

9 Gas-phase Molecular Spectroscopy

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Introduction

Gas-phase molecular spectroscopy is still in the growth phase, and perhaps 10^3 papers would have good claims to be discussed in this review, which we have limited for the most part to work published in 1980 and 1981. We have occasionally included some 1982 publications which came to our attention during writing, when they were of particular significance to the discussion.

The emphasis of our 1979 report¹ was on technique; this was almost inevitable, since we considered several years work in which there had been tremendous development of experimental methods. We have to some extent built upon our earlier report, and in a number of cases we refer the reader back to it for further explanation or key references (we refer to it in the text as Part I). In this way we have been able to devote more space in the current report to applications and results, whilst, we hope, keeping the text accessible to the non-specialist reader. We have also considered somewhat more fully spectroscopy at high frequencies, such as photoelectron spectroscopy, although we have still generally restricted ourselves to transitions involving valence electrons.

Many reviews and books on spectroscopic topics have appeared in the last two years: we later refer to some of these in the sections to which they are particularly relevant. One book in which the daunting task of covering almost the whole of gas phase spectroscopy was taken on is 'High Resolution Molecular Spectroscopy', by J. M. Hollas.² Coverage is from microwave to photoelectron, and whilst theory is certainly extensively considered, the author's chosen bias is towards experimental aspects. There are numerous examples (and a molecule index), and also an up-to-date chapter on laser spectroscopy.

Further detail on laser spectroscopy may be found in the book of that name by W. Demtröder.³ This covers much of the fundamental physics of laser operation and spectroscopy, as well as applications, for various spectral regions.

Contributions to the symposium in celebration of the 50th anniversary of R. S.

¹ M. T. Macpherson and R. F. Barrow, *Annu. Rep. Prog. Chem., Sect. C*, 1979, **76**, 51.

² J. M. Hollas, 'High Resolution Molecular Spectroscopy', Butterworths, London, 1982.

³ W. Demtröder, 'Laser Spectroscopy' (Springer Series in Chemical Physics Vol. 5), Springer, Berlin & Heidelberg, 1981.

Mulliken's election to the faculty at the University of Chicago have been published,⁴ as have papers from the colloquium celebrating the 65th birthday of A. Lagerqvist.⁵ The full proceedings of the Faraday Discussion on High Resolution Spectroscopy have appeared, with a number of interesting discussion comments as well as the presented papers.⁶ A supplement to the Bibliography of *Ab Initio* Molecular Wave Functions has been published;⁷ we have only occasionally included references to *ab initio* studies, when they seemed particularly appropriate in the context of the discussion or table.

Organization of the Report.—The report is divided into three main sections, on rotational, vibrational, and electronic spectroscopy (thus studies of transitions between electronic states would appear in Section 3, even if they involved infrared radiation, and information specifically on the electronic ground state would also appear in Section 3 if it were derived from electronic spectroscopy). The division is only occasionally non-rigorous when, for example, out of convenience we include RF transitions in Section 1, and IR transitions between spin states in Section 2.

The other obvious division is between text and tables. Since our field of coverage is so wide, we have inevitably had to be very selective (often apparently arbitrarily so, no doubt) of the work which we have discussed in the text, particularly as we did not wish it to read like a catalogue of references. Catalogues of references can be useful, however, so we have provided these also. The various tables contain information on papers published in 1980 and 1981, and are fairly comprehensive. The arrangement is by type of spectroscopy, and by molecule.*† We hope that these tables will provide a guide to recent work in specific areas, and offer starting points for the recovery of spectroscopic information from the ever multiplying literature.

1 Rotational Spectroscopy

Table 1 Rotational (and other low frequency) spectroscopic studies of diatomic molecules. Molecules are listed in alphabetical order

Molecule	Technique	Comments	Ref.
BF	MW (low T flame and from high T reactions)		8
BaS	MMW (low pressure flame, Ba + OCS → Ba + CO)	extensive experimental details	9
BrCl	MMW		10
BrF	MMW		10
BrO	MMW (microwave discharge Br ₂ + O ₂)	hfs	11

* It has not been possible always to specify all isotopic species of a given molecule which have been studied, especially in microwave spectroscopy where they are often numerous, although we have tried to mention species of particular interest where appropriate.

† All double resonance experiments are listed in the section appropriate to the higher frequency photon.

⁴ *J. Phys. Chem.*, 1980, **84**, 2091–2141.

⁵ *Phys. Scr.*, 1982, **25**, 241–390.

⁶ 'High Resolution Spectroscopy', Royal Society of Chemistry, Faraday Division, General Discussion No. 71, 1981.

⁷ W. G. Richards, P. R. Scott, V. Sackwild, and S. A. Robins, 'A Bibliography of *Ab Initio* Molecular Wave Functions,' Supplement for 1978–80. Clarendon Press, Oxford, 1981.

⁸ Ch. Ryzlewics and T. Töring, *Chem. Phys.*, 1980, **51**, 329.

⁹ D. A. Helms, M. Winnewisser, and G. Winnewisser, *J. Phys. Chem.*, 1980, **84**, 1758.

¹⁰ R. E. Willis, jun., and W. W. Clark, *J. Chem. Phys.*, 1980, **72**, 4946.

¹¹ E. A. Cohen, H. M. Pickett, and M. Geller, *J. Mol. Spectrosc.*, 1981, **87**, 459.

Table 1 (continued)

Molecule	Technique	Comments	Ref.
C1F	MMW		10
CO ⁺	MMW, SMMW (glow discharge)		12
GaBr	MMW (flame reaction, saturation modulation)	high rotational transition in $v = 0-3$	13
Gal	MW	hfs, $eq_v Q$	14
HCl	CH ₃ OH laser absorption	pressure broadened line shapes	15
² HI	MMW, mol. beam absorption	hfs	16
IBr	MMW		10
ICl	MMW		10
N ₂	CARS (3 colour pulsed laser) analysis	quantitative agreement between calc. and obs. lineshapes collision-induced absorption, fit of experimental lineshapes	17
Na ¹ H, Na ² H	MMW (glow discharge absorption)	significant Born–Oppenheimer breakdown	19
NO	tunable laser sidebands	852–1053 GHz	20
O ₂	MMW	¹⁶ O ¹⁷ O, ¹⁷ O ¹⁸ O hfs	21
O ₂	CARS	see N ₂ above	17
O ₂	MW	magnetic dipole transitions, line strengths greater than expected. (Relevant to stratospheric emission)	22
O ₂	LMR	magnetic dipole transitions in $a^1\Delta_g, v = 0$ of ¹⁶ O ₂	23
O ₂	MBMR	coherent dynamics; inhomogeneous dephasing can be used to find translational temperature of beam	24
OH	MW Zeeman	molecular g factors	25
O ¹ H, O ² H	LMR	118.8, 96.5, and 215.4 μ m	26
O ¹ H, O ² H	LMR	in vibrationally excited states	27
OH	LMR	Lamb dips allow resolution of proton hfs	28
SeD	LMR	r_e estimate	29

¹² K. V. L. N. Sastry, *Astrophys. J. Lett.*, 1981, **250**, L91.

¹³ K. P. Rajappan Nair, H.-U. Schütze-Pahlman, and J. Hoeft, *Chem. Phys. Lett.*, 1981, **80**, 149.

¹⁴ K. P. R. Nair and J. Hoeft, *J. Mol. Spectrosc.*, 1981, **85**, 301; *Chem. Phys. Lett.*, 1980, **70**, 583.

¹⁵ J. Pourcin, A. Jacquemoz, A. Fournel, and H. Sielmann, *J. Mol. Spectrosc.*, 1981, **90**, 43.

¹⁶ B. Sivery, J. Demaison, J. Burie, and A. Dubrulle, *J. Mol. Spectrosc.*, 1981, **88**, 434.

¹⁷ C. M. Roland and W. A. Steele, *J. Chem. Phys.*, 1980, **73**, 5919.

¹⁸ J. D. Poll and J. L. Hunt, *Can. J. Phys.*, 1981, **59**, 1449.

¹⁹ K. V. L. N. Sastry, E. Herbst, and F. C. de Lucia, *J. Chem. Phys.*, 1981, **74**, 4753; *Astrophys. J. Lett.*, 1981, **248**, L53.

²⁰ F. C. van den Henvel, W. L. Meerts, and A. Dymanus, *J. Mol. Spectrosc.*, 1980, **84**, 162.

²¹ G. Cazzoli, *Nuovo Cimento*, 1981, **62B**, 243.

²² T. A. Clark and D. J. W. Kendall, *J. Quant. Spectrosc. Radiat. Transfer*, 1980, **24**, 65.

²³ A. Scalabrin, R. J. Saykally, K. M. Evenson, H. E. Radford, and M. Mizushima, *J. Mol. Spectrosc.*, 1981, **89**, 344.

²⁴ A. Amirav, U. Even, J. Jortner, and L. Kleinman, *J. Chem. Phys.*, 1980, **73**, 4217.

²⁵ K. V. L. N. Sastry and J. Vanderlinde, *J. Mol. Spectrosc.*, 1980, **83**, 332.

²⁶ J. S. Geiger, D. R. Smith, and J. D. Bonnett, *Chem. Phys. Lett.*, 1980, **70**, 600.

²⁷ P. B. Davies, W. Hack, and H. G. Wagner, *Faraday Discuss. Chem. Soc.*, 1981, **71**, 15.

²⁸ J. M. Brown, C. M. L. Kerr, F. D. Wayne, K. M. Evenson, and H. E. Radford, *J. Mol. Spectrosc.*, 1981, **86**, 544.

²⁹ D. I. Cliff, P. B. Davies, B. J. Handy, B. A. Thrush, and E. K. Murray Lloyd, *Chem. Phys. Lett.*, 1980, **75**, 9.

Table 2 Rotational (and other low frequency) spectroscopic studies of triatomic molecules. Molecules are listed in alphabetical order

Molecule	Technique	Comments	Ref.
C ₂ H	MMW, SMMW (glow discharge)	good agreement with radio astronomy	30
ClB=S	MW [1000 °C, Cl ₂ S ₂ (g) + B(s)]	hfs, vibration-rotation analysis	31
ClCN	MBER	hfs, inc. in excited state of ¹⁴ N nucleus	32
Cl ₂ O	MW	detrn. of equilibrium structure by a modified mass dependence method	33
C ₂ N, C ₂ N ⁺ , C ₃ H	calculation	theoretical MW spectral constants (also hyperfine constants for HNC, ² HNC and HNCH ⁺)	34
CO ₂	MW	¹⁸ O substitution produces dipole sufficient to observe pure rotational transitions	35
FCP	MW	dipole moment, vibration-rotation data	36
FSO	MW (OCS + O ₃ /CF ₄ , microwave discharge)	hfs, spin-rotation, dipole moment structure. Ground state is ² A'' measurements of <i>T</i> ₂ (polarization relaxation time)	37
HCN	MW coherent transients		38
HCO ⁺	MW (glow discharge)	pressure broadening of <i>J</i> = 0-1 transition by H ₂	39
HCO ⁺	MW (glow discharge)	<i>r</i> _s structure	40
HCO ⁺	MMW (rf discharge)	centrifugal distortion	41
HO ₂	MW	dipole moment	42
² HO ₂	LMR	structure: also revised	43
H ₂ O	quantum beats	molecular geometry for ¹ HO ₂ beats between magnetic hf levels	44
H ₂ ^{17,18} O	FTFIR	50-730 cm ⁻¹	45
H ₂ ^{16,17,18} O	FTFIR	10-47 cm ⁻¹	46
H ₂ ^{16,17,18} O	analysis	centrifugal distortion	47

³⁰ K. V. L. N. Sastry, P. Helminger, A. Charo, E. Herbst, and F. C. de Lucia, *Astrophys. J.*, 1981, **251**, L119.

³¹ C. Kirby and H. W. Kroto, *J. Mol. Spectrosc.*, 1980, **83**, 130.

³² J. M. L. J. Reinartz, W. L. Meerts, and A. Dymanus, *Chem. Phys.*, 1980, **45**, 387.

³³ M. Nakata, M. Sugie, H. Takeo, C. Matsumura, T. Fukuyama, and K. Kuchitsu, *J. Mol. Spectrosc.*, 1981, **86**, 241.

³⁴ S. Green, *Astrophys. J.*, 1980, **240**, 962.

³⁵ Y. Endo, K. Yoshida, S. Saito, and E. Hirota, *J. Chem. Phys.*, 1980, **73**, 3511.

³⁶ H. W. Kroto, J. F. Nixon, and N. P. C. Simmons, *J. Mol. Spectrosc.*, 1980, **82**, 185.

³⁷ Y. Endo, S. Saito, and E. Hirota, *J. Chem. Phys.*, 1981, **74**, 1568.

³⁸ M. Charron, T. G. Anderson, and J. I. Steinfeld, *J. Chem. Phys.*, 1980, **73**, 1494.

³⁹ T. G. Anderson, C. S. Gudeman, T. A. Dixon, and R. C. Woods, *J. Chem. Phys.*, 1980, **72**, 1332.

⁴⁰ R. C. Woods, R. J. Saykally, T. G. Anderson, T. A. Dixon, and P. G. Szanto, *J. Chem. Phys.*, 1981, **75**, 4256.

⁴¹ M. Bogey, C. Demuynck, and J. L. Destombes, *Mol. Phys.*, 1981, **43**, 1043.

⁴² S. Saito and C. Matsymura, *J. Mol. Spectrosc.*, 1980, **80**, 39.

⁴³ C. E. Barnes, J. M. Brown, and H. E. Radford, *J. Mol. Spectrosc.*, 1980, **84**, 179.

⁴⁴ N. M. Lawandy and D. W. Robinson, *Appl. Phys. Lett.*, 1981, **38**, 750.

⁴⁵ J. Kauppinen and E. Kyro, *J. Mol. Spectrosc.*, 1980, **84**, 405.

⁴⁶ R. H. Partridge, *J. Mol. Spectrosc.*, 1981, **87**, 429.

⁴⁷ E. Kyro, *J. Mol. Spectrosc.*, 1981, **88**, 167.

Table 2 (continued)

Molecule	Technique	Comments	Ref.
HCS ⁺	MW (glow discharge, CO/H ₂ S)		48
HCS ⁺	interstellar observation	also possibly HO ₂ C ⁺ or HO-CN	49
NF	LMR	a ¹ Δ, J = 7 → 8	50
N ₂ H ⁺	MW	substitution structure	51
N ₂ ¹ H ⁺ , N ₂ ² H ⁺	MMW, SMMW (glow discharge)		52
NH ₂	MMW, SMMW (N ₂ H ₄ + microwave discharge of H ₂ O)	hfs	53
NO	MBER	Zeeman, molecular g factors, hfs	54a
OCS	MW/supersonic beam	stark modulated MW spectroscopy in CW supersonic mol. beam	54b
OCS	MW	line shift measurements	55
OCS	MW	observed in highly excited vibrational levels produced by energy transfer from N ₂ improved molecular constants	56
OCS	MMW, molecular beam absorption		57
OCS	SMMW		58
ONCl	MW	cubic force field, structure	59
ONF	MW	Zeeman: g values, hfs	60

**Table 3 Rotational (and other low frequency) spectroscopic studies of tetra-atomic molecules.
Molecules are listed in alphabetical order**

Molecule	Technique	Comments	Ref.
AsH ₃	intracavity RF	pure nuclear quadrupole resonance transitions	61
C ₃ H ⁺	calculation	theoretical MW spectral constants	62
C ₂ ² H ₂	MW	excited vibrational states; dipole moments	63
COCl ₂	MW	r _s , r _m , r _e structures	64

⁴⁸ C. S. Gudeman, N. H. Haese, N. D. Piltch, and R. C. Woods, *Astrophys. J.*, 1981, **246**, L47.⁴⁹ P. Thaddeus, M. Guelin, and R. A. Linke, *Astrophys. J.*, 1981, **246**, L41.⁵⁰ P. B. Davies and F. Temps, *J. Chem. Phys.*, 1981, **74**, 6556.⁵¹ P. G. Szanto, T. G. Anderson, R. J. Saykally, N. D. Piltch, T. A. Dixon, and R. C. Woods, *J. Chem. Phys.*, 1981, **75**, 4261.⁵² K. V. L. N. Sastry, P. Helminger, E. Herbst, and F. C. de Lucia, *Chem. Phys. Lett.*, 1981, **84**, 286.⁵³ A. Charo, K. V. L. N. Sastry, E. Herbst, and F. C. de Lucia, *Astrophys. J.*, 1981, **244**, L111.⁵⁴ (a) W. L. Meerts and L. Vesetti, *J. Mol. Spectrosc.*, 1980, **82**, 202; (b) H. S. Zivi, A. Bauder, and Hs.H. Gunthard, *Chem. Phys. Lett.*, 1981, **83**, 469.⁵⁵ W. A. Wensink, C. Noorman, and H. A. Dijkerman, *J. Phys. B*, 1981, **14**, 2813.⁵⁶ M. Bogey and A. Bauer, *J. Mol. Spectrosc.*, 1980, **84**, 170.⁵⁷ A. Dubrulle, J. Demaison, J. Burie, and D. Boucher, *Z. Naturforsch., Teil A*, 1980, **35**, 471.⁵⁸ A. V. Burenin, A. N. Val'dov, E. N. Karyakin, A. F. Krupnov, and S. M. Shapin, *J. Mol. Spectrosc.*, 1981, **87**, 312.⁵⁹ A. M. Mirri, R. Cervellati, and G. Cazzoli, *J. Mol. Spectrosc.*, 1980, **83**, 202.⁶⁰ F. Rohwer and A. Guarneri, *Z. Naturforsch., Teil A*, 1980, **35**, 336.⁶¹ F. Scappini and T. Oka, *J. Mol. Spectrosc.*, 1981, **85**, 390.⁶² S. Wilson and S. Green, *Astrophys. J.*, 1980, **240**, 968.⁶³ K. Matsumura, T. Tanaka, Y. Endo, S. Saito, and E. Hirota, *J. Phys. Chem.*, 1980, **84**, 1793.⁶⁴ M. Nakata, T. Fukuyama, and K. Kuchitsu, *J. Mol. Spectrosc.*, 1980, **83**, 118.

Table 3 (continued)

Molecule	Technique	Comments	Ref.
COCl ₂	MW	<i>r</i> _z structure and isotope effect	65
COF ₂	MW		66
FCIO ₂	analysis	harmonic force field, structure recalculated	67
H ₂ CO	MW	hfs, ¹⁷ O species	68
H ₂ CO	MW	¹⁷ O, ¹⁸ O species	69
H ₂ CO	MW	ground-state parameters compatible with IR and UV data	70
H ₂ CO	MWDR	time-resolved four-level system, rotation relaxation studies	71
HCICO	MW	centrifugal distortion, force field	72
HNCH ⁺	<i>ab initio</i>	prediction of <i>J</i> = 1 ← 0 frequency	73
HNCO	MW	<i>r</i> _z structure and harmonic force field. (MW, MMW, SMMW data used)	74
HNCO	FTFIR	80–350 cm ⁻¹ , <i>r</i> _s structure	75
HNCS	MW	ground-state constants, molecule is <i>trans</i>	76
HN ₃	MW	substitution structure	77
HNO ₂	MMW, SMMW	<i>cis</i> and <i>trans</i> ; spectral maps available for SMM region based on these molecules, and HNO ₃	78
H ₂ O ₂	MW	dipole moment	79
H ₂ O ₂	MMW	higher K ₋₁ states	80
H ₂ O ₂	FIR	rotational-torsion spectrum, 80–700 GHz	81
¹⁴ NH ₃ , ¹⁵ NH ₃	MW	<i>v</i> ₄ inversion spectra	82
¹⁵ NH ₃	SMMW (RAD)	inversion, inversion-rotation	83
¹⁵ NH ₃	FTFIR	rotation-inversion, 38–280 cm ⁻¹	84
¹⁴ NH ₃	MW	heating gas to produce new inversion lines	85
¹⁵ NH ₃	MW	inversion spectrum	86
PH ₃	MW	allowed and forbidden transitions	87

- ⁶⁵ M. Nakata, K. Kohata, T. Fukuyama, and K. Kuchitsu, *J. Mol. Spectrosc.*, 1980, **83**, 105.
⁶⁶ M. Nakata, K. Kohata, T. Fukuyama, K. Kuchitsu, and C. J. Wilkins, *J. Mol. Struct.*, 1980, **68**, 271.
⁶⁷ A. G. Robiette, C. R. Parent, and M. C. L. Gerry, *J. Mol. Spectrosc.*, 1981, **86**, 455.
⁶⁸ R. Cornet, B. M. Landsberg, and G. Winnewisser, *J. Mol. Spectrosc.*, 1980, **82**, 253.
⁶⁹ D. T. Davies, R. J. Richards, and M. C. L. Gerry, *J. Mol. Spectrosc.*, 1980, **80**, 307.
⁷⁰ R. Cornet and G. Winnewisser, *J. Mol. Spectrosc.*, 1980, **80**, 438.
⁷¹ D. A. Andrews, *Chem. Phys.*, 1981, **56**, 231.
⁷² M. Suzuki, K. Yamada, and M. Takami, *J. Mol. Spectrosc.*, 1981, **88**, 207.
⁷³ P. S. Dardi and C. E. Dykstra, *Astrophys. J.*, 1980, **240**, L171.
⁷⁴ L. Fusina and I. M. Mills, *J. Mol. Spectrosc.*, 1981, **86**, 488.
⁷⁵ K. Yamada, *J. Mol. Spectrosc.*, 1980, **79**, 323.
⁷⁶ Y. Hamada, M. Winnewisser, G. Winnewisser, L. B. Szalkanski, and M. C. L. Gerry, *J. Mol. Spectrosc.*, 1980, **79**, 295.
⁷⁷ B. P. Winnewisser, *J. Mol. Spectrosc.*, 1980, **82**, 220.
⁷⁸ W. C. Bowman, F. C. de Lucia, and P. Helminger, *J. Mol. Spectrosc.*, 1981, **88**, 431.
⁷⁹ E. A. Cohen and H. M. Pickett, *J. Mol. Spectrosc.*, 1981, **87**, 582.
⁸⁰ W. C. Bowman, F. C. de Lucia, and P. Helminger, *J. Mol. Spectrosc.*, 1981, **87**, 571.
⁸¹ P. Helminger, W. C. Bowman, and F. C. de Lucia, *J. Mol. Spectrosc.*, 1981, **85**, 120.
⁸² E. A. Cohen, *J. Mol. Spectrosc.*, 1980, **79**, 496.
⁸³ S. P. Belov, L. I. Gershstein, A. F. Krupnov, A. V. Malovskij, S. Urban, V. Spirko, and D. Papousek, *J. Mol. Spectrosc.*, 1980, **84**, 288.
⁸⁴ M. Carlotti, A. Trombetti, B. Velino, and J. Vrbancich, *J. Mol. Spectrosc.*, 1980, **83**, 401.
⁸⁵ B. V. Sinha and P. D. P. Smith, *J. Mol. Spectrosc.*, 1980, **80**, 231.
⁸⁶ H. Sasada, *J. Mol. Spectrosc.*, 1980, **83**, 15.
⁸⁷ S. P. Belov, A. V. Burenin, L. I. Gershstein, A. F. Krupnov, V. N. Markov, A. V. Maslovsky, and S. M. Shapin, *J. Mol. Spectrosc.*, 1981, **86**, 184.

Table 3 (continued)

Molecule	Technique	Comments	Ref.
PH ₃	analysis (of SMMW measurements)	representation of effective rotational Hamiltonian operator in form of Pade operator (esp. for molecules with small moments of inertia)	88
PH ₃	MW	dipole moment in $v_4 = 1$	89
PH ₃	MW	1-type doubling transitions in $v_4 = 1$	90

Table 4 Rotational (and other low frequency) spectroscopic studies of polyatomic molecules.
Molecules are listed with increasing number of carbon atoms. For molecules containing carbon, listing is then with increasing number of hydrogen atoms. Listing is otherwise alphabetical

Molecule	Technique	Comments	Ref.
BH ₃ NH ₃	MW		91
ClO ₃ F	MBER		92
GeH ₄	MBMR	avoided crossing spectroscopy	93
HNO ₃	MW	harmonic force field	94
IF ₅	MW	$v_5 = 1, v_9 = 1$ Coriolis resonance	95
IF ₅	MW	$v_5 = 1, v_9 = 1$	96
OPF ₃	MMW	$v_6 = 2, cf. v_6 = 1$	97
SiH ₄	MBMR	avoided crossing spectroscopy	93
SiH ₂ F ₂	MW	harmonic force field, cf. other fluorosilanes	98
CF ₃ Br } CF ₃ I }	MW	hfs; rf pumping of quadrupole sub-levels of ¹³ C species	99
CHF ₃	MBER	avoided crossings	100
CHO ₆ N ₃ [HC(NO ₂) ₃]	MW	twist of NO ₂ groups	101
CH ₂ Cl ₂	MW	harmonic force fields, methylene chloride, dichlorosilane	102
CH ₂ O ₂ (HCOOH)	MW	harmonic force field; ¹³ C or ¹⁸ O species	103
CH ₂ N ₂ (H ₂ N-NC)	MMW	0 ⁺⁻ inversion state splitting <10 cm ⁻¹	104

⁸⁸ S. P. Belov, A. V. Burenin, O. L. Polyansky, and S. M. Shapin, *J. Mol. Spectrosc.*, 1981, **90**, 579.⁸⁹ F. Scappini and R. Schwarz, *Chem. Phys. Lett.*, 1981, **80**, 350.⁹⁰ A. Guarneri, F. Scappini, and G. di Longo, *Chem. Phys. Lett.*, 1981, **82**, 321.⁹¹ R. D. Suenram and L. R. Thorne, *Chem. Phys. Lett.*, 1981, **78**, 157.⁹² R. L. de Leon and J. S. Muenter, *J. Mol. Spectrosc.*, 1980, **83**, 469.⁹³ W. M. Itano and N. F. Ramsay, *J. Chem. Phys.*, 1980, **72**, 4941.⁹⁴ P. N. Ghosh, C. E. Blom, and A. Bauder, *J. Mol. Spectrosc.*, 1981, **89**, 159.⁹⁵ B. Balikci and P. N. Brier, *J. Mol. Spectrosc.*, 1981, **85**, 109.⁹⁶ B. Balikci and P. N. Brier, *J. Mol. Spectrosc.*, 1981, **89**, 254.⁹⁷ J. G. Smith, *J. Mol. Spectrosc.*, 1981, **88**, 126.⁹⁸ R. W. Davis, A. G. Robiette, and M. C. L. Gerry, *J. Mol. Spectrosc.*, 1980, **83**, 185.⁹⁹ A. P. Cox, G. Duxbury, J. A. Hardy, and Y. Kawashima, *J. Chem. Soc., Faraday Trans. 2*, 1980, **76**, 339.¹⁰⁰ W. L. Meerts and I. Ozier, *J. Chem. Phys.*, 1981, **75**, 597.¹⁰¹ W. Caminati and E. B. Wilson, *J. Mol. Spectrosc.*, 1980, **81**, 507.¹⁰² R. W. Davis, A. G. Robiette, and M. C. L. Gerry, *J. Mol. Spectrosc.*, 1981, **85**, 399.¹⁰³ R. W. Davis, A. G. Robiette, M. C. L. Gerry, E. Bjarnov, and G. Winnewisser, *J. Mol. Spectrosc.*, 1980, **81**, 93.¹⁰⁴ E. Schafer, M. Winnewisser, and J. J. Christiansen, *Chem. Phys. Lett.*, 1981, **81**, 380.

Table 4 (continued)

Molecule	Technique	Comments	Ref.
CH ₃ BS	MW	hfs, vibration-rotation	105
CH ₃ Br	MW	molecular constants for $\nu_6 = 1$	106
CH ₃ Cl			
CH ₃ I			
CH ₃ F	MBER	$\mu = 1.85840D$ (for calibrating IR laser Stark experiments)	107
CH ₃ O (methoxy)	LMR	precise parameters for ² E g.s.	108
CH ₃ O (CH ₂ OH)	LMR	detected	109
CH ₃ O ₂ N (<i>cis</i> -methyl nitrite)	MW	barrier to internal rotation, <i>cis/trans</i> energy difference	110
CH ₃ ONSi (silyl isocyanate)	MW	r_s ; quasi-linear SiNCO chain	111
CH ₃ P (CH ₂ =PH)	MW		112
CH ₄	interstellar	spectroscopic constants calculated	113
CH ₄	MBMR	mixing of levels by nuclear hyperfine interaction leads to avoided crossings	114
CH ₄ O (CH ₃ OH)	MW	dipole moments	115
CH ₄ O (CH ₃ O ² H)	MW	torsional constant, dipole moment	116
CH ₄ O (CH ₃ O ² H, C ² H ₃ O ² H)	FTFIR	internal rotation, 80–250 cm ⁻¹	117
C ₂ H ₂ N ₂ (CH ₂ =N—CN)	assignments		118
C ₂ H ₃ N (CH ₃ C ¹⁵ N)	MW		119
C ₂ H ₃ OCIS (CICISCH ₃)	MW	barrier to internal rotation, hfs; CH ₃ <i>syn</i> to CO	120
C ₂ H ₃ OF ₃ (CF ₃ OCH ₃)	MW	r_s ; barrier to internal rotation; <i>gauche</i>	121
C ₂ H ₃ OFS (FCOSCH ₃)	MW	torsional interactions; CH ₃ <i>syn</i> to CO	122
C ₂ H ₄ (C ₂ ² H ₄)	MW	r_z , dipole moment	123

¹⁰⁵ C. Kirby and H. W. Kroto, *J. Mol. Spectrosc.*, 1980, **83**, 1.¹⁰⁶ A. Dubrule, J. Burie, D. Boucher, F. Herlemont, and J. Demaison, *J. Mol. Spectrosc.*, 1981, **88**, 394.¹⁰⁷ M. D. Marshall and J. S. Muenter, *J. Mol. Spectrosc.*, 1980, **83**, 279.¹⁰⁸ D. K. Russell and H. E. Radford, *J. Chem. Phys.*, 1980, **72**, 2750.¹⁰⁹ H. E. Radford, K. M. Evenson, and D. A. Jennings, *Chem. Phys. Lett.*, 1981, **78**, 589.¹¹⁰ P. N. Ghosh, A. Bauder, and Hs.H. Gunthard, *Chem. Phys.*, 1980, **53**, 39.¹¹¹ J. A. Duckett, A. G. Robiette and M. C. L. Gerry, *J. Mol. Spectrosc.*, 1981, **90**, 374.¹¹² H. W. Kroto, J. F. Nixon, and K. Ohno, *J. Mol. Spectrosc.*, 1981, **90**, 367.¹¹³ K. Fox, D. E. Jennings, and Dag Nhu Mai, *J. Phys. Chem.*, 1980, **84**, 1765.¹¹⁴ W. M. Itano and I. Ozier, *J. Chem. Phys.*, 1980, **72**, 3700.¹¹⁵ K. V. L. N. Sastry, R. M. Lees, and J. van der Linde, *J. Mol. Spectrosc.*, 1981, **88**, 228.¹¹⁶ V. K. Kaushik, T. Takagi, and C. Matsumura, *J. Mol. Spectrosc.*, 1980, **82**, 418.¹¹⁷ V. Stern, N. Goff, J. Kachmarsky, and K. D. Moller, *J. Mol. Spectrosc.*, 1980, **79**, 345.¹¹⁸ B. Bak and H. Svahnholz, *Chem. Phys. Lett.*, 1980, **75**, 528.¹¹⁹ J. K. Messer and J. A. Roberts, *J. Mol. Spectrosc.*, 1981, **88**, 231.¹²⁰ W. Caminati, R. K. Bohn, and N. S. True, *J. Mol. Spectrosc.*, 1980, **84**, 355.¹²¹ J. Nakagawa, H. Kato, and M. Hayashi, *J. Mol. Spectrosc.*, 1981, **90**, 467.¹²² W. Caminati and R. Meyer, *J. Mol. Spectrosc.*, 1981, **90**, 303.¹²³ E. Hirota, Y. Endo, S. Saito, K. Yoshida and I. Yamaguchi, and K. Machida, *J. Mol. Spectrosc.*, 1981, **89**, 223.

Table 4 (continued)

Molecule	Technique	Comments	Ref.
C ₂ H ₄ O ₂ (CH ₃ COOH)	MW	internal rotation splittings; substitution structure	124
C ₂ H ₄ OS (HCOSCH ₃)	MW	barrier to internal rotation	125
C ₂ H ₄ Si (H ₃ SiC≡CH)	MW	2v ₁₀ ; vibrational anharmonic constant	126
C ₂ H ₅ I	MW	hfs	127
C ₂ H ₆ Cl ₂ Si (dimethyl dichlorosilane)	MW	hfs	128
C ₂ H ₆ O ₂ (glycol-O-d ₂)	MW, MWMWDR	internal rotation of OD groups	129
C ₂ H ₆ O ₂ (glycol)	MW, RFMWDR	semi-rigid rotor; tunnelling of hydroxyl protons	130
C ₂ H ₆ S (dimethyl sulphide)	MW	moment of inertia of methyl top	131
C ₂ H ₆ S (dimethyl sulphide-d ₆)	MW	molecular rotation – methyl top rotation interaction	132
C ₂ H ₇ P (dimethyl phosphide-d ₃)	MW	also IR, Raman, barrier to internal rotation	133
C ₃ HP (H—C≡C—C≡P)	MW		134
C ₃ H ₂ O (propynal-d ₁)	MMW (some IRMWDR)		135
C ₃ H ₃ O ₂ N (CH ₃ CO · NCO)	MW	barrier to internal rotation, dipole moments	136
C ₃ H ₃ ONS (NC—COSCH ₃)	MW, RFMWDR	failure of semi-rigid rotor pattern for A species; barrier to internal rotation	137
C ₃ H ₃ P (CH ₂ · CH · C≡P)	MW	planar	138
C ₃ H ₄ (methyl acetylene)	MW	v ₅ = 1	139
C ₃ H ₄ (methyl acetylene)	FTFIR	10—60 cm ⁻¹	140
C ₃ H ₄ N ₂ (2-cyanoaziridine)	MW	hfs; only cis isomer detected	141
C ₃ H ₄ S (<i>trans</i> -2-propenethiol)	MW	planar	142
C ₃ H ₅ I (3-iodopropene)	theory	quadrupole hfs	143
C ₃ H ₅ F ₃ (CF ₃ OC ₂ H ₅)	MW	GT isomer; r _s structure; barrier to internal rotation	144

- ¹²⁴ B. P. van Eijek, J. van Opheusden, M. M. M. van Schaik, and E. van Zoeren, *J. Mol. Spectrosc.*, 1981, **86**, 465.
- ¹²⁵ W. Caminati, B. P. van Eijek, and D. G. Lister, *J. Mol. Spectrosc.*, 1981, **90**, 15.
- ¹²⁶ J. Carlier and A. Bauer, *J. Mol. Spectrosc.*, 1981, **88**, 219.
- ¹²⁷ D. Boucher, A. Dubrule, and J. Demaison, *J. Mol. Spectrosc.*, 1980, **84**, 375.
- ¹²⁸ M. Nakata, H. Takeo, and C. Matsumura, *J. Mol. Spectrosc.*, 1980, **82**, 117.
- ¹²⁹ E. Walder, A. Bauder, and Hs.H. Gunthard, *Chem. Phys.*, 1980, **51**, 223.
- ¹³⁰ W. Caminati and G. Corbelli, *J. Mol. Spectrosc.*, 1981, **90**, 572.
- ¹³¹ J. Demaison, D. Schwoch, B. T. Tan, and H. D. Rudolph, *J. Mol. Spectrosc.*, 1980, **83**, 391.
- ¹³² J. Demaison, B. T. Tan, V. Typke, and H. D. Rudolph, *J. Mol. Spectrosc.*, 1981, **86**, 406.
- ¹³³ J. R. Durig, S. D. Hudson, M. R. Jalilian, and Y. S. Li, *J. Chem. Phys.*, 1981, **74**, 772.
- ¹³⁴ H. W. Kroto, J. F. Nixon, and K. Ohno, *J. Mol. Spectrosc.*, 1981, **90**, 512.
- ¹³⁵ M. Takami, *J. Mol. Spectrosc.*, 1980, **80**, 301.
- ¹³⁶ B. Landsberg and K. Iqbal, *J. Chem. Soc., Faraday Trans. 2*, 1980, **76**, 1208.
- ¹³⁷ W. Caminati, *J. Mol. Spectrosc.*, 1981, **90**, 315.
- ¹³⁸ K. Ohno, H. W. Kroto, and J. F. Nixon, *J. Mol. Spectrosc.*, 1981, **90**, 507.
- ¹³⁹ P. M. Burrell, E. Bjarnov, and R. H. Schwendeman, *J. Mol. Spectrosc.*, 1980, **82**, 193.
- ¹⁴⁰ C. Meyer and M. Sergen-Rozey, *J. Mol. Spectrosc.*, 1980, **83**, 343.
- ¹⁴¹ R. D. Brown, P. D. Godfrey, and A. L. Ottrey, *J. Mol. Spectrosc.*, 1980, **82**, 73.
- ¹⁴² K. Georgiou and H. W. Kroto, *J. Mol. Spectrosc.*, 1980, **83**, 94.
- ¹⁴³ I. Ohkoshi, Y. Niide, M. Takano, and Y. Sasada, *J. Mol. Spectrosc.*, 1980, **82**, 27.
- ¹⁴⁴ M. Hayashi, H. Kato, and M. Oyamada, *J. Mol. Spectrosc.*, 1980, **83**, 408.

Table 4 (continued)

Molecule	Technique	Comments	Ref.
C ₃ H ₆ F ₂ (CH ₃ CF ₂ CH ₃)	MW, MMW	barrier to internal rotation, dipole moment	145
C ₃ H ₆ N ₂ (1-pyrazoline)	MW	ring-puckering vibration excited	146
C ₃ H ₆ O ₂ (methyl acetate)	MW, MWMWDR	internal rotation barriers for the two non-equivalent methyl groups	147
C ₃ H ₆ O ₃ (trioxane)	MW	graphical method for assignment of rotational spectrum of slightly asymmetric molecule (¹³ C or ¹⁸ O)	148
C ₃ H ₈ O ₂ (1,2-propanediol)	MW	intramolecular H bond	149
C ₃ H ₈ S (CH ₃ SC ₂ H ₅)	MW	barrier to internal rotation of SCH ₃	150
C ₃ H ₉ ON (2-methoxyethylamine)	MW	gauche, with intramolecular H-bond; barrier to internal rotation	151
C ₃ H ₉ SiBr [(CH ₃) ₃ SiBr]	MW		152
C ₃ H ₁₀ Si (propyl silane)	MW	antiperiplanar isomer	153
C ₄ H ⁺	theory	microwave spectral constants	62
C ₄ H ₄ O ₃ (2,4-dioxabicyclo[3.1.0] hexan-3-one)	MW		154
C ₄ H ₅ Cl (cis-1-chlorobuta- 1,3-diene)	MW	planar; hfs	155
C ₄ H ₄ N (cyclopropyl cyanide)	MW	hfs	156
C ₄ H ₆ O (HC≡CCH ₂ · O · CH ₃)	MW	barrier to internal rotation	157
C ₄ H ₆ O ₂ (O=CH · CCH ₃ · CHOH)	MW	vibration-torsion interaction; intramolecular H-bonded	158
C ₄ H ₈ (1,1-d ₂ -but-1-ene)	MW	skew form	159
C ₄ H ₉ O ₂ N (2-methyl-2-nitropropane)	MW	barrier to t-butyl internal rotation	160
C ₄ H ₉ SN (thiomorpholine)	MW	chair equatorial conformers	161
C ₄ H ₁₀	Raman	structure assigned to torsional modes; asymmetric potential	162

¹⁴⁵ J. R. Durig, G. A. Guirgis, and Y. S. Li, *J. Chem. Phys.*, 1981, **74**, 5946.¹⁴⁶ L. Halonen, E. Friz, A. G. Robiette, and I. M. Mills, *J. Mol. Spectrosc.*, 1980, **79**, 432.¹⁴⁷ J. Sheridan, W. Bossert, and A. Bauder, *J. Mol. Spectrosc.*, 1980, **80**, 1.¹⁴⁸ J.-M. Colmont, *J. Mol. Spectrosc.*, 1980, **80**, 166.¹⁴⁹ W. Caminati, *J. Mol. Spectrosc.*, 1981, **86**, 193.¹⁵⁰ M. Hayashi, M. Adachi, and J. Nakagawa, *J. Mol. Spectrosc.*, 1981, **86**, 129.¹⁵¹ W. Caminati and E. B. Wilson, *J. Mol. Spectrosc.*, 1980, **81**, 356.¹⁵² M. D. Harmony and M. R. Strand, *J. Mol. Spectrosc.*, 1980, **81**, 308.¹⁵³ M. Hayashi, J. Nakagawa, and Y. Aguni, *Bull. Chem. Soc. Jpn.*, 1980, **53**, 2468.¹⁵⁴ S. Bomar, E. Bay, H.-G. Kraft, and J. W. Bevan, *J. Mol. Spectrosc.*, 1981, **87**, 482.¹⁵⁵ F. Karlsson and Z. Smith, *J. Mol. Spectrosc.*, 1980, **81**, 327.¹⁵⁶ R. D. Brown, P. D. Godfrey, and A. L. Ottrey, *J. Mol. Spectrosc.*, 1980, **81**, 303.¹⁵⁷ M. Hayashi, J. Nakagawa, and H. Kato, *J. Mol. Spectrosc.*, 1980, **84**, 362.¹⁵⁸ N. D. Sanders, *J. Mol. Spectrosc.*, 1981, **86**, 27.¹⁵⁹ A. Bouchy and M. J. Ledoux, *J. Mol. Spectrosc.*, 1980, **80**, 453.¹⁶⁰ P. R. R. Langridge-Smith, R. Stevens, and A. P. Cox, *J. Chem. Soc., Faraday Trans. 2*, 1980, **76**, 330.¹⁶¹ A. C. Fantoni, R. R. Filgueira, L. M. Boggia, and W. Caminati, *J. Mol. Spectrosc.*, 1980, **84**, 493.¹⁶² D. A. C. Compton, S. Montero, and W. F. Murphy, *J. Phys. Chem.*, 1980, **84**, 3587.

Table 4 (continued)

Molecule	Technique	Comments	Ref.
C ₄ H ₁₀ O (<i>trans, trans</i> -methyl propyl ether)	MW	<i>r</i> _s , barrier to internal rotation of CH ₃ C group	163
C ₅ HN (cyanobutadiyne)	MW	excited states of ν ₁₀ and ν ₁₁	164
C ₅ H ₄ NBr (3-bromopyridine)	MW	hfs	165
C ₅ H ₈ O (tetrahydropyran-4-one)	MW	chair conformation; dipole moment	166
C ₅ H ₈ SO (4-thiacyclohexanone)	MW, RFMWDR	chair conformation	167
C ₅ H ₁₀ (<i>cis</i> -2-pentene)	MW	barrier to internal rotation about C ₁ -C ₂ axis; excited states of C ₃ -C ₄ torsion exhibit further spectral splitting due to tunnelling between the 2 equivalent skew conformations	168
C ₆ H ₅ FO (3-fluorophenol)	MW	<i>r</i> ₀ structure proposed	169
C ₆ H ₉ N (cyanocyclopentane)	MW	axial and equatorial conformers	170
C ₇ HN (cyanohexatriyne)	MW		171
C ₇ H ₈ (All ¹³ C monosubstituted toluenes)	MW	substitution structure; elongation of ring along symmetry axis, short ring-methyl C-C bond	172
C ₇ H ₁₄ Si (1-silabicyclo[2.2.2.]octane)	MW	skeletal torsion with double minimum function	173

Table 5 Rotational (and other low frequency) spectroscopic studies of loosely bound complexes

Molecule	Technique	Comments	Ref.
ArC ₂ H ₂	MBER	hfs; T-shaped	174
ArCH ₃ Cl	MBER	T-shaped	175
ArClCN	FTMW	hfs; T-shaped	176
ArH ₂	MBR	hfs; partial potential	177
ArHBr	MBER	hfs (Br, D); linear (but large amplitude motion)	178
ArHBr	FTMW	hfs (Br); linear	179

¹⁶³ H. Kato, J. Nakagawa, and M. Hayashi, *J. Mol. Spectrosc.*, 1980, **80**, 272.

¹⁶⁴ M. Hutchinson, H. W. Kroto, and D. R. M. Walton, *J. Mol. Spectrosc.*, 1980, **82**, 394.

¹⁶⁵ S. Doraiswamy and S. D. Sharma, *J. Mol. Spectrosc.*, 1981, **88**, 95.

¹⁶⁶ J. L. Alonso, *J. Mol. Spectrosc.*, 1980, **84**, 520.

¹⁶⁷ J. L. Alonso, *J. Mol. Spectrosc.*, 1981, **87**, 110.

¹⁶⁸ B. P. van Eijck, *J. Mol. Spectrosc.*, 1981, **85**, 189.

¹⁶⁹ A. I. Jaman, R. N. Nandi, and D. K. Ghosh, *J. Mol. Spectrosc.*, 1981, **86**, 269.

¹⁷⁰ Jong-In Choe and M. D. Harmony, *J. Mol. Spectrosc.*, 1980, **81**, 480.

¹⁷¹ C. Kirby, H. W. Kroto, and D. R. M. Walton, *J. Mol. Spectrosc.*, 1980, **83**, 261.

¹⁷² V. Amir-Ebrahimi, A. Choplin, J. Demaison, and G. Roussy, *J. Mol. Spectrosc.*, 1981, **89**, 42.

¹⁷³ A. Kawaguchi, T. Tanaka, E. Hirota, K. Mochida, and H. Sakurai, *J. Mol. Spectrosc.*, 1980, **79**, 168.

¹⁷⁴ R. L. DeLeon and J. S. Muentner, *J. Chem. Phys.*, 1980, **72**, 6020.

¹⁷⁵ R. L. DeLeon and J. S. Muentner, *J. Chem. Phys.*, 1981, **75**, 1113.

¹⁷⁶ M. R. Keenan, D. B. Wozniak, and W. H. Flygare, *J. Chem. Phys.*, 1981, **75**, 631.

¹⁷⁷ M. Waaijer, and J. Reuss, *Chem. Phys.*, 1981, **63**, 263.

¹⁷⁸ K. C. Jackson, P. R. R. Langridge-Smith, and B. J. Howard, *Mol. Phys.*, 1980, **39**, 817.

¹⁷⁹ M. R. Keenan, E. J. Campbell, T. J. Balle, W. Buxton, T. K. Minton, P. D. Soper, and W. H. Flygare, *J. Chem. Phys.*, 1980, **72**, 3070.

Table 5 (continued)

Molecule	Technique	Comments	Ref.
ArHCl	calculation	rotation and vibrational energy levels	180
ArHCl	data fitting	anisotropic PES obtained using mol. beam spectra, line broadening, 2nd virial coefficients and scattering X-sections	181
ArHCl	MBER	centrifugal distortion of eQq in $\text{Ar} \cdots \text{H}(\text{D})^{35}\text{Cl}$	182
ArHCl	FTSMMW	spectra from internal rotary motion of HCl sub-unit	183
Ar ² HF	FTMW	nuclear spin–nuclear spin interactions	184
ArHF	MBER	hfs; hyperfine parameters with 1 kHz resolution	185
ArN ₂ O	MBER	tunnels through low barrier at C_{2v} ,	186
ArSO ₂	MBER	interchanging the two O atoms	187
ArSO ₃	MBER	symmetric rotor	188
KrH ₂	MBR	hfs; partial potential	177
KrHBr	FTMW	hfs; linear	179
KrHCl	FTSMMW	spectra from internal rotary motion of HCl sub-unit	183
KrHCl	FTMW	^{82,84,86} Kr, ^{1,2} H ^{35,37} Cl: all combinations	189
KrHCl	MBER	linear; nuclear spin–spin and spin–rotation	190
KrHCl	FTMW	⁸³ Kr eQq	191
KrHF	FTMW	includes ⁸³ Kr eQq	192
KrHF	FTMW	includes ⁸³ Kr eQq	193
NeH ₂	MBR	hfs; potential	177
Ne ² HCl	MBER	linear, extremely non-rigid; (Ne ¹ HCl seems non-polar)	194
XeHCl	FTMW	includes ¹³¹ Xe eQq	195
Xe ² HCl	FTMW	includes ¹³¹ Xe eQq	191
XeHCl	FTSMMW	spectra from internal rotary motion of HCl sub-unit	183
XeHF	MBER	includes ¹³¹ Xe eQq	196
(Br ₂) ₂	electric deflection	polar	197

¹⁸⁰ I. F. Kidd, G. G. Balint-Kurti, and M. Shapiro, *Faraday Discuss. Chem. Soc.*, 1981, **71**, 287.¹⁸¹ J. M. Hutson and B. J. Howard, *Mol. Phys.*, 1981, **43**, 493.¹⁸² J. M. Hutson and B. J. Howard, *J. Chem. Phys.*, 1981, **74**, 6520.¹⁸³ E. W. Boom and J. van der Elsken, *J. Chem. Phys.*, 1980, **73**, 15.¹⁸⁴ M. R. Keenan, L. W. Buxton, E. J. Campbell, A. C. Legon, and W. H. Flygare, *J. Chem. Phys.*, 1981, **74**, 2133.¹⁸⁵ T. A. Dixon, C. H. Joyner, F. A. Baiocchi and W. Klemperer, *J. Chem. Phys.*, 1981, **74**, 6539.¹⁸⁶ C. H. Joyner, T. A. Dixon, F. A. Baiocchi and W. Klemperer, *J. Chem. Phys.*, 1981, **75**, 5285.¹⁸⁷ R. L. DeLeon, A. Yokozeki, and J. S. Muenter, *J. Chem. Phys.*, 1980, **73**, 2044.¹⁸⁸ K. H. Bowen, K. R. Leopold, and W. Klemperer, *J. Chem. Phys.*, 1980, **73**, 137.¹⁸⁹ T. J. Balle, E. J. Campbell, M. R. Keenan, and W. H. Flygare, *J. Chem. Phys.*, 1980, **72**, 923.¹⁹⁰ A. E. Barton, T. J. Henderson, P. R. R. Langridge-Smith, and B. J. Howard, *Chem. Phys.*, 1980, **45**, 429.¹⁹¹ E. J. Campbell, L. W. Buxton, M. R. Keenan, and W. H. Flygare, *Phys. Rev. A*, 1981, **24**, 812.¹⁹² E. J. Campbell, M. R. Keenan, L. W. Buxton, T. J. Balle, P. D. Soper, A. C. Legon, and W. H. Flygare, *Chem. Phys. Lett.*, 1980, **70**, 420.¹⁹³ L. W. Buxton, E. J. Campbell, M. R. Keenan, T. J. Balle, and W. H. Flygare, *Chem. Phys.*, 1981, **54**, 173.¹⁹⁴ A. E. Barton, D. J. B. Howlett, and B. J. Howard, *Mol. Phys.*, 1980, **41**, 619.¹⁹⁵ M. R. Keenan, L. W. Buxton, E. J. Campbell, T. J. Balle, and W. H. Flygare, *J. Chem. Phys.*, 1980, **73**, 3523.¹⁹⁶ F. A. Baiocchi, T. A. Dixon, C. H. Joyner, and W. Klemperer, *J. Chem. Phys.*, 1981, **75**, 2041.¹⁹⁷ K. V. Chance, K. H. Bowen, J. S. Winn, and W. Klemperer, *J. Chem. Phys.*, 1980, **72**, 791.

Table 5 (continued)

Molecule	Technique	Comments	Ref.
(ClF) ₂	electric deflection	polar	197
(F ₂) ₂	electric deflection	slightly polar	197
(H ₂) ₂	MBER	<i>o-o</i> and <i>o-p</i> dimers, hfs	198
(H ₂) ₂	analysis of ref. 198	<i>o-p</i> dimer, hfs; takes into account continuum states	199
(H ₂ O) ₂	MBER	partially deuteriated; symmetry plane, <i>trans</i> and quasi-linear H-bond; hfs \Rightarrow tunnelling rotational levels	200
H ₂ O · HF	MW		201
(ICl) ₂ , (ICl) ₃	electric deflection	both polar	197
(NO) ₂	MBER	<i>cis</i> planar; large spin rotation constants \Rightarrow low lying electronic states	202
N ₂ O · HF	MBER	not similar to CO ₂ · HF	203
N ₂ SO ₃	MBER	symmetric rotor	188
(SO ₃) ₂ , (SO ₃) ₃	electric deflection	both planar	188
CO · HX (X = F, Cl, Br)	FTMW	OC \cdots HX bond	204
CO · HF	FTMW	¹⁹ F nuclear spin–nuclear spin, ² H nuclear quadrupole coupling; linear equilibrium geometry	205
CO · HCl	FTMW	hfs	206
CO ₂ HF	MBER	nearly linear OCO–HF	207
HCN · HF	MW		208
SCO · HF	MBER		207
CH ₃ CN · HF	MW		209
C ₂ H ₂ · HCl	FTMW	hfs; T-shaped π complex, C _{2v} planar	210
C ₂ H ₄ · HCl	FTMW	hfs; non-planar, near prolate asymmetric top (equilibrium C _{2v})	211
(CH ₂) ₂ O · HF	MW	also IR	212
C ₂ N ₂ · HF	FTMW	hfs	213
(HCN) ₂	FTMW		214
C ₃ H ₆ · HF (cyclopropane)	FTMW	hfs – HF \perp to Δ edge, and in plane of ring	215
(CH ₃) ₃ NN · HF	MW	also IR	216

¹⁹⁸ J. Verberne and J. Reuss, *Chem. Phys.*, 1980, **50**, 137.¹⁹⁹ M. Waaijer, M. Jacobs, and J. Reuss, *Chem. Phys.*, 1981, **63**, 257.²⁰⁰ J. A. Odutola and T. R. Dyke, *J. Chem. Phys.*, 1980, **72**, 5062.²⁰¹ J. W. Bevan, Z. Kisiel, A. C. Legon, D. J. Millen, and S. C. Rogers, *Proc. R. Soc. London, Ser. A*, 1980, **372**, 441.²⁰² C. M. Western, P. R. R. Langridge-Smith, B. J. Howard, and S. E. Novick, *Mol. Phys.*, 1981, **44**, 145.²⁰³ C. H. Joyner, T. A. Dixon, F. A. Baiocchi, and W. Klemperer, *J. Chem. Phys.*, 1981, **74**, 6550.²⁰⁴ A. C. Legon, P. D. Soper, M. R. Keenan, T. K. Minton, T. J. Balle, and W. H. Flygare, *J. Chem. Phys.*, 1980, **73**, 583.²⁰⁵ A. C. Legon, P. D. Soper, and W. H. Flygare, *J. Chem. Phys.*, 1981, **74**, 4944.²⁰⁶ P. D. Soper, A. C. Legon, and W. H. Flygare, *J. Chem. Phys.*, 1981, **74**, 2138.²⁰⁷ F. A. Baiocchi, T. A. Dixon, C. H. Joyner, and W. Klemperer, *J. Chem. Phys.*, 1981, **74**, 6544.²⁰⁸ A. C. Legon, D. J. Millen, and S. C. Rogers, *Proc. R. Soc. London, Ser. A*, 1980, **370**, 213.²⁰⁹ J. W. Bevan, A. C. Legon, D. J. Millen, and S. C. Rogers, *Proc. R. Soc. London, Ser. A*, 1980, **370**, 239.²¹⁰ A. C. Legon, P. D. Aldrich, and W. H. Flygare, *J. Chem. Phys.*, 1981, **75**, 625.²¹¹ P. A. Aldrich, A. C. Legon, and W. H. Flygare, *J. Chem. Phys.*, 1981, **75**, 2126.²¹² A. S. Georgiou, A. C. Legon, and D. J. Millen, *Proc. R. Soc. London, Ser. A*, 1980, **373**, 511.²¹³ A. C. Legon, P. D. Soper, and W. H. Flygare, *J. Chem. Phys.*, 1981, **74**, 4936.²¹⁴ L. W. Buxton, E. J. Campbell, and W. H. Flygare, *Chem. Phys.*, 1981, **56**, 399.²¹⁵ L. W. Buxton, P. D. Aldrich, J. A. Shea, A. C. Legon, and W. H. Flygare, *J. Chem. Phys.*, 1981, **75**, 2681.²¹⁶ A. S. Georgiou, A. C. Legon, and D. J. Millen, *Proc. R. Soc. London, Ser. A*, 1980, **370**, 257.

The Microwave Region.—A guide to the current state of much of the art of microwave spectroscopy exists as the compendium ‘Modern Aspects of Microwave Spectroscopy’, edited by G. W. Chantry.²¹⁷ This contains articles on microwave spectrometers (Roussy and Chantry), MWMW double resonance (Baker), IRMW double resonance (Jones), submillimetre scanning spectroscopy (Krupnov), interferometric spectrometry at millimetre and submillimetre wavelengths (Fleming), and the astrophysics of interstellar molecules (Winnewisser, Churchwell, and Walmsley).

We shall return later to recent developments in some of these areas, but shall first consider one of the principal objectives of conventional microwave spectroscopy, namely the determination of molecular structure. An example of continuing development in this area is provided by studies on phosgene, COCl₂, which in particular illustrate some of the different approximations to ‘structure’ which may be derived, although their discussion is necessarily somewhat involved.

Carpenter and Rimmer²¹⁸ measured the microwave spectrum of phosgene, and determined a harmonic force field. They obtained a ground-state structure for the molecule (the *r*₀ structure), and also an average or *r*_z structure. The *r*_z structure was produced using the *r*₀ structure and the harmonic force field, using rotational constants calculated as

$$A_z = A_0 + \frac{1}{2} \sum_i (\alpha_i^A)_{\text{harmonic}}$$

where the contributions from the harmonic force field are summed over normal modes.

Microwave spectroscopy cannot supply a complete set of geometrical parameters for one isotopic species of even a fairly simple polyatomic molecule like COCl₂, because the number of rotational constants which can be determined for a single species is less than the number of parameters required. Measurements for different isotopic species were made in the study mentioned above. The *r*_z structure, however, changes on any isotopic substitution, but such changes are usually neglected in the analysis because to do otherwise would require information (not generally available) on the anharmonicity of molecular vibrations. Nakata *et al.*⁶⁵ have considered this problem: in the relatively favourable case when the substitution is of a heavy atom, only small changes in *r*_z parameters result (less than $\pm 0.002 \text{ \AA}$ for bond lengths and $\pm 0.01^\circ$ for bond angles), but, they point out, even such small uncertainties may produce consequent uncertainties of $\sim 0.01 \text{ \AA}$ or $\sim 1^\circ$ when using isotopic rotational constants to derive *r*_z structural parameters.

COCl₂ was convenient to study because it is comparatively easy to prepare a number of different isotopic species (the eight molecules where *C*_{2v} symmetry is preserved, and analysis thus simplified, being particularly desirable), and also because it was possible to obtain complementary electron diffraction structural data.⁶⁵ (The electron diffraction data represent an average over the species at natural isotopic abundance, but here it was possible to neglect isotopic dependence in the analysis, since isotopic differences were much smaller than structure uncertainties.) Microwave and electron diffraction results were shown to be mutually consistent within their confidence limits; indeed for COCl₂ the structure, free of isotope effects, could be determined by electron diffraction data alone. Thus by analysing the microwave data

²¹⁷ G. W. Chantry, ed., ‘Modern Aspects of Microwave Spectroscopy’, Academic Press, New York, 1979.

²¹⁸ J. H. Carpenter and D. F. Rimmer, *J. Chem. Soc., Faraday Trans. 2*, 1979, **74**, 466.

using a model anharmonic potential, it was possible to obtain information *about* anharmonic potential constants: information on isotopic differences could be obtained from rotational constants for the different isotopic species.

Allowing for, as opposed to neglecting entirely, isotopic variations when calculating the r_z structure changed structural parameters by up to $\pm 0.02 \text{ \AA}$ and $\pm 1^\circ$. Even calculations made using anharmonic constants for the constituent diatomic molecules of phosgene, CO and CCl, were not entirely satisfactory. It was shown that, when neglecting isotopic differences, the r_z parameters obtained depended strongly on the set of isotopic species used in the analysis, although this last systematic error could be greatly reduced by incorporating data from different sets of species. The effective anharmonic constants were further combined with the r_z parameters to obtain equilibrium r_e bond lengths for the molecule, parameters which cannot normally be derived without additional vibrational information.

The lack of vibrational information, or the existence of perturbations, *etc.*, even when it is available, may make the determination of the r_e structure very difficult. Because of this difficulty, an approximation to the r_e structure, which uses data from the substitution structure* and the zero-point moments of inertia, was proposed; this is the mass-dependent (r_m) structure.[†] In an additional paper Nakata *et al.*⁶⁴ using Kraitchman's equations, obtained eight substitution structures from four pairs of isotopic species of phosgene, then used the r_s co-ordinates to obtain r_m structural parameters. Phosgene was a suitable molecule with which to extend r_m structure determination beyond a three atom system. Attention was paid to the relationship between I_m and I_e , and to which r_m parameters should be a good approximation to corresponding r_e parameters. Those r_m parameters were combined with the r_e bond distances determined earlier (from the MW and electron diffraction studies) to provide a set of precise r_e parameters: $r_e(\text{C}=\text{O}) = 1.1756 \pm 0.0023 \text{ \AA}$; $r_e(\text{C}-\text{Cl}) = 1.7381 \pm 0.0019 \text{ \AA}$; $\angle_e \text{Cl}-\text{C}-\text{Cl} = 111.79 \pm 0.24^\circ$.

Another determination of r_z structure combining MW and electron diffraction data was carried out for COF_2 .⁶⁶ In this case the values obtained for the structural parameters [$r_z(\text{C}=\text{O}) = 1.1717 \pm 0.013 \text{ \AA}$; $r_z(\text{C}-\text{F}) = 1.3157 \pm 0.005 \text{ \AA}$; $\angle_z \text{F}-\text{C}-\text{F} = 107.71 \pm 0.08^\circ$] agree well with those which had been derived earlier from rotational constants alone,²²² but in this study it was additionally possible to estimate effective constants for the cubic anharmonicity of bond stretching vibrations.

The comparison between r_m and r_e structures is further considered in an

* The substitution structure is obtained by locating each atom from the change in experimental moment of inertia which results when one atom in a molecule is isotopically substituted: the relatively simple equations of Kraitchman²¹⁹ provide a means of doing this. They have been extended to allow for limited multiple substitution, and Wilson and Smith²²⁰ have produced generalized equations valid for multiple substitution in planar molecules and molecules which retain a symmetry plane on substitution.

† Watson²²¹ proposed the mass-dependent structure. It is based on the approximation

$$I_e = 2I_s - I_0$$

derived from a first-order treatment of isotope effects appropriate for certain types of molecule. ' I_e ' so derived is normally denoted I_m .

²¹⁹ J. Kraitchman, *Am. J. Phys.*, 1953, **21**, 17.

²²⁰ E. B. Wilson and Z. Smith, *J. Mol. Spectrosc.*, 1981, **87**, 569.

²²¹ J. K. G. Watson, *J. Mol. Spectrosc.*, 1973, **48**, 479.

²²² J. H. Carpenter, *J. Mol. Spectrosc.*, 1974, **50**, 182.

investigation of Cl_2O .³³ Here it is suggested that a good approximation to the equilibrium structure may be achieved by calculating the so called r_c structure; this takes an average of r_m structures from complementary pairs of isotopic species chosen in such a way as to cancel out second-order differences between equilibrium and mass dependent parameters.

Transient Species. Microwave spectroscopy continues to be an important probe of transient species. Several isotopic variants of methyl sulphido boron, ($\text{CH}_3\text{B}=\text{S}$), have been studied in the range 26.5—40.0 GHz, and around 9.1 GHz.¹⁰⁵ It was prepared by passing dimethyl disulphide over crystalline boron at 1000 °C, and found to have a half-life of 1—2 s at a pressure of 20 μm Hg (no CH_3SB was observed). A complete substitution structure was obtained, and the value for r_s (C—B), $1.5352 \pm 0.0041 \text{ \AA}$, is the first determination of bond length between an sp hybridized boron atom and an sp^3 hybridized carbon atom. Dipole and quadrupole moments were also determined, and a vibration-rotation analysis carried out.

The new radical FSO has been identified from analysis of its microwave spectrum.³⁷ It was generated by allowing carbonyl sulphide to react with the products of a microwave discharge of an oxygen/carbon tetrafluoride mixture. Spectra were measured in the region 30—80 GHz, and involved the ground vibrational state of the normal and ^{34}S species, and the first excited bending state of the normal species. Hyperfine interaction constants and dipole moment were measured, and an r_0 structure and harmonic force field calculated. By considering spin-rotation and hyperfine interaction constants, it was inferred that the ground electronic state of FSO is ${}^2\text{A}''$ (for example, the components of the spin-rotation interaction constant indicate that the unpaired electron is located in a p -type MO perpendicular to the plane of the molecule). FSO has also been detected by LMR.²²³

The technique of observing coherent transients by pulsed Fourier transform microwave spectroscopy, which was described in Part I,¹ has been applied to many molecular species, and applications to loosely bound complexes will be discussed later. A semi-classical description of the experiment, using density matrix formalism, has been presented,²²⁴ and the technique has been used to study the gas dynamics of the pulsed supersonic nozzle source that forms part of the experiment.²²⁵

Microwave Stark modulation spectroscopy has also been performed on continuous supersonic molecular beams. The $J = 1 \rightarrow 0$ transition in OCS, in pure, and argon and helium seeded, beams has been observed. The beam and microwave radiation were in a parallel configuration, and high resolution was obtained.^{54b} The method of power switching in the creation of microwave coherent transients has been advocated by Shimizu *et al.*²²⁶ Their technique avoids large changes in radiation power at the detector which would make signal detection difficult, and has been applied to relaxation studies, particularly of NH_3 , whilst transitions in H_2O , OCS, and O_2 have also been observed.

²²³ F. D. Wayne and H. E. Radford, unpublished, report in ref. 37.

²²⁴ E. J. Campbell, L. W. Buxton, T. J. Balle, and W. H. Flygare, *J. Chem. Phys.*, 1981, **74**, 813.

²²⁵ E. J. Campbell, L. W. Buxton, T. J. Balle, M. R. Keenan, and W. H. Flygare, *J. Chem. Phys.*, 1981, **74**, 829.

²²⁶ T. Shimizu, N. Morita, T. Kasuga, H. Sasada, F. Matsushima, and N. Konishi, *Appl. Phys.*, 1980, **21**, 29.

Interstellar Molecules. Over fifty molecules have now been spectroscopically identified in the interstellar medium, many of these by transitions which occur in the radio and microwave regions. Conclusive assignment generally relies on the preparation and investigation of particular species in the laboratory, and this is often difficult. Wilson²²⁷ has reviewed the contribution which theoretical studies have made to the assignment of interstellar spectral lines, particularly with regard to radicals and ions, and discussed some assignments which have subsequently been confirmed in laboratory studies. Earthbound studies of prospective interstellar molecules continue; cyanohexatriyne, HC_6N , has been successfully synthesized and its microwave spectrum measured¹⁷¹ (see Figure 1) despite problems with the sample decomposing during the run, and it has

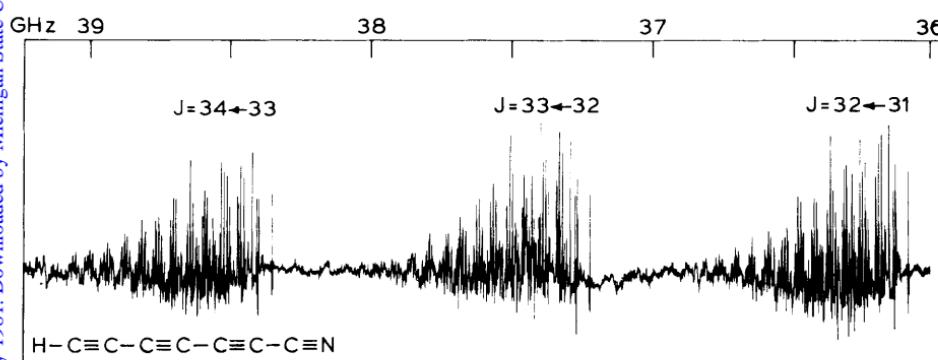


Figure 1 Rotational spectrum of $\text{H}(\text{C}\equiv\text{C})_3\text{CN}$ in the range 36–39 GHz. Each $\Delta J = +1$ transition consists of a readily identified ground-state transition followed to higher frequency by a plethora of vibrational satellites. This run was made from low to high frequency and the sample was decomposing as the run progressed

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been identified in the interstellar medium. [The identification in space of HC_9N , reported in Part I,¹ was based on an extrapolation technique using data from studies on lower members of the series HC_nN ($n = 1, 3, 5, 7$).²²⁸]

Kroto²²⁹ has written a wide ranging review of the spectra of interstellar molecules. It covers fundamentals of both the spectroscopy and the astronomy, the nature of the interstellar medium, the types of spectra which are observed (not only in the MW region) and discusses some of the possible pathways of interstellar chemistry. Data on transitions in interstellar molecules has been evaluated, and tables of 'recommended rest frequencies' produced.²³⁰

The Millimetre/Submillimetre Wave Region.—Many light molecules undergo their strongest rotational transitions at frequencies greater than those associated with the conventional microwave region, but on leaving this region the provision of a suitable source of radiation becomes more difficult. We discussed some methods for resolving

²²⁷ S. Wilson, *Chem. Rev.*, 1980, **80**, 263.

²²⁸ T. Oka, *J. Mol. Spectrosc.*, 1978, **72**, 172.

²²⁹ H. W. Kroto, *Int. Rev. Phys. Chem.*, 1981, **1**, 309.

²³⁰ F. J. Lovas, L. E. Snyder, and D. R. Johnson, *Astrophys. J. Suppl. Ser.*, 1979, **41**, 451.

this difficulty in Part I.¹ De Lucia *et al.*²³¹ have reviewed gas-phase approaches to the source problem for the 'near millimetre wave' region (100—1000 GHz), and in particular discuss various methods of pumping 'NMMW' lasers.

Sub-Doppler submillimetre spectroscopy has been performed on molecular beam samples using tunable laser sidebands as the radiation source.²³² The output from a submillimetre laser (*e.g.* the 432 μm line of HCOOH) was mixed with tunable microwave radiation using the non-linearity of a Schottky diode, and the resulting tunable sidebands interacted with molecular beams effusing out of an array of parallel capillary tubes. For strong transitions, linewidths an order of magnitude narrower than the Doppler width were observed, as illustrated in Figure 2.

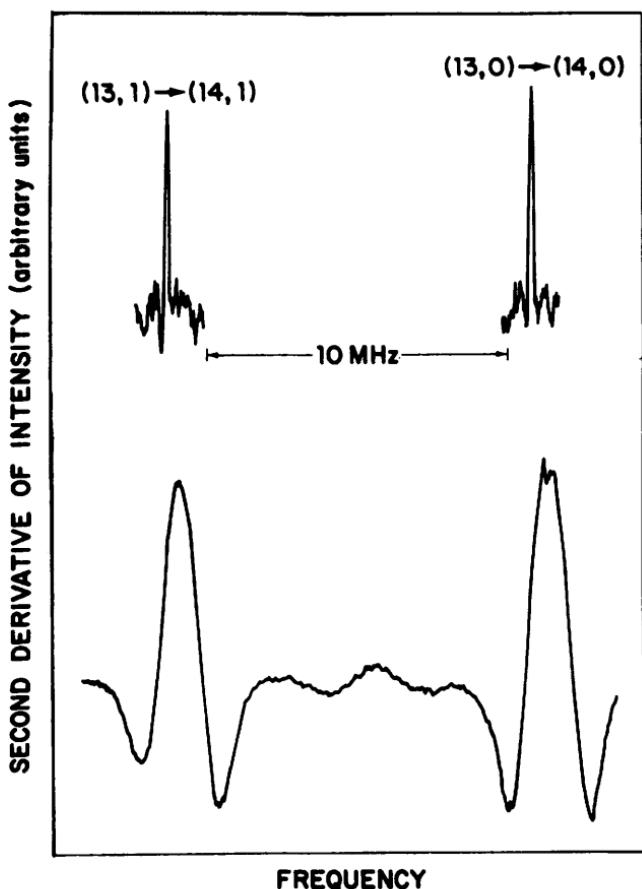


Figure 2 Sub-Doppler submillimetre spectroscopy using molecular beams. Top: second derivatives of Sub-Doppler linewidth absorptions due to the $(J, K) = (13, 0) \rightarrow (14, 0)$ and $(13, 1) \rightarrow (14, 1)$ rotational transitions in the ground state of CH_3F obtained with the molecular beam spectrometer. The driving pressure was 0.50 Torr. Bottom: the same transition observed with static cell

(Reproduced by permission from *Appl. Phys. Lett.*, 1981, **39**, 857)

²³¹ F. C. de Lucia, E. Herbst, M. S. Feld, and W. Harper, *IEEE J. Quant. Electron.*, 1981, **17**, 2171.

²³² W. A. M. Blumberg, D. D. Peck, and H. R. Fetterman, *Appl. Phys. Lett.*, 1981, **39**, 857.

Progress has been made in the measurement of millimetre wave spectra of high temperature species. Helms, Winnewisser, and Winnewisser⁹ have studied BaS in a low pressure flame, and have provided a detailed description of their experiment, which has been extended into the submillimetre region. They attribute improvements in sensitivity and spectral coverage to the use of a larger volume low pressure flame reaction sphere, better source stabilization, and the use of a helium-cooled InSb photoconducting detector.

The ethynyl radical, C₂H, had exhibited a reluctance to show itself conclusively in the laboratory, but its spectrum has now been measured in the 174—350 GHz region, the radical having been produced in a glow discharge.³⁰ Spectral constants are reported to be in excellent agreement with those derived from radioastronomical observations. (C₂H has also been detected by LMR,^{233,234} and an electronically excited state has been observed — see Section 3).

Raman Spectroscopy.—Molecular hydrogen, with its high B values, is a molecule more amenable than most to rotational Raman spectroscopy. Dayan and Viennot²³⁵ have observed the effects of high pressures (up to 400 bar) of foreign gases (N₂, CO₂, C₂H₄, C₂H₆) on the linewidth of the H₂ anti-Stokes rotational line $J = 3 \rightarrow 1$ at 595 cm⁻¹. They show that the broadening is characteristic of the foreign gas, and suggest that the quadrupole-quadrupole interaction dominates the anisotropic intermolecular potential (there being no permanent dipoles).

The low B values of non-hydrides present a problem also for rotational CARS experiments. CARS is generally a three-colour experiment. Two lasers, of frequencies ω_1 and ω_2 , irradiate a sample, usually collinearly. At least one of these lasers is normally a dye laser, and when the tuning is such that $\omega_1 - \omega_2$ is the frequency ω_r of a Raman active transition of the molecule, a coherent signal is generated at a frequency $\omega_3 = 2\omega_1 - \omega_2$. The direction of this emission depends on the wave vectors of the input beams. When ω_r is small, as it is for rotational transitions, $\omega_1 \approx \omega_2 \approx \omega_3$, and it becomes difficult to separate the signal beam both from the input beams and from the considerable superradiance which is emitted by the tunable laser at the signal frequency.

One way around these problems was found by Beattie *et al.*,²³⁶ performing a four-colour experiment (see Figure 3). They used two tunable dye lasers with orthogonally polarized outputs of frequencies ω_1 and ω_2 , and one fixed-frequency (doubled Nd:YAG) laser of frequency ω_3 considerably different to ω_1 and ω_2 . Because of this difference it was not difficult to separate ω_1 and ω_2 from ω_3 , and the separation of ω_3 from the associated CARS signal ω_4 could be achieved because of their different polarization. The superradiance problem was made negligible by the use of a fixed-frequency solid-state laser in place of a dye laser. Using this technique ¹⁴N₂ and ¹⁶O₂ bands in air were observed, and resolution of 0.01 cm⁻¹ was achieved (0.2 cm⁻¹ was routine).

Roland and Steele¹⁷ have approached the same problem with a three-colour experiment. Again by management of polarizations, but by using an interference filter to block superradiance and a monochromator for beam separation, they also observed

²³³ R. J. Saykally, D. M. Renter, L. M. Ziurys, and K. M. Evenson, unpublished, reported in ref. 30.

²³⁴ R. J. Saykally and K. M. Evenson, 33rd Symposium on Molecular Spectroscopy, 1978, Columbus, Ohio.

²³⁵ E. Dayan and J. P. Viennot, *J. Raman Spectrosc.*, 1980, **9**, 344.

²³⁶ I. R. Beattie, T. R. Gilson, and D. A. Greenhalgh, *Nature (London)*, 1978, **276**, 378.

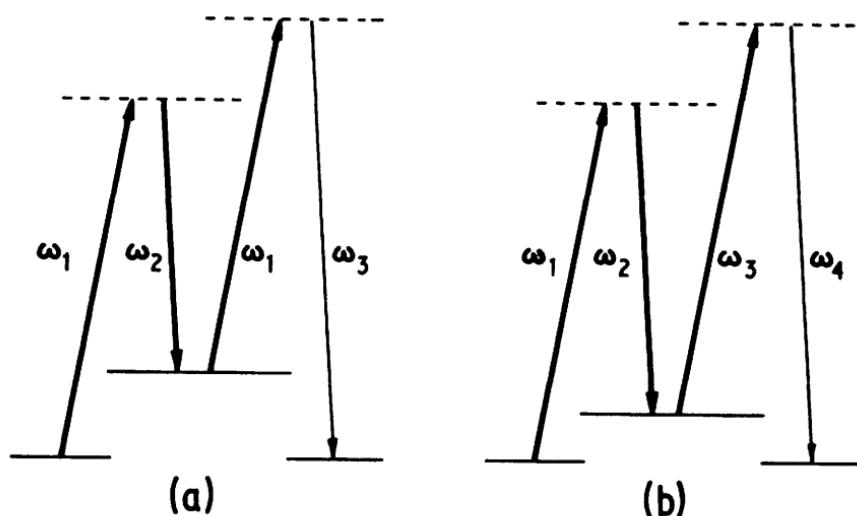


Figure 3 (a) Three- and (b) four-colour Raman spectroscopy
(After *Nature*, 1978, **276**, 378)

N_2 and O_2 transitions in air, and found good agreement between measured and calculated lineshapes and intensities. The techniques are good down to frequencies ω_r of about 40 cm^{-1} .

Laser Magnetic Resonance Spectroscopy.—Laser magnetic resonance spectroscopy is now a well established technique for the study of rotational transitions which lie in the far infrared, and typical apparatus was shown in Part I.¹ In the Spiers Memorial Lecture to the Faraday Society, Evenson²³⁷ considered far infrared LMR, and presented a comprehensive summary of all FIRLMR papers to date (May 1981), as well as a number of pre-publication results. A more discursive review of this branch of spectroscopy has been presented by Evenson *et al.*,²³⁸ and Davies²³⁹ has described LMR spectroscopy and its application in kinetics and laboratory astrophysics.

FIRLMR spectroscopy has the potential to produce precise molecular parameters, and this has been realized following analysis of the spectrum of CH_3O :¹⁰⁸ these parameters reflect the effect of Jahn-Teller perturbations (expected because of the unpaired electron and E symmetry of the ground state). The technique can also be used to probe transitions in metastable excited states (*e.g.*, $\text{PH}^1\Delta$, $\text{CO } a^3\Pi$, $\text{NF}^1\Delta$; see ref. 237). Five rotational transitions ($J = 4 \leftarrow 3$, $5 \leftarrow 4$, $7 \leftarrow 6$, $8 \leftarrow 7$, $9 \leftarrow 8$) of the ${}^{16}\text{O}_2$ molecule in $v = 0$ of its $a^1\Delta_g$ state have been observed, all of these being magnetic dipole transitions.²³ It was possible to saturate transitions and observe inverse Lamb dips. LMR, it is proposed, may become an important probe of this species in

²³⁷ K. M. Evenson, *Faraday Discuss. Chem. Soc.*, 1981, **71**, 7.

²³⁸ K. M. Evenson, R. J. Saykally, D. A. Jennings, R. F. Curl, jun., and J. M. Brown, 'Far infrared laser magnetic resonance' in 'Chemical and Biochemical Applications of Lasers', ed. C. B. Moore, Academic Press, New York, 1980, Vol. 5, p. 95.

²³⁹ P. B. Davies, *J. Phys. Chem.*, 1981, **85**, 2599.

atmosphere processes, and also provide information of importance in biological systems.

Ions.—‘Gaseous molecular ions are involved in some of the most intriguing problems in modern science.’ Thus Saykally and Woods begin their review of the high resolution spectroscopy of molecular ions.^{240a} The results of molecular ion spectroscopy may be significant in the elucidation of these problems, and spectroscopic developments are described. For example, the advance of rotational LMR to include molecular ions (reported in Part I¹) is discussed, as are microwave spectroscopy of ions and associated radioastronomical studies.

The molecular structure of HCO^+ has been determined by the microwave ($J = 0 \rightarrow 1$ transition) substitution method, the first determination of an r_s structure for a molecular ion [$r_s(\text{CO}) = 1.1071(2)$ Å; $r_s(\text{CH}) = 1.0930(1)$ Å].⁴⁰ The various isotopic species of HCO^+ were produced in a DC discharge. There was very good agreement between measurement and *ab initio* theoretical prediction, although satisfactory comparison is not strictly possible because theory predicts r_e rather than r_s structure (vibrational satellite spectra could not be found, and so the r_e structure could not be determined). A similar study⁵¹ has been carried out on N_2H^+ , and structure parameters [$r_s(\text{NN}) = 1.0947(4)$ Å; $r_s(\text{NH}) = 1.0320(1)$ Å] obtained which agreed ‘beautifully’ with *ab initio* calculations.

N_2H^+ and N_2D^+ , produced in a glow discharge, have also been observed in the millimetre and submillimetre regions of the spectrum,⁵² $J = 4 \rightarrow 5$ for N_2H^+ and $J = 5 \rightarrow 6$ for N_2D^+ . Further refinement of the structure of HCO^+ was presented in a study of its millimetre wave spectrum by Bogey *et al.*,⁴¹ the ions being produced in an electrodeless RF discharge of H_2/CO (D_2/CO). These results are combined with those of Woods *et al.*,⁴⁰ to yield centrifugal distortion constants.

The $J = 0 \rightarrow 1$ transition has been seen for the molecule HOC^+ (including ^{18}O and ^{13}C isotopic variants) in a glow discharge, and there is a strong suggestion of a large amplitude bending vibration.^{240b}

Loosely Bound Complexes.—In this sub-section we consider van der Waals and intramolecularly hydrogen-bonded complexes, although the greater amount of recent effort has been directed towards the investigation and understanding of van der Waals molecules. There have of course been studies of electronic transitions in such molecules, and these are reported later; for the moment we restrict coverage of experiments to low frequency spectroscopic investigations. The technique which has been most widely applied in such investigations is molecular beam electric resonance (MBER) spectroscopy, although in the last two years a large number of species have been studied using the pulsed Fourier transform microwave (FTMW) method. Both these techniques were described in Part I,¹ where some results were also discussed.

In a comprehensive review of this field by Le Roy and Carley,²⁴¹ particular attention is paid to the potential energy surfaces of van der Waals molecules, and the relationship between P.E. surfaces and spectroscopic information. For weakly bound diatomic molecules, Winn²⁴² has presented a systematic review which is also concerned

²⁴⁰ (a) R. J. Saykally and R. C. Woods, *Annu. Rev. Phys. Chem.*, 1981, **32**, 403; (b) C. S. Gudemann and R. C. Woods, *Phys. Rev. Lett.*, 1982, **48**, 1344.

²⁴¹ R. J. Le Roy and J. S. Carley, *Adv. Chem. Phys.*, 1980, **42**, 353.

²⁴² J. S. Winn, *Acc. Chem. Res.*, 1981, **14**, 341.

with potential energy curves. The potential well characteristics of a large number of weakly bound diatomics are considered so that some general and comparative conclusions may be drawn. Weak bonding, it is seen, is not generally associated with extensive charge delocalization (delocalization being taken to mean 'those changes in electronic structure that occur in the vicinity of R_e which contribute to bonding by reducing the relative rate of increase of the total electronic kinetic energy'), but there are notable variations in the degree of persistence of long range forces to shorter distances, and in the relative rates of appearance of repulsive forces. The onset of repulsion is abrupt in the heteronuclear rare gas dimers relative to the more gentle potential curvature of the alkaline-earth dimers, for example.

Caution is advised²⁴² in interpretation of potential well parameters because of the lack of experimental data corroborated by different techniques, and because of the occasional ability of different potentials to reproduce the same experimental results. Problems in characterizing potential energy surfaces for polyatomic complexes are of course even greater, but there has been progress in this area, particularly for atom-diatom complexes. Howard²⁴³ has shown how molecular beam rotational spectroscopic data can be used to characterize the well in the region around the minimum, and Hutson and Howard²⁴⁴ have demonstrated, with reference to ArHCl, a method for extracting good spectroscopic constants from a proposed surface. This is based on the BOARS (Born-Oppenheimer Angular Radial Separation) approximation. Conceptually similar to the Born-Oppenheimer separation of electronic and nuclear motion, BOARS is valid if the vibrational-rotational motion of the diatom in the complex is fast compared to the stretching frequency of the van der Waals bond, or the vibrational-rotational motion is not strongly dependent on the stretching co-ordinate. It allows the expression of the eigenfunctions as the product $Q(\theta;R)\chi(R)$ of separated angular and radial functions. Solving the angular problem at each value of R yielded eigenfunctions $Q_b(\theta;R)$ but for sufficiently accurate calculations it was found necessary to include the non-adiabatic coupling of different $Q_b(\theta;R)$. This could be done rapidly using a specially developed technique with general application, and the whole procedure was then termed the CBO (Corrected Born-Oppenheimer) method. It has also been applied to molecular beam spectroscopic data for (HF)₂.²⁴⁵

MBER spectroscopic results can, as we have said, only illuminate a particular region of the potential surface, although other experiments can probe different regions. Hutson and Howard¹⁸¹ have extended the region of determination of the anisotropic surface of ArHCl by simultaneous least-squares fitting to data from molecular beam spectra, rotational line-broadening cross sections, second virial coefficients and molecular beam total differential cross-sections. The equilibrium configuration is shown to be linear with the configuration Ar·HCl at a centre of mass Ar-HCl distance of 4 Å. The surface is well determined except in the region of a supposed shallow minimum near the linear Ar·Cl-H configuration, which is not sampled by the complex in its ground vibrational state.

The rare gas atom-hydrogen halides comprise the class of complexes most studied recently by low frequency spectroscopy. Balle *et al.*¹⁸⁹ chose to demonstrate their new

²⁴³ B. J. Howard, *Faraday Discuss. Chem. Soc.*, 1981, **71**, 23.

²⁴⁴ J. M. Hutson and B. J. Howard, *Mol. Phys.*, 1980, **41**, 1123.

²⁴⁵ A. E. Barton and B. J. Howard, *Faraday Discuss. R. Soc. Chem.*, 1982, **73**.

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technique of pulsed Fourier transform microwave spectroscopy by observing the rotational spectra of several isotopic species of KrHCl, including those containing ^{82}Kr , ^{84}Kr , and ^{86}Kr . As is typical for such complexes, the equilibrium configuration was found to be linear $\text{Kr} \cdot \text{HCl}$, but there is large amplitude vibration of H relative to the Kr–Cl internuclear axis. For isotopic species where data overlapped, there was generally good agreement with constants derived from a study of this complex by MBER spectroscopy,¹⁹⁰ in which it was possible to determine nuclear spin–spin and spin–rotation constants.

ArHCl has been more frequently studied and data incorporated in the potential energy surface determination; an interesting aspect of study concerns the centrifugal distortion of the nuclear quadrupole coupling constant.¹⁸² Such distortion occurs because the van der Waals bond stretches as the complex rotates, and at a slightly increased average molecular distance, the complex is subject to a slightly different angular potential. The measured effect is small, but indicates that the bending force constant increases with increasing intermolecular distance.

The X–Cl distance increases down the series ArHCl, KrHCl, XeHCl, because of the increase in size of the rare gas atom, with the overlap of the van der Waals radii remaining approximately constant. Increasing polarizability of the rare gas atom causes a reduction in bending amplitude.¹⁹⁰ This series of complexes has also been observed by Fourier transform spectroscopy at low temperature in the far infrared; these spectra were thought to originate from internal rotatory motion of the HCl sub-unit.¹⁸³

The rotational spectra and structures of ArHBr and KrHBr have been investigated (ArHBr by MBER¹⁷⁸ and both by pulsed FTMW¹⁷⁹), again revealing a linear $\text{Ar} \cdot \text{HF}$ configuration, and large amplitude vibrations. An MBER study of $\text{Ar} \cdot \text{HF}$ ¹⁸⁵ showed that the potential surface of this species is quite anharmonic even in the zero-point region, which is typical for such systems. In fact, the amplitude of zero-point bending remains fairly constant along the series ArHF, ArHCl, ArHBr. Since this amplitude depends roughly on the ratio of the anisotropy of interaction (expressed as the bending force constant) to the rotational constant of the diatomic sub-unit, the anisotropy must decrease along the series (in parallel with the rotational constant).¹⁷⁸

The nature of the bonding in van der Waals molecules has been the subject of considerable speculation. In Part I¹ we discussed the idea that the constituent atoms or molecules of a van der Waals complex might be thought of as a Lewis acid–base pair. Bonding would arise from a weak charge transfer interaction, and HOMO–LUMO considerations could lead to predictions of geometry for some complexes. Particularly interesting, then, are some studies carried out on rare gas–hydrogen halide complexes involving ^{83}Kr or ^{131}Xe , where it was possible to measure the quadrupole coupling constants for these nuclei.

The nuclear quadrupole coupling constant of a free rare gas atom is zero, but a measurable effect may result on complexing, when the atom's spherical symmetry is lost. Since this coupling constant reflects the electric field gradient at the nucleus, it is an indication of the electronic environment of the rare gas atom in the complex.

The first measurements of quadrupole coupling for a rare gas atom in a van der Waals molecule was for $^{83}\text{KrHF}$, using pulsed FTMW.¹⁹² Analysis of the coupling constant required a consideration of so called Sternheimer shielding (an induction effect on the rare gas atom by the hydrogen halide). Use of an incorrect shielding constant led to the initial conclusion that a weak charge-transfer effect was present, but

recalculation with the correct value, and subsequent work on $^{83}\text{KrDF}$, showed that there was *no* evidence for significant charge transfer on complex formation.¹⁹³ A study carried out on $^{131}\text{XeHCl}$ ¹⁹⁵ also revealed no evidence for Lewis acid–base type bonding; the electric field gradient was again interpreted in terms of Sternheimer shielding, and the measured dipole moment could be explained without recourse to charge transfer.

Further FTMW studies of $^{83}\text{KrCl}$ and $^{131}\text{XeDCl}$ failed to indicate charge transfer from the rare gas atom in the bonding.¹⁹¹ By considering electric multipole moments of the hydrogen halide molecules, electric field gradients along the molecular axis were calculated at the rare gas nucleus site. A direct proportionality was found between these field gradients and the ^{83}Kr and ^{131}Xe nuclear quadrupole coupling constants.

Similar results have been obtained by Baiocchi *et al.*¹⁹⁶ in the MBER spectroscopy of $^{131}\text{XeHF}$, who also concluded that field gradient at the Xe nucleus was probably due almost entirely to induction (Sternheimer) effects. They carefully distinguished charge overlap and charge transfer; charge overlap does apparently occur, since the complex bond length is shorter than the sum of the van der Waals radii. However, they estimated what might be the expected effects of charge transfer in two ways, from results on excited state Xe atoms (with one electron transferred out of the p shell), and for Xe in stable molecules. In each case the observed field gradients in the van der Waals molecules were only 2–3% of the magnitude estimated for true charge transfer. Further insight into the nature of the bonding might be possible from the evident scaling of the field gradient with the polarization of the hydrogen halide molecule; this suggests that an electrostatic model could be appropriate for the calculation of charge distribution in these van der Waals molecules. (The electrostatic model, however, should be a good approximation when charges are well separated, whereas the structural evidence is for charge overlap in these molecules, and so this last inference is somewhat surprising.) The generality of these conclusions awaits further investigation.

The rationalization of structures of loosely bound complexes by HOMO–LUMO Lewis acid–base has of course nevertheless had some success (although it may be that in many cases electrostatic considerations would predict the same structure). The application of simple molecular orbital theory along HOMO–LUMO lines has been described by Burdett.²⁴⁶ Such a notion fails for ArCH_3Cl , however, where it is found that the Ar atom is located away from the C–Cl axis, and the complex is T-shaped.¹⁷⁵

CO_2HF , OCSHF,²⁰⁷ and N_2OHF ²⁰³ have been studied by MBER spectroscopy. CO_2HF is linear ($\text{OCO} \cdots \text{HF}$), as is OCSHF ($\text{SCO} \cdots \text{HF}$), whereas the donor–acceptor model would predict a bent hydrogen-bonded geometry. N_2OHF , on the other hand, does have a bent structure, and whilst it is possible to offer a donor–acceptor rationalization of this,²⁰³ the validity of such an explanation may be questioned in view of the CO_2HF result. Similarly contrasting results have been obtained, using MBER spectroscopy, for the dimers of H_2O ²⁰⁰ and HF.²⁴⁵ An intra-complex angle in $(\text{H}_2\text{O})_2$ is rather close to the HOMO–LUMO prediction, whereas in $(\text{HF}_2)_2$ it is somewhat removed.

2 Vibrational Spectroscopy

Table 6 Vibration–rotation spectroscopic studies of diatomic molecules. Molecules are listed in alphabetical order

Molecule	Technique	Comments	Ref.
AsO	LMR	$v = 1 \leftarrow 0$ in $X^2\Pi_{3/2}$ hfs due to ^{75}As	247
BrO	LMR	$^2\Pi_{1/2} \leftarrow ^2\Pi_{3/2}$ magnetic dipole transition	248
CCl	diode laser	fundamental, 870 cm^{-1}	249
CF	diode laser	31 lines of fundamental vibration–rotation band at 1286 cm^{-1}	250
^{14}CO	FTIR	fundamental	251
CO	IR	2–0 band absorption intensity, pressure broadening	252
CO	IR	$P(6); T$ dependence of linewidth and absorption	253, 254
CO	diode laser	fundamental; line strength and collision widths	255
CO	diode laser	broadened by H_2O	256
CO	IRDR, time-resolved	population and alignment studied	257
CO	cw CO laser	extended to $8.18\text{ }\mu\text{m}$ (36–35 band); liquid N_2 cooled	258
ClO	LMR	2–0 band of $X^2\Pi_{3/2}$ at $6\text{ }\mu\text{m}$	259
ClO	IR	spectral line parameters for fundamental	260
FO	LMR	fundamental vibration	261
Fe ₂ , FeNi	RR	matrix	262
H ₂	CARS	optical Stark effect	263
H ₂	IR, 77 K	quadrupolar double transitions $S_1(J) + S_0(J)$: colliding pair	264
H ₂	IR, 77 K	hexadecapolar U-branch transitions; collision induced	265
$^1\text{H}_2, ^2\text{H}_2$	IR	induced spectrum in matrix	266
$^2\text{H}_2$	SRS	sub-Doppler saturation spectroscopy	267
$^2\text{H}_2, ^1\text{H}^2\text{H}$	calculation	vibrational eigenenergies: relates vibrational energy level to quantum number v	268

²⁴⁷ H. Uehara, *Chem. Phys. Lett.*, 1981, **84**, 539.

²⁴⁸ A. R. W. McKellar, *J. Mol. Spectrosc.*, 1981, **86**, 43.

²⁴⁹ C. Yamada, K. Nagai, and E. Hirota, *J. Mol. Spectrosc.*, 1981, **85**, 416.

²⁵⁰ K. Kawaguchi, C. Yamada, Y. Hamada, and E. Hirota, *J. Mol. Spectrosc.*, 1981, **86**, 136.

²⁵¹ J. Mink, A. Ayoub, G. Kemeny, and F. King, *J. Mol. Spectrosc.*, 1981, **86**, 258.

²⁵² G. Ghandaish and G. R. Hebert, *Can. J. Phys.*, 1981, **59**, 1367.

²⁵³ J. A. Sell, *J. Quant. Spectrosc., Radiat. Transfer*, 1980, **23**, 595.

²⁵⁴ P. Varanasi, *J. Quant. Spectrosc., Radiat. Transfer*, 1980, **25**, 187.

²⁵⁵ P. L. Varghese and R. K. Hanson, *J. Quant. Spectrosc. Radiat. Transfer*, 1980, **24**, 479.

²⁵⁶ P. L. Varghese and R. K. Hanson, *J. Mol. Spectrosc.*, 1981, **88**, 234.

²⁵⁷ Ph. Brechignac, A. Picard-Bersellini, and R. Charneau, *J. Phys. B*, 1980, **13**, 135.

²⁵⁸ T. X. Lin, W. Rohrbeck, and W. Urban, *Appl. Phys. B*, 1981, **26**, 73.

²⁵⁹ R. S. Low and A. R. W. McKellar, *J. Mol. Spectrosc.*, 1980, **79**, 424.

²⁶⁰ J. R. Gillis and A. Goldman, *J. Quant. Spectrosc., Radiat. Transfer*, 1981, **26**, 23.

²⁶¹ A. R. W. McKellar, *Can. J. Phys.*, 1979, **57**, 2106.

²⁶² M. Moskowitz and D. P. LiLella, *J. Chem. Phys.*, 1980, **73**, 4917.

²⁶³ L. A. Rahn, R. L. Farrow, M. L. Koszykowski, and P. L. Mattern, *Phys. Rev. Lett.*, 1980, **45**, 620.

²⁶⁴ A. Sen, R. D. G. Prasad, and S. Paddi Reddy, *J. Chem. Phys.*, 1980, **72**, 1716.

²⁶⁵ S. Paddi Reddy, A. Sen, and R. D. G. Prasad, *J. Chem. Phys.*, 1980, **72**, 6102.

²⁶⁶ J. A. Warren, G. R. Smith, and W. A. Guillory, *J. Chem. Phys.*, 1980, **72**, 4901.

²⁶⁷ A. Owyong and P. Esherick, *Opt. Lett.*, 1980, **5**, 421.

²⁶⁸ C. L. Beckel and R. B. Kwong, *J. Chem. Phys.*, 1980, **73**, 4698.

Table 6 (continued)

Molecule	Technique	Comments	Ref.
$^2\text{H}^3\text{H}$	Raman	rotation and rotation-vibration	269
H_2	solar FTIR	4-0 $S(1)$ quadrupole line strength and pressure shift	270
$^1\text{H}^2\text{H}$	Fabry-Perot	absorption strengths for lines in 4-0 and 5-0	271
$^1\text{H}^2\text{H}$	intracavity, photoacoustic	5-0; calibration of photoacoustic detector	272
$^1\text{H}^2\text{H}$	direct pumping, photoacoustic	$v = 5, 6$; collisional relaxation	273
$^1\text{H}^2\text{H}^+$	ion beam IR photodissociation	18-16 band, hfs	274
HCl	IR/SISAM	$v = 0-1$ perturbed by $\text{N}_2, \text{O}_2, \text{H}_2$ at 298 and 163 K	275
$^{1,2}\text{HCl}$	FTIR	2840-8450 cm^{-1} ; 3-0, 1-0 bands	276
HCl	intracavity dye laser quenching, and photoacoustic	(5-0), (6-0), (7-0)	277
HCl	FTIR	pressure broadening of (4-0)-(7-0)	278
HCl	FTIR	intensities of (4-0)-(7-0)	279
HF	DFS	(1-0) collisional narrowing	280
HI	diode laser	hfs	281
$^{1,2}\text{HI}$	FTIR	(2-0)-(5-0), hfs at low J in (2-0)	282
HeH^+	ion beam IR photodissociation	bound to quasi-bound vibration-rotation transitions	283
N_2	CARS	improved constants for electronic g.s.	284
NF	diode laser	fundamental of $a^1\Delta$, ~8.6, μm , hfs	285
NO	FTIR emission dc discharge	$\Delta v = 2$ sequence	286
NO	IRRFDR	$X^2\Pi_{1/2}, v = 0, 1$; hfs	287
NO	spin-flip laser, magnetic modulation	lineshape analysis, g_J factors	288

²⁶⁹ J. E. Barefield, L. H. Jones, and R. Liepens, *J. Mol. Spectrosc.*, 1980, **80**, 233.²⁷⁰ J. W. Brault and W. H. Smith, *Astrophys. J. Lett.*, 1980, **235**, L177.²⁷¹ M. E. Mickelson, L. E. Larson, and J. T. Trauger, *Icarus*, 1980, **41**, 142.²⁷² W. H. Smith and J. Gelfand, *J. Quant. Spectrosc. Radiat. Transfer*, 1980, **24**, 15.²⁷³ E. A. Rohlffing, J. Gelfand, R. B. Miles, and H. Rabitz, *J. Chem. Phys.*, 1981, **75**, 4893.²⁷⁴ A. Carrington and J. Buttenshaw, *Mol. Phys.*, 1981, **44**, 267.²⁷⁵ J. P. Houdeau, M. Larvor, and C. Haeusler, *Can. J. Phys.*, 1980, **58**, 318.²⁷⁶ G. Guelachvili, P. Niay, and P. Bernage, *J. Mol. Spectrosc.*, 1981, **85**, 271.²⁷⁷ K. V. Reddy, *J. Mol. Spectrosc.*, 1980, **82**, 127.²⁷⁸ M. Zughul, J. Gelfand, H. Rabitz, and A. E. de Pristo, *J. Quant. Spectrosc. Radiat. Transfer*, 1980, **24**, 371.²⁷⁹ J. Gelfand, M. Zughul, H. Rabitz, and C. J. Han, *J. Quant. Spectrosc. Radiat. Transfer*, 1981, **26**, 303.²⁸⁰ A. S. Pine, *J. Mol. Spectrosc.*, 1980, **82**, 435.²⁸¹ L. L. Strow, *Opt. Lett.*, 1980, **5**, 166.²⁸² G. Guelachvili, P. Niay, and P. Bernage, *J. Mol. Spectrosc.*, 1981, **85**, 253.²⁸³ A. Carrington, J. Buttenshaw, R. A. Kennedy, and T. P. Softley, *Mol. Phys.*, 1981, **44**, 1233.²⁸⁴ T. R. Gilson, I. R. Beattie, J. D. Black, D. A. Greenhaigh, and S. N. Jenny, *J. Raman Spectrosc.*, 1980, **9**, 361.²⁸⁵ P. B. Davies, P. A. Hamilton, and M. Okumura, *J. Chem. Phys.*, 1981, **75**, 4294.²⁸⁶ C. Amiot and J. Verges, *J. Mol. Spectrosc.*, 1980, **81**, 424.²⁸⁷ R. S. Lowe, A. R. W. McKellar, and P. Veillette, *J. Mol. Spectrosc.*, 1981, **88**, 372.²⁸⁸ W. Herrmann, W. Rohrbeck, and W. Urban, *Appl. Phys.*, 1980, **22**, 71.

Table 6 (continued)

Molecule	Technique	Comments	Ref.
$^{15}\text{N}^{16,18}\text{O}$	IR	(1–0), (2–0), (3–0)	289
NO	CARS	Q branch series for $\text{X}^2\Pi_{1/2}$, $\text{X}^2\Pi_{3/2}$; ratio of differential Raman X-sections	290
NO	IR fluorescence (electron irradiation of $\text{N}_2 + \text{O}_2$)	Einstein coefficients, $v \leq 9$	291
NO	diode laser	line broadening by H_2O , N_2	292
NO	FTIR	intensity and self-broadening in fundamental	293
NS	diode laser	1204 cm^{-1} ; ${}^2\Pi_{1/2}-{}^2\Pi_{1/2}$, ${}^2\Pi_{3/2}-{}^2\Pi_{3/2}$, (1, 0) bands	294
O_2	diode laser	electric quadrupole $S(5)$ and $S(7)$ in (1, 0)	295
O_2	calculation	line positions and intensities for (1, 0) electric quadrupole transitions	296
O_2	Raman	$^{17}\text{O}^{18}\text{O}$, ^{17}O , so observed for first time	297
O_2	CARS	O_2 as photofragment from O_3 , dissociation	298
O^2H	FTIR ${}^2\text{H}_2/\text{O}_2$ flame	$\sim 2 \mu\text{m}$; analysis incorporates electronic and MW data	299
OH	colour centre laser, magnetic rotation	cf. Zeeman modulation technique	300
P^2H	LMR	$v = 1 \leftarrow 0$; rotation, spin–spin and spin–rotation constants for $v = 0, 1$	301
PN	diode laser	800–1050 °C	302
S^2H	LMR	$\text{X}^2\Pi_{3/2}Q(1.5)$, 1885.76 cm^{-1}	303
Se^2H	LR	${}^2\Pi_{1/2}-{}^2\Pi_{3/2}$; magnetic and electric dipole transitions, $\sim 1770 \text{ cm}^{-1}$; spin–orbit, spin–rotation interactions for $\text{Se}^{1,2}\text{H}$	304
SeO	LMR	$v = 1 \leftarrow 0$, $\text{X}^3\Sigma^-$	305
SiO	diode laser	(1, 0)–(5, 4) bands; SiO maser	306
SiO	calculation	intensities, astrophysical implications	307
TiN	FTIR	matrix	308

289 J. L. Teffo, A. Henry, P. Cardinet, and A. Valentin, *J. Mol. Spectrosc.*, 1980, **82**, 348.290 A. Beckmann, H. Fietz, W. Kiefer, and J. Laane, *Phys. Rev. A*, 1981, **24**, 2518.291 B. D. Green, G. E. Caledonia, and R. E. Murphy, *J. Quant. Spectrosc. Radiat. Transfer*, 1981, **26**, 215.292 J. A. Sell, *J. Quant. Spectrosc. Radiat. Transfer*, 1981, **25**, 19.293 J. Y. Mandin, C. Amiot, and G. Guelachvili, *Ann. Phys.*, 1980, **5**, 91.294 K. Matsumura, K. Kawaguchi, K. Nagai, C. Yamada, and E. Hirota, *J. Mol. Spectrosc.*, 1980, **84**, 68.295 J. Reid, R. L. Sinclair, A. M. Robinson, and A. R. W. McKellar, *Phys. Rev. A*, 1981, **24**, 1944.296 L. S. Rothman and A. Goldman, *Appl. Opt.*, 1981, **20**, 2182.297 H. G. M. Edwards, D. A. Long, K. A. B. Najm, and M. Thomson, *J. Raman Spectrosc.*, 1981, **10**, 60.298 J. J. Valentini, D. S. Moore, and D. S. Bomse, *Chem. Phys. Lett.*, 1981, **83**, 217.299 C. Amiot, J.-P. Maillard, and J. Chauville, *J. Mol. Spectrosc.*, 1981, **87**, 196.300 J. Pfeiffer, D. Kirsten, P. Kalkert, and W. Urban, *Appl. Phys. B*, 1981, **26**, 173.301 H. Uehara and K. Hakuta, *J. Chem. Phys.*, 1981, **74**, 4326.302 A. G. Maki and F. J. Lovas, *J. Mol. Spectrosc.*, 1981, **85**, 368.303 W. Rohrbeck, A. Hinz, and W. Urban, *Mol. Phys.*, 1980, **41**, 925; R. S. Lowe, *ibid.*, p. 929.304 J. M. Brown, A. Carrington, and A. D. Fackerell, *Chem. Phys. Lett.*, 1980, **75**, 13.305 K. Hakuta and H. Uehara, *J. Mol. Spectrosc.*, 1981, **85**, 97.306 F. J. Lovas, A. G. Maki, and W. B. Olson, *J. Mol. Spectrosc.*, 1981, **87**, 449.307 R. H. Tipping and C. Chackerian, *J. Mol. Spectrosc.*, 1981, **88**, 352.308 F. W. Froben and F. Rogge, *Chem. Phys. Lett.*, 1981, **78**, 264.

Table 7 Vibration-rotation spectroscopic studies of triatomic molecules. Molecules are listed in alphabetical order

Molecule	Technique	Comments	Ref.
BO ₂	diode laser	vibronic interaction between $\tilde{\chi}^2\Pi_u$ and $\tilde{\chi}^2\Pi_g$ states	309
C ₃	potential surface	reproduces data on energy, geometry, force constants ($\tilde{\chi}^1\Sigma_g^+$)	310
CF ₂	diode laser	$\tilde{\chi}^1A_1$, ν_1 band	311
CO ₂	DFS	930—985 K, 00°1 ← 00°0	312
CO ₂	IR Zeeman, co-propagating waves	Doppler-free resonances, magnetic parameters for individual vibrational states	313
CO ₂	FTIR	1.4—1.7 μm atmospheric window	314
CO ₂	calculation	vibration excitation cross section for electron impact at 10 eV	315
CO ₂	FTIR	ν_2 540—830 cm^{-1}	316
CO ₂	FTIR	ν_3 bands, 4.3 μm	317
CO ₂	FTIR emission	hot bands, 4.5 μm	318
¹³ CO ₂	IR	$0\nu_2^1\nu_3 - 0\nu_2^1(\nu_3 - 1)$, $\nu_2 = 1$ line strengths, ν_3 , 4.3 μm	319
¹³ C ¹⁸ O ₂	FTIR	ν_2 , ν_3	320
C ¹⁷ O ₂ , C ¹⁷ O ¹⁸ O	FTIR	ν_2 , 15 μm	321
¹³ CO ₂	diode laser	(01 ¹ 0)—(000) Q branches	322
CO ₂	CARS	2 ν_2 , polarized and depolarized, vibrational relaxation	323
CO ₂	FTIR	3 ν_3 , 1.43 μm , self-shifting; negative shifts as p increases from 4—280 Torr	324
CO ₂	IR	energy levels and intensities of all absorption transitions of atmospheric interest	325
CO ₂	IR	201 ₁₁ —000 band at 4978 cm^{-1} ; line intensities and self-broadening at 197 and 294 K	326
CO ₂	diode laser	15 μm bands, intensities and half-widths, 200—325 K	327
CO ₂	IR	line strengths, ν_3 , 4.3 μm	328

³⁰⁹ K. Kawaguchi, E. Hirota, and C. Yamada, *Mol. Phys.*, 1981, **44**, 509.³¹⁰ S. Carter, I. M. Mills, and J. N. Murrell, *J. Mol. Spectrosc.*, 1980, **81**, 110.³¹¹ P. B. Davies, W. Lewis-Bevan, and D. K. Russell, *J. Chem. Phys.*, 1981, **75**, 5602.³¹² A. S. Pine and G. Guelachvili, *J. Mol. Spectrosc.*, 1980, **79**, 84.³¹³ J. E. Thomas, *Opt. Lett.*, 1980, **5**, 123.³¹⁴ J. P. Maillard, M. Cuisenier, P. L. Arcas, E. Arie, and C. Amiot, *Can. J. Phys.*, 1980, **58**, 1560.³¹⁵ D. Thirumalai, K. Onda, and D. G. Truhlar, *J. Phys. B.*, 1980, **13**, L619.³¹⁶ R. Paso, J. Kauppinen, and R. Anttila, *J. Mol. Spectrosc.*, 1980, **79**, 236.³¹⁷ G. Guelachvili, *J. Mol. Spectrosc.*, 1980, **79**, 72.³¹⁸ D. Baily, R. Farreng, G. Guelachvili, and C. Rossetti, *J. Mol. Spectrosc.*, 1981, **90**, 74.³¹⁹ C. P. Rinsland, A. Baldacci, and K. N. Rao, *J. Mol. Spectrosc.*, 1980, **81**, 256.³²⁰ M. J. Reisfeld, H. Flicker, and M. Goldblatt, *J. Mol. Spectrosc.*, 1980, **83**, 175.³²¹ M. J. Reisfeld, H. Flicker, and M. Goldblatt, *J. Mol. Spectrosc.*, 1980, **82**, 411.³²² N. Nereson, H. Flicker, and M. J. Reisfeld, *J. Mol. Spectrosc.*, 1980, **82**, 452.³²³ C. M. Roland and W. A. Steele, *J. Chem. Phys.*, 1981, **74**, 2733.³²⁴ Ph. Arcas, E. Arie, C. Boulet, and J. P. Maillard, *J. Chem. Phys.*, 1980, **73**, 5383.³²⁵ L. S. Rothman and L. D. G. Young, *J. Quant. Spectrosc. Radiat. Transfer*, 1981, **25**, 505.³²⁶ F. P. J. Valero, C. B. Suarez, and R. W. Boese, *J. Quant. Spectrosc. Radiat. Transfer*, 1980, **23**, 337.³²⁷ G. L. Tettener and W. G. Planet, *J. Quant. Spectrosc. Radiat. Transfer*, 1980, **24**, 343.³²⁸ B. Fridovich, W. C. Braun, G. R. Smith, and E. E. Champion, *J. Mol. Spectrosc.*, 1980, **81**, 248.

Table 7 (continued)

Molecule	Technique	Comments	Ref.
CO ₂	IR	line strengths, (11 ¹ 0, 03 ¹ 0) ₁₁ —(00 ⁰ 0), 1932 cm ⁻¹	329
CS ₂	FTIR	ν_2	330
¹³ CS ₂	FTIR	250—430 cm ⁻¹	331
CS ₂	calculation	anharmonic force field	332
CSe ₂	IR	$2\nu_1 + \nu_3, 2\nu_2 + \nu_3$	333
ClO ₂	FTIR	ν_1	334
ClO ₂	MWIRDR	$\nu_1 = 1$ constants	335
ClO ₂	MWIRDR	$\nu_3 = 1$; also triple resonances	336
ClO ₂	MWIRDR	extensive set of constants, r_e structures	337
FCO	diode laser	ν_1, ν_2 bands	338
H ₃ ⁺	IR absorption + DFS	ν_2	339
HCN	RFIRDR, colour centre laser	(010) → (011)	340
HCN	potential surface	reproduces data on energy, geometry, force constants ($\tilde{X}^1\Sigma^+$)	310
HCO	LMR	ν_2 fundamental, constants for (010)	341
² HCO	LMR	ν_1, ν_3 bands	342
HCP	IR	ν_3	343
HCP	IR	$\nu_2, 2\nu_2$ and hot bands; ν_1 and ν_2 of H ¹³ CP seen	344
HO ₂	diode laser	ν_2 band	345
H ₂ O	FTIR	4 ν_2 , 5930—6400 cm ⁻¹	346
H ₂ ¹⁸ O	IR	line positions and intensities for 2 ν_2 , ν_1 and ν_3 bands	347
H ₂ ^{17,18} O	FTIR	(020), (100), (001)	348
¹ H ² HO	HeXe laser, Zeeman tuned Stark modulation	$\nu_1, 2\nu_2$	349
² H ₂ O	² H ₂ O laser	separation of 5 ₅ —5 ₃ , 5 ₄ —5 ₂ in ν_2	350
² H ₂ O	IR	ν_1, ν_3	351

329 P. Arcas, E. Arie, P. Cardinet, A. Valentin, and A. Henry, *J. Mol. Spectrosc.*, 1980, **81**, 262.

330 K. Jolma and J. Kauppinen, *J. Mol. Spectrosc.*, 1980, **82**, 214.

331 J. Kauppinen and K. Jolma, *J. Mol. Spectrosc.*, 1981, **85**, 314.

332 M. Lacy and D. H. Whiffen, *Mol. Phys.*, 1981, **43**, 1205.

333 A. G. Maki and R. L. Sams, *J. Mol. Spectrosc.*, 1981, **90**, 215.

334 Y. Hamada and M. Tsuboi, *J. Mol. Spectrosc.*, 1980, **83**, 373.

335 H. Jones, *Chem. Phys. Lett.*, 1980, **69**, 483.

336 H. Jones and W. Lienert, *Chem. Phys. Lett.*, 1980, **73**, 417.

337 H. Jones and J. M. Brown, *J. Mol. Spectrosc.*, 1981, **90**, 222.

338 K. Nagai, C. Yamada, Y. Endo, and E. Hirota, *J. Mol. Spectrosc.*, 1981, **90**, 249.

339 T. Oka, *Phys. Rev. Lett.*, 1980, **45**, 531.

340 R. L. De Leon, P. H. Jones, and J. S. Muenster, *Appl. Opt.*, 1981, **20**, 525.

341 J. M. Brown, J. Buttenshaw, A. Carrington, K. Dumper, and C. R. Parent, *J. Mol. Spectrosc.*, 1980, **79**, 47.

342 R. S. Lowe and A. R. W. McKellar, *J. Chem. Phys.*, 1981, **74**, 2686.

343 J.-M. Garneau and A. Cabona, *J. Mol. Spectrosc.*, 1980, **79**, 502.

344 J.-M. Garneau and A. Cabona, *J. Mol. Spectrosc.*, 1981, **87**, 490.

345 K. Nagai, Y. Endo, and E. Hirota, *J. Mol. Spectrosc.*, 1981, **89**, 520.

346 C. Camy-Peyret, J.-M. Flaud, and J.-P. Maillard, *J. Phys. Lett.*, 1980, **41**, L23.

347 J.-M. Flaud, C. Camy-Peyret, and R. A. Toth, *Can. J. Phys.*, 1980, **58**, 1748.

348 C. Camy-Peyret, J.-M. Flaud, and R. A. Toth, *J. Mol. Spectrosc.*, 1981, **87**, 233.

349 K. Uehara, K. Takagi, and T. Kasuya, *Appl. Phys.*, 1981, **24**, 187.

350 G. Dodel and N. G. Douglas, *J. Mol. Spectrosc.*, 1981, **87**, 297.

351 V. D. Gupta, *J. Phys. B*, 1981, **14**, 1761.

Table 7 (continued)

Molecule	Technique	Comments	Ref.
H_2O	FTIR	2170—3090 cm^{-1} ; $2\nu_2$, ν_1 , ν_3	352
H_2O	FTIR	ν_2 self broadening	353
HOCl	IR, diode laser	1238 cm^{-1}	354
NO_2	IR	$2\nu_2/\nu_3$ Coriolis perturbation	355
NO_2	diode laser	ν_2 ; 687—720 cm^{-1} , 820—865 cm^{-1}	356
NO_2	RFIRDR	spin-rotation and hyperfine parameters for (001)	357
NO_2	discrete resonance CARS	ν_1 , ν_2	358
NO_2	diode laser	ν_2 ; intensities, self and N_2 broadening	359
NO_2	IR	(101) band line strengths, spin splittings, and (111)—(010); 2863—2934 cm^{-1}	360
N_2O	co-propagating lasers, Doppler-free resonances	(100—001) band hfs	361
N_2O	IR	(24°0)—(00°0), (01°2—00°0) line strengths	362
NH_2	LMR	constants for g.s. and $\nu_2 = 1$	363
NH_2	IR	constants of (020), also fitting (020), (010), (000)	364
Ni_3	RR	Ar matrix, g.s. Δ_u ?, apex angle between 90° and 100°	365
O_3	IR	10 μm and 4.8 μm region; combines various data sets	366
O_3	FTIR	ν_1 , ν_3 and $(\nu_1 + \nu_2) - \nu_2$	367
O_3	interferometer, line-tunable CO_2 laser	ν_3 from anomalous dispersion at 10 μm	368
O_3	IR/SISAM	$2\nu_3$, $\nu_1 + \nu_3$, $2\nu_1$ line positions and intensities	369
O_3	variational calculations	strengths of fundamentals	370
OBF	IR, shock tube	intensities of fundamentals	371
$\text{O}^{12,13}\text{CS}$	IR	ν_3	372

³⁵² N. Papineau, J.-M. Flaud, C. Camy-Peyret, and G. Guelachvili, *J. Mol. Spectrosc.*, 1981, **87**, 219.

³⁵³ J.-Y. Maudin, J.-M. Flaud, and C. Camy-Peyret, *J. Quant. Spectrosc. Radiat. Transfer*, 1980, **23**, 351.

³⁵⁴ R. L. Sams and W. B. Olson, *J. Mol. Spectrosc.*, 1980, **84**, 113.

³⁵⁵ A. R. Hoy, *J. Mol. Spectrosc.*, 1981, **86**, 55.

³⁵⁶ J.-M. Flaud, C. Camy-Peyret, V. M. Devi, P. P. Das, and K. N. Rao, *J. Mol. Spectrosc.*, 1980, **84**, 234.

³⁵⁷ M. Allegrini, A. R. W. McKellar, P. Pinson, and J. M. Brown, *J. Chem. Phys.*, 1980, **73**, 6087.

³⁵⁸ M. E. McIlwain and J. C. Hindman, *J. Chem. Phys.*, 1980, **73**, 68.

³⁵⁹ V. M. Devi, P. P. Das, A. Bano, K. N. Rao, J.-M. Flaud, C. Camy-Peyret, and J.-P. Chevillard, *J. Mol. Spectrosc.*, 1981, **88**, 251.

³⁶⁰ R. A. Toth and R. H. Hunt, *J. Mol. Spectrosc.*, 1980, **79**, 182.

³⁶¹ J. E. Thomas, M. Burns, and A. Javan, *Opt. Lett.*, 1980, **5**, 18.

³⁶² N. Lacome and A. Levy, *J. Mol. Spectrosc.*, 1981, **85**, 205.

³⁶³ K. Kawaguchi, C. Yamada, E. Hirota, J. M. Brown, J. Buttenshaw, C. R. Parent, and T. J. Sears, *J. Mol. Spectrosc.*, 1980, **81**, 60.

³⁶⁴ F. W. Birss, M. F. Merienne-Lafore, D. A. Ramsay, and M. Vervloet, *J. Mol. Spectrosc.*, 1981, **85**, 493.

³⁶⁵ M. Moskovits and D. P. DiLella, *J. Chem. Phys.*, 1980, **72**, 2267.

³⁶⁶ J. M. Flaud, C. Camy-Peyret, and L. S. Rothman, *Appl. Opt.*, 1980, **19**, 655.

³⁶⁷ A. Barbe, C. Secroun, P. Jouve, A. Goldman, and D. G. Murcray, *J. Mol. Spectrosc.*, 1981, **86**, 286.

³⁶⁸ C. Secroun, A. Barbe, P. Jouve, P. Arcas, and E. Arie, *J. Mol. Spectrosc.*, 1981, **85**, 8 (87, 587 erratum).

³⁶⁹ J.-M. Flaud, C. Camy-Peyret, A. Barbe, C. Secroun, and P. Jouve, *J. Mol. Spectrosc.*, 1980, **80**, 185.

³⁷⁰ G. D. Carney, S. Giogianni, and K. N. Rao, *J. Mol. Spectrosc.*, 1980, **80**, 158.

³⁷¹ D. W. Boyer, *J. Quant. Spectrosc. Radiat. Transfer*, 1980, **24**, 269.

³⁷² G. Blanquet, J. Walrand, C. P. Courtoy, and A. Fayt, *J. Mol. Spectrosc.*, 1980, **81**, 473.

Table 7 (continued)

Molecule	Technique	Comments	Ref.
OCS	diode	line strengths at 12 μm	373
OCS	CO ₂ laser heterodyne	1050 cm^{-1} ; frequency differences to 8.6 GHz	374
OCS	IR, diode laser	859, 1711 cm^{-1} bands; calibration of diode lasers	375
OCS	potential surface	fitting to spectroscopic observations	376
SF ₂	FTIR	780—860 cm^{-1} ; ν_1 , ν_3	377
SO ₂	diode laser heterodyne	ν_1	378
SO ₂	DFS	4 μm , $\nu_1 + \nu_3$ band	379
SO ₂	FTIR	ν_1 , ν_2 ; Coriolis interactions $\nu_1 - \nu_2$ and $\nu_2 - \nu_3$	380
SO ₂	Zeeman effect	$2_{02} \rightarrow 1_{11}$: magnetic field calibration standard	381
S ^{16,18} O ₂	Raman	fundamentals, (010) \rightarrow (110)	382
SiF ₂	FTIR	stretching fundamentals, vibrational transition moments	383

Table 8 Vibration-rotation spectroscopic studies of tetra-atomic molecules. Molecules are listed in alphabetical order

Molecule	Technique	Comments	Ref.
AsH ₃	RFIR double resonance		61
CF ₃ H	FTIR	a very close resonance ν_1 , $6\nu_6$	384
CH ₃	diode laser	ν_2 , 600—750 cm^{-1}	385
C ₂ H ₂	diode laser	ν_5 , 15 μm	386
C ₂ H ₂	FTIR	ν_5 fundamental region	387
C ₂ H ₂	Raman	3950 cm^{-1} ; anharmonicity constants	388
C ₂ ² H ₂ , C ₂ ¹ H ₂ H	Raman	ν_1 , ν_2 (and ν'_4 C ₂ H ₂)	389
C ₂ H ₂	Raman	ν_1 , ν_2 , ν'_4	390
C ₂ H ₂	CARS, pulsed s/s beam	ν_2 Q branch, 1974 cm^{-1}	391
C ₂ H ₂	CARS, pulsed s/s beam	ν_2 Q branch, saturation broadening	392
C ₂ H ₂	IR	5 ν_3 self-broadening	393

373 V. M. Devi, P. P. Das, A. Bano, and K. N. Rao, *J. Mol. Spectrosc.*, 1981, **87**, 578.374 J. P. Sattler, T. L. Worchesky, A. G. Maki, and W. J. Lafferty, *J. Mol. Spectrosc.*, 1981, **90**, 460.375 A. G. Maki, W. B. Olson, and R. L. Sams, *J. Mol. Spectrosc.*, 1980, **81**, 122.376 D. H. Whiffen, *Mol. Phys.*, 1980, **39**, 391.377 J. C. Deroche, H. Burger, P. Schulz, and H. Willner, *J. Mol. Spectrosc.*, 1981, **89**, 269.378 J. P. Sattler, T. L. Worchesky, and W. J. Lafferty, *J. Mol. Spectrosc.*, 1981, **88**, 364.379 A. S. Pine and M. Dang-Nhu, *J. Mol. Spectrosc.*, 1980, **84**, 132.380 T. Nakanaga, S. Kondo, and S. Saeki, *J. Mol. Spectrosc.*, 1980, **81**, 413.381 D. J. Miller, R. de Leon, and J. S. Muenter, *J. Mol. Spectrosc.*, 1980, **83**, 283.382 M. H. Brooker and H. H. Eysil, *J. Raman Spectrosc.*, 1981, **11**, 322.383 G. L. Caldow, C. M. Deeley, P. H. Turner, and I. M. Mills, *Chem. Phys. Lett.*, 1981, **82**, 434.384 H.-R. Dubal and M. Quack, *Chem. Phys. Lett.*, 1981, **80**, 439.385 C. Yamada, E. Hirota, and K. Kawaguchi, *J. Chem. Phys.*, 1981, **75**, 5256.386 P. P. Das, V. M. Devi, and K. N. Rao, *J. Mol. Spectrosc.*, 1980, **84**, 313.387 J. Hietanen and J. Kauppinen, *Mol. Phys.*, 1981, **42**, 411.388 H. Finsterholz, H. W. Schrotter, and G. Strey, *J. Raman Spectrosc.*, 1981, **11**, 375.389 E. Kostyk and H. L. Welsh, *Can. J. Phys.*, 1980, **58**, 912.390 E. Kostyk and H. L. Welsh, *Can. J. Phys.*, 1980, **58**, 534.391 M. D. Duncan, P. Oesterlin, and R. L. Byer, *Opt. Lett.*, 1981, **6**, 90.392 M. D. Duncan, P. Oesterlin, F. Konig, and R. L. Byer, *Chem. Phys. Lett.*, 1981, **80**, 253.393 J. S. Wong, *J. Mol. Spectrosc.*, 1980, **82**, 449.

Table 8 (continued)

Molecule	Technique	Comments	Ref.
$\text{C}^{1,2}\text{H}_2\text{F}$	IR	from $\text{F}+\text{CH}_3\text{F}$ in matrix; also some H-bonded products	394
C_2HF	laser Stark, IRMWDR	dipole moments for ten vibrational states	395
CH_2I	IR photofragment fluorescence	vibrationally excited	396
$^{1,2}\text{HBF}_2$	IR, (MW)	harmonic force field, r_z structure	397
HBO_2	IR, shock tube	intensities of fundamentals	371
$\text{H}_2^{12,13}\text{CO}$	diode laser	ν_2	398
$^2\text{H}_2\text{CO}$	waveguide laser intracavity	Lamb dips by IR fluorescence detection	399
$^{1,2}\text{H}_2\text{CS}$	FTIR	harmonic force field, r_z structure	400
H_2CS	CO_2 laser Stark, multiple absorption	$\nu_3, \nu_4, 2\nu_2$; $\sim 10 \mu\text{m}$	401
HN_3	diode laser, Stark modulation	ν_3	402
HN_3	Raman	ν_2 , Q branches of hot bands $\nu_5 \rightarrow \nu_2 + \nu_5, \nu_6 \rightarrow \nu_2 + \nu_6$	403
$^2\text{HNCO}$	IR	ν_1 , interaction with $2\nu_3$	404
HNO_2 cis, trans	CO laser Stark	ν_2 ; trans more stable than cis by ~ 400 cal/mole	405
$^2\text{HNSO}$	IR	$\nu_1, 2\nu_1$	406
HNSO	IR	300—4100 cm^{-1}	407
H_2O_2	IR	ν_6 band at 1266 cm^{-1}	408
$^2\text{HHSe}$	IR	$2\nu_1$	409
NH_3	FTIR, s/s expansion	ν_2 ; rotational cooling	410
NH_3	diode laser	Zeeman effect in IR spectrum of molecule without electronic moment	411
NH_3	diode, CO/CO_2 lasers, IRIRDR	sub-Doppler; line narrowing, collision-induced resonances	412a,b
NH_3	laser Stark	refined molecular constants	413
NH_3	diode laser heterodyne	9—10 μm , frequency measurements of 32 lines	414

394 M. E. Jacox, *Chem. Phys.*, 1981, **59**, 199.395 K. Matsumura, K. Tanaka, C. Yamada, and T. Tanaka, *J. Mol. Spectrosc.*, 1980, **80**, 209.396 S. L. Baughcum and S. R. Leone, *J. Chem. Phys.*, 1980, **72**, 6531.397 A. G. Robiette and M. C. L. Gerry, *J. Mol. Spectrosc.*, 1980, **80**, 403.398 D. M. Sweger and R. L. Sams, *J. Mol. Spectrosc.*, 1981, **87**, 18.399 F. Herlemont, J. Fleury, and J. Lamaire, *Opt. Commun.*, 1981, **37**, 403.400 P. H. Turner, L. Halonen, and I. M. Mills, *J. Mol. Spectrosc.*, 1981, **88**, 402.401 D. J. Bedwell and G. Duxbury, *J. Mol. Spectrosc.*, 1980, **84**, 531.402 K. Yamada and M. Takami, *J. Mol. Spectrosc.*, 1980, **84**, 431.403 J. Bendtsen, *J. Raman Spectrosc.*, 1980, **9**, 162.404 D. A. Steiner, S. R. Polo, T. K. McCubbin, jun., and K. A. Wishah, *Can. J. Phys.*, 1981, **59**, 1313.405 M. Allegrini, J. W. C. Johns, A. R. W. McKellar, and P. Pinson, *J. Mol. Spectrosc.*, 1980, **79**, 446.406 M. Carlotti, G. di Lonardo, G. Galloni, and A. Trombettini, *J. Mol. Spectrosc.*, 1980, **80**, 291.407 M. Carlotti, G. di Lonardo, G. Galloni, and A. Trombettini, *J. Mol. Spectrosc.*, 1980, **84**, 155.408 F. P. J. Valero, D. Goorvitch, F. S. Bonomo, and R. W. Boese, *Appl. Opt.*, 1981, **20**, 4097.409 J. R. Gillis and T. H. Edwards, *J. Mol. Spectrosc.*, 1980, **81**, 373.410 D. L. Snavely, S. D. Colson, and K. B. Wibery, *J. Chem. Phys.*, 1981, **74**, 6975.411 V. G. Kolosovnikov, Yu. A. Kuritsyn, I. Pak, N. I. Ulitskiy, B. M. Kharlamov, A. D. Britov, I. I. Zasavitsky, and S. P. Shotov, *Opt. Commun.*, 1980, **35**, 213.412 (a) W. H. Weber and R. W. Terhume, *Opt. Lett.*, 1981, **6**, 455; (b) R. Guccione-Gush, *Phys. Rev. A*, 1981, **23**, 2740.413 K. Shimoda, Y. Ueda, and J. Iwahori, *Appl. Phys.*, 1980, **21**, 181.414 J. P. Sattler, L. S. Miller, and T. L. Worchesky, *J. Mol. Spectrosc.*, 1981, **88**, 347.

Table 8 (continued)

Molecule	Technique	Comments	Ref.
NH ₃	diode laser	931—954 cm ⁻¹	415
N ² H ₃	saturation laser Stark, intracavity	inverse Lamb dips	416
NH ₃	IR, diode laser, FIR	Coriolis and 1-type interactions in ν_2 , $2\nu_2$ and ν_4	417
NH ₃	diode laser	ν_2 multiplets ~8.4 μm	418
NH ₃	diode laser	frequency measurements	419
NH ₃	IRMWDR, FTIR	920—1080 cm ⁻¹	420
14,15N ² H ₃	diode laser	ν_2 inversion levels	421
14,15N ² H ₃	FTIR	ν_2 , intensities, vibrational transition moments	422
¹⁵ NH ₃	saturation laser Stark, intracavity	ν_2 , Lamb dips; dipole moment for $\nu_2 = 1$	423
14,15NH ₃	IR	intensities and line shapes in ν_2 fundamentals	424
N ₂ H ₂	IR	7.6 μm ; ν_4 , ν_6 Coriolis interactions	425
P ₄	Raman	ν_2 region, molecular constants	426
PH ₃	FTIR	ν_2 , ν_4	427
PH ₃	IR	ν_1 , ν_3	428
PH ₃	IR	ν_2 , ν_4 ; 9—10 μm	429
PH ₃	laser Stark	dipole moment in $\nu_2 = 1$, $\nu_4 = 1$	430
P ³ H ₃	FTIR	4 fundamentals, Coriolis interactions, equilibrium structure	431

Table 9 Vibrational spectroscopic studies of polyatomic molecules. Molecules are listed with increasing number of carbon atoms. For molecules containing carbon, listing is then with increasing number of hydrogen atoms. Listing is otherwise alphabetical

Molecule	Technique	Comments	Ref.
B ₂ ^{1,2} H ₆	IR	complete assignment of all 18 frequencies	432

⁴¹⁵ G. Baldacchini, S. Marchetti, and V. Montelatici, *J. Mol. Spectrosc.*, 1981, **86**, 115.

⁴¹⁶ G. di Lonardo and A. Trombetti, *Chem. Phys. Lett.*, 1981, **84**, 327.

⁴¹⁷ S. Urban, V. Spirko, D. Papousek, R. S. McDowall, N. G. Nereson, S. P. Belov, L. I. Gershstein, A. V. Maslovskij, A. F. Krupnov, J. Curtis, and K. N. Rao, *J. Mol. Spectrosc.*, 1980, **79**, 455.

⁴¹⁸ S. Giorgianni, F. Cappellani, and G. Restelli, *J. Mol. Spectrosc.*, 1980, **83**, 228.

⁴¹⁹ J. P. Sattler and T. L. Worchesky, *J. Mol. Spectrosc.*, 1981, **90**, 297.

⁴²⁰ S. Urban, V. Spirko, D. Papousek, J. Kauppinen, S. P. Belov, L. I. Gershstein, and A. F. Krupnov, *J. Mol. Spectrosc.*, 1981, **88**, 274.

⁴²¹ V. M. Devi, P. P. Das, K. N. Rao, S. Urban, D. Papousek, and V. Spirko, *J. Mol. Spectrosc.*, 1981, **88**, 293.

⁴²² B. J. Krohn and L. H. Jones, *J. Mol. Spectrosc.*, 1981, **86**, 16.

⁴²³ G. di Lonardo, A. Trombetti, and B. Velino, *Chem. Phys. Lett.*, 1981, **80**, 352.

⁴²⁴ P. Varanasi and P. Wyant, *J. Quant. Spectrosc. Radiat. Transfer*, 1981, **25**, 311.

⁴²⁵ K.-E. J. Hallin, J. W. C. John, and A. Trombetti, *Can. J. Phys.*, 1981, **59**, 663.

⁴²⁶ N. J. Brassington, H. G. M. Edwards, and D. A. Long, *J. Raman Spectrosc.*, 1981, **11**, 346.

⁴²⁷ A. Goldman, G. R. Cook, and F. S. Bonomo, *J. Quant. Spectrosc. Radiat. Transfer*, 1980, **24**, 211.

⁴²⁸ A. Baldacci, V. M. Devi, K. N. Rao, and G. Tarrago, *J. Mol. Spectrosc.*, 1980, **81**, 179.

⁴²⁹ G. Tarrago, M. Dang-Nhu, and A. Goldman, *J. Mol. Spectrosc.*, 1981, **88**, 311.

⁴³⁰ G. di Lonardo and A. Trombetti, *Chem. Phys. Lett.*, 1980, **76**, 307.

⁴³¹ K. Kijima and T. Tanaka, *J. Mol. Spectrosc.*, 1981, **89**, 62.

⁴³² J. L. Duncan, D. C. McKean, I. Torto, and G. D. Nivellini, *J. Mol. Spectrosc.*, 1981, **85**, 16.

Table 9 (continued)

Molecule	Technique	Comments	Ref.
B_2H_6	FTIR	$\nu_{17}, \nu_{18}, \nu_{14}, \nu_9 + \nu_{15}$	433
B_2^2H_6	FTIR	$\nu_{17}, \nu_{18}, \nu_5 + \nu_{15}, \nu_8, \nu_{14}$	434
GeH_4	CARS, IR	ν_1, ν_3	435
GeH_4	FTIR	ν_2, ν_4	436
HNO_3	diode laser	$\nu_2, 1690-1727 \text{ cm}^{-1}$	437
MoF_6	diode laser	ν_3 Q branch, $740-750 \text{ cm}^{-1}$; laser isotope separation of Mo?	438
NOF_3	FTIR	350-1800 cm^{-1}	439
POF_3	IRMWDR three and four level	ν_4 fundamental; B, dipole moment for $\nu_4 = 1$	440
SF_6	cw CO_2 laser	absorption coefficients for 10.6 and 9.4 μm bands	441
SF_6	IRDR (diode laser)	line shape analysis	442
SF_6	diode laser	ν_5 and ν_6 bands, Coriolis interactions	443
SF_6	cw laser, s/s beam, bolometer	$P(3)$ and $P(4)$ of ν_3 ; oscillations and adiabatic rapid passage	444
SF_6	DFS	$3\nu_3$	445
SF_6	DFS	$3\nu_3, 160 \text{ K}$	446
SF_6	CARS, CSRS	ν_1, ν_2 ; anharmonicity, vibration-rotation	447
SiH_4	inverse Raman	quasi-cw, near Doppler limit	448
SiH_4	CARS, IR	ν_1, ν_3	435
$\text{Si}^2\text{H}_3\text{H}$	IR	ν_1	449
$\text{SiH}^{35,37}\text{Cl}$	FTIR	$\nu_3, 2\nu_3$	450
SiH_3I	FTIR	ν_3	451
UF_6, WF_6	cw CO_2 laser	absorption coefficients for 10.6 and 9.4 μm bands	441
CClF_3	FTIR	anharmonic force field; Coriolis and anharmonic coefficients	452
CF_4	diode laser	$\nu_4, 16 \mu\text{m}$; CF_4 laser?	453

433 E. Hamilton and J. L. Duncan, *J. Mol. Spectrosc.*, 1981, **90**, 129.

434 E. Hamilton and J. L. Duncan, *J. Mol. Spectrosc.*, 1981, **90**, 517.

435 G. Ya. Zueva, D. N. Kozlov, P. V. Nickles, A. M. Prokhorov, V. V. Smirnov, and S. M. Tchuksin, *Opt. Commun.*, 1980, **35**, 218.

436 W. A. Kreiner, R. Obferkuch, A. G. Robiette, and P. H. Turner, *J. Mol. Spectrosc.*, 1981, **85**, 442.

437 A. G. Maki and J. S. Wells, *J. Mol. Spectrosc.*, 1980, **82**, 427.

438 J. C. Cummings, *J. Mol. Spectrosc.*, 1980, **83**, 417.

439 P. Nectoux, A. Vinit, and M. Gilbert, *J. Mol. Spectrosc.*, 1980, **84**, 146.

440 T. Amano and R. H. Schwendeman, *Chem. Phys.*, 1981, **57**, 333.

441 D. M. Cox and A. Gnauck, *J. Mol. Spectrosc.*, 1980, **81**, 207.

442 C. Reiser, J. I. Steinfeld, and H. W. Galbraith, *J. Chem. Phys.*, 1981, **74**, 2189.

443 S. Marchetti, *J. Phys. B*, 1981, **14**, L827.

444 S. Avrillier, J.-M. Raimond, Ch. J. Borde, D. Bassi, and G. Scoles, *Opt. Commun.*, 1981, **39**, 311.

445 A. S. Pine and A. G. Robiette, *J. Mol. Spectrosc.*, 1980, **80**, 388.

446 C. W. Patterson and B. J. Krohn, *J. Mol. Spectrosc.*, 1981, **88**, 133.

447 J. Cahen-de Villardi, M. Clerc, P. Isnard, and J. M. Weulersse, *J. Mol. Spectrosc.*, 1980, **84**, 319.

448 A. Owyoung, P. Esherick, A. G. Robiette, and R. S. McDowell, *J. Mol. Spectrosc.*, 1981, **86**, 209.

449 C. Frommer, R. W. Lovejoy, R. L. Sams, and W. B. Olson, *J. Mol. Spectrosc.*, 1981, **89**, 261.

450 H. Burger, J. Cichon, S. Dobos, R. Eujen, and P. Schulz, *J. Mol. Spectrosc.*, 1981, **86**, 298.

451 H. Burger, S. Dobos, P. Schulz, and A. Ruoff, *J. Mol. Spectrosc.*, 1980, **84**, 478.

452 K. Scanlon, I. Suzuki, and J. Overend, *J. Chem. Phys.*, 1981, **74**, 3735.

453 R. S. McDowell, M. J. Reisfeld, H. W. Galbraith, B. J. Krohn, H. Flicker, R. C. Kennedy, J. P. Aldridge, and N. G. Nereson, *J. Mol. Spectrosc.*, 1980, **83**, 440.

Table 9 (continued)

Molecule	Technique	Comments	Ref.
CF ₄	diode laser	$\nu_2 + \nu_4$	454
CF ₄	FTIR	ν_4	455
CF ₄	FTIR	$2\nu_1 + \nu_4$, 2445 cm ⁻¹	456
CF ₄	IRRFD	(diode laser)	457
CF ₄	IRMWDR	(diode laser)	458
CF ₄	inverse Raman	ν_1 (Q branch) and $\nu_1 + \nu_2 \leftarrow \nu_2$ hot band	459
CF ₄	Raman	all fundamentals plus some overtones and hot bands	460
CF ₄	CO ₂ laser	self-broadening, cf. Ar-CF ₄	461
CF ₃ Cl	IR	600—2100 cm ⁻¹	462
CF ₂ Cl ₂	IR/SISAM	8.6 and 10.6 μm	463
CF ₃ I	MWIRDR	9.4 μm CO ₂ laser; analysis incomplete	464
CHF ₃	IR	fundamental and 1st overtone C—H	465
CHF ₃	diode laser	ν_4 , Coriolis $\nu_4 - 2\nu_3$	466
CH ₂ F ₂	FTIR, 11 atm.	intensities, Coriolis interaction	467
CH ₂ OS (HCOSH)	IR	force field, torsional potential	468
CH ₃ Br	IR	review of perturbation, r_e structure (142 refs)	469
C ² H ₃ Br	FTIR	Coriolis interaction $\nu_2 - \nu_5$	470
C ² H ₃ Br	IR	ν_4 , Coriolis interactions	471
C ² H ₃ Br	FTIR	ν_6 , 713 cm ⁻¹	472
CH ₃ Br	IRRFD intracavity	ν_6 , $2\nu_5$, $\nu_3 + \nu_6$; hfs	473
CH ₃ Cl	FTIR	2280—2580 cm ⁻¹ ; $\nu_2 + \nu_6$, $\nu_5 + \nu_6$, $2\nu_3 + \nu_6$	474
CH ₃ ^{35,37} Cl	FTIR, Raman	r_e structure	475
CH ₃ F	tunable laser sidebands	ν_3 , Stark effect	476

⁴⁵⁴ C. W. Patterson, R. S. McDowell, N. G. Nereson, R. F. Begley, H. W. Galbraith, and B. J. Krohn, *J. Mol. Spectrosc.*, 1980, **80**, 71.

⁴⁵⁵ G. Tarrago, G. Poussigul, M. Dang-Nhu, and J. Kauppinen, *J. Mol. Spectrosc.*, 1981, **86**, 232.

⁴⁵⁶ M. Dang-Nhu, G. Graner, and G. Guelachvili, *J. Mol. Spectrosc.*, 1981, **85**, 358.

⁴⁵⁷ M. Takami, *J. Chem. Phys.*, 1980, **73**, 2665.

⁴⁵⁸ M. Takami, *J. Chem. Phys.*, 1981, **74**, 4276.

⁴⁵⁹ P. Esherick, A. Owyoung, and C. W. Patterson, *J. Mol. Spectrosc.*, 1981, **86**, 250.

⁴⁶⁰ J.-E. Lolck, *J. Raman Spectrosc.*, 1981, **11**, 294.

⁴⁶¹ R. Eckhardt, J. Telle, and L. Haynes, *J. Mol. Spectrosc.*, 1981, **90**, 321.

⁴⁶² S. Giorgianni, A. Gambi, R. Visinoni, and S. Gherardi, *J. Mol. Spectrosc.*, 1981, **90**, 51.

⁴⁶³ M. Morillon-Chapey, A. O. Diallo, and J.-C. Deroche, *J. Mol. Spectrosc.*, 1981, **88**, 424.

⁴⁶⁴ F. Kohler, H. Jones, and H. D. Rudolph, *J. Mol. Spectrosc.*, 1980, **80**, 56.

⁴⁶⁵ H.-R. Dubal and M. Quack, *Chem. Phys. Lett.*, 1980, **72**, 342.

⁴⁶⁶ S. Sofue, K. Kawaguchi, E. Hirota, and T. Fujiyama, *Bull. Chem. Soc. Jpn.*, 1981, **54**, 897.

⁴⁶⁷ S. Kondo, T. Nakanago, and S. Saeki, *J. Chem. Phys.*, 1980, **73**, 5409.

⁴⁶⁸ B. P. Winnewisser and W. H. Hocking, *J. Phys. Chem.*, 1980, **84**, 1771.

⁴⁶⁹ G. Graner, *J. Mol. Spectrosc.*, 1981, **90**, 394.

⁴⁷⁰ C. Betrencourt-Stirnemann, R. Paso, J. Kauppinen, and R. Anttila, *J. Mol. Spectrosc.*, 1981, **87**, 506.

⁴⁷¹ P. M. Wilt, F. W. Hecker, J. D. Fehribach, D. E. Bardin, and T. H. Edwards, *J. Mol. Spectrosc.*, 1981, **90**, 33.

⁴⁷² R. Paso, J. Kauppinen, R. Anttila, and C. Betrencourt-Stirnemann, *J. Mol. Spectrosc.*, 1981, **85**, 232.

⁴⁷³ E. Arimondo, J. G. Baker, P. Glorieux, T. Oka, and J. Sakai, *J. Mol. Spectrosc.*, 1980, **82**, 54.

⁴⁷⁴ C. di Lauro and C. Alamichel, *J. Mol. Spectrosc.*, 1980, **81**, 390.

⁴⁷⁵ P. Jensen, S. Brodersen, and G. Guelachvili, *J. Mol. Spectrosc.*, 1981, **88**, 378.

⁴⁷⁶ G. Magerl, W. Schupita, E. Bonek, and W. A. Kreiner, *J. Mol. Spectrosc.*, 1980, **83**, 431.

Table 9 (continued)

Molecule	Technique	Comments	Ref.
CH ₃ F	IRIRDR molecular beam	Doppler-free hot band transition, $2\nu_3 \leftarrow \nu_3$	477
C ² H ₃ F	laser Stark	ν_5 , vibration-rotation, dipole moment	478
CH ₃ I	FTIR	2880—3160 cm ⁻¹ , seven overlapping bands	479
CH ₂ ² HI	diode laser	ν_6''	480
¹³ CH ₃ I	diode laser	ν_6	480
C ² H ₃ I	FTIR	$\nu_3 \sim 500$ cm ⁻¹	481
C ² H ₃ I	FTIR	ν_6	482
CH ₃ I	diode laser	isotope shift for ¹²⁹ I in ν_6 band	483
CH ₃ I	IRRFDR	ν_6 , 1-type doubling	484
CH ₃ O (CH ₂ OH)	IR	Ar matrix (Ar*, F + CH ₃ OH)	485
CH ₄	FTIR	$3\nu_3$, ~9000 cm ⁻¹ ; use of T dependence of line intensity ratios for analysis	486
^{12,13} CH ₄	FTIR	$\nu_2 + \nu_3$, 4400—4650 cm ⁻¹ (perturbed)	487
CH ₃ ² H	FTIR analysis	ν_2	488
CH ₄	FTIR	$\nu_3 + \nu_4 - \nu_4$	489
CH ₄	FTIR	$\nu_3 + \nu_4$	490
¹³ CH ₃ ² H	FTIR	ν_2	491
CH ₄	inverse Raman, free jet expansion	non-Boltzman population because of nuclear spin effects	492
CH ₄	analysis	$\nu_1, \nu_3, 2\nu_2, \nu_2 + \nu_4, 2\nu_4$; interacting states	493
CH ₄	IRRFDR	ν_2, ν_4	494
¹³ CH ₄	inverse Raman quasi-cw	ν_1 , fundamental	495
CH ₃ ² H	IR	2 ν_6 , 4.5 μm	496
CH ₃ ² H	IR	ν_3 , 7.6 μm	497
C ² H ₃ H	IR	900—1400 cm ⁻¹ , vibration-rotation constants for $\nu_5 = 1$	498

⁴⁷⁷ F. Matsushima, N. Morita, Y. Honguh, and T. Shimizu, *Appl. Phys.*, 1981, **24**, 219.

⁴⁷⁸ G. L. Caldow and G. Duxbury, *J. Mol. Spectrosc.*, 1981, **89**, 93.

⁴⁷⁹ G. Graner and G. Guelachvili, *J. Mol. Spectrosc.*, 1981, **89**, 19.

⁴⁸⁰ P. P. Das, V. M. Devi, and K. N. Rao, *J. Mol. Spectrosc.*, 1981, **86**, 202.

⁴⁸¹ R. Anttila, M. Koivusaari, J. Kauppinen, and E. Kyro, *J. Mol. Spectrosc.*, 1980, **84**, 225.

⁴⁸² M. Koivusaari, J. Kauppinen, A.-M. Kelhala, and R. Anttila, *J. Mol. Spectrosc.*, 1980, **84**, 342.

⁴⁸³ M. Wahlen and G. Tucker, *Opt. Commun.*, 1981, **36**, 39.

⁴⁸⁴ E. Arimondo and P. Glorieux, *J. Mol. Spectrosc.*, 1980, **84**, 559.

⁴⁸⁵ M. E. Jacox, *Chem. Phys.*, 1981, **59**, 213.

⁴⁸⁶ G. Pierre, J.-C. Hilico, C. de Bergh, and J.-P. Maillard, *J. Mol. Spectrosc.*, 1980, **82**, 379.

⁴⁸⁷ J.-C. Hilico, J. Degni, J. P. Champion, and G. Guelachvili, *J. Mol. Spectrosc.*, 1980, **81**, 277.

⁴⁸⁸ C. Chackerian and G. Guelachvili, *J. Mol. Spectrosc.*, 1980, **84**, 447.

⁴⁸⁹ R. H. Hunt, L. R. Brown, R. A. Toth, and J. W. Brault, *J. Mol. Spectrosc.*, 1981, **86**, 170.

⁴⁹⁰ R. H. Hunt, L. R. Brown, R. A. Toth, and J. W. Brault, *J. Mol. Spectrosc.*, 1981, **86**, 159.

⁴⁹¹ C. Chackerian and G. Guelachvili, *J. Mol. Spectrosc.*, 1980, **80**, 244.

⁴⁹² J. J. Valentini, P. Esherick, and A. Owyoung, *Chem. Phys. Lett.*, 1980, **75**, 590.

⁴⁹³ J.-E. Lolck and A. G. Robiette, *J. Mol. Spectrosc.*, 1981, **88**, 14.

⁴⁹⁴ A. G. Robiette, *J. Mol. Spectrosc.*, 1981, **86**, 143.

⁴⁹⁵ W. A. Kreiner and A. G. Robiette, *J. Chem. Phys.*, 1981, **74**, 3713.

⁴⁹⁶ R. S. McDowell, C. W. Patterson, and A. Owyoung, *J. Chem. Phys.*, 1980, **72**, 1071.

⁴⁹⁷ G. Poussigul, G. Tarrago, P. Cardinet, and A. Valentin, *J. Mol. Spectrosc.*, 1980, **82**, 35.

⁴⁹⁸ G. Tarrago, K. N. Rao, and L. W. Pinkley, *J. Mol. Spectrosc.*, 1980, **79**, 31.

⁴⁹⁹ J. Dupré-Maquaire, J. Dupré, and G. Tarrago, *J. Mol. Spectrosc.*, 1981, **90**, 63.

Table 9 (continued)

Molecule	Technique	Comments	Ref.
$^{13}\text{CH}_4$	IR	$2\nu_3$, 1.67 μm	500
CH_4	IR	ν_3 transition moments and line strengths	501
$\text{C}^{1,2}\text{H}_4$	IR	absolute intensities, dipole moment derivatives, and bond charge parameters	502
$\text{CH}_4\text{O} (\text{CH}_3\text{OH})$	IRMWDR	Stark effect in g.s. and 1st excited C—O stretch	503
$\text{CH}_4\text{O} (\text{CH}_3\text{OH})$	diode laser	C—O stretch fundamental, 1034 cm^{-1}	504
$\text{CH}_4\text{O} (\text{CH}_3\text{OH})$	laser Stark (HCN laser)	significant variation of dipole moment parameters with torsion—rotation state	505
$\text{CH}_4\text{O} (\text{C}^2\text{H}_3\text{OH})$	laser Stark (diode laser)	Doppler limited $P(J)$ and $R(J)$ multiplets for $J \leq 10$ of 10 μm C—O stretch band	506
$\text{CH}_4\text{O} (\text{CH}_3\text{OH})$	CH_3OH laser	C—O stretch fundamental, Stark effect used in analysis	507
$\text{CH}_4\text{O} (\text{CH}_3\text{OH})$ $\text{C}_2\text{F}_5\text{Cl}$	CH_3OH laser IRMPPE, IR fluorescence	perturbation of C—O stretch onset of quasi-continuum at vibrational state density of $\sim 400/\text{cm}^{-1}$	508 509
$\text{C}_2\text{F}_4\text{S}_2$	IR	band intensities near 1080 and 965 cm^{-1} , significance for IR photochemistry	510
$\text{C}_2\text{HCl}_3\text{O} (\text{CCl}_3\text{CHO})$	Raman	20–3200 cm^{-1} , low frequency torsion	511
$\text{C}_2\text{H}_2\text{F}$	IR	in Ar matrix (from $\text{F} + \text{C}_2\text{H}_2$)	512
$\text{C}_2\text{H}_2\text{F}_2$	diode laser heterodyne (wideband)	ν_4 , ν_9	513
$\text{C}_2\text{H}_2\text{F}_2$	diode laser	ν_4 , ν_9	514
$\text{C}_2\text{H}_2\text{N}_4$ (s-tetrazine)	CARS	resonant, and delayed, CARS	515
$\text{C}_2\text{H}_2\text{N} (\text{CH}_3\text{NC})$	intracavity cw dye laser	$5\nu_{\text{CH}}$, $6\nu_{\text{CH}}$, $5\nu_{\text{CH}} + \nu_1$ laser isotope separation	516
$\text{C}_2^{1,2}\text{H}_4$	FTIR	ν_{12} fundamentals	517
$\text{C}_2\text{H}_3^{2\text{H}}$	IR	Fermi resonance, $\nu_1 - (\nu_2 + \nu_{12})$, $\sim 3000 \text{ cm}^{-1}$	518

500 K. Fox, G. W. Halsey, and D. E. Jennings, *J. Mol. Spectrosc.*, 1980, **83**, 213.501 S. Gherissi, A. Henry, M. Loete, and A. Valentini, *J. Mol. Spectrosc.*, 1981, **86**, 344.502 J. H. G. Bode and W. M. A. Smit, *J. Phys. Chem.*, 1980, **84**, 198.503 T. Amano, *J. Mol. Spectrosc.*, 1981, **88**, 194.504 J. O. Henningsen, *J. Mol. Spectrosc.*, 1981, **85**, 282.505 L. H. Johnston, R. P. Srivastava, and R. M. Lees, *J. Mol. Spectrosc.*, 1980, **84**, 1.506 W. H. Weber, D. H. Leslie, and C. W. Peters, *J. Mol. Spectrosc.*, 1981, **89**, 214.507 J. O. Henningsen, *J. Mol. Spectrosc.*, 1980, **83**, 70508 R. M. Lees, M. A. Walton, and J. O. Henningsen, *J. Mol. Spectrosc.*, 1981, **88**, 90.509 J. W. Hudgens and J. D. McDonald, *J. Chem. Phys.*, 1981, **74**, 1510.510 M. Quack and G. Seyfang, *Chem. Phys. Lett.*, 1981, **84**, 541.511 J. R. Durig and W. J. Natter, *J. Raman Spectrosc.*, 1981, **11**, 32.512 M. E. Jacox, *Chem. Phys.*, 1980, **53**, 307.513 J. P. Sattler, T. L. Worchesky, K. J. Ritter, and W. J. Lafferty, *Opt. Lett.*, 1980, **5**, 21.514 W. J. Lafferty, J. P. Sattler, T. L. Worchesky, and K. J. Ritter, *J. Mol. Spectrosc.*, 1981, **87**, 416.515 T. J. Aartsma, W. H. Hesselink, and D. A. Wiersma, *Chem. Phys. Lett.*, 1980, **71**, 424.516 K. V. Reddy and M. J. Berry, *Chem. Phys. Lett.*, 1980, **72**, 29.517 J. Harper, A. R. Morrison, and J. L. Duncan, *Chem. Phys. Lett.*, 1981, **82**, 32.518 Y. Verbist-Scieur, C. P. Courtoy, and A. Fayt, *J. Mol. Spectrosc.*, 1981, **85**, 480.

Table 9 (continued)

Molecule	Technique	Comments	Ref.
$\text{C}_2\text{H}_2^{2}\text{H}_2$	IR	a -axis Coriolis interacting band system	519
C_2H_4	IR, diode laser, waveguide laser	$\sim 10 \mu\text{m}$; ν_7 , ν_{10} and (inactive) ν_4	520
$^{12}\text{C}^{13}\text{CH}_4$	IR	$\nu_5 + \nu_{12}$, $\nu_1 + \nu_{12}$; $\sim 4500 \text{ cm}^{-1}$	521
$\text{C}_2\text{H}_3^{2}\text{H}$	IR	ν_3	522
C_2^{2}H_4	IR		523
C_2^{2}H_4	diode laser	ν_{11} , 2200 cm^{-1}	524
C_2H_4	analysis of vibration	generalized isotope rules for molecular vibration	525
$\text{C}_2\text{H}_4\text{O}$ (ethyl oxide)	IR	fundamental bands, Coriolis interactions, intensity borrowing, force fields	526
$\text{C}_2\text{H}_4\text{O}$ (acetaldehyde)	IR	torsional vibrational levels, restricted rotational potentials, RKR	527
C_2H_6	IR	$1940 - 2152 \text{ cm}^{-1}$	528
C_2H_6	IR	ν_7	529
C_2H_6	FTIR	ν_9 , $12.17 \mu\text{m}$	530
C_2H_6		overtones; pure CH_3 local mode overtone dominant	531
$\text{C}_2\text{H}_3^{2}\text{H}_3$	FTIR		532
$\text{C}_2\text{H}_3^{2}\text{H}_3$	IR	$2\nu_3$	533
$\text{C}_2\text{H}_3^{2}\text{H}_3$	IR	ν_7	534
$\text{C}_2\text{H}_4\text{F}$	IR	Ar matrix (from $\text{F} + \text{C}_2\text{H}_4$)	535
$\text{C}_2\text{H}_7\text{P}$ (dimethyl phosphine-d ₃)	IR, Raman	assignment, normal co-ordinate analysis	133
$\text{C}_2\text{H}_8\text{Si}_2$ (1,3-disilacyclobutane-1,1,3-d)	IR	ring puckering combination bands, isotope effect	536
C_3F_6^+	IR, matrix photoionization		537
C_3O_2	FTIR	$1800 - 2600 \text{ cm}^{-1}$, ν_3 and $\nu_2 + \nu_4$	538

519 F. Hegelund and J. L. Duncan, *Mol. Phys.*, 1981, **44**, 803.520 C. Lambeau, A. Fayt, J. L. Duncan, and T. Nakagawa, *J. Mol. Spectrosc.*, 1980, **81**, 227.521 M. de Vleeschouwer, C. Lambeau, D. van Lerberghe, E. Janssens, and A. Fayt, *J. Mol. Spectrosc.*, 1981, **90**, 273.522 P. Herbin, G. Blanquet, J. Walrand, C. P. Courtoy, and A. Fayt, *J. Mol. Spectrosc.*, 1981, **86**, 310.523 J. L. Duncan, E. Hamilton, A. Fayt, D. van Lerberghe, and F. Hegelund, *Mol. Phys.*, 1981, **43**, 737.524 N. Ohashi, K. Kawaguchi, and E. Hirota, *J. Mol. Spectrosc.*, 1981, **85**, 427.525 T. Wolfram and A. Asgharian, *J. Chem. Phys.*, 1981, **74**, 1661.526 T. Nakanaga, *J. Chem. Phys.*, 1980, **73**, 5451.527 P. Pajunen, *J. Mol. Spectrosc.*, 1981, **88**, 64.528 K. F. Lin, W. E. Blass, and N. M. Gailar, *J. Mol. Spectrosc.*, 1980, **79**, 151.529 A. R. H. Cole, K. J. Cross, J. A. Cugley, and H. M. Heise, *J. Mol. Spectrosc.*, 1980, **83**, 233.530 S. J. Daunt, W. E. Blass, G. W. Halsey, K. Fox, R. J. Lovell, H. Flicker, and J. D. King, *J. Mol. Spectrosc.*, 1981, **86**, 327.531 B. R. Henry and W. R. A. Greenlay, *J. Chem. Phys.*, 1980, **72**, 5516.532 J. L. Duncan, J. Harper, A. R. Morrisson, G. D. Nivellini, and F. Tullini, *J. Mol. Spectrosc.*, 1981, **90**, 197.533 H. M. Heise and A. R. H. Cole, *J. Mol. Spectrosc.*, 1980, **83**, 245.534 H. M. Heise and A. R. H. Cole, *J. Mol. Spectrosc.*, 1980, **80**, 320.535 M. E. Jacox, *Chem. Phys.*, 1981, **58**, 289.536 P. W. Jagodzinski, R. M. Irwin, J. M. Cooke, and J. Laane, *J. Mol. Spectrosc.*, 1980, **84**, 139.537 B. J. Kelsall and L. Andrews, *J. Phys. Chem.*, 1981, **85**, 1288.538 L. Fusina, I. M. Mills, and G. Guelachvili, *J. Mol. Spectrosc.*, 1980, **79**, 101.

Table 9 (continued)

Molecule	Technique	Comments	Ref.
C_2O_2	FTIR	vibrational Renner-Teller effect	539
C_2O_2	fitting	semi-rigid bender Hamiltonian	540
C_3HN (HCC^{13}CN)	diode laser	ν_2 , 5 μm	541
$\text{C}_3\text{H}_2\text{O}$ (propynal-d ₁)	IRMWDR	MW transitions in $\nu_2 = 1$	542
$\text{C}_3\text{H}_2\text{O}$ (propynal)	IRMWDR (also triple resonance)	ν_2 ; also two photon inverse Lamb dips	543
C_3H_4 (allene-d ₄)	FTIR	Coriolis resonance	544
C_3H_4 (allene-d ₄)	FTIR	ν_{11}	545
C_3H_4 (allene-d ₄)	FTIR	hot bands, $\nu_9 + \nu_{11} - \nu_{11}$, $\nu_{10} + \nu_{11} - \nu_{11}$	546
C_3H_4 (allene-d ₄)	FTIR	ν_7	547
C_3H_4 (allene)	analysis	experimental signs of dipole moment derivatives	548
$\text{C}_3\text{H}_5\text{N}$ (propionitrile, inc. d ₀ , d ₂ , d ₃ and ^{13}CN)	FTIR/Raman	100—6000 cm^{-1}	549
C_3H_6 (cyclopropane)	diode laser	$\nu_{10} + \nu_{11}$	550
C_3H_6 (cyclopropane)	IR	ν_6 , ~3100 cm^{-1}	551
C_3H_6 (cyclopropane-d ₆)	IR	ν_6	552
$\text{C}_3\text{H}_6\text{O}$ (propanal)	IR, Raman, FIR	potential functions	553
$\text{C}_3\text{H}_7\text{N}$ (allylamine)	IRMWDR, triple resonance	IR transitions in two distinct rotameric forms observed	554
$\text{C}_4\text{HF}_9[(\text{CF}_3)_3\text{CH}]$	IR	bandshape and intensity, fundamental and first CH overtone	465
C_4H_2 (diacetylene)	MW	$\nu_8 - \nu_6$ band	555
C_4H_2 (diacetylene)	IR	ν_4 , 3 μm region	556
C_4H_8 (1-butene)	IR	conformation, torsional potential	557
C_4H_9 (t-butyl)	IR	matrix isolation	558
C_5H_{12} (neopentane)		overtones: $\Delta\nu_{\text{CH}} = 3, 4, 5$	559
$\text{C}_6\text{H}_3\text{F}_3$ (1,3,5-trifluoro benzene, and -d ₃)	Raman, IR	Coriolis coupling	560

⁵³⁹ L. Halonen, I. M. Mills, and J. Kauppinen, *Mol. Phys.*, 1981, **43**, 913.

⁵⁴⁰ P. R. Bunker, *J. Mol. Spectrosc.*, 1980, **80**, 422.

⁵⁴¹ K. Yamada and G. Winnewisser, *J. Mol. Spectrosc.*, 1981, **90**, 596.

⁵⁴² M. Takami and M. Suzuki, *J. Chem. Phys.*, 1980, **72**, 4089.

⁵⁴³ H. Jones, *J. Mol. Spectrosc.*, 1980, **81**, 21.

⁵⁴⁴ F. Hegelund, J. Kauppinen, and R. Anttila, *J. Mol. Spectrosc.*, 1981, **86**, 429.

⁵⁴⁵ F. Hegelund, R. Anttila, and J. Kauppinen, *J. Mol. Spectrosc.*, 1980, **81**, 164.

⁵⁴⁶ F. Hegelund, P. Lund, R. Anttila, and J. Kauppinen, *J. Mol. Spectrosc.*, 1981, **89**, 174.

⁵⁴⁷ R. Anttila, M. Koivusaari, J. Kauppinen, and F. Hegelund, *J. Mol. Spectrosc.*, 1981, **87**, 393.

⁵⁴⁸ M. N. Ramos, A. B. M. S. Bassi, and R. E. Bruns, *J. Mol. Spectrosc.*, 1981, **87**, 298.

⁵⁴⁹ H. M. Heise, F. Winther, and H. Lutz, *J. Mol. Spectrosc.*, 1981, **90**, 531.

⁵⁵⁰ W. H. Weber, D. H. Leslie, C. W. Peters, and R. W. Terhune, *J. Mol. Spectrosc.*, 1980, **81**, 316.

⁵⁵¹ B. Rubin, S. R. Polo, and T. K. McCubbin, *J. Mol. Spectrosc.*, 1980, **84**, 487.

⁵⁵² A. H. Nielsen, S. J. Daunt, and G. W. Halsey, *J. Mol. Spectrosc.*, 1980, **81**, 494.

⁵⁵³ J. R. Durig, D. A. C. Compton, and A. Q. McArver, *J. Chem. Phys.*, 1980, **73**, 719.

⁵⁵⁴ I. Botskor and H. Jones, *J. Mol. Spectrosc.*, 1980, **81**, 1.

⁵⁵⁵ K. Matsumura, T. Etoh, and T. Tanaka, *J. Mol. Spectrosc.*, 1981, **90**, 106.

⁵⁵⁶ H. L. Buijs and D. A. Ramsay, *Astrophys. J.*, 1980, **235**, L115.

⁵⁵⁷ J. R. Durig and D. A. C. Compton, *J. Phys. Chem.*, 1980, **84**, 773; **85**, 462.

⁵⁵⁸ J. Pacausty and J. S. Chang, *J. Chem. Phys.*, 1981, **74**, 5539.

⁵⁵⁹ B. R. Henry and M. A. Mohammadi, *Chem. Phys. Lett.*, 1980, **75**, 99.

⁵⁶⁰ J. Korppi-Tommola, H. F. Shurvell, S. J. Daunt, and D. Steele, *J. Mol. Spectrosc.*, 1981, **87**, 382.

Table 9 (continued)

Molecule	Technique	Comments	Ref.
C ₆ H ₆	FTIR	<i>B</i> ₀ constant of ν ₁₁	561
C ₆ H ₆	IR	band intensities	562
C ₆ ¹² H ₆ (and partially deuteriated species)	laser photoacoustic	overtones	563
C ₆ ¹² H ₁₂ (cyclohexane)	IR	degenerate bands; Coriolis coupling constants from band contour simulations	564
C ₆ H ₁₂ (cyclohexane)	FTIR	50—700 cm ⁻¹ , combination bands	565
C ₆ H ₁₂ O ₂ (tetramethyl dioxetane)	dye laser/mol. beam	4ν _{CH} , intramolecular relaxation	566
C ₇ H ₇ ⁻	IRMPD electron detachment	spectroscopic and mechanistic applications	567

Table 10 *Vibrational spectroscopic studies of loosely bound complexes. Molecules are listed in alphabetical order*

Molecule	Technique	Comments	Ref.
ArBCl ₃	cw CO ₂ laser	spectra broadened by predissociation	568
(Bi) _n	resonance Raman, matrix	Bi ₂ , ? Bi ₄	569
(C ₂ H ₄) _n , C ₂ H ₄ · Ar, Ne, Kr, C ₂ F ₄	IR	photodissociation spectra	570
(C ₆ H ₆) _n	OPO excitation	CH stretch range (3000—3100 cm ⁻¹); vibrational predissociation	571
CH ₃ F, HF }	IR, FTIR solid Ar		572
CH ₃ ⁺ , HF }			
(CO ₂) _n	CCL, molecular beam	IR spectra and vibrational predissociation; spectra close to (ν ₁ + ν ₃) and (2ν ₂ + ν ₃)	573
(Cs) _n	IR	?X ³ Σ _u ⁺ of (Cs) ₂ , ?Cs ₃ , Cs ₄	574
(H ₂ O) _n	IR	absorption by molecular water vapour, responsible for atmospheric IR continuum	575
NH ₄ (NH ₃) _n ⁺ , <i>n</i> = 0 to 4	pulsed IR	2—5 μm; isotope effects	576

561 J. Kauppinen, P. Jensen, and S. Brodersen, *J. Mol. Spectrosc.*, 1980, **83**, 161.562 M. Akiyama, *J. Mol. Spectrosc.*, 1980, **84**, 49.563 K. V. Reddy, D. F. Heller, and M. J. Berry, *J. Phys. Chem.*, 1982, **76**, 2814.564 T. Bien, G. Doege, and R. Arndt, *J. Raman Spectrosc.*, 1981, **11**, 112.565 T. L. Smithson and H. Wieser, *J. Chem. Phys.*, 1980, **72**, 2340.566 G. A. West, R. P. Mariella, jun., J. A. Pete, W. B. Hammond, and D. F. Heller, *J. Chem. Phys.*, 1981, **75**, 2006.567 C. Wight and J. L. Beauchamp, *J. Am. Chem. Soc.*, 1981, **103**, 6499.568 M. P. Casassa, D. S. Bomse, and K. C. Janda, *J. Phys. Chem.*, 1981, **85**, 2623.569 K. Manzel, U. Engelhardt, H. Abe, W. Schulze, and F. W. Froben, *Chem. Phys. Lett.*, 1981, **77**, 514.570 M. P. Casassa, D. S. Bomse, and K. C. Janda, *J. Chem. Phys.*, 1981, **74**, 5044.571 M. F. Vernon, J. M. Lisy, H. S. Kwok, D. J. Krajnovich, A. Tramer, Y. R. Shen, and Y. T. Lee, *J. Phys. Chem.*, 1981, **85**, 3327.572 G. L. Johnson and L. Andrews, *J. Am. Chem. Soc.*, 1980, **102**, 5736.573 T. E. Gough, R. E. Miller, and G. Scoles, *J. Phys. Chem.*, 1981, **85**, 4041.574 E. Zouboulis, N. D. Bhaskar, A. Vasilakis, and W. Happer, *J. Chem. Phys.*, 1980, **72**, 2356.575 H. R. Carlon, *J. Appl. Phys.*, 1981, **52**, 3111.576 H. A. Schwarz, *J. Chem. Phys.*, 1980, **72**, 284.

The Infrared Region.—Electric quadrupole vibration–rotation transitions have been observed in the fundamental band of O₂ around 1600 cm⁻¹, the first laboratory observation of such transitions in a molecule other than hydrogen.⁴⁹ This was achieved using the tunable diode laser/long path absorption technique which had earlier allowed the observation of the electric quadrupole rotational spectrum of H₂ reported in Part I.¹ The O₂ lines detected were S(5) and S(7) of the (1 ← 0) band, and each is a close triplet split by the spin of the X³Σ_g⁻ state. Magnetic dipole transitions were searched for but not found, which contrasts with results in the microwave and millimetre wave regions, where rotational magnetic dipole spectra of O₂ are well known, but quadrupole transitions seem absent. This different behaviour was explained by considering the magnetic dipole moment of O₂, which is molecule-fixed and rotates with it to give the rotational spectrum, but it is not expected to vary significantly with the stretching co-ordinate, and so the magnetic dipole vibrational spectrum is not observed. The electric quadrupole vibrational spectrum is observed, however, because of the expected quite strong dependence of the molecular quadrupole moment on vibrational motion.

These results have allowed the identification of the same transitions in the atmospheric solar spectrum, and have suggested a similar assignment for some lines in the 2400 cm⁻¹ region of the solar spectrum of N₂.⁵⁷⁷

Such experiments well illustrate the type of investigation which may now be attempted in the infrared. A glance at the tables covering recent spectroscopic studies in this region shows the extent to which diode laser spectroscopy and also Fourier transform spectroscopy are taking over in normal infrared experiments. (Operating principles of both diode lasers and Fourier transform spectrometers were described in Part I.¹) The diode laser still retains to some extent the temperament of a research instrument, whereas the commercial development of Fourier transform spectrometers has made their routine use possible even in analytical laboratories. Clearly some experiments require an intense monochromatic light source, and the diode laser also has the edge in resolution over the FTS, but commercially available Fourier transform spectrometers are now very good indeed (with resolution of <0.01 cm⁻¹), and suited to taking survey spectra as well as carrying out high resolution work.

A further glance at the tables quickly advises against attempting to comment upon or rationalize the results of all the work which has been carried out; Legon⁵⁷⁸ has presented a rationalization of the equilibrium conformations of 4- and 5-membered cyclic molecules, and that review alone runs to 450 references.

The reduction of the mass of spectroscopic data to forms which are manageable and preferably of physical significance is of importance, and a desirable method of doing this is by the construction of potential surfaces which reproduce the data. (We saw some examples of this in Section 1, in the sub-section on microwave spectroscopy and when considering van der Waals molecules, but the potential usefulness of information about vibrational levels soon became clear.)

There are well known methods of fitting data for diatomic molecules to potential curves, but Whiffen³⁷⁶ has considered the problem for a linear triatomic, taking carbonyl sulphide as an example. Rather than applying perturbation theory, he uses a matrix diagonalization method which is compatible with a least-squares technique,

⁵⁷⁷ A. Goldman, J. Reid, and L. S. Rothman, *Geophys. Res. Lett.*, 1981, **8**, 77.

⁵⁷⁸ A. C. Legon, *Chem. Rev.*, 1980, **80**, 231.

and he also compares the method with other possible strategies. Some modifications to this method are discussed in a determination of the anharmonic force field of CS_2 ,³³² and a numerical technique for the comparison of different potential surfaces is applied.

Another approach to the construction of ground-state potential surfaces has been taken by Murrell, Mills, and co-workers, for example in the cases of C_3 and HCN .³¹⁰ They fit data on energy, geometry, and force constants in all stable conformations, together with data on dissociation products and results of *ab initio* energy calculations for other conformations. Analytic functions are employed, where the triatomic potential surface is written as the sum of 1-atom, 2-atom, and 3-atom terms, and they interpolate between equilibrium configurations and dissociation products for which the functions fit exactly.

Developments in Experimental Technique, and some Interesting New Experiments.— Altmann *et al.*⁵⁷⁹ have described the construction of a simple multipass absorption cell suitable for use with a laser. Two parallel concave mirrors are used, and adjusting the distance between them varies the number of passes: a 1 m long cell provided path lengths between 3 and 150 m.

A wavelength meter for tunable diode lasers has been constructed by Nagai *et al.*⁵⁸⁰ Its standard is a single frequency He–Ne laser, and it consists of moving corner reflectors which form a Michelson interferometer. When measuring CO_2 laser wavelengths, an absolute accuracy of 10^{-7} was obtained.

A method of measuring absolute line strengths has been demonstrated by Jennings⁵⁸¹ for lines in the v_4 band of CH_4 . This splits the output of a diode laser to allow double beam operation, and acquires signal using ‘sweep integration’ (*i.e.*, with a dual-channel signal averager). Techniques are described to minimize refractive and calibration errors. Calibration is achieved by heterodyne beating with a stabilized CO_2 laser.

‘Wideband, rapid and accurate’ diode laser heterodyne spectroscopy has been developed by Sattler *et al.*,⁵¹³ and applied to the v_4 and v_9 bands of 1,1-difluoroethylene. Their technique operates at up to ± 6.5 GHz from a CO_2 laser emission line.

Fridovich *et al.* have derived a simple procedure, applicable for example to diode laser spectra, whereby the distortion of a Doppler line by a Gaussian instrument function may be calculated.⁵⁸²

An absorption cell in which gas may be heated, designed with Fourier transform spectroscopy in mind, has been described by Dalton and Sakai.⁵⁸³ They chose the configuration of Pfund rather than that of White for the multi-reflection optics, because in the White cell the features which allow easy adjustment of the optical path length may cause instability. The Pfund arrangement is less flexible, but more stable in the severe mechanical environment of high temperature. Experiments on CO_2 and H_2O at temperatures up to 1300 K are described.

A study of the $\Delta v = 2$ sequence ($v < 15$) of NO^{286} provides an example of the

⁵⁷⁹ J. Altmann, R. Baumgart, and C. Weitkamp, *Appl. Opt.*, 1981, **20**, 995.

⁵⁸⁰ K. Nagai, K. Kawaguchi, C. Yamada, K. Hayakawa, Y. Takagi, and E. Hirota, *J. Mol. Spectrosc.*, 1980, **84**, 197.

⁵⁸¹ D. E. Jennings, *Appl. Opt.*, 1980, **19**, 2695.

⁵⁸² B. Fridovich, V. M. Devi, and P. P. Das, *J. Mol. Spectrosc.*, 1980, **81**, 269.

⁵⁸³ W. S. Dalton and H. Sakai, *Appl. Opt.*, 1980, **19**, 2413.

application of Fourier transform spectroscopy to a system in emission. It is hoped that its versatility might extend also to fast-scan real time-resolved studies. In Part I¹ we reported the observation by Mantz of HCO, using time-resolved FTS, following the flash photolysis of acetaldehyde. This work has been questioned by Garrison *et al.*,⁵⁸⁴ who present strong evidence that the transient spectra were misinterpreted and that they were due to artefacts. They are optimistic, however, that the technique may be viable given revised experimental conditions.

FTIR spectroscopy has also been used to obtain broad band infrared spectra from molecules in a supersonic expansion. A cryopumped jet assembly was mounted inside the sample chamber of a commercial spectrometer, and the system used to study collision-induced rotational energy transfer (rotational cooling) in ammonia; statistically significant deviations from a Boltzmann distribution were found, indicative of a $\Delta K = 0$ propensity rule.⁴¹⁰

There have been advances in the application of tunable infrared laser sources (in addition to diode lasers) to spectroscopy. There have been several studies (see Tables) using the cw difference frequency spectrometer (DFS).⁵⁸⁵ This operates in the 2.2—4.2 μm region, coherent infrared radiation resulting from the mixing of two visible lasers (argon ion and dye) in LiNbO₃ crystal, coupled with careful phase-matching. An extensive study has, for example, been made of the two IR-active vibrational bands of the $3\nu_3$ manifold of SF₆, at a temperature of 160 K and with near Doppler-limited resolution.⁴⁴⁶ Analysis showed that the weak (2, 1, 0) sub-band of $3\nu_3$, having only a very small intrinsic dipole transition moment, derives most of its strength by intensity borrowing from the (3, 0, 0) sub-band.

Colour centre lasers (CCL's),^{586,587} which can operate pulsed or cw, may have a cw output power of 50 mW (or several mW single mode), and are beginning to show their usefulness in molecular spectroscopy.* Such a laser has been incorporated in a computer-controlled spectrometer described by Litfin *et al.*⁵⁸⁸ They have also reported sensitivity enhancement in CCL studies by using the magnetic rotation Faraday effect.⁵⁸⁹ This experiment is similar in principle to polarization spectroscopy (see Part I¹), although it does not require saturation. When a magnetic field is applied to a paramagnetic molecule, the transition of interest splits into components which respond differently to the right and left circular components of linearly polarized light, and so when the laser is tuned to one component of the transition, its axis of polarization is rotated. This enables transmission of the laser beam by crossed polarizers, and so an absorption signal may be detected. The effect allows the signal to be modulated, and discriminates against diamagnetic background. It has been applied to the first NO overtone, and the fundamental of OH.

Pfeiffer *et al.*³⁰⁰ have also used this technique to study OH. They have obtained effective molecular *g*-values, and measured OH radical concentrations of 10^{13} cc^{-1} ,

* We shall see later the use of CCL's in the spectroscopy of electronically excited states also.

⁵⁸⁴ A. A. Garrison, R. A. Crocombe, G. Mamantov, and J. A. de Haseth, *Appl. Spectrosc.*, 1980, **34**, 399.

⁵⁸⁵ A. S. Pine, *J. Opt. Soc. Am.*, 1976, **66**, 97.

⁵⁸⁶ L. F. Mollenauer, 'Colour Centre Lasers', in 'Methods of Experimental Physics', ed. C. L. Rang, Vol. 15, Part B, 1979, p.1.

⁵⁸⁷ W. Gellerman, K. P. Koch, and F. Luty, *Laser Focus*, 1982, April, 71.

⁵⁸⁸ G. Litfin, C. R. Pollock, J. V. V. Kasper, R. F. Curl, jun., and F. K. Tittel, *IEEE J. Quant. Electron.*, 1980, **16**, 1154.

⁵⁸⁹ G. Litfin, C. R. Pollock, R. F. Curl, jun., and F. K. Tittel, *J. Chem. Phys.*, 1980, **72**, 6602.

and so the technique is presently less sensitive than LMR, although potentially more flexible. Increased sensitivity has subsequently been reported – see p. 338.

The colour centre laser is fairly noisy, and magnetic modulation is therefore more practical than Zeeman modulation for signal enhancement, but a Zeeman modulation technique has been used with a spin-flip Raman laser. A small magnetic field modulates the line centre of the absorbing paramagnetic molecule, thus modulating the transmitted laser intensity. Signal intensity and lineshape are quite different from those for a conventional absorption spectrum, and so these have been investigated in the case of NO for comparison with theory.²⁸⁸ The sign of g_J was predicted to change for high rotational states, and this was observed experimentally.

There has been increased use in molecular spectroscopy of techniques other than those which directly monitor the absorption or emission of photons. Whilst some studies using these techniques remain at the level of detection only, others have permitted extensive spectroscopy to be carried out. Foremost in the latter category is optoacoustic spectroscopy, in which sound waves resulting from non-radiative relaxation are picked up using a microphone.^{590,591} This technique is very sensitive, and when coupled with stable laser light sources is ideal for studying weak absorptions, such as high vibrational overtones, as we shall discuss later in this Section. One example of such a study, however, illustrates the sensitivity of the technique: Smith and Gelfand²⁷² calibrated their intracavity photoacoustic spectrometer on transitions in the (5, 0) band of HD. Measured line-strengths agreed very well with those obtained from an earlier conventional spectroscopic study, but they had used a pressure-pathlength product of only 10^{-6} of that of the earlier study. Whilst the authors pointed out that comparison of these figures is not strictly valid, the implication remains clear.

Optoacoustic detection has been coupled with a colour centre laser to study transitions to rotational levels of the v_3 band of HCN.⁵⁹² Lieto *et al.*⁵⁹³ have designed an optoacoustic cell suitable for laser-Stark spectroscopy; it may be a very appropriate application, because the sensitivity of the technique requires that the field be applied only over a small volume cell.

Optoacoustic detection is limited in operation at lower pressures by the need for collision partners to build up a signal which can be detected by the microphone. An alternative detection technique uses a sensitive thermal element (an optothermal receiver) such as a foil or ceramic pyrodetector.⁵⁹⁴ Optothermal spectroscopy has achieved sub-Doppler resolution in studies of SF₆.⁵⁹⁵

In Part I¹ we reported the use of photoacoustic Raman spectroscopy (PARS) in the study of pure rotational transitions. PARS has now been applied to many compounds and to vibration–rotation transitions, and in particular is advanced as a detection technique (with sensitivity of ~1 ppm for CH₄, CO₂, and N₂O in N₂).⁵⁹⁶ Another sensitive detection technique, developed by Davis and co-workers,^{597,598} is phase

⁵⁹⁰ A. Rosencwaig, 'Photoacoustics and Photoacoustic Spectroscopy' (Chemical Analysis, 1980, Vol. 57).

⁵⁹¹ T. F. Hunter and P. C. Turtle, *Adv. Infrared Raman Spectrosc.*, 1980, **7**, 283.

⁵⁹² K. R. German and W. S. Gornall, *J. Opt. Soc. Am.*, 1981, **71**, 1452.

⁵⁹³ A. Di Lieto, P. Minguzzi, and M. Tonelli, *Appl. Phys. B*, 1982, **27**, 1.

⁵⁹⁴ C. Hartung and R. Jurgeit, *Opt. Spectrosc.*, 1979, **46**, 660.

⁵⁹⁵ C. Hartung, R. Jurgeit, and H.-H. Ritze, *Appl. Phys.*, 1980, **23**, 407.

⁵⁹⁶ D. R. Siebert, G. A. West, and J. J. Barrett, *Appl. Opt.*, 1980, **19**, 53.

⁵⁹⁷ C. C. Davis, *Appl. Phys. Lett.*, 1980, **36**, 515.

⁵⁹⁸ C. C. Davis and S. J. Petuchowski, *Appl. Opt.*, 1981, **20**, 2539.

fluctuation optical heterodyne (PFLOH) spectroscopy. This involves the coherent detection of the small change which occurs in the phase of a single frequency probe laser when it passes through a sample which to the probe beam is transparent, but which has absorbed energy from some other source. The phase change results from the alteration in density, and thus refractive index, of the sample. Sensitivities of 10 ppb for SF₆ in air and 40 ppb for CH₃OH in helium, and absorption coefficients below 10⁻¹⁰ cm⁻¹, are reported.

Thermal lensing (TL) spectroscopy has been used for some time, and relies on the alteration of the spatial characteristics of a laser beam which undergoes some absorption by the sample.⁵⁹⁹ Perhaps somewhere between TL and PFLOH comes PDS(!), photothermal deflection spectroscopy.^{600,601} Like PFLOH, this uses a probe beam which is not absorbed, but what is monitored is deflection from its original path. Sensitivity of 5 ppb ethylene (10⁻⁷ cm⁻¹) is reported.

Double Resonance Studies.—Double resonance studies were discussed in Part I.¹ Briefly the principle is this. A transition between two vibrational levels (say) can begin and end in a variety of rotational levels, and so rovibrational spectra of polyatomic molecules can be very confusing. How much simpler they would be if all the transitions with the same lower (or upper) level could somehow be identified; this is the aim of double resonance spectroscopy. Transitions in the microwave and infrared are pumped simultaneously. When the application of one radiation field modifies the absorption of the other, this means that the two transitions have a level in common (or have levels collisionally coupled), and a double resonance has occurred. So for example, if a known ground-state rotational level is depleted by strong MW pumping, lines in the rovibrational spectrum originating from that level will be uniquely diminished, immediately performing half the spectral assignment and making the other half much easier.

Obviously, a modification to the signal would also occur if the population of a level were increased rather than depleted by pumping, and in this case an extra advantage might be conferred, in that it may be possible to observe transitions in absorption normally absent because of insufficient lower state population.

Infrared-microwave double resonance (IRMWDR) has been reviewed by Jones.²¹⁷ A 'textbook example' of the application of the technique has been presented by Jones and Brown, who studied ClO₂.³³⁷ This is not an obvious candidate for an IRMWDR investigation, because large B values mean few rotational transitions occur in the conventional microwave, and symmetry considerations further remove half of the rotational levels. However, there are many fine and hyperfine components, and double resonance signals were obtained with about a quarter of the 120 CO₂ and N₂O laser lines available. In fact, extensive sets of precise data were obtained, and r_e structures derived for both ³⁷ClO₂ and ³⁵ClO₂. Infrared band centres were calculated from the known frequencies of those laser lines found to be resonant with fine or hyperfine components, using appropriate fine and hyperfine constants; these calculations could be checked when more than one component of a band was coincident with one of the

⁵⁹⁹ D. S. Klijger, *Acc. Chem. Res.*, 1980, **13**, 129.

⁶⁰⁰ D. Fournier, A. C. Boccara, N. M. Amer, and R. Gerlach, *Appl. Phys. Lett.*, 1980, **519**.

⁶⁰¹ W. B. Jackson, N. M. Amer, A. C. Boccara, and D. Fournier, *Appl. Opt.*, 1981, **20**, 1333.

laser lines, and they were found to be very reliable. Another interesting aspect of this study was the molecule's apparent disregard for the selection rule in ΔF , since $\Delta F = 0, 1, 2$ and 3 transitions were observed (the technique is very sensitive, however).

In the ClO_2 study mentioned above, some use was made of the technique of triple resonance, and triple resonance was used extensively to permit the assignment of the complex non-rigid rotor spectrum of allylamine.⁵⁵⁴ Two strong microwave pumping fields were employed, and the signal was carried by the infrared (CO_2) laser monitored absorption. Triple resonance may be thought of as occurring when the application of the second microwave pump modifies the double resonance signal. The technique aids in the assignment of double resonance signals, and can effectively extend the tuning range of the microwave excitation. The experimental arrangement is shown in Figure 4.

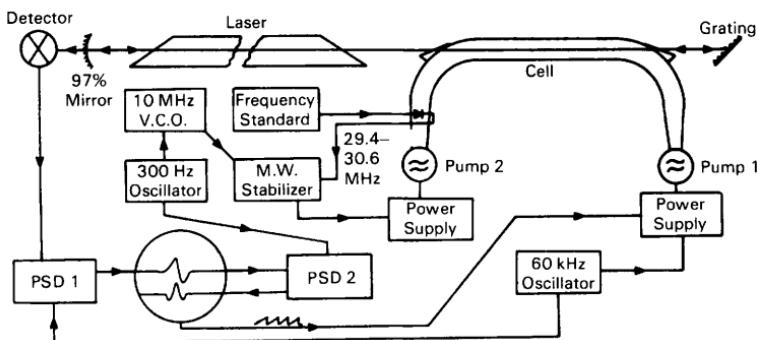


Figure 4 Experimental arrangement for double and triple resonance spectroscopy. A wide-band waveguide cell was placed within the CO_2 laser resonator. The output of microwave pump 1 was frequency modulated at 60 kHz and swept by the sawtooth from the display oscilloscope. Pump 2 was frequency modulated at 300 Hz and stabilized at the desired frequency. This was accomplished by sweeping the 30 MHz intermediate frequency of the microwave stabilizing loop between 29.4 and 30.6 MHz; i.e., a 300 Hz frequency modulation with a depth of 1.2 MHz was produced. Double resonance signals were observed as the output of the phase-sensitive detector PSD1, which was tuned to 60 Hz. Triple-resonance signals were produced by feeding the output of PSD1 into PSD2, which was tuned to 300 Hz. Double-resonance signals appeared as a first derivative, triple-resonance signals as a quasi-second derivative lineshape.

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Some energy-level systems are shown in Figure 5 and Figure 6 shows a triple resonance signal. Application of this technique allowed IR transitions in two distinct rotameric forms of allylamine to be identified.

At first, double resonance experiments were only possible in the microwave region, because only there were strong, coherent sources available which could disturb equilibrium populations. The advent of lasers extended the region of the technique's applicability, and even in the infrared, where lasers were generally of fixed frequency (or line tunable), a microwave source could provide some tunability, as we have seen. The limited tuning of infrared lasers restricted the usefulness of double resonance

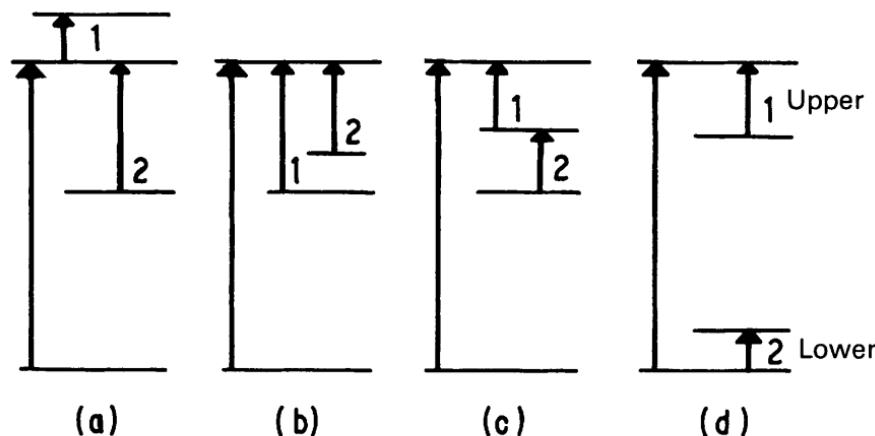


Figure 5 Four characteristic types of energy-level system possible in triple-resonance experiments. The long arrow represents laser radiation; the two shorter arrows marked 1 and 2 represent microwave pumps 1 and 2, respectively. There are, of course, many more possible combinations than those shown here. Part (a) is a 'ladder-type' three-level system; (b) a three-level system in which the common level is above (or it could equally well be below) the other two levels; (c) a system in which the laser-induced population shift is transferred by pump 1 to one of the levels of the rotational transition resonant with pump 2, thus allowing measurement; (d) a triple-resonance scheme in which the two microwave pumps are resonant with rotational transitions, one in the lower vibrational state, the other in the upper vibrational state. The situations represented by (a), (b) and (c) with both rotational transitions in the lower state are also possible

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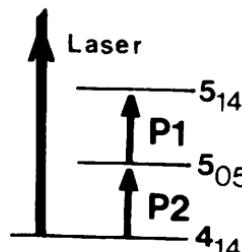
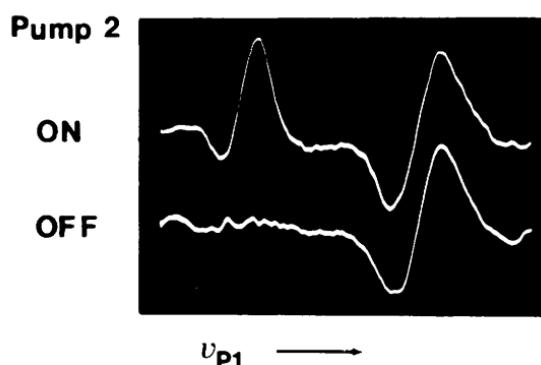


Figure 6 Triple-resonance signal at 20 013 MHz on the $5_{1,4} - 5_{0,5}$ ground-state transition of the NGLG1 isomer of allylamine with pump 2 in a cw mode resonant with $5_{0,5} - 4_{1,4}$. Upper trace, pump 2 on; lower trace, pump 2 off. The signal present in both traces is an unidentified double-resonance signal at 20 024.8 MHz

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experiments involving two infrared lasers (IRIRDR), although possibilities for tuning exist and are increasing.

Within limits, one may Stark tune transitions into resonance with fixed frequency lasers, and in Part I¹ we reported the IRIRDR experiment of Matsumisha *et al.* where in each of the two regions where a laser field was applied to a molecular beam sample, a separate Stark field was applied. This approach was used particularly to study collisional relaxation, and has now been employed to observe Doppler-free hot-band transitions.⁴⁷⁷ The first laser is used to increase the number of molecules in otherwise sparsely populated excited vibrational levels, and the second probes transitions out of these levels.

Orr and Oka⁶⁰² have reviewed their IRIRDR technique of Doppler-free spectroscopy, which requires the use of just one single frequency laser. Radiation from this laser is passed through an electro-optic modulator driven at a variable radiofrequency, and this amplitude modulation generates sidebands to the original laser radiation. These sidebands provide the two infrared frequencies necessary for the experiment. (Because excitation frequencies can be selected such that each field samples the same velocity group of molecules, sub-Doppler resolution can be obtained – see Part I¹ for further details of sub-Doppler spectroscopy.) The technique has been applied to Stark effect studies of a number of molecules, and allows the measurements of very small dipole moments, for example of GeH₄ and CH₃D. (A related technique reported in Part I¹ is that of Bedwell and Duxbury, who use acousto-optically generated sidebands.) Orr and Oka look forward to the increased versatility their techniques could achieve using a tunable laser, and of course it need not be restricted to Stark effect studies.

Weber and Terhume^{412a} have performed a sub-Doppler Stark-tuned double resonance experiment on NH₃, using a CO laser and a tunable diode laser. Some double resonance signals were observed which involved levels not directly pumped by the CO laser but were connected only by collisions. Line narrowing was still observed in these signals, which means that state changing collisions were occurring which were not velocity changing – the molecule remains in the same velocity group and so the line is narrower than the Doppler width. It is not uncommon to detect this type of phenomenon in double resonance studies. Doppler-free 2-photon absorption has also been observed in NH₃ in the 10 μm region, using a diode laser and a CO₂ laser.^{412b}

Bréchignac *et al.*²⁵⁷ have looked at the collisional process in more detail, and have used time-resolved IRIRDR to observe collision-induced reorientation in CO. The degree of reorientation could be measured through the use of polarized CO lasers to prepare the molecule in an aligned vibrationally excited state and to probe the residual anisotropy after collisions. They were able to estimate elastic and inelastic contributions to the dephasing, finding the elastic contribution to be about 20%. This study provides the first experimental evidence of a significant elastic reorientational effect on a linear molecule in its electronic ground state.

Molecules in Excited Vibrational States.—We consider here some work of relevance to infrared multipole photon absorption, and also the excitation of high overtones by single photons. Such studies may provide insight into both excitation and relaxation processes, but a full discussion of energy redistribution and intramolecular dynamics is

⁶⁰² J. Orr and T. Oka, *Appl. Phys.*, 1980, **21**, 293.

not presented; there are a number of specific reviews and articles which consider that topic (e.g., refs 603—607).

The process by which polyatomic molecules absorb multiple photons of infrared light is not yet fully understood. Cantrell *et al.*⁶⁰⁸ have considered theoretical arguments for the importance of coherent pulse propagation effects to this process, whereby the interaction between the fields of the laser radiation and the molecule produces coherent sidebands at frequencies of all molecular transitions accessible from the initial energy levels. They have taken the example of SF₆, and, summarizing currently available spectroscopic information, they ask how a CO₂ laser operating at moderate intensity can pump the very large number of rotational states in SF₆ which it apparently does. The only explanation which they find acceptable is that it occurs because of the generation of the new sideband radiation frequencies. (MPD of SF₆ has nevertheless been observed in a molecular beam, and also at low laser power).

Quack and co-workers have discussed the importance of spectral bandshape and intensity to the detailed understanding of the multiphoton absorption process, and have examined these properties in the infrared spectroscopy of CF₃H and C₄F₉H (these molecules being chosen because the CH chromophore, which they wanted to examine, is well separated in the spectrum from others in the molecule).⁴⁶⁵ They explain that the broadness of even the fundamental and first overtone bands in C₄F₉H is due to vibrational effects, because of the very high densities of vibrational states even at fairly low energies.

In a study of the ring compound tetrafluoro-1,3-dithietane (C₂F₄S₂)⁵¹⁰ they measured rate coefficients for infrared photochemistry (C₂F₄S₂ → 2CF₂S) following laser irradiation of three different bands, and compared these rates with theoretical estimates derived using measured vibrational band intensities. It was found that the model, which contained no adjustable parameters, reproduced the trend of the experimental results.

There has been much interest in the spectra of high vibrational overtones. Gas-phase studies have been stimulated by the availability of very sensitive laser techniques such as intracavity dye laser photoacoustic spectroscopy, appropriate to these weak absorptions.

Vibrational spectra of polyatomic molecules have long been explained in terms of bond modes,⁶⁰⁹ in particular normal modes; a normal mode involves the in-phase vibration of the atoms in a molecule, which thus all pass through their equilibrium positions at the same time. The usual derivation of normal mode analysis assumes, however, that vibrational amplitudes are very small, and terms beyond quadratic in the potential are neglected. Molecular vibrations are of course anharmonic, and so it might not be surprising if at high energies the relatively simple normal mode description were to be found unsuitable, and something much more complicated were to be required. That may be the case for *very* high energies, but many overtone spectra of X—H vibrations, where X is C, O, N, show a striking simplicity in that the positions of bands

⁶⁰³ P. Brumer, *Adv. Chem. Phys.*, 1981, **47**, 201.

⁶⁰⁴ E. J. Heller, *J. Chem. Phys.*, 1980, **72**, 1337.

⁶⁰⁵ P. R. Stannard and W. M. Gelbart, *J. Phys. Chem.*, 1981, **85**, 3592.

⁶⁰⁶ S. A. Rice, *Adv. Chem. Phys.*, 1981, **47**, 117.

⁶⁰⁷ D. W. Noid, M. L. Koszykowski, and R. A. Marcus, *Ann. Rev. Phys. Chem.*, 1981, **32**, 267.

⁶⁰⁸ C. D. Cantrell, A. A. Makarov, and W. H. Louisell, *Adv. Chem. Phys.*, 1981, **47**, Part 1, 583.

⁶⁰⁹ M. L. Sage and J. Jortner, *Adv. Chem. Phys.*, 1981, **47**, Part 1, 293.

can be predicted from a one-dimensional anharmonic oscillator model. Such oscillators are not strongly coupled, and it appears that quite large amounts of energy can be localized in one oscillator – a *local mode*.

Some localization can certainly be modelled whilst maintaining a normal mode basis by allowing superpositions of anharmonically coupled normal modes, and this approach may have some success in rationalizing the average energies of XH overtone stretching spectra. Overtone bands in general are narrower than would be predicted in this way, however, and the spectra are simpler, not showing all the symmetry allowed components that would be expected.⁶¹⁰

It seems that local modes may represent a more appropriate basis for the interpretation of these spectra. But can local modes provide a ‘good’ description of the system, ask Heller and Gelbart,⁶¹¹ when the broad overtone bands are taken to indicate very fast decay? Yes, in principle, they reply, because the description may be good for the preparation of the initial excited state, and the coupling of the radiation field and molecule, without having to refer to the state’s subsequent decay. They concede the difficulty, however, of deriving separate information on each of these two processes from only the spectrum.

So we have a description involving normal modes at low energies and local modes at higher energies. Their relative predominance has been assessed by Lawton and Child⁶¹² for the stretching vibrations of H₂O. At low energies (below about 2200 cm⁻¹) they found only normal trajectories, but with increasing energy local trajectories were found to occupy an increasing fraction of the phase space. Local trajectories are characterized as those which do not retain the symmetry of the surface, whilst normal trajectories do – see Figure 7. (Both these types of trajectory they call regular, but at

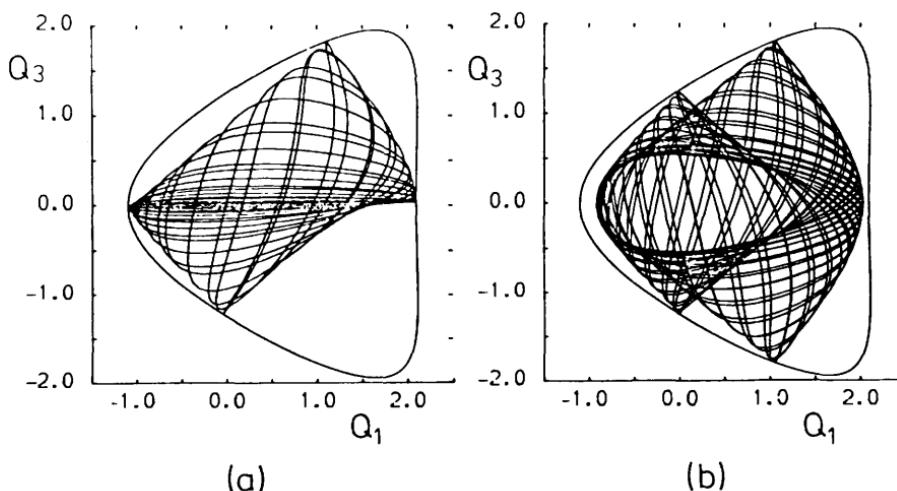


Figure 7 (a) Local and (b) normal trajectories at $E = 26\ 367\ \text{cm}^{-1}$. The notation on the diagrams is with the units: mass ($10^{-28}\ \text{kg}$), length ($10^{-10}\ \text{m}$), and time ($10^{-15}\ \text{s}$)
(Reproduced by permission from *Mol. Phys.*, 1981, **44**, 709)

⁶¹⁰ B. R. Henry, *Acc. Chem. Res.*, 1977, **10**, 207.

⁶¹¹ E. J. Heller and W. M. Gelbart, *J. Chem. Phys.*, 1980, **73**, 626.

⁶¹² R. T. Lawton and M. S. Child, *Mol. Phys.*, 1981, **44**, 709.

an energy of about $30\ 000\ \text{cm}^{-1}$ irregular motions begin to appear, characterized by trajectories which are not bounded by sharp caustics.)

Although normal mode and local mode behaviour can be distinguished, it is not convenient to have to describe different parts of the spectrum in terms of different models. It has been proposed that the whole spectrum (at least below the irregular region, if it occurs) is best analysed on the basis of one type of vibrational state, the local mode state (which would thus be used even in the region where the local mode model is not the more appropriate).^{613,614}

Child and Lawton⁶¹³ have presented this type of model. We have seen that the coupling of oscillators to produce normal mode behaviour requires that the oscillators be harmonic. Child and Lawton employ harmonically coupled *anharmonic* oscillators, and propose that even if bond vibrations are coupled through potential or kinetic energy terms in the Hamiltonian, the coupling can be quenched by strong bond anharmonicity. If in this way there is a significant reduction in the coupling, then the tendency would be towards local mode behaviour, manifested as a trend towards *degeneracy* of levels which in a conventional analysis of a triatomic would be considered as due to the symmetric and antisymmetric stretch. Local mode behaviour would be characterized by a very small value for the ratio of coupling strength to bond anharmonicity, whereas a large value for this ratio would indicate normal mode behaviour.

On application of the model to acetylene, the tendency found was towards local mode behaviour in C_2H_2 , but normal mode behaviour in C_2D_2 . This was attributed to greater interbond coupling in C_2D_2 , specifically indirect coupling through the C–C bond, which occurs because of the close resonance between C–C and C–D vibrational frequencies.

The overtone spectrum of SO_2 has also been considered, as an extreme example of a normal type of spectrum, and was modelled satisfactorily. Normal mode behaviour occurs because of the large value of the interbond coupling (here direct momentum coupling, principally) compared to the very small bond anharmonicity.

H_2O , on the other hand, has a large bond anharmonicity, and a disposition towards local mode behaviour is seen. Indeed for this molecule the model has been successfully applied to the analysis of the high resolution vibration–rotation spectrum.⁶¹⁴ If two identical bonds in the molecule are coupled, then two vibrational states will exist with a splitting related to the coupling strength. For H_2O , it is seen that these states move, as predicted, dramatically closer to degeneracy as higher overtones are excited, indicating a progressive reduction in interbond coupling and so a localization of the bond modes.

A similar sort of analysis has been proposed by Mortensen *et al.*, who have termed it the ‘local mode picture’.⁶¹⁵

There have been numerous recent studies of high overtone spectra, but the most extensive gas-phase investigation, by Reddy, Heller, and Berry, is of benzene (C_6H_6 , C_6D_6 , C_6HD_5), toluene and fluorobenzenes ($\text{C}_6\text{H}_5\text{F}$, C_6HF_5).⁵⁶³ They used cw intracavity dye laser photoacoustic spectroscopy in the visible, and pulsed photoacoustic spectroscopy in the infrared, where a dye laser focused into a stimulated Raman scattering cell provided the radiation source.

⁶¹³ M. S. Child and R. T. Lawton, *Faraday Discuss. Chem. Soc.*, 1981, **71**, 273.

⁶¹⁴ M. S. Child and R. T. Lawton, *Chem. Phys. Lett.*, 1982, **87**, 217.

⁶¹⁵ O. S. Mortensen, B. R. Henry, and M. A. Mohammadi, *J. Chem. Phys.*, 1981, **75**, 4800.

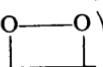
We consider C_6HD_5 , and adopt their notation, where $\{n\}$ states are the permutations and combinations of n quanta which may be distributed over the several sites, those available being one CH site plus five CD sites in this case. Each group of states of the same n produces an energy 'band'. They obtained the striking result that within each band of $\{n\}$ states, only two states appear spectroscopically, and these correspond to '*single site excitations*', with all n quanta on one of the five CD sites or the single CH site. Throughout their studies on benzenes and substituted benzenes, they found no sure spectroscopic evidence for excitation of multiple sites; no evidence in the case of the $\{6\}$ band, for example, of say one quantum on a CD site and the other five on a CH site.

They did find some local mode/normal mode combination bands of extremely low intensity, and draw attention to the enormous density of other vibrational states present at these high overtone energies. These states may be involved in a very weak absorption continuum that can just be detected beneath the discrete spectrum, or they may be dark. (This weak continuum is in fact much weaker again than some earlier experimental results had led them to believe.)

That certain bands of C_6H_6 and C_6D_6 , with even v , were observed at all led to the conclusion that there is a lowering of the symmetry, since such transitions would be forbidden under D_{6h} . It was held that this is because of the localized bond mode nature of the excitation, i.e., that it is a dynamical symmetry lowering.

Lifetimes for the overtone states were estimated from bandwidths, assuming homogeneous Lorentzian broadening (although some bands not displaying a Lorentzian lineshape were found), and these estimates led to the deduction that the decay was non-statistical, in that it did not appear that transitions from a given initial states to all possible final states were equally probable. The decays were fast (~ 50 – 500 fs), but in benzene, for example, they remained the same within a factor of four over a range of energy encompassing a six orders of magnitude variation in the densities of vibrational states. Similarly, the $5v_{CH}$ bandwidths in benzene and toluene were almost the same, despite the differences in their densities of states.

This and other evidence convinced the authors that state-to-state intramolecular rate processes were occurring (and therefore that such processes might occur irrespective of the method of preparation of the highly excited vibrational states, e.g., by radiationless transitions as well as direct one photon excitation). Furthermore, extrapolation of their calculations suggested increasing spectral isolation of CH (CD) stretching modes at energies higher than they had used. This in turn made them wonder about the validity of current thinking on ergodicity in highly vibrationally excited polyatomic molecules, and whether highly excited benzene might have such a comparatively small number of coupled levels as to be treated as a 'quasi-intermediate' case.

Cannon and Crim^{616a,b} have also considered relaxation following overtone excitation, but they actually measured reaction rates, by observing in real time the chemiluminescent products of tetramethyl dioxetane  decomposition.

Measuring the rates following excitation in $4v_{CH}$ and $5v_{CH}$, they found that they could be well modelled by RRKM theory.

⁶¹⁶ (a) B. D. Cannon and F. F. Crim, *J. Chem. Phys.*, 1981, **75**, 1752; (b) B. D. Cannon, E. S. McGinley, and F. F. Crim, *Ber. Bunsenges. Phys. Chem.*, 1982, **86**, 467.

Is the lineshape, then, a good source of information on intramolecular vibrational relaxation? West *et al.*⁵⁶ using the same molecule, have performed an experiment to isolate possible contributions to the lineshape. Both inhomogeneous contributions (from underlying rotational levels or hot bands) and contributions from homogeneous intramolecular vibrational dephasing (due to the thermal, randomly fluctuating molecular motions) would be expected to be strongly temperature dependent. They therefore measured the vibrational excitation spectrum of supercooled tetramethyl-dioxetane, using a pulsed molecular beam/alexandrite laser system and monitoring blue fluorescence from electronically excited acetone produced by the photodissociation. Comparison of this spectrum with a room temperature photoacoustic spectrum showed the line shape to be virtually insensitive to temperature over the range encompassed. Their conclusion is that a T_1 type vibrational relaxation out of the CH oscillator is occurring on a time scale of about 50 fs, a similar conclusion to that reached by Reddy *et al.* for the case of the substituted benzenes.

Transient Species.—The sensitivity of laser techniques has allowed great progress in the infrared spectroscopy of short-lived species, as illustrated, for example, in the review of Hirota.⁶¹⁷ The lasers which have been particularly involved are the tunable diode laser, in absorption spectroscopy, and fixed frequency lasers such as the CO laser, in laser magnetic resonance spectroscopy,* and we shall discuss just a few examples.

Diatomeric species such as CCl^{249} and CF^{250} are amongst a number of transient molecules studied using diode laser spectroscopy by Hirota and co-workers. To improve sensitivity, they used a multiple reflection White cell, and also applied Zeeman modulation. This discriminates in favour of paramagnetic lines, and also reduces fringe noise which arises because of reflection of the laser light by optical elements. In the case of CF, Zeeman modulation allowed detection of lines in the $^2\Pi_{1/2}$ state, as well as in $^2\Pi_{3/2}$, because of the considerable deviation from Hund's case (a). [In pure Hund's case (a), spin and orbital magnetic moments cancel in the $^2\Pi_{1/2}$ state to leave the molecule diamagnetic, but because of the small spin-orbit coupling constant and the quite large rotational constant for the case of CF, $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$ sub-levels mix, and so the ' $^2\Pi_{1/2}$ ' lines are modulated by a Zeeman field.] The CF radicals were generated in an AC discharge, at an estimated concentration of 6×10^{11} molecules cm^{-3} . They calculate that the minimum detectable quantity would be about 6×10^8 molecules cm^{-3} , which is comparable with the sensitivity of far-infrared LMR.

The radical NF has been studied in its $a^1\Delta$ electronically excited state using a diode laser.²⁸⁵ The species, which has a long radiative lifetime (5.6 s), was produced by allowing H atoms from a microwave discharge to react with NF_2 from thermal dissociation of N_2F_4 . The fundamental vibration-rotation band was observed, with both N and F nuclear hyperfine structure.

The $(0, 0, 1) \leftarrow (0, 0, 0)$ and $(0, 0, 2) \leftarrow (0, 0, 1)$ bands of the linear radical BO_2 have been studied.³⁰⁹ The ν_3 mode (antisymmetric stretch) was found to have a large negative anharmonicity (*i.e.*, x_{33} is large and positive), and to have an unusually low

* For a short introduction to LMR spectroscopy, and to its use in kinetics and atmospheric chemistry, see B. A. Thrush, *Acc. Chem. Res.*, 1981, **14**, 116.

⁶¹⁷ E. Hirota, 'Structural studies of transient molecules by laser spectroscopy', in 'Chemical and Biochemical Applications of Lasers,' ed. C. B. Moore, Academic Press, New York, 1980, Vol. 5.

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fundamental frequency (1278.3 cm^{-1} , compared to 1071 cm^{-1} for v_1 of $^{11}\text{BO}_2$). This behaviour was attributed to a breakdown of the Born–Oppenheimer approximation, specifically a vibronic interaction between the $\tilde{\chi}^2\Pi_g$ and $\tilde{\Lambda}\Pi_u^2$ states through the v_3 mode. Evidence was also found for higher-order Renner–Teller interactions in the v_2 state.

A diode laser study of the methyl radical in the gas phase has confirmed its planarity in the ground vibronic state.³⁸⁵ The mode studied was v_2 , the out of plane bend, which has a fundamental frequency of 606.4531 cm^{-1} . The $(2 \leftarrow 1)$ and $(3 \leftarrow 2)$ bands were also observed. The potential function for this mode has a large negative anharmonicity again ascribed to vibronic interaction with excited electronic states. The concentration of species observed was estimated at $10^{13}\text{ molecules cm}^{-3}$, and its lifetime (in the AC discharge) was about 1.4 ms.

Using a CO₂ laser, the LMR spectrum of the $v = 1 \leftarrow 0$ band of the X $^2\Pi_{3/2}$ state of AsO has been observed, the first study of this radical at frequencies below the electronic region. It was possible for the first time to see hyperfine splitting due to the ⁷⁵As nucleus.²⁴⁷

LMR has also been used to study a vibrational overtone of a radical, the $v = 2 \leftarrow 0$ band of ClO, X $^2\Pi_{3/2}$ state. It occurs at about $6\text{ }\mu\text{m}$, and so a CO laser was used.²⁵⁹ This transition was calculated to be weaker than the fundamental by a factor of 230.

Of course, transitions occur in this region which are not vibrational in nature, and LMR spectroscopy has been used to probe fine-structure transitions of the radical SeD at $5.6\text{ }\mu\text{m}$.³⁰⁴ Magnetic and electric dipole transitions between the X $^2\Pi_{1/2}$ and X $^2\Pi_{3/2}$ states were observed, and data combined with those for SeH to provide spin–orbit and spin–rotation interaction parameters. Magnetic dipole transitions were also seen by LMR spectroscopy of BrO, using CO₂ laser lines between 964 and 970 cm^{-1} .²⁴⁸ Transitions between the $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$ components of the ground state were observed, this being the first direct observation of the $^2\Pi_{1/2}$ state. The spin–spin splitting parameters were determined for species of both bromine isotopes.

Ions.—The reaction $\text{H}_2 + \text{H}_2^+ \rightarrow \text{H}_3^+ + \text{H}$ is efficient and exothermic, which is why H₃⁺ is the most abundant ion in a hydrogen discharge. H₂ has a high proton affinity so that H₃⁺ has a high energy of dissociation. Absorption lines in the region 2450–2950 cm⁻¹ have been assigned to the v_2 fundamental of H₃⁺ following detection and measurement in a difficult experiment.³³⁹ The radiation source was the difference frequency generated by mixing an argon ion laser and dye laser, which was discussed on p. 263, and absorption was detected following sixteen traversals of a 2 m multiple reflexion discharge cell cooled in liquid nitrogen. The density of ions was estimated at $3 \times 10^{10}\text{ cm}^{-3}$, and the sensitivity of the detection system was checked by observation of the $v = 1 \leftarrow 0$ quadrupole spectrum of D₂. Constants derived from a fit to fifteen measured lines include $v_2 = 2521.564(135)\text{ cm}^{-1}$, $B_0 = 43.568(48)\text{ cm}^{-1}$, $C_0 = 20.708(48)\text{ cm}^{-1}$, where B_0 and C_0 were separated with a value of the inertial defect, $\Delta = 3h/4\pi^2Cv_2$, and the uncertainties are the standard deviations. The values are in good agreement with *ab initio* predictions for this the simplest of polyatomic species.⁶¹⁸

Experiments have also been performed to observe the infrared spectrum of D₃⁺,⁶¹⁹ using the Doppler tuned fast ion beam method already used to make high precision

⁶¹⁸ G. D. Carney and R. N. Porter, *Phys. Rev. Lett.*, 1980, **45**, 537.

⁶¹⁹ J.-T. Shy, J. W. Farley, W. E. Lamb, jun., and W. H. Wing, *Phys. Rev. Lett.*, 1980, **45**, 535.

measurements on HD^+ and HeH^+ . In this technique, ions are Doppler shifted into resonance with lines of a CO laser, and resonance is detected by changes in the cross-sections for charge exchange on collision of the excited ion with a target gas. Four transitions, measured to 0.0005 cm^{-1} (at 70% confidence level), were assigned to the fundamental v_2 band: four others, around 1811 cm^{-1} , were not identified.

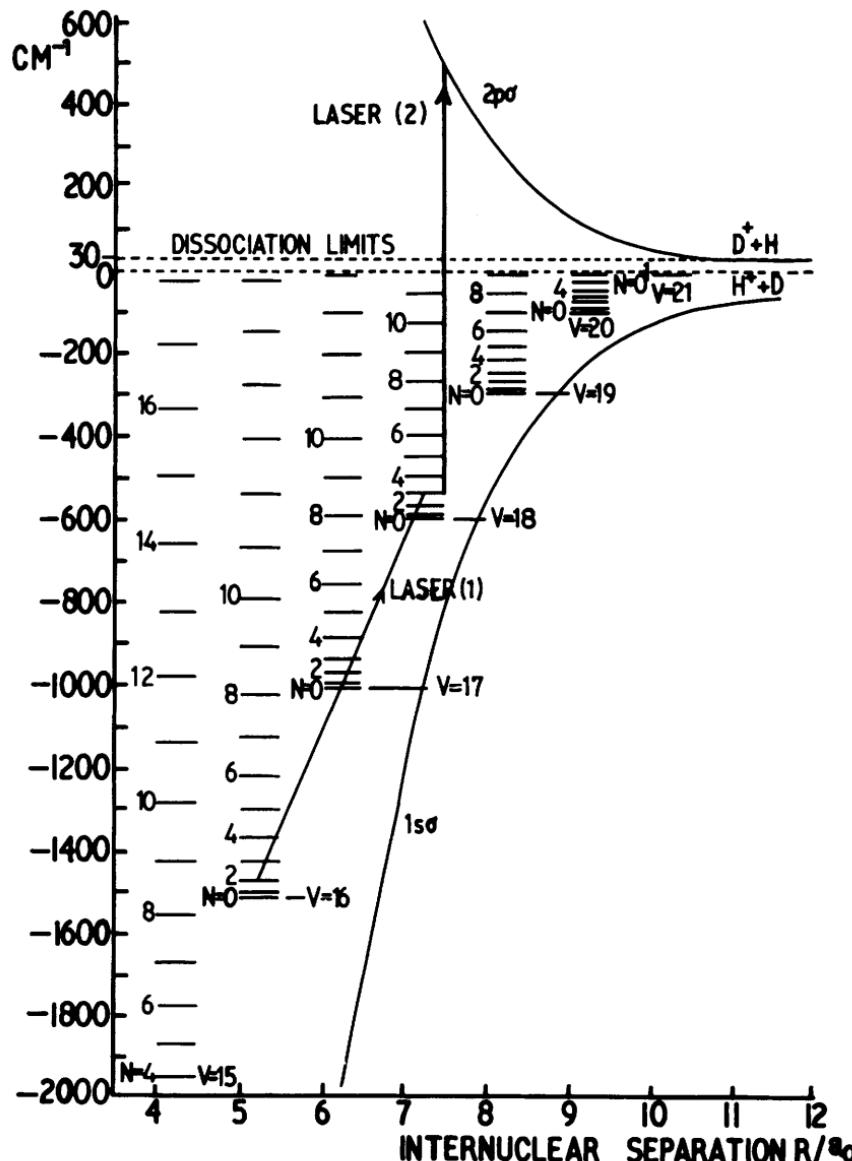


Figure 8 Principles of the two-photon infrared dissociation technique for HD^+
(Reproduced by permission from *Mol. Phys.*, 1981, **44**, 267)

It has also been possible to observe transitions of species in an ion beam by performing infrared photodissociation from levels close to the dissociation limit. The application of this technique to HD⁺ was reported in Part I,¹ and this has now been fully described.²⁷⁴ Ions are produced by electron impact, and then dissociated by two infrared photons as shown in Figure 8. The first photon probes the transitions of interest, here in the $v = 18 \leftarrow 16$ band, which are Doppler-tuned into resonance. At resonance, a photon from a second laser dissociates the species, and so transitions are detected as a variation in photofragment (H⁺ or D⁺) yield.

In the above experiment, there was insufficient energy in one CO₂ laser photon to dissociate HD⁺ from $v = 16$. However, in a similar experiment on HeH⁺, one proton was sufficient to cause dissociation from high vibrational levels. Even though excitation was thus from below the dissociation limit to above it, scanning the spectrum (by tuning the beam velocity) produced considerable structure; the observations were thus of bound to quasibound vibration-rotation transitions, the quasibound levels lying above the dissociation limit but below the maximum of the centrifugal energy barrier.²⁸³ Infrared transitions have also been observed in H₃⁺⁶²⁰ and CH⁺⁶²¹ using this technique. Many lines have been observed but their assignments are not clear.

The low resolution IR spectrum of C₆H₇⁻ has been obtained by infrared multiphoton electron detachment, using a low power line-tunable cw CO₂ laser. The technique could distinguish the isomeric benzyl and cyclopentadienyl anions, and is proposed as a general method for extending the diagnostic capabilities of mass spectrometry.⁵⁶⁷

Infrared spectroscopy of molecular ions in noble gas matrices has been reviewed by Andrews,⁶²² who considers both ions which are chemically bound, and those isolated by matrix atoms from the counter ion.

Raman Spectroscopy.—Multiplex photoelectric detection has been successfully employed in several branches of Raman spectroscopy. For example, an optical multichannel analyser, with to some degree the combined advantages of a photomultiplier and a photographic plate, has been used to increase detection sensitivity by a factor of more than 1000.⁶²³ Chao⁶²⁴ has considered the use of such instruments in weak emission signal averaging, and in transient pulsed laser experiments, particularly picosecond laser Raman spectroscopy.

There continues to be much interest in non-linear Raman spectroscopy. Theory and practice of many of the various techniques have been reviewed by Levenson and Song,⁶²⁵ and discussed in a recent book by Eesley.⁶²⁶ The terminology in this area may be confusing – Eesley reports Levenson's remark that 'At midnight on January first of every year, the coherent Raman physicists have conspired to permute the acronyms for these techniques... just to keep the chemists confused' – and we discussed some of the varieties in Part I.¹

⁶²⁰ A. Carrington, J. Buttenshaw, and R. A. Kennedy, *Mol. Phys.*, 1982, **45**, 753.

⁶²¹ A. Carrington, J. Buttenshaw, R. A. Kennedy, and T. P. Softley, *Mol. Phys.*, 1982, **45**, 747.

⁶²² L. Andrews, *Adv. Infrared Raman Spectrosc.*, 1980, **7**, 59.

⁶²³ J. J. Freedman, J. Heaviside, P. J. Hendra, J. Prior, and E. S. Read, *Appl. Spectrosc.*, 1981, **35**, 196.

⁶²⁴ J. L. Chao, *Appl. Spectrosc.*, 1981, **35**, 281.

⁶²⁵ M. D. Levenson and J. J. Song, 'Coherent Raman Spectroscopy', in 'Coherent Nonlinear Optics: Recent Advances' (Topics in Current Physics Vol. 21), ed. M. S. Feld and V. S. Letokhov, Springer, Berlin, 1980.

⁶²⁶ G. L. Eesley, 'Coherent Raman Spectroscopy', Pergamon, Oxford, 1981.

Of these, CARS remains the most well known, and the principles are as discussed on p. 239. Resonant enhancement of such emission from NO_2 ,³⁵⁸ and s-tetrazine⁵¹⁵ has been reported.

When CARS spectral lines are closely spaced, as they are for example in the Q-branches of diatomic molecules, there may be interference between the lines due to the real component of the third-order non-linear susceptibility. This interference causes an asymmetry in band profile, and should show a pressure dependence. In a study of NO, Beckmann *et al.*²⁹⁰ observed the pressure dependence of CARS signals in order to distinguish contributions from the real and imaginary parts of the third-order susceptibility. They also measured the differential Raman scattering cross-sections for the states $\text{X}^2\Pi_{1/2}$ and $\text{X}^2\Pi_{3/2}$, and found them to be identical.

Another interesting CARS experiment has allowed the observation of an optical Stark effect. Rahn *et al.*²⁶³ have shown that vibrational and rotational Raman transitions are shifted to lower frequency when a *nonresonant* intense optical field is applied; this is interpreted as due to a change in internuclear separation (and polarizability), with applied laser field. Depending on the experimental configuration, the effect may be observable as a spectral shift or an inhomogeneous broadening. There may be important consequences for ultimate resolution and sensitivity in CARS type experiments, but also possibly advantages for infrared laser photolysis.

Because of its rejection of incoherent background light, CARS is particularly suited to use in luminous environments such as flames and plasmas; a measurement of vibrational populations in low-pressure hydrogen plasma had a sensitivity of 10^{12} cm^{-3} for a given rovibrational state (additionally, an asymmetric broadening of the $v = 1$ line may be partly due to a Stark effect, as we have just discussed).⁶²⁷

Noting sensitivity 'per rovibrational state' is particularly significant for CARS, since signal strength depends on the square of the number density of the molecules in the lower level of the transition. This prompted the study of N_2 in a supersonic expansion reported in Part I,¹ and the feasibility of high resolution studies has now been demonstrated using C_2H_2 in a pulsed jet.³⁹¹ The pulsing of the jet allows relatively high molecular densities to be coupled with the advantage of rotational cooling. In an extension of the C_2H_2 investigation, saturation broadening was observed in the v_2 Q-branch.³⁹² The broadening occurs because the population difference at the line centre is (given strong radiation) reduced more than in the wings. The measured value of 1050 MHz for this effect is significantly greater than the calculated value (<100 MHz) of the Stark effect broadening of the type discussed above, and so is another factor to be borne in mind when considering ultimate resolution and sensitivity of CARS experiments.

Broadband CARS spectra have been reported for a number of molecules (N_2 , O_2 , H_2 , D_2 , C_2H_2) in supersonic jets, in an experiment directed towards temperature measurement and rotational relaxation studies.⁶²⁸

CARS does not rely on the existence of fluorescent states, nor is its time resolution limited by radiative lifetimes. These are ideal qualities for a technique to probe collision-free photofragments, and it has now been demonstrated that sensitivity too is sufficient to permit studies of molecular dynamics in a bulb experiment.²⁹⁸ Nascent

⁶²⁷ M. Lealat, J. P. E. Taran, J. Taillet, M. Bacal, and A. M. Bruneteau, *J. Appl. Phys.*, 1981, **52**, 2687.

⁶²⁸ P. Huber-Walchli and J. W. Nibler, *J. Chem. Phys.*, 1982, **76**, 273.

rovibrational distributions of molecular oxygen have been obtained following photodissociation of ozone, in an experiment at 2 Torr. This was possible because the average time between collisions is estimated at 100 ns, whereas the pump and probe processes both occur within a 6 ns laser pulse.

Raman techniques may also be used to study molecules in transient states which are subject to intramolecular decay. Spontaneous Raman scattering has been employed to probe infrared multiple photon excited molecules,⁶²⁹ and CARS spectra have been obtained from transient species (as yet unidentified) during the photoisomerization of cycloheptatrienes;⁶³⁰ the time resolution potentially available in such studies may be very important.

Stimulated Raman spectroscopy produces a coherent signal the strength of which is *linearly* dependent on number density of species present. It involves the application of a strong pump laser (frequency ω_1) and a weaker probe laser (frequency ω_2), and when the tuning is such that the frequency difference corresponds to the excitation frequency of a Raman active mode, the intensity of the probe beam is modified. If $\omega_2 < \omega_1$, a gain is produced (stimulated Raman gain spectroscopy, SRGS), and when $\omega_1 < \omega_2$, a loss results (stimulated Raman loss, or inverse Raman spectroscopy, IRS).^{626, 631}

In IRS, the signal which is observed is an induced Raman absorption of the probe beam, and since the probe is at shorter wavelength than the pump, this configuration should provide better suppression of background light than SRGS. High resolution has been combined with high sensitivity in IRS by using the 'quasi-cw' approach,⁶³¹ where the probe beam is a stable single-mode cw laser (a low noise source on which signal can be more easily detected), but the pump is a high-power repetitively pulsed laser (strong enough to provide the necessary perturbation of the molecular system).

A schematic representation of the quasi-cw IRS experiment is shown in Figure 9. The pulsed pump laser is a single-mode dye oscillator pulse amplified to 2MW by three dye amplifiers pumped themselves by a frequency-doubled Nd:YAG laser. The pulses emitted have bandwidth <100 MHz and 6 ns duration. The probe is a single mode argon ion laser. A Doppler-limited spectrum of $^{13}\text{CH}_4$ was recorded (at a pressure of 1.3 Torr) with a sensitivity almost four orders of magnitude greater than in previous cw studies.⁴⁹⁶ The v_1 mode was studied, and found to be very different to the v_1 band in $^{12}\text{CH}_4$, due principally to a much smaller value of ΔB for the ^{13}C species which causes overlapping of transitions near the band origin. A Coriolis interaction with the nearby combination band $v_2 + v_4$ was thought to be responsible for the difference in ΔB .

Extensions of this technique have also been reported to take the resolution inside the Doppler width. The first is sub-Doppler Raman saturation spectroscopy, which can be either a four-beam or a three-beam technique. With four beams, two narrow-band intense pulsed sources selectively saturate a Raman transition for a velocity sub-group of molecules. This system is then interrogated by a pump and a probe beam, as before. In the three-beam configuration, the original saturating pump beam is reflected back into the system, to provide the pump beam for the interrogation too. Here it interacts with the counter-propagating weak probe beam on which the reduced width signal is

⁶²⁹ V. N. Bagratashvili, Yu.G. Vainer, V. S. Doljikov, S. F. Koliakov, A. A. Makarov, L. P. Malyavkin, E. A. Ryabov, E. G. Silkis, and V. D. Titov, *Appl. Phys.*, 1980, **22**, 101.

⁶³⁰ K. Luther and W. Wieters, *J. Chem. Phys.*, 1980, **73**, 4131.

⁶³¹ A. Owyong, 'High Resolution Stimulated Raman Spectroscopy' in 'Advances in Infrared and Raman Spectroscopy', ed. R. J. H. Clark and R. E. Hester, Vol. 9, Heyden & Son, London, 1982.

recorded. Such experiments have been performed on D₂. The arrangement is similar to that shown in Figure 9 with the addition that the cw argon ion laser is used both as the measurement probe beam, and as the input to an amplifier chain (two coumarin 500 dye amplifiers transversely pumped by the third harmonic of the pulsed Nd:YAG) to provide the second saturating beam.²⁶⁷

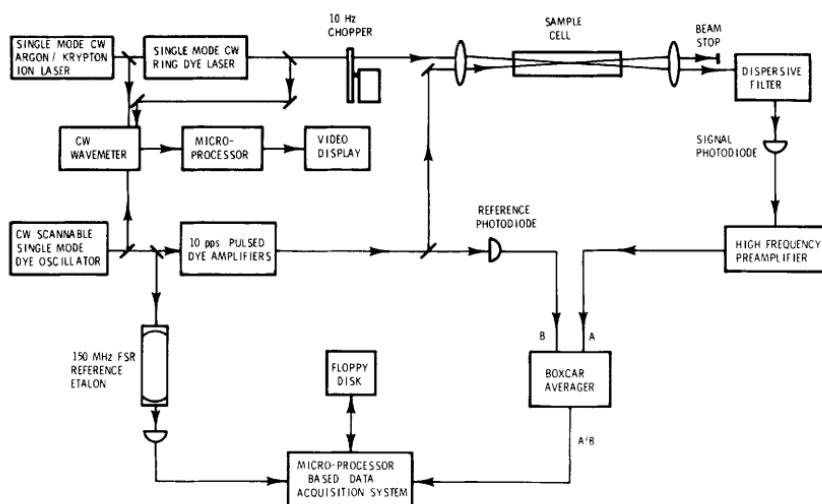


Figure 9 Schematic diagram of the quasi-cw inverse Raman experiment

(Reproduced, by permission, from 'High-resolution Stimulated Raman Spectroscopy', in 'Advances in Infrared and Raman Spectroscopy', ed. R. J. H. Clark and R. E. Hester, Vol. 9, Heyden and Son, London, 1982).

The second experiment to produce sub-Doppler spectra uses a supersonic free jet. The degree of line narrowing is related to the fraction of the molecules sampled from the diverging jet, and this technique also confers its usual advantage of spectral simplification. Results on ¹²CH₄ are shown in Figure 10. Observed rotational state distributions are non-Boltzmann, due to nuclear spin effects. Conversion between *ortho*, *para*, and *meta* states of the molecule is very slow, and as absolute zero is approached, the relative populations for *J* = 0 (*meta*), 1 (*ortho*), and 2 (*para*) will approach the room temperature abundance ratios of the nuclear spin species, 5:9:2.⁴⁹² This study was on a cw expansion, and higher sensitivities are confidently expected for pulsed jets.

Loosely Bound Complexes.—Even at quite high pressures and low temperatures, the concentration of van der Waals complexes in bulk gases is usually small. It is possible to record infrared spectra for some species under these conditions, but many interesting complexes, including larger cluster compounds, only exist in sufficient concentrations for experiment in the cold environment of supersonic expansions.

Vibrational predissociation has been studied in a number of these species, using infrared lasers and molecular beams. Weak bonding means that dissociation is energetically facile, and the process is self-detecting, as it is revealed as a modification

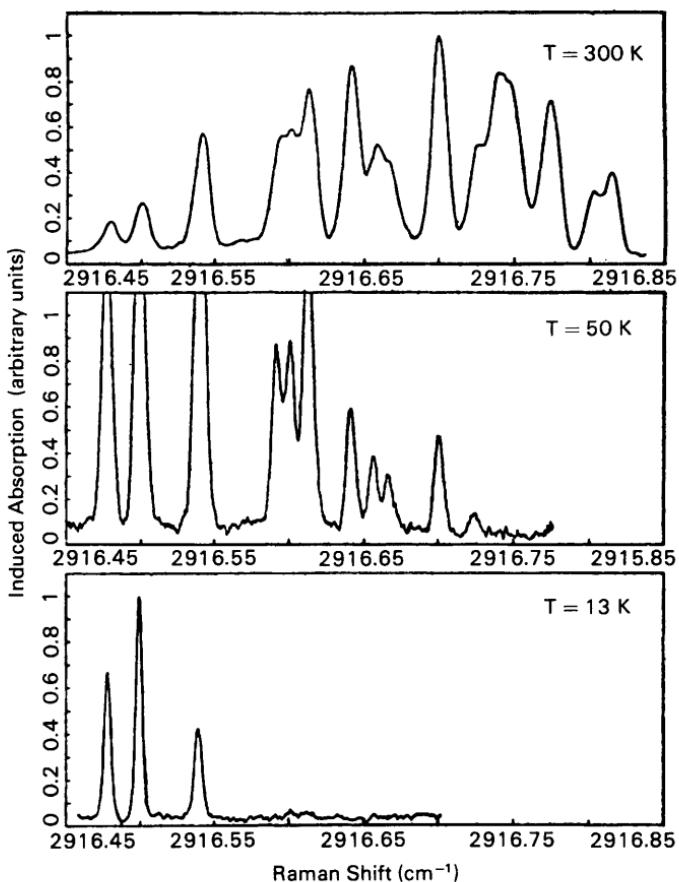


Figure 10 Inverse Raman spectra of v_1 Q branch of $^{12}\text{CH}_4$. Bandhead at 2916.472 cm^{-1} , with higher J transitions extending to higher frequency. (a) Static gas, 1 Torr, 300 K, $\approx 1^\circ$ optical crossing angle; (b) molecular jet, 350 μm nozzle, 4.8 psi backing pressure, 1.8 mm downstream, estimated density $1.5 \times 10^{16}\text{ cm}^{-3}$, $\approx 5^\circ$ optical crossing angle; (c) molecular jet, 100 μm nozzle, 55 psi backing pressure, 4.5 mm downstream, estimated density $2.2 \times 10^{15}\text{ cm}^{-3}$, $\approx 5^\circ$ optical crossing angle

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in molecular flux to the beam detector when the laser is in resonance with a predissociating transition.

The first of these experiments, using tunable diode laser photolysis, involved $(\text{N}_2\text{O})_n$ (see Part I¹), and further studies, now using a colour centre laser, have been performed on $(\text{CO}_2)_n$.⁵⁷³ A schematic representation of the experiment is given in Figure 11. Sensitive detection is by microcalorimetry, using a bolometer, and also by mass spectrometer for additional identification. (Levy^{632a} has called bolometric detection the 'molecular beam analogue of photoacoustic detection in a static gas'; it can be sensitive

⁶³² (a) D. H. Levy, *Ann. Rev. Phys. Chem.*, 1980, **31**, 197; (b) H. P. Godfried and I. F. Silvera, *Phys. Rev. Lett.*, 1982, **48**, 1337.

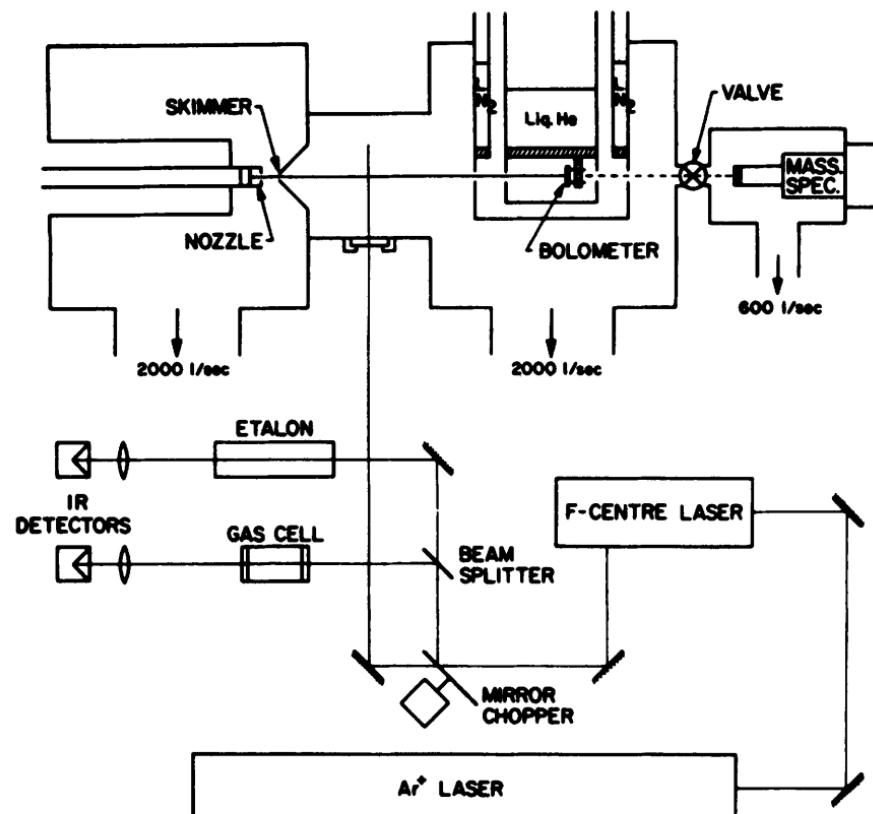


Figure 11 Schematic diagram of the laser-molecular beam experiment on infrared spectra and vibrational predissociation
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not only to translational kinetic energy and beam flux, but also to the internal excitation of molecules which strike it.) Signal is enhanced by multiple crossing of the beam by the laser, always at 90°. Spectra were observed which lie very close to the ($\nu_1 + \nu_3$) and ($2\nu_2 + \nu_3$) bands of CO₂. Vibrational predissociation was apparent even for large clusters containing a few hundred molecules.

Other studies of this type have used mass spectrometric detection. A cw CO₂ laser was used to excite ethylene dimers and clusters, and ethylene bound to Ne, Ar, Kr, and C₂F₄.⁵⁷⁰ It was thought that predissociation was preceded by direct intramolecular energy flow from ethylene ν_7 to the van der Waals bond. A similar study of Ar·BCl₃ found that exciting one quantum of 'BCl₃ ν_3 ' resulted in a predissociation lifetime between 1 and 3 ps.⁵⁶⁸

An optical parametric oscillator (see Part I¹) provided the necessary tunable IR radiation to predissociate benzene clusters by exciting in the region of the C-H stretching frequency. The wavelength dependence of the vibrational predissociation was found to resemble the IR spectrum of liquid benzene at room temperature. Translational energy distributions were also measured for benzene monomers

produced by cluster predissociation, and they revealed that energy surplus to bond breaking requirements is partitioned entirely into fragment rotation and vibration.⁵⁷⁰

Predissociation of van der Waals complexes has also been studied by electronic spectroscopy, and we shall return to this subject in Section 3.

Raman spectroscopy has recently been performed on van der Waals species. Both rotational and vibrational spectra of argon dimers have been observed in an expansion seeded with N₂, using crossed expansion-intracavity laser geometry.^{632b} The spectra were explained in terms of a dipole-induced-dipole model for the dimer polarizability. The dimer to monomer ratio was determined to be 0.020(4).

3 Electronic Spectroscopy

References for Table 11. (pp. 291–312)

- ⁶³³ G. V. Marr, R. M. Holmes, and K. Codling, *J. Phys. B*, 1980, **13**, 283.
- ⁶³⁴ M. Raoult, Ch. Jungen, and D. Dill, *J. Chem. Phys.*, 1980, **77**, 599.
- ⁶³⁵ J. R. Hiskes, *J. Appl. Phys.*, 1980, **51**, 4592.
- ⁶³⁶ A. W. Fliflet and V. McKoy, *Phys. Rev. A*, 1980, **21**, 1863.
- ⁶³⁷ M. D. Burrows, L. C. McIntyre, S. R. Ryan, and W. E. Lamb, *Phys. Rev. A*, 1980, **21**, 1841.
- ⁶³⁸ Y. Morioka, S. Hara, and M. Nakamura, *Phys. Rev. A*, 1980, **22**, 177.
- ⁶³⁹ C. A. Weatherford, *Phys. Rev. A*, 1980, **22**, 2519.
- ⁶⁴⁰ L. G. J. Boesten and H. G. M. Heideman, *Physica B + C*, 1980, **98**, 242.
- ⁶⁴¹ S. M. Tarr, J. A. Schiavone, and R. S. Freund, *Phys. Rev. Lett.*, 1980, **44**, 1660.
- ⁶⁴² P. M. Dehmer and W. A. Chupka, *Chem. Phys. Lett.*, 1980, **70**, 127.
- ⁶⁴³ M. Rothschild, H. Egger, R. T. Hawkins, H. Pummer, C. K. Rhodes, *Chem. Phys. Lett.*, 1980, **72**, 404.
- ⁶⁴⁴ J. Breton, P. M. Guyon, and M. Glass-Maujean, *Phys. Rev. A*, 1980, **21**, 1909.
- ⁶⁴⁵ M. Larzilliere, F. Launay, and J.-Y. Roncin, *J. Phys. (Paris)*, 1980, **41**, 1431.
- ⁶⁴⁶ D. Mathur, *Int. J. Mass. Spectrom. Ion. Phys.*, 1981, **40**, 235.
- ⁶⁴⁷ I. P. Bogdanova, G. V. Efremova, B. P. Lavrov, V. N. Ostrovskii, V. I. Ustimov, and V. I. Yakovleva, *Opt. Spectrosc.*, 1981, **50**, 63.
- ⁶⁴⁸ (a) M. Landau, R. I. Hall, and F. Pichou, *J. Phys. B*, 1981, **14**, 1509; (b) J. P. Johnson and J. L. Franklin, *Int. J. Mass. Spectrom. Ion. Phys.*, 1980, **33**, 393.
- ⁶⁴⁹ N. Bose and F. Linder, *J. Phys. B*, 1981, **14**, 2499.
- ⁶⁵⁰ E. E. Eyler and F. M. Pipkin, *Phys. Rev. Lett.*, 1981, **47**, 1270.
- ⁶⁵¹ M. Rothschild, H. Egger, R. T. Hawkins, J. Bokor, H. Pummer, and C. K. Rhodes, *Phys. Rev. A*, 1981, **23**, 206.
- ⁶⁵² P. Quadrelli and K. Dressler, *J. Mol. Spectrosc.*, 1981, **86**, 316.
- ⁶⁵³ W. Kolos, *J. Mol. Spectrosc.*, 1981, **86**, 420.
- ⁶⁵⁴ K. Dressler and L. Wolniewicz, *J. Mol. Spectrosc.*, 1981, **86**, 534.
- ⁶⁵⁵ W. Kolos and J. Rychlewski, *J. Mol. Spectrosc.*, 1981, **88**, 1.
- ⁶⁵⁶ G. O. Brink, *J. Mol. Spectrosc.*, 1981, **90**, 353.
- ⁶⁵⁷ V. Kumar and E. Krishnakumar, *J. Electron Spectrosc.*, 1981, **24**, 1.
- ⁶⁵⁸ Ch. Jungen and M. Raoult, *Faraday Discuss. Chem. Soc.*, 1981, **71**, 253.
- ⁶⁵⁹ A. Heutz and J. Mazeau, *J. Phys. B*, 1981, **14**, L591.
- ⁶⁶⁰ P. Rosmus and E. A. Reinsch, *Z. Naturforsch., Teil A*, 1980, **35**, 1066.
- ⁶⁶¹ W. T. Zemke and W. C. Stwalley, *J. Chem. Phys.*, 1980, **73**, 5584.
- ⁶⁶² (a) M. Brieger, A. Hese, A. Renn, and A. Sodeik, *Chem. Phys. Lett.*, 1980, **76**, 465; (b) P. J. Dagdigian, *J. Chem. Phys.*, 1980, **73**, 2049.
- ⁶⁶³ G. Ennen, B. Fiedler, and Ch. Ottinger, *J. Chem. Phys.*, 1981, **75**, 59.
- ⁶⁶⁴ F. B. Orth, W. C. Stwalley, S.-C. Yang, and Y.-K. Hsieh, *J. Mol. Spectrosc.*, 1980, **79**, 314.
- ⁶⁶⁵ M. Brieger, A. Hese, A. Renn, and A. Sodeik, *Chem. Phys. Lett.*, 1981, **78**, 153.
- ⁶⁶⁶ M. Giroud and O. Nedelec, *J. Chem. Phys.*, 1980, **73**, 4151.
- ⁶⁶⁷ S.-C. Yang, Y.-K. Hsieh, K. K. Verma, and W. C. Stwalley, *J. Mol. Spectrosc.*, 1980, **83**, 304.
- ⁶⁶⁸ Y.-K. Hsieh, S.-C. Yang, A. C. Tam, K. K. Verma, W. C. Stwalley, *J. Mol. Spectrosc.*, 1980, **83**, 311.
- ⁶⁶⁹ S.-C. Yang, K.-K. Hsieh, A. C. Tam, W. T. Zemke, K. K. Verma, and W. C. Stwalley, *J. Chem. Phys.*, 1981, **75**, 3679.
- ⁶⁷⁰ W. J. Balfour, *J. Mol. Spectrosc.*, 1980, **79**, 507.
- ⁶⁷¹ B. Kaving and B. Lindgren, *Phys. Scr.*, 1981, **24**, 752.
- ⁶⁷² L. Klynnings and H. Martin, *J. Phys. B*, 1981, **14**, L365.
- ⁶⁷³ B. Kaving, University of Stockholm Institute of Physics Report, 81—08.
- ⁶⁷⁴ K. J. Snowdon, R. J. MacDonald, and E. Veje, *J. Phys. B*, 1980, **13**, 1413.

- ⁶⁷⁵ K. H. Becker, H. H. Boenig, and T. Tatarczyk, *Chem. Phys. Lett.*, 1980, **71**, 242.
⁶⁷⁶ B. Bhatnagar, J. L. Wilkerson, G. R. Smith, and W. A. Guillory, *J. Mol. Spectrosc.*, 1981, **85**, 348.
⁶⁷⁷ I. Kusonoki and C. Ottinger, *J. Chem. Phys.*, 1980, **73**, 2069.
⁶⁷⁸ P. C. Cosby, H. Helm, and J. T. Moseley, *Astrophys. J.*, 1980, **235**, 52.
⁶⁷⁹ P. M. Mul, J. B. A. Mitchell, V. S. D'Angelo, P. Defrance, J. W. McGowan, and H. R. Froelich, *J. Phys. B*, 1981, **14**, 1353.
⁶⁸⁰ M. M. Graff and J. T. Moseley, *Chem. Phys. Lett.*, 1981, **83**, 97.
⁶⁸¹ (a) F. J. Grieman, B. H. Mahan, A. O'Keefe, and J. S. Winn, *Faraday Discuss. Chem. Soc.*, 1981, **71**, 191; (b) B. H. Mahan and A. O'Keefe, *Astrophys. J.*, 1981, **248**, 1209.
⁶⁸² P. Bollmark, B. Lindgren, and U. Sassenberg, *Phys. Scr.*, 1981, **24**, 542.
⁶⁸³ T. Bergeman, P. Erman, and M. Larsson, *Chem. Phys.*, 1980, **54**, 55.
⁶⁸⁴ P. Erman and M. Larsson, *Phys. Scr.*, 1980, **22**, 348.
⁶⁸⁵ I. L. Chidsey and D. R. Crosby, *J. Quant. Spectrosc. Radiat. Transfer*, 1980, **23**, 187.
⁶⁸⁶ C. C. Wang and C.-M. Huang, *Phys. Rev. A*, 1980, **21**, 1235.
⁶⁸⁷ C. C. Wang, D. K. Killinger, and C.-M. Huang, *Phys. Rev. A*, 1980, **22**, 188.
⁶⁸⁸ J. A. Coxon, *Can. J. Phys.*, 1980, **58**, 933.
⁶⁸⁹ F. Raab, T. Bergeman, D. Lieberman, and H. Metcalf, *Opt. Lett.*, 1980, **5**, 427.
⁶⁹⁰ T. Bergeman, P. Erman, Z. Hartaym, and M. Larsson, *Phys. Scr.*, 1981, **23**, 45.
⁶⁹¹ (a) A. Goldman and J. R. Gillis, *J. Quant. Spectrosc. Radiat. Transfer*, 1981, **25**, 111; (b) I. S. McDermid and J. B. Laudenslager, *J. Chem. Phys.*, 1982, **76**, 1824.
⁶⁹² D. P. Dewangen and D. R. Flower, *J. Phys. B*, 1981, **14**, L425.
⁶⁹³ F. J. Grieman, B. H. Mahan, and A. O'Keefe, *J. Chem. Phys.*, 1980, **72**, 4246.
⁶⁹⁴ K. Checkland, D. L. Cooper, and W. G. Richards, *J. Phys. B*, 1981, **14**, 2545.
⁶⁹⁵ F. Breyer, P. Frey, and H. Hotop, *Z. Phys. A*, 1981, **300**, 7.
⁶⁹⁶ (a) B. K. Janousek and J. I. Brauman, *Phys. Rev. A*, 1981, **23**, 1673; (b) S. J. Dunlavy, J. M. Dyke, N. K. Fayad, N. Jonathan, and A. Morris, *Mol. Phys.*, 1981, **44**, 265.
⁶⁹⁷ P. Bollmark, B. Lindgren, and U. Sassenberg, *Phys. Scr.*, 1980, **21**, 811.
⁶⁹⁸ C. E. Brion, S. T. Hood, I. H. Suzuki, E. Weigold, and G. R. J. Williams, *J. Electron Spectrosc.*, 1980, **21**, 71.
⁶⁹⁹ R. Abouaf and D. Teillet-Billy, *J. Phys. B*, 1980, **13**, L275; *Chem. Phys. Lett.* 1980, **73**, 106.
⁷⁰⁰ D. Spence, *J. Phys. B*, 1981, **14**, L107.
⁷⁰² A. P. Hitchcock and C. E. Brion, *Chem. Phys.*, 1981, **61**, 281; *J. Phys. B*, 1980, **13**, L677.
⁷⁰³ G. A. Segal and K. Wolf, *J. Phys. B*, 1981, **14**, 2291.
⁷⁰⁴ F. Carnovale, R. Tseng, and C. E. Brion, *J. Phys. B*, 1981, **14**, 4771.
⁷⁰⁵ J. M. Hutson and D. L. Cooper, *J. Chem. Phys.*, 1981, **75**, 4502.
⁷⁰⁶ P. L. Smith, K. Yoshino, J. H. Black, and W. H. Parkinson, *Astrophys. J.*, 1980, **238**, 874.
⁷⁰⁷ D. S. Ginter and M. L. Ginter, *J. Mol. Spectrosc.*, 1981, **90**, 177.
⁷⁰⁸ M. G. White, S. H. Southworth, P. Kobrin, and D. A. Shirley, *J. Electron Spectrosc.*, 1980, **19**, 115.
⁷⁰⁹ M. A. Baig, J. Hormes, J. P. Connerade, and W. R. S. Garton, *J. Phys. B*, 1981, **14**, L147.
⁷¹⁰ D. S. Ginter, M. L. Ginter, and S. G. Tilford, *J. Mol. Spectrosc.*, 1981, **90**, 152.
⁷¹¹ L. Klynning and M. Kronekvist, *Phys. Scr.*, 1981, **24**, 21.
⁷¹² D. S. Ginter and M. L. Ginter, *J. Mol. Spectrosc.*, 1980, **82**, 152.
⁷¹³ G. N. Gerasimov and L. V. Egorova, *Opt. Spectrosc.*, 1980, **48**, 566.
⁷¹⁴ R. Panock, R. R. Freeman, R. H. Storz, and T. A. Miller, *Chem. Phys. Lett.*, 1980, **74**, 203.
⁷¹⁵ Y. Matsuura and K. Fukuda, *J. Phys. Soc. Jpn.*, 1980, **49**, 308.
⁷¹⁶ S. Takao, M. Kogoma, T. Oka, M. Imamura, and S. Arai, *J. Chem. Phys.*, 1980, **73**, 148.
⁷¹⁷ Y. Matsuura and K. Fukuda, *J. Phys. Soc. Jpn.*, 1981, **50**, 933.
⁷¹⁸ T. D. Bonifield, F. H. K. Rainbow, G. K. Walters, M. V. McCusker, D. C. Lorents, and R. A. Gutcheck, *Chem. Phys. Lett.*, 1980, **69**, 290.
⁷¹⁹ A. Luches, V. Nassici, A. Perrone, and M. R. Perrone, *Opt. Commun.*, 1981, **39**, 307.
⁷²⁰ T. D. Bonifield, F. H. K. Rainbow, G. K. Walters, M. V. McCusker, D. C. Lorents, and R. A. Gutcheck, *J. Chem. Phys.*, 1980, **72**, 2914.
⁷²¹ O. Dutuit, M. C. Castex, J. Le Calve, and M. Lavallee, *J. Chem. Phys.*, 1980, **73**, 3107.
⁷²² H. P. Grieneisen, K. Hohla, and K. L. Kompa, *Opt. Commun.*, 1981, **37**, 97.
⁷²³ (a) I. Dabrowski, G. Herzberg, and K. Yoshino, *J. Mol. Spectrosc.*, 1981, **89**, 491; (b) P. M. Dehmer and E. D. Poliakoff, *Chem. Phys. Lett.*, 1981, **77**, 326.
⁷²⁴ G. Klein and M. J. Carvalho, *J. Phys. B*, 1981, **14**, 1283.
⁷²⁵ P. Millet, A. M. Barrie, A. Birot, H. Brunet, H. Dijols, J. Galy, and Y. Salamero, *J. Phys. B*, 1981, **14**, 459.
⁷²⁶ H. Haberland and W. Weber, *J. Phys. B*, 1980, **13**, 4147.
⁷²⁷ M. D. Havey, S. E. Froking, and J. J. Wright, *Phys. Rev. Lett.*, 1980, **45**, 1783.
⁷²⁸ W. P. Lapatovich, R. Ahmad-Bitar, P. E. Mookowitz, I. Renorn, R. A. Gottscho, and D. E. Pritchard, *J. Chem. Phys.*, 1980, **73**, 5418.
⁷²⁹ R. A. Gottscho, R. Ahmad-Bitar, W. P. Lapatovich, I. Renhorn, and D. E. Pritchard, *J. Chem. Phys.*, 1981, **75**, 2546.

- ⁷³⁰ D. L. Cooper, *J. Chem. Phys.*, 1981, **75**, 4157.
⁷³¹ B. Sayer, M. Ferray, J. P. Visticot, and J. Lozingot, *J. Phys. B*, 1980, **13**, 177.
⁷³² M. Ferray, J. P. Visticot, L. Lozingot, and B. Sayer, *J. Phys. B*, 1980, **13**, 2571.
⁷³³ M. E. Dolan and F. Masnou-Seeuws, *J. Phys. B*, 1981, **14**, L583.
⁷³⁴ M. A. Islam, A. Kponou, B. Suleman, and W. Hopper, *Phys. Rev. Lett.*, 1981, **47**, 643.
⁷³⁵ J. P. Visticot, J. Szudy, and B. Sayer, *J. Phys. B*, 1981, **14**, 2329.
⁷³⁶ J. P. Visticot, J. Szudy, and B. Sayer, *J. Phys. B*, 1981, **14**, 4755.
⁷³⁷ J. M. Salter and E. L. Lewis, *J. Phys. B*, 1980, **13**, L315.
⁷³⁸ C. B. Collins, J. A. Anderson, F. W. Lee, P. A. Vicharelli, D. Popescu, and I. Popescu, *Phys. Rev. Lett.*, 1980, **44**, 139.
⁷³⁹ K. Niemax, *J. Phys. B*, 1980, **13**, 1791.
⁷⁴⁰ C. R. Webster and F. Rostas, *J. Phys. B*, 1981, **14**, 4497.
⁷⁴¹ J. Tellinghuisen and R. J. Exton, *J. Phys. B*, 1980, **13**, 4781.
⁷⁴² R. J. LeRoy and W.-H. Lam, *Chem. Phys. Lett.*, 1980, **71**, 544.
⁷⁴³ D. C. Hartman and J. S. Winn, *J. Chem. Phys.*, 1981, **74**, 4320.
⁷⁴⁴ T. Grycuk and E. Czerwosz, *Physica C*, 1981, **106**, 431.
⁷⁴⁵ M. C. Castex, J. le Calve, D. Haats, B. Jordan, and G. Zimmerer, *Chem. Phys. Lett.*, 1980, **70**, 106.
⁷⁴⁶ T. G. Dreiling and D. W. Setser, *J. Chem. Phys.*, 1981, **75**, 4360.
⁷⁴⁷ K. Tamagake, D. W. Setser, and J. H. Kolts, *J. Chem. Phys.*, 1981, **74**, 4286.
⁷⁴⁸ M. Armentane, A. Brancaccio, E. Burattini, V. Santoro, N. Spinelli, and F. Vanoli, *Int. J. Mass Spectrom. Ion Phys.*, 1980, **36**, 213.
⁷⁴⁹ E. C. Zifp and M. R. Gorman, *J. Chem. Phys.*, 1980, **73**, 813.
⁷⁵⁰ A. Y.-M. Ung, *J. Chem. Phys.*, 1980, **72**, 3731.
⁷⁵¹ A. Huetz, F. Gresteau, R. I. Hall, and J. Mazeau, *J. Chem. Phys.*, 1980, **72**, 5297.
⁷⁵² J. Derouard, T. D. Nguyen, and N. Sadeghi, *J. Chem. Phys.*, 1980, **72**, 6698.
⁷⁵³ J. B. West, A. C. Parr, B. E. Cole, D. L. Ederer, R. Stockbauer, and J. L. Dehmer, *J. Phys. B*, 1980, **13**, L105.
⁷⁵⁴ I. Nadler, D. W. Setser, and S. Rosenwaks, *Chem. Phys. Lett.*, 1980, **72**, 536.
⁷⁵⁵ S. M. Tarr, J. A. Schiavone, and R. S. Freund, *Phys. Rev. Lett.*, 1980, **44**, 1660.
⁷⁵⁶ A. C. Parr, D. L. Ederer, B. E. Cole, J. B. West, R. Stockbauer, K. Codling, and J. L. Dehmer, *Phys. Rev. Lett.*, 1981, **46**, 22.
⁷⁵⁷ D. Cerny, R. Bacis, R. W. Field, and R. A. McFarlane, *J. Phys. Chem.*, 1981, **85**, 2626.
⁷⁵⁸ T. Suzuki, *Opt. Commun.*, 1981, **38**, 364.
⁷⁵⁹ G. Cernogora, L. Hochard, M. Touzeau, and C. M. Ferreira, *J. Phys. B*, 1981, **14**, 2977.
⁷⁶⁰ W. R. Green and J. Lukasik, *Opt. Lett.*, 1980, **5**, 537.
⁷⁶¹ N. Oda and T. Osawa, *J. Phys. B*, 1981, **14**, L563.
⁷⁶² D. V. Zhuk, D. K. Otorbaev, V. N. Ochkin, S. Yu. Savinov, and N. N. Sobolev, *Opt. Spectrosc.*, 1981, **50**, 323.
⁷⁶³ D. Cerny, F. Roux, C. Effantin, J. d'Incan, and J. Verges, *J. Mol. Spectrosc.*, 1980, **81**, 216.
⁷⁶⁴ B. M. DeKoven, D. H. Levy, H. H. Harris, B. R. Zegarski, and T. A. Miller, *J. Chem. Phys.*, 1981, **74**, 5659.
⁷⁶⁵ H. Oertl, M. Kratzat, J. Imschweiler, and T. Noll, *Chem. Phys. Lett.*, 1981, **82**, 552.
⁷⁶⁶ J. A. Michejda, L. J. Dube, and P. D. Burrow, *J. Appl. Phys.*, 1981, **52**, 3121.
⁷⁶⁷ W. B. Lewis and W. R. Wadt, *Chem. Phys. Lett.*, 1981, **78**, 266.
⁷⁶⁸ D. Coe, F. Robben, and L. Talbot, *J. Opt. Soc. Am.*, 1980, **70**, 1238.
⁷⁶⁹ L. A. Collins, D. C. Cartwright, and W. R. Wadt, *J. Phys. B*, 1980, **13**, L613.
⁷⁷⁰ W. Benesch, D. Rivers, and J. Moore, *J. Opt. Soc. Am.*, 1980, **70**, 792.
⁷⁷¹ F. A. Grimm, *J. Electron Spectrosc.*, 1980, **20**, 245.
⁷⁷² A. Carrington and R. P. Tuckett, *Chem. Phys. Lett.*, 1980, **74**, 19.
⁷⁷³ B. H. Mahan and A. O'Keefe, *J. Chem. Phys.*, 1981, **74**, 5606.
⁷⁷⁴ E. D. Poliakoff, J. L. Dehmer, D. Dill, A. C. Parr, K. H. Jackson, and R. N. Zare, *Phys. Rev. Lett.*, 1981, **46**, 907.
⁷⁷⁵ J. Chevaleyre and J. P. Perrot, *J. Mol. Spectrosc.*, 1981, **85**, 85.
⁷⁷⁶ A. Ding, K. Richter, and M. Menzinger, *Chem. Phys. Lett.*, 1981, **77**, 523.
⁷⁷⁷ (a) J. B. West, K. Codling, A. C. Parr, D. L. Ederer, B. E. Cole, R. Stockbauer, and J. L. Dehmer, *J. Phys. B*, 1981, **14**, 1791; (b) T. A. Carlson, M. O. Krause, D. McHaffy, J. W. Taylor, F. A. Grimm, and J. D. Allen, jun., *J. Chem. Phys.*, 1980, **73**, 6056.
⁷⁷⁸ A. Huetz, F. Gresteau, and J. Mazeau, *J. Phys. B*, 1980, **13**, 3275.
⁷⁷⁹ A. Huetz, I. Cadet, F. Gresteau, R. I. Hall, D. Vichon, and J. Mazeau, *Phys. Rev. A*, 1980, **21**, 622.
⁷⁸⁰ S. C. Wallace and K. K. Innes, *J. Chem. Phys.*, 1980, **72**, 4805.
⁷⁸¹ (a) E. Miescher, *J. Chem. Phys.*, 1980, **73**, 3088; (b) Y. Ono, S. H. Linn, H. F. Prest, C. Y. Ng, and E. Miescher, *ibid.*, p. 4855.
⁷⁸² R. Freedman and R. W. Nicholls, *J. Mol. Spectrosc.*, 1980, **83**, 223.
⁷⁸³ H. Zacharias, H. Rottke, and K. H. Welge, *Opt. Commun.*, 1980, **35**, 185.
⁷⁸⁴ (a) J. C. Miller and R. N. Compton, *J. Chem. Phys.*, 1981, **75**, 22; (b) C. E. Otis and P. M. Johnson, *Chem. Phys. Lett.*, 1981, **83**, 73.

- 785 P. Arrowsmith, W. J. Jones, and R. P. Tuckett, *J. Mol. Spectrosc.*, 1981, **86**, 216.
 786 P. A. Freedman and P. L. Radioff, *J. Mol. Spectrosc.*, 1981, **88**, 225.
 787 A. Timmermann and R. Wallenstein, *Opt. Commun.*, 1981, **39**, 239.
 788 K. Dressler, Ch. Jungen, and E. Miescher, *J. Phys. B*, 1981, **14**, L701.
 789 J. A. Guest and L. C. Lee, *J. Phys. B*, 1981, **14**, 3401.
 790 C. E. Brion and K. H. Tan, *J. Electron Spectrosc.*, 1981, **23**, 1.
 791 K. Dressler and E. Miescher, *J. Chem. Phys.*, 1981, **75**, 4310.
 792 C. Amiot, *Chem. Phys. Lett.*, 1981, **83**, 40.
 793 F. Lahmani, C. Lardeux, and D. Solgadi, *Chem. Phys. Lett.*, 1981, **81**, 531.
 794 J. R. Banic, R. H. Lipson, T. Efthimiopoulos, and B. P. Stoicheff, *Opt. Lett.*, 1981, **6**, 461.
 795 T. Gustafsson and H. J. Levinson, *Chem. Phys. Lett.*, 1981, **78**, 28.
 796 P. Esherick and R. J. M. Anderson, *Chem. Phys. Lett.*, 1980, **70**, 621.
 797 T. Hikida, S. Yagi, and Y. Mori, *Chem. Phys.*, 1980, **52**, 399.
 798 L. G. Dage, J. Dusek, and M. F. Zabielski, *J. Quant. Spectrosc. Radiat. Transfer*, 1980, **24**, 237.
 799 (a) W. E. Sharp and D. W. Rusch, *J. Quant. Spectrosc. Radiat. Transfer*, 1981, **25**, 413; (b) R. E. Demaray, C. Otis, K. Aron, and P. Johnson, *J. Chem. Phys.*, 1980, **72**, 5772.
 800 P. C. Cosby and H. Helm, *J. Chem. Phys.*, 1981, **75**, 3882.
 801 V. A. Pavloschuk, Yu. G. Pikus, and L. I. Shanskii, *Opt. Spectrosc.*, 1980, **45**, 474.
 802 A. Gerwer, C. Asaro, B. V. McKoy, and P. W. Langhoff, *J. Chem. Phys.*, 1980, **72**, 713.
 803 H. van Lonkhuyzen, H. G. Muller, and C. A. DeLange, *J. Electron Spectrosc.*, 1980, **21**, 241.
 804 R. P. Saxon and B. Liu, *J. Chem. Phys.*, 1980, **73**, 870 and 876.
 805 J. W. Brault, *J. Mol. Spectrosc.*, 1980, **80**, 384.
 806 D. Spence, *J. Chem. Phys.*, 1981, **74**, 3898.
 807 M. A. Dillon and D. Spence, *J. Chem. Phys.*, 1981, **74**, 6070.
 808 P. C. Wright, *Chem. Phys. Lett.*, 1980, **71**, 127.
 809 D. H. Katayama and Y. Tanaka, *J. Mol. Spectrosc.*, 1981, **88**, 41.
 810 C. Amiot and J. Verges, *Can. J. Phys.*, 1981, **59**, 1391; see also L. S. Rothman, *Appl. Opt.*, 1982, **21**, 2428.
 811 B. R. Lewis, H. Carver, T. I. Hobbs, D. G. McCoy, and H. P. F. Gies, *J. Quant. Spectrosc. Radiat. Transfer*, 1980, **24**, 365.
 812 C. C. Chiang and G. B. Skinner, *J. Quant. Spectrosc. Radiat. Transfer*, 1980, **24**, 525.
 813 P. Morin, I. Nenner, P. M. Guyon, O. Dutuit, and K. Ito, *J. Chem. Phys.*, 1980, **72**, 605.
 814 V. Kumar and E. Krishnakumar, *J. Electron Spectrosc. Relat. Phenom.*, 1981, **22**, 109.
 815 (a) A. L. Roche, K. Kirby, S. L. Guberman, and A. Dalgarno, *J. Electron Spectrosc. Relat. Phenom.*, 1981, **22**, 223; (b) A. Chutjian and J. M. Ajello, *Chem. Phys. Lett.*, 1980, **72**, 504; (c) J. H. D. Eland, *J. Chem. Phys.*, 1980, **72**, 6015.
 816 P. C. Cosby and J.-B. Ozanne, J. T. Moseley, and D. L. Albritton, *J. Mol. Spectrosc.*, 1980, **79**, 203.
 817 (a) M. Carre, M. Druetta, M. L. Gaillard, H. H. Bukow, M. Horain, A. L. Roche, and M. Velghe, *Mol. Phys.*, 1980, **40**, 1453; (b) M. Broyer, M. Larzilliere, M. Carre, M. L. Gaillard, M. Velghe, and J. B. Ozenne, *Chem. Phys.*, 1981, **63**, 445.
 818 P. M. Guyon and I. Nenner, *Appl. Opt.*, 1980, **19**, 4068.
 819 F. J. Grieman, J. T. Moseley, R. P. Saxon, and P. C. Cosby, *Chem. Phys.*, 1980, **51**, 169.
 820 H. Helm, P. C. Cosby, and D. L. Huestis, *J. Chem. Phys.*, 1980, **73**, 2629.
 821 D. S. Pesic, D. Rakotoarajimy, and S. Weniger, *Astrophys. J. Suppl.*, 1981, **45**, 507.
 822 R. Bombach, A. Schmelzer, and J.-P. Stadelmann, *Chem. Phys.*, 1981, **61**, 214.
 823 J. M. Brown, D. J. Milton, J. K. G. Watson, R. N. Zare, D. L. Albritton, M. Horani, and J. Rostas, *J. Mol. Spectrosc.*, 1981, **90**, 139.
 824 K. Codling, A. C. Parr, D. L. Ederer, R. Stockbauer, J. B. West, B. E. Cole, and J. L. Dehmer, *J. Phys. B*, 1981, **14**, 657.
 825 R. G. C. Blyth, I. Powis, and C. J. Danby, *Chem. Phys. Lett.*, 1981, **84**, 272.
 826 J. C. Hansen, M. M. Graff, J. T. Moseley, and P. C. Cosby, *J. Chem. Phys.*, 1981, **74**, 2195.
 827 A. Tabche-Fonhaile, I. Nenner, P. M. Guyon, and J. Delwiche, *J. Chem. Phys.*, 1981, **75**, 1129.
 828 D. S. Belic and R. I. Hall, *J. Phys. B*, 1981, **14**, 365.
 829 B. Couillaud, A. Ducasse, L. Sarger, and D. Boscher, *Appl. Phys. Lett.*, 1980, **36**, 407.
 830 B. J. Sullivan and D. A. Dowd, *Chem. Phys.*, 1980, **46**, 231.
 831 G. W. King, I. M. Littlewood, J. R. Robins, and N. T. Wijeratne, *Chem. Phys.*, 1980, **50**, 291.
 832 J. P. Pique, F. Stoeckel, and F. Hartmann, *Opt. Commun.*, 1980, **33**, 23.
 833 R. P. Hackel, L. A. Hackel, and S. Ezekiel, *Phys. Rev. A*, 1980, **21**, 1342.
 834 P. Luc, *J. Mol. Spectrosc.*, 1980, **80**, 41.
 835 R. Bacis, S. Churassy, R. W. Field, J. B. Koffend, and J. Verges, *J. Chem. Phys.*, 1980, **72**, 34.
 836 J. B. Koffend, F. J. Wodarczyk, R. Bacis, and R. W. Field, *J. Chem. Phys.*, 1980, **72**, 478.
 837 A. Yokozeki and J. S. Muenter, *J. Chem. Phys.*, 1980, **72**, 3796.
 838 D. W. Callahan, A. Yokozeki, and J. S. Muenter, *J. Chem. Phys.*, 1980, **72**, 4791.
 839 A. L. Guy, K. S. Viswanathan, A. Sur, and J. Tellinghuisen, *Chem. Phys. Lett.*, 1980, **73**, 582.
 840 K. A. Truesdell, R. A. Keller, and E. F. Zalewski, *J. Chem. Phys.*, 1980, **73**, 1117.
 841 R. Bacis, M. Broyer, S. Churassy, J. Verges, and J. Vigne, *J. Chem. Phys.*, 1980, **73**, 2641.

- 842 R. J. LeRoy, *J. Chem. Phys.*, 1980, **73**, 6003.
 843 H. Hemmati and G. J. Collins, *Chem. Phys. Lett.*, 1980, **75**, 488.
 844 J. Tellinghuisen, M. R. McKeever, and A. Sur, *J. Mol. Spectrosc.*, 1980, **82**, 225.
 845 R. A. Ashby and C. W. Johnson, *J. Mol. Spectrosc.*, 1980, **84**, 41.
 846 S. Gerstenkorn, P. Luc, and J. Sinzelle, *J. Phys. (Paris)*, 1980, **41**, 1419.
 847 S. Gerstenkorn, P. Luc, and R. Vetter, *Rev. Phys. Appl.*, 1981, **16**, 529.
 848 C. Demuynck and J. L. DesTombes, *IEEE J. Quantum Elect.*, 1981, **OE17**, 575.
 849 D. E. Cooper, C. M. Klimcak, and J. E. Wessel, *Phys. Rev. Lett.*, 1981, **46**, 324.
 850 K. S. Viswanathan, A. Sur, and J. Tellinghuisen, *J. Mol. Spectrosc.*, 1981, **86**, 393.
 851 T. K. Balasubramanian, G. L. Bhale, M. N. Dixit, and N. A. Narasimham, *J. Mol. Spectrosc.*, 1981, **88**, 259.
 852 C. T. Rettner, C. R. Webster, and R. N. Zare, *J. Phys. Chem.*, 1981, **85**, 1105.
 853 G. W. King, I. M. Littlewood, and J. R. Robins, *Chem. Phys.*, 1981, **56**, 145.
 854 M. S. de Vries, N. J. A. van Veen, T. Baller, and A. E. de Vries, *Chem. Phys.*, 1981, **56**, 157.
 855 J. R. Wiesenfeld and R. H. Young, *Chem. Phys.*, 1981, **58**, 51.
 856 C. Tai and H. J. Simon, *Opt. Lett.*, 1981, **6**, 133.
 857 S. Gerstenkorn, P. Luc, and J. Verges, *J. Phys. B*, 1981, **14**, L193.
 858 K. Kasatani, Y. Tanaka, K. Shibuya, M. Kawasaki, K. Obi, H. Sato, and I. Tanaka, *J. Chem. Phys.*, 1981, **74**, 895.
 859 W. R. Lambert, P. M. Felker, and A. H. Zewail, *J. Chem. Phys.*, 1981, **74**, 4732.
 860 J. L. Hall, L. Hollberg, T. Baer, and H. G. Robinson, *Appl. Phys. Lett.*, 1981, **39**, 680.
 861 G. C. Bjorklund and M. D. Levenson, *Phys. Rev. A*, 1981, **24**, 166.
 862 C. Tai, *Phys. Rev. A*, 1981, **24**, 294.
 863 C. J. Borde, G. Camy, B. Decomps, J.-P. Descoubes, and J. Vigue, *J. Phys. (Paris)*, 1981, **42**, 1393.
 864 M. Martin, C. Fotakis, R. J. Donovan, and M. J. Shaw, *Nuovo Cimento B*, 1981, **63**, 300.
 865 J. Vigue, M. Broyer, and J. C. Lehmann, *J. Phys. (Paris)*, 1981, **42**, 937, 949, and 961.
 866 S. Gerstenkorn and P. Luc, *Opt. Commun.*, 1981, **36**, 322.
 867 J. P. Pique, F. Hartmann, R. Bacis, and S. Churassy, *Opt. Commun.*, 1981, **36**, 354.
 868 W. Thieme and E. Fill, *Opt. Commun.*, 1981, **36**, 361.
 869 M. Glaser, D. Kegung, and H. J. Foth, *Opt. Commun.*, 1981, **38**, 119.
 870 R. Vasudev and W. M. McClain, *Opt. Commun.*, 1981, **38**, 348.
 871 J. C. D. Brand, A. K. Kalukar, and A. B. Yamashita, *Opt. Commun.*, 1981, **39**, 235.
 872 S. Churassy, F. Martin, R. Bacis, J. Verges, and R. W. Field, *J. Chem. Phys.*, 1981, **75**, 4863.
 873 W. Lenth, C. Ortiz, and G. C. Bjorklund, *Opt. Lett.*, 1981, **6**, 351.
 874 Ch. Ottinger and M. Schroder, *J. Phys. B*, 1980, **13**, 4163.
 875 R. A. Bernheim, L. P. Gold, P. B. Kelly, C. Kittrell, and D. K. Veirs, *Chem. Phys. Lett.*, 1980, **70**, 104.
 876 K. K. Verma, M. E. Koch, and W. C. Stwalley, *J. Mol. Spectrosc.*, 1981, **87**, 548.
 877 R. A. Bernheim, L. P. Gold, P. B. Kelly, T. Tipton, and D. K. Veirs, *J. Chem. Phys.*, 1981, **74**, 2749.
 878 R. A. Bernheim, L. P. Gold, P. B. Kelly, C. Tomczyk, and D. K. Veirs, *J. Chem. Phys.*, 1981, **74**, 3249.
 879 J. R. Balz, R. A. Bernheim, L. P. Gold, P. B. Kelly, and D. K. Veirs, *J. Chem. Phys.*, 1981, **75**, 5226.
 880 G. Ennen, Ch. Ottinger, K. K. Verma, and W. C. Stwalley, *J. Mol. Spectrosc.*, 1981, **89**, 413.
 881 E. W. Rothe, U. Krause, and R. Duren, *Chem. Phys. Lett.*, 1980, **72**, 100.
 882 M. Allegri and L. Moi, *Opt. Commun.*, 1980, **32**, 91.
 883 N. W. Carlson, A. J. Taylor, and A. L. Schawlow, *Phys. Rev. Lett.*, 1980, **45**, 18.
 884 N. W. Carlson, A. J. Taylor, K. M. Jones, and A. W. Schawlow, *Phys. Rev. A*, 1981, **24**, 822.
 885 A. Valence and Nguyen Tuan Q, *Phys. Lett. A*, 1981, **82**, 116.
 886 K. K. Verma, W. C. Stwalley, and W. T. Zemke, *J. Appl. Phys.*, 1981, **52**, 5419.
 887 K. K. Verma, J. Bahns, and W. C. Stwalley, *J. Phys. Chem.*, 1981, **85**, 2884.
 888 K. K. Verma, T. H. Vu, and W. C. Stwalley, *J. Mol. Spectrosc.*, 1981, **85**, 131.
 889 W. T. Zemke, K. K. Verma, T. Vu, and W. C. Stwalley, *J. Mol. Spectrosc.*, 1981, **85**, 150.
 890 E. W. Rothe, F. Ranjbar, D. Sinha, and G. P. Reck, *Chem. Phys. Lett.*, 1981, **78**, 16.
 891 G. W. King, I. M. Littlewood, and N. T. Littlewood, *Chem. Phys. Lett.*, 1981, **80**, 215.
 892 J. P. Woerdman and J. J. de Groot, *Chem. Phys. Lett.*, 1981, **80**, 220.
 893 H. Itoh, M. Hayakawa, Y. Fukuda, and M. Matsuoka, *Opt. Commun.*, 1981, **36**, 131.
 894 A. J. Taylor, K. M. Jones, and A. L. Schawlow, *Opt. Commun.*, 1981, **39**, 47.
 895 H.-R. Xia, G.-Y. Yan, and A. L. Schawlow, *Opt. Commun.*, 1981, **39**, 153.
 896 F. Roussel, *J. Phys. B*, 1981, **14**, L313.
 897 E. J. Breford, F. Engelke, G. Ennen, and K. H. Meiweis, *Faraday Discuss. Chem. Soc.*, 1981, **71**, 233.
 898 R. Hotop and K. Niemax, *J. Phys. B*, 1980, **13**, L93.
 899 E. J. Breford and F. Engelke, *Chem. Phys. Lett.*, 1980, **75**, 132.
 900 C. D. Caldwell, F. Engelke, and H. Hage, *Chem. Phys.*, 1980, **54**, 21.
 901 J. Tellinghuisen, G. Pichler, W. L. Snow, M. E. Hillard, and R. J. Exton, *Chem. Phys.*, 1980, **50**, 313.
 902 J. Tellinghuisen and M. B. Moeller, *Chem. Phys.*, 1980, **50**, 301.
 903 J. Morellec and D. Normand, *J. Phys. B*, 1981, **14**, 3919.
 904 N. J. A. van Veen, M. S. de Vries, J. D. Sokol, T. Baller, and A. E. de Vries, *Chem. Phys.*, 1981, **56**, 81.

- ⁹⁰⁵ L. Vuskovic and S. K. Srivastava, *J. Phys. B*, 1981, **14**, 2677.
- ⁹⁰⁶ J. C. Miller, R. L. Mowery, E. R. Krausz, S. M. Jacobs, H. W. Kim, P. N. Schatz, and L. Andrews, *J. Chem. Phys.*, 1981, **74**, 6349.
- ⁹⁰⁷ C. R. Vidal, *J. Chem. Phys.*, 1980, **72**, 1864.
- ⁹⁰⁸ T. Bergeman and P. F. Liao, *J. Chem. Phys.*, 1980, **72**, 887.
- ⁹⁰⁹ C. W. Bauschlicher, jun., B. H. Lengsfeld, III, and R. Yarkony, *J. Chem. Phys.*, 1980, **73**, 5702.
- ⁹¹⁰ G. Taieb, *J. Phys. (Paris)*, 1981, **42**, 537.
- ⁹¹¹ Z. A. Svyatkin, L. A. Kuznetsova, and Yu. Ya. Kuzyakov, *J. Quant. Spectrosc. Radiat. Transfer*, 1980, **23**, 307 and **24**, 25.
- ⁹¹² A. Lagerqvist and I. Renhorn, *J. Mol. Spectrosc.*, 1981, **87**, 300.
- ⁹¹³ Y. C. Hsu, B. Hegemann, and J. G. Pruitt, *J. Chem. Phys.*, 1980, **72**, 6437.
- ⁹¹⁴ R. A. Gottscho, R. W. Field, R. Bacis, and S. J. Silvers, *J. Chem. Phys.*, 1980, **73**, 599.
- ⁹¹⁵ S. J. Silvers, R. A. Gottscho, and R. W. Field, *J. Chem. Phys.*, 1981, **74**, 6000.
- ⁹¹⁶ R. A. Gottscho, P. S. Weiss, R. W. Field, and J. G. Pruitt, *J. Mol. Spectrosc.*, 1980, **82**, 283.
- ⁹¹⁷ R. A. Gottscho, J. B. Koffend, and R. W. Field, *J. Mol. Spectrosc.*, 1980, **82**, 310.
- ⁹¹⁸ R. S. Kolman, L. Schoonveld, and S. Sundaram, *J. Quant. Spectrosc. Radiat. Transfer*, 1981, **25**, 445.
- ⁹¹⁹ P. G. Cummins, R. W. Field, and I. Renhorn, *J. Mol. Spectrosc.*, 1981, **90**, 327.
- ⁹²⁰ D. L. Cooper, S. J. Prosser, and W. G. Richards, *J. Phys. B*, 1981, **14**, L487.
- ⁹²¹ P. F. Bernath, P. G. Cummins, and R. W. Field, *Chem. Phys. Lett.*, 1980, **70**, 618.
- ⁹²² P. F. Bernath and R. W. Field, *J. Mol. Spectrosc.*, 1980, **82**, 339.
- ⁹²³ W. J. Childs and L. S. Goodman, *Phys. Rev. A*, 1980, **21**, 1216.
- ⁹²⁴ W. J. Childs, G. L. Goodman, and L. S. Goodman, *J. Mol. Spectrosc.*, 1981, **86**, 365.
- ⁹²⁵ M. Dulick, P. F. Bernath, and R. W. Field, *Can. J. Phys.*, 1980, **58**, 703.
- ⁹²⁶ L.-E. Berg, L. Klynnning, and H. Martin, *Phys. Scr.*, 1980, **21**, 173.
- ⁹²⁷ L.-E. Berg, L. Klynnning, and H. Martin, *Phys. Scr.*, 1980, **22**, 216.
- ⁹²⁸ L. Klynnning and H. Martin, *Phys. Scr.*, 1980, **22**, 221.
- ⁹²⁹ L.-E. Berg, L. Klynnning, H. Martin, A. Pereira, and P. Royen, *Phys. Scr.*, 1981, **24**, 23.
- ⁹³⁰ L. Klynnning and H. Martin, *Phys. Scr.*, 1981, **24**, 25.
- ⁹³¹ L. Klynnning and H. Martin, *Phys. Scr.*, 1981, **24**, 33.
- ⁹³² W. J. Childs, D. R. Cok, L. S. Goodman, and O. Poulsom, *Phys. Rev. Lett.*, 1981, **47**, 1389.
- ⁹³³ J. M. Brown, D. J. Milton, and T. C. Steimle, *Faraday Discuss. Chem. Soc.*, 1981, **71**, 151.
- ⁹³⁴ P. F. Bernath, R. W. Field, B. Pinchemel, Y. Lefebvre, and J. Schamps, *J. Mol. Spectrosc.*, 1981, **88**, 175.
- ⁹³⁵ P. Bernath, B. Pinchemel, R. W. Field, K. Moller, and T. Törring, *J. Mol. Spectrosc.*, 1981, **88**, 420.
- ⁹³⁶ W. J. Childs, D. R. Cok, and L. S. Goodman, *Can. J. Phys.*, 1981, **59**, 1308.
- ⁹³⁷ W. J. Childs, D. R. Cok, G. L. Goodman, and L. S. Goodman, *J. Chem. Phys.*, 1981, **75**, 501.
- ⁹³⁸ P. F. Bernath, B. Pinchemel, and R. W. Field, *J. Chem. Phys.*, 1981, **74**, 5508.
- ⁹³⁹ D. E. Reisner, P. F. Bernath, and R. W. Field, *J. Mol. Spectrosc.*, 1981, **89**, 107.
- ⁹⁴⁰ W. J. Childs, L. S. Goodman, and I. Renhorn, *J. Mol. Spectrosc.*, 1981, **87**, 522.
- ⁹⁴¹ J. Nakagawa and D. O. Harris, *J. Mol. Spectrosc.*, 1981, **86**, 65.
- ⁹⁴² P. C. F. Ip, P. F. Bernath, and R. W. Field, *J. Mol. Spectrosc.*, 1981, **89**, 53.
- ⁹⁴³ M. A. Johnson, C. R. Webster, and R. N. Zare, *J. Chem. Phys.*, 1981, **75**, 5575.
- ⁹⁴⁴ M. A. A. Clyne and M. C. Heaven, *Chem. Phys.*, 1980, **51**, 299.
- ⁹⁴⁵ J. A. Coxon and S. C. Foster, *J. Mol. Spectrosc.*, 1981, **88**, 428.
- ⁹⁴⁶ G. R. Hebert, R. W. Nicholls, and C. Linton, *J. Quant. Spectrosc. Radiat. Transfer*, 1980, **23**, 229.
- ⁹⁴⁷ H. Lavendy, *J. Phys. B*, 1980, **13**, 1151.
- ⁹⁴⁸ A. C. LeFloc'h, J. Lebreton, F. Launay, J. Ferran, and J. Rostas, *J. Phys. B*, 1980, **13**, 3989.
- ⁹⁴⁹ J. Borkowska-Barnecka and W. Zyrnicki, *Physica B + C*, 1980, **100**, 124.
- ⁹⁵⁰ G. Lakshminarayana and A. Sethumadhavan, *J. Quant. Spectrosc. Radiat. Transfer*, 1980, **23**, 343.
- ⁹⁵¹ P. Erman, *Phys. Scr.*, 1980, **22**, 108.
- ⁹⁵² S. J. Harris and A. M. Weiner, *Opt. Lett.*, 1981, **6**, 434.
- ⁹⁵³ P. L. Jones, R. D. Mead, B. E. Kohler, S. D. Rosner, and W. C. Lineberger, *J. Chem. Phys.*, 1980, **73**, 4419.
- ⁹⁵⁴ I. Dubois and H. Leclercq, *J. Phys. B*, 1981, **14**, 2807.
- ⁹⁵⁵ M. A. Epting, M. T. McKenzie, jun., and E. R. Nixon, *J. Chem. Phys.*, 1980, **73**, 134.
- ⁹⁵⁶ V. E. Bondybey and J. H. English, *J. Mol. Spectrosc.*, 1980, **84**, 388.
- ⁹⁵⁷ L.-E. Berg, S. Ismail, L. Klynnning, H. Martin, A. Pereira, and P. Royen, *Phys. Scr.*, 1981, **23**, 1047.
- ⁹⁵⁸ V. E. Bondybey and J. H. English, *J. Chem. Phys.*, 1981, **74**, 6978.
- ⁹⁵⁹ K. Manzel, W. Schulze, and F. W. Froben, *Chem. Phys. Lett.*, 1981, **82**, 557.
- ⁹⁶⁰ D. D. Stranz and R. K. Khanna, *J. Chem. Phys.*, 1981, **74**, 2116.
- ⁹⁶¹ A. J. Kotlar, R. W. Field, J. I. Steinfeld, and J. A. Coxon, *J. Mol. Spectrosc.*, 1980, **80**, 86.
- ⁹⁶² W. C. Paske, J. R. Twist, A. W. Garrett, and D. E. Golden, *J. Chem. Phys.*, 1980, **72**, 6134.
- ⁹⁶³ J. Fournier, H. Mohammad, J. Deson, and C. Vermeil, *J. Chem. Phys.*, 1980, **73**, 6039.
- ⁹⁶⁴ B. Ritchie and G. P. Tambe, *J. Phys. B*, 1980, **13**, L225.
- ⁹⁶⁵ H. Zacharias, H. Rottke, and K. H. Welge, *Opt. Commun.*, 1980, **35**, 185.

- ⁹⁶⁶ J.-H. Fock, P. Gurtler, and E. E. Koch, *Chem. Phys.*, 1980, **47**, 87.
⁹⁶⁷ D. M. Cooper and S. R. Langhoff, *J. Chem. Phys.*, 1981, **74**, 1200.
⁹⁶⁸ (a) L. C. Lee and J. A. Guest, *J. Phys. B*, 1981, **14**, 3415; (b) M. Trone, R. Azria, and Y. Le Coat, *Ibid.*, 1980, **13**, 2327.
⁹⁶⁹ D. L. Ederer, A. C. Parr, B. E. Cole, R. Stockbauer, J. L. Dehmer, J. B. West, and K. Codling, *Proc. R. Soc. London, Ser. A.*, 1981, **378**, 423.
⁹⁷⁰ M. A. A. Clyne and M. C. Heaven, *J. Chem. Soc., Faraday Trans. 2* 1981, **77**, 1375.
⁹⁷¹ J. M. Ajello, A. Chutjian, and R. Winchell, *J. Electron Spectrosc.*, 1980, **19**, 197.
⁹⁷² G. Hancock and H. Zacharias, *Chem. Phys. Lett.*, 1981, **82**, 402.
⁹⁷³ F. Arquerous and J. Campos, *Physica C*, 1982, **112**, 131.
⁹⁷⁴ (a) F. Arquerous and J. Campos, *J. Phys. B*, 1981, **14**, 2159; (b) D. L. Ederer, *Proc. R. Soc. London, Ser. A.*, 1981, **378**, 423.
⁹⁷⁵ R. D. Brown, P. D. Godfrey, D. C. McGilvery, and J. G. Crofts, *Chem. Phys. Lett.*, 1981, **84**, 437.
⁹⁷⁶ D. H. Katayama and J. A. Welsh, *J. Chem. Phys.*, 1981, **75**, 4224.
⁹⁷⁷ R. Abouaf, D. Teillet-Billy, and S. Gowsand, *J. Phys. B*, 1981, **14**, 3517.
⁹⁷⁸ T. Bergeman and D. Cossart, *J. Mol. Spectrosc.*, 1981, **87**, 119.
⁹⁷⁹ D. Cossart, *J. Phys. (Paris)*, 1980, **41**, 489.
⁹⁸⁰ A. J. Hynes and J. H. Brophy, *Chem. Phys. Lett.*, 1980, **75**, 52.
⁹⁸¹ P. Erman and M. Larsson, *Phys. Scr.*, 1981, **23**, 1052.
⁹⁸² G. Bosser and J. Lebreton, *J. Phys. B*, 1981, **14**, 1445.
⁹⁸³ C. Linton, *J. Mol. Spectrosc.*, 1980, **80**, 279.
⁹⁸⁴ M. A. Baig and J. P. Connerade, *J. Mol. Spectrosc.*, 1980, **83**, 31.
⁹⁸⁵ C. Linton, *J. Mol. Spectrosc.*, 1980, **79**, 90.
⁹⁸⁶ P. Magat, A. C. LeFloch, and J. Lebreton, *J. Phys. B*, 1980, **13**, 4143.
⁹⁸⁷ M. A. A. Clyne and M. C. Heaven, *Faraday Discuss. Chem. Soc.*, 1981, **71**, 213.
⁹⁸⁸ D. J. Greenwood, C. Linton, and R. F. Barrow, *J. Mol. Spectrosc.*, 1981, **89**, 134.
⁹⁸⁹ J. M. Brom and W. H. Beattie, *J. Mol. Spectrosc.*, 1980, **81**, 445.
⁹⁹⁰ B. Burtin, M. Carleer, R. Colin, C. Dreze, and T. Ndikumana, *J. Phys. B*, 1980, **13**, 3783.
⁹⁹¹ D. J. Greenwood, R. F. Barrow, and C. Linton, *J. Mol. Spectrosc.*, 1981, **86**, 480.
⁹⁹² Y. Houbrechts, I. Dubois, and H. Bredohl, *J. Phys. B*, 1980, **13**, 3369.
⁹⁹³ H. Bredohl, Ph. Demoulin, Y. Houbrechts, and F. Melen, *J. Phys. B*, 1981, **14**, 1771.
⁹⁹⁴ F. Melen, Y. Houbrechts, I. Dubois, B. Le. Huyen, and H. Bredohl, *J. Phys. B*, 1981, **14**, 3637.
⁹⁹⁵ M. Tsuji, T. Mizuguchi, and Y. Nishimura, *Can. J. Phys.*, 1981, **59**, 985.
⁹⁹⁶ M. Tsuji, T. Mizuguchi, and Y. Nishimura, *Chem. Phys. Lett.*, 1981, **84**, 318.
⁹⁹⁷ M. Tsuji, Y. Nishimura, and T. Mizuguchi, *Chem. Phys. Lett.*, 1981, **83**, 483.
⁹⁹⁸ B. Coquart and J. C. Prudhomme, *J. Mol. Spectrosc.*, 1981, **87**, 75.
⁹⁹⁹ H. Obase, M. Tsuji, and Y. Nishimura, *Chem. Phys. Lett.*, 1981, **81**, 119.
¹⁰⁰⁰ P. K. Carroll and A. T. Nulty, *J. Mol. Spectrosc.*, 1980, **79**, 62.
¹⁰⁰¹ P. Perdigon and F. Martin, *J. Mol. Spectrosc.*, 1980, **83**, 40.
¹⁰⁰² G. Gerber and G. Kuscher, *Chem. Phys.*, 1981, **60**, 119.
¹⁰⁰³ V. E. Bondybey, G. P. Schwartz, and J. E. Griffiths, *J. Mol. Spectrosc.*, 1981, **89**, 328.
¹⁰⁰⁴ V. E. Bondybey and J. H. English, *J. Chem. Phys.*, 1980, **73**, 42.
¹⁰⁰⁵ J. M. Blondeau, G. Gandara, P. Carette, and J. Messelyn, *Chem. Phys. Lett.*, 1980, **71**, 246.
¹⁰⁰⁶ V. E. Bondybey, G. P. Schwartz, J. E. Griffiths, and J. H. English, *Chem. Phys. Lett.*, 1980, **76**, 30.
¹⁰⁰⁷ F. Ahmed and E. R. Nixon, *J. Chem. Phys.*, 1981, **74**, 2156.
¹⁰⁰⁸ F. Ahmed and E. R. Nixon, *J. Chem. Phys.*, 1981, **75**, 110.
¹⁰⁰⁹ M. A. A. Clyne and M. C. Heaven, *Chem. Phys.*, 1981, **58**, 145.
¹⁰¹⁰ R. Tripathi, S. B. Rai, and K. N. Upadhyaya, *J. Phys. B*, 1981, **14**, 441.
¹⁰¹¹ A. Jenouvrier and B. Pascat, *Can. J. Phys.*, 1980, **58**, 1275.
¹⁰¹² A. T. Pitt, D. Patel, and R. D. Coombe, *J. Mol. Spectrosc.*, 1981, **87**, 401.
¹⁰¹³ W. E. Jones and T. D. McLean, *J. Mol. Spectrosc.*, 1980, **83**, 317.
¹⁰¹⁴ W. E. Jones and T. D. McLean, *J. Mol. Spectrosc.*, 1981, **90**, 481.
¹⁰¹⁵ R. P. Saxon and B. Liu, *J. Chem. Phys.*, 1980, **73**, 5174.
¹⁰¹⁶ V. E. Bondybey and J. H. English, *J. Chem. Phys.*, 1980, **72**, 3113.
¹⁰¹⁷ C. R. Quick, jun., and R. E. Weston, jun., *J. Chem. Phys.*, 1981, **74**, 4951.
¹⁰¹⁸ G. Theodorakopoulos, S. D. Peyerimhoff, and R. J. Buenker, *Chem. Phys. Lett.*, 1981, **81**, 413.
¹⁰¹⁹ A. L. Smith and J. B. Hopkins, *J. Chem. Phys.*, 1981, **75**, 2080.
¹⁰²⁰ A. J. Capel, J. H. D. Eland, and R. F. Barrow, *Chem. Phys. Lett.*, 1981, **82**, 496.
¹⁰²¹ L. F. Phillips, *J. Phys. Chem.*, 1981, **85**, 399A.
¹⁰²² S. P. Reddy and K. K. Verma, *J. Mol. Spectrosc.*, 1980, **84**, 89.
¹⁰²³ R. Winter, I. Barnes, E. H. Fink, J. Wildt, and F. Zabel, *Chem. Phys. Lett.*, 1980, **73**, 297.
¹⁰²⁴ F. Ahmed and E. R. Nixon, *J. Mol. Spectrosc.*, 1981, **87**, 101.
¹⁰²⁵ S. J. Prosser, R. F. Barrow, J. Verges, C. Effantin, and J. d'Incan, *J. Phys. B*, 1980, **13**, L547.
¹⁰²⁶ F. Ahmed and E. R. Nixon, *J. Mol. Spectrosc.*, 1980, **83**, 64.
¹⁰²⁷ V. E. Bondybey and J. H. English, *J. Chem. Phys.*, 1980, **72**, 6479.

- 1028 G. Gouedard and J. C. Lehmann, *Faraday Discuss. Chem. Soc.*, 1981, **71**, 143.
 1029 K. G. Ibbs and A. J. McCaffery, *J. Chem. Soc., Faraday Trans 2*, 1981, **77**, 631.
 1030 C. Effantin, J. d'Incan, J. Verges, M. T. Macpherson, and R. F. Barrow, *Chem. Phys. Lett.*, 1980, **70**, 560.
 1031 D. E. Newlin, G. W. Stewart, and J. L. Gole, *Can. J. Phys.*, 1981, **59**, 441.
 1032 M. A. A. Clyne and E. Martinez, *J. Chem. Soc., Faraday Trans. 2*, 1980, **76**, 1275.
 1033 M. A. A. Clyne and E. Martinez, *J. Chem. Soc., Faraday Trans. 2*, 1980, **76**, 1561.
 1034 J. A. Coxon, *J. Mol. Spectrosc.*, 1980, **82**, 264.
 1035 A. E. Douglas, *Can. J. Phys.*, 1981, **59**, 835.
 1036 J. Le Calve, M. C. Castex, D. Haaks, B. Jordan, and G. Zimmierer, *Nuovo Cimento B*, 1981, **63**, 265.
 1037 I. S. McDermid, *J. Chem. Soc., Faraday Trans. 2*, 1981, **77**, 519.
 1038 I. S. McDermid and J. B. Laudenslager, *Chem. Phys. Lett.*, 1981, **79**, 370.
 1039 R. S. Hosack, A. P. Kennedy, and K. B. McAfee, *J. Mol. Spectrosc.*, 1980, **80**, 239.
 1040 R. Luypaert, G. de Vlieger, and J. Van Craen, *J. Chem. Phys.*, 1980, **72**, 6283.
 1041 G. de Vlieger, F. Claesens, and H. Eisendrath, *J. Mol. Spectrosc.*, 1980, **83**, 339.
 1042 M. S. Child, *J. Phys. B*, 1980, **13**, 2557.
 1043 M. A. A. Clyne, M. C. Heaven, and E. Martinez, *J. Chem. Soc., Faraday Trans. 2*, 1980, **76**, 177.
 1044 M. A. A. Clyne, M. C. Heaven, and E. Martinez, *J. Chem. Soc., Faraday Trans. 2*, 1980, **76**, 405.
 1045 M. A. A. Clyne, M. C. Heaven, and S. J. Davis, *J. Chem. Soc., Faraday Trans. 2*, 1980, **76**, 961.
 1046 S. J. Bullman, J. W. Farthing, and J. C. Whitehead, *Mol. Phys.*, 1981, **44**, 97.
 1047 R. Luypaert, J. van Craen, J. Coremans, and G. de Vlieger, *J. Phys. B*, 1981, **14**, 2575.
 1048 A. Sur and J. Tellinghuisen, *J. Mol. Spectrosc.*, 1981, **88**, 323.
 1049 R. J. S. Morrison and E. R. Grant, *J. Chem. Phys.*, 1981, **75**, 49.
 1050 J. Tellinghuisen, P. Berwanger, J. G. Ashmore, and K. S. Viswanathan, *Chem. Phys. Lett.*, 1981, **84**, 528.
 1051 N. Bettin, H. Knockel, and E. Tiemann, *Chem. Phys. Lett.*, 1981, **80**, 386.
 1052 M. V. Kurepa, D. S. Babic, and D. S. Belic, *J. Phys. B*, 1981, **14**, 375.
 1053 M. A. A. Clyne and J. P. Liddy, *J. Chem. Soc., Faraday Trans. 2*, 1980, **76**, 1561.
 1054 J. A. Coxon and M. A. Wickramaaratchi, *J. Mol. Spectrosc.*, 1981, **87**, 85.
 1055 S. B. Hutchison, J. G. Eden, and J. T. Verdeyen, *Appl. Phys. Lett.*, 1980, **37**, 374.
 1056 J. A. Coxon, R. M. Gordon, and M. A. Wickramaaratchi, *J. Mol. Spectrosc.*, 1980, **79**, 363.
 1057 J. A. Coxon and M. A. Wickramaaratchi, *J. Mol. Spectrosc.*, 1980, **79**, 380.
 1058 M. S. de Vries, N. J. A. van Veen, M. Hutchinson, and A. E. de Vries, *Chem. Phys.*, 1980, **51**, 159.
 1059 M. A. A. Clyne and M. C. Heaven, *J. Chem. Soc., Faraday Trans. 2*, 1980, **76**, 49.
 1060 G. W. King, I. M. Littlewood, and J. R. Robins, *Chem. Phys.*, 1981, **62**, 359.
 1061 (a) H. Knockel, E. Tiemann, and D. Zoglowski, *J. Mol. Spectrosc.*, 1981, **85**, 225; (b) J. M. Dyke, N. Jonathan, J. D. Mills, and A. Morris, *Mol. Phys.*, 1980, **40**, 1177.
 1062 A. Loewenschuss, J. C. Miller, and L. Andrews, *J. Mol. Spectrosc.*, 1980, **80**, 351.
 1063 P. R. Bunker and P. C. Klein, *Chem. Phys. Lett.*, 1981, **78**, 553.
 1064 A. D. Smirnov, N. E. Kuzmenko, and Yu. Ya. Kuzyakov, *Opt. Spectrosc.*, 1980, **48**, 111.
 1065 M. Pelissier, *J. Chem. Phys.*, 1981, **75**, 775.
 1066 C. M. Brown and M. L. Ginter, *J. Mol. Spectrosc.*, 1980, **80**, 145.
 1067 O. Appelblad, A. Lagerqvist, I. Renhorn, and R. W. Field, *Phys. Scr.*, 1980, **22**, 603.
 1068 G. P. Mishra, S. B. Rai, and K. N. Upadhyay, *Can. J. Phys.*, 1981, **59**, 289.
 1069 G. P. Mishra, R. Tripathi, S. B. Rai, K. N. Upadhyay, and D. K. Rai, *J. Mol. Spectrosc.*, 1981, **85**, 245.
 1070 R. Tripathi, S. B. Rai, and K. N. Upadhyay, *J. Phys. B*, 1981, **14**, L575.
 1071 S. B. Rai and D. K. Rai, *Chem. Phys. Lett.*, 1981, **80**, 606.
 1072 G. P. Mishra, S. B. Rai, and K. N. Upadhyay, *Can. J. Phys.*, 1979, **57**, 824.
 1073 V. I. Srdanov and D. S. Pesic, *J. Mol. Spectrosc.*, 1981, **90**, 27.
 1074 S. A. Mitchell, G. A. Kenney-Wallace, and G. A. Ozin, *J. Am. Chem. Soc.*, 1981, **103**, 6030.
 1075 C. Bousquet and N. Bras, *J. Phys. (Paris)*, 1980, **41**, 19.
 1076 E. Laboucher and N. Hoe, *J. Phys. Lett. (Paris)*, 1980, **41**, L57.
 1077 A. B. Callear and K.-L. Lai, *Chem. Phys. Lett.*, 1980, **75**, 234.
 1078 M. H. R. Hutchinson and E. S. Theocarous, *Chem. Phys. Lett.*, 1981, **81**, 553.
 1079 H. Helvajian and C. Wittig, *Appl. Phys. Lett.*, 1981, **38**, 731.
 1080 H. C. Braynan, D. R. Fischell, and T. A. Cool, *J. Chem. Phys.*, 1980, **73**, 4260.
 1081 A. Bernard and R. Gravina, *Astrophys. J. Suppl.*, 1980, **44**, 223.
 1082 R. Gopal, L. K. Singh, and M. M. Joshi, *J. Mol. Spectrosc.*, 1981, **89**, 15.
 1083 A. Bernard, S. Roux, and J. Verges, *J. Mol. Spectrosc.*, 1980, **80**, 374.
 1084 A. Bernard and A. M. Sibai, *Z. Naturforsch. Teil A*, 1980, **35**, 1313.
 1085 E. A. Shenyavskaya and L. V. Gurvich, *J. Mol. Spectrosc.*, 1980, **81**, 152.
 1086 C. Cosse, M. Fouassier, T. Mejean, M. Tranquille, D. P. DiLella, and M. Moskovits, *J. Chem. Phys.*, 1980, **73**, 6076.
 1087 A. E. Douglas and P. M. Veillette, *J. Chem. Phys.*, 1980, **72**, 5378.
 1088 D. C. Galehouse, J. W. Brault, and S. P. Davis, *Astrophys. J. Suppl.*, 1980, **42**, 241.

- 1089 D. Powell, R. Brittain, and M. Vala, *Chem. Phys.*, 1981, **58**, 355.
1090 P. D. Hammer and S. P. Davis, *Astrophys. J.*, 1980, **237**, L51.
1091 P. D. Hammer and S. P. Davis, *Astrophys. J. Suppl.*, 1981, **47**, 201.
1092 P. S. Murty, *Astrophys. J.*, 1980, **240**, 363.
1093 P. D. Hammer, S. P. Davis, and A. C. Zook, *J. Chem. Phys.*, 1981, **74**, 5320.
1094 W. J. Balfour and B. Lindgren, *Phys. Ser.*, 1980, **22**, 36.
1095 J. G. Phillips, S. P. Davis, and D. C. Galehouse, *Astrophys. J. Suppl.*, 1980, **43**, 417.
1096 W. H. Hocking, A. J. Merer, and D. J. Milton, *Can. J. Phys.*, 1981, **59**, 266.
1097 A. S.-C. Cheung, R. C. Hansen, A. M. Lyryra, and A. J. Merer, *J. Mol. Spectrosc.*, 1981, **86**, 526.
1098 W. E. Jones and G. Krishnamurty, *J. Phys. B*, 1980, **13**, 3375.
1099 W. H. Hocking, A. J. Merer, D. J. Milton, W. E. Jones, and G. Krishnamurty, *Can. J. Phys.*, 1980, **58**, 516.
1100 G. Balducci, G. Gigli, and M. Guido, *J. Chem. Soc., Faraday Trans. 2*, 1981, **77**, 1107.
1101 R. J. Van Zee, C. A. Baumann, and W. Welner, jun., *J. Chem. Phys.*, 1981, **74**, 6977.
1102 R. M. Gordon and A. J. Merer, *Can. J. Phys.*, 1980, **58**, 642.
1103 S. M. Harris and R. F. Barrow, *J. Mol. Spectrosc.*, 1980, **84**, 334.
1104 A. S.-C. Cheung, R. M. Gordon, and A. J. Merer, *J. Mol. Spectrosc.*, 1981, **87**, 289.
1105 J. M. Delaval, C. Dufour, and J. Schamps, *J. Phys. B*, 1980, **13**, 4757.
1106 B. Pinchemel, *J. Phys. B*, 1981, **14**, 2569.
1107 C. Linton, M. Dulick, R. W. Field, P. Carette, and R. F. Barrow, *J. Chem. Phys.*, 1981, **74**, 189.
1108 C. Linton and M. Dulick, *J. Mol. Spectrosc.*, 1981, **89**, 569.
1109 M. Dulick, R. W. Field, and J. C. Beaufils, *J. Mol. Spectrosc.*, 1981, **87**, 268.
1110 M. Dulick, R. W. Field, J. C. Beaufils, and J. Schamps, *J. Mol. Spectrosc.*, 1981, **87**, 278.
1111 B. R. Yadav, S. B. Rai, and D. K. Rai, *J. Mol. Spectrosc.*, 1981, **89**, 1.
1112 L. A. Kaledin and E. A. Shenyavskaya, *J. Mol. Spectrosc.*, 1981, **90**, 590.
1113 R. Brittain, D. Powell, M. Kreglewski, and M. Vala, *Chem. Phys.*, 1980, **54**, 71.
1114 A. N. Samoilova, Yu. M. Efremov, and L. V. Gurvich, *J. Mol. Spectrosc.*, 1981, **86**, 1.
1115 W. J. Balfour and F. B. Orth, *J. Mol. Spectrosc.*, 1980, **84**, 424.

Table 11 Electronic spectroscopic studies of diatomic molecules (Molecules are listed in the following order: H₂, hydrides, He₂, rare gas molecules, N₂, NO, O₂, I₂, Groups I-VII, transition metal diatomics. This table includes van der Waals diatomic molecules)

Molecule	Technique	States	Comments	Constants	Ref.
H ₂	synchrotron analysis	18—30 eV 804—736 Å	$\Delta N = 2$ transitions contribute vibrational/rotational preionization: MCQD	angular distribution of photoelectrons	633
H ₂	electron impact	$e + H_2 \rightarrow B' \Sigma_u^+; C' \Pi_u^- \rightarrow H_2, X' \Sigma_g^+, v''$	angular distribution of photoelectrons	cross-sections	634
H ₂	analysis: electron impact	cross-sections for excitation of $b' \Sigma_u^+, B' \Sigma_u^+$			635
H ₂	electron impact	30—100 eV autoionizing states $Q_1' \Sigma_u^+$ and $Q_1' \Pi_u^-$	large isotope effects	energy distributions of ion fragments	636
H ₂	photoelectron electron impact	$b^3 \Sigma_u^+$	rotational intensity distribution		638
H ₂	electron impact	$b^3 \Sigma_u^+$	$e + H_2 \rightarrow H^- + e$ significant near $'\Sigma_g^+$ dissociation threshold		639
H ₂	electron impact		$n \sim 35$		640
H ₂	electron impact	excitation of states of high n, l in threshold energy collisions			641
H ₂	predisociation	$3 p\pi D' \Pi_u^{(e)}$	isotope effect		642
H ₂	predisociation	$B'^1 \Sigma_u^+ \sim B' ^1 \Sigma_u^+$	interference effects H ₂ , HD		643
H ₂	synchrotron fluorescence	super excited levels above $H(n=1) + H(n=2)$ and above ionization limit	fluorescence observed above IP especially for $'\Pi_u^{(e)}$ levels		644
H ₂	emission	$3 p\pi D' \Pi_u^{(e)} \rightarrow X' \Sigma_g^+$	dissociative ionization;		645
H ₂	electron impact		significant proton production below dissociation limit		646
H ₂	electron impact	$d^3 \Pi_u^{(e)}$ excitation states 23—29 eV and one unknown at 22.3 eV	$\sigma-H_2$, autoionizing states near threshold	cross-sections	647
H ₂	electron impact				648

Table 11 (continued)

Molecule	Technique	States	Comments	Constants	Ref.
H ₂	electron impact		energy and angular distribution of H ⁺		648b
H ₂	electron-photon coincidences	H ₂ , D ₂ , 12.2 to 16 eV	decay of excited singlet states:		649
H ₂	delayed coincidence	excitation: i(3d) ³ Π _u ← c(2p)- jΠ _u ⁺ ← X ¹ Σ _g ⁺ fluorescence: i(3d) ³ Π _u → b(2p) ¹ Σ _u ⁺ D' ¹ Π _u , D' ³ Π _u , B' ¹ Σ _u ⁺ states of H ₂ , HD, D ₂ around 830 Å	effect of predissociation	τ	650
H ₂	VUV laser		line profiles, Doppler and Fano	absorption cross-section	651
H ₂	theoretical	3dπ ¹ Π _g ⁽⁰⁾ and J ¹ Δ _g ⁽⁰⁾	H ₂ , HD and D ₂ , adiabatic corrections	R, V, E	652
H ₂	theoretical	B'' ¹ Σ _g ⁺ , HH ¹ Σ _g ⁺ ,	H ₂ , HD and D ₂ , adiabatic calculation	E, V	653
H ₂	theoretical	B' ¹ Σ _u ⁺	adiabatic corrections	E	654
H ₂	laser intracavity absorption	c ³ Π observed in absorption	electrons, 0.02—1.14 eV produced by PES	scattering cross-section	655
H ₂	electron scattering analysis	ionization continuum: vibrational-rotational preionization dissociation of H ₂ ⁻	multichannel quantum defect theory	656	657
H ₂	electron impact <i>ab initio</i>	H ⁻ (n = 2) + H(1s)			658
H ₂ ⁻ NeH ⁺ KrH ⁺ LiH		X ¹ Σ ⁺	radiative transition probabilities lifetimes and dipole moments		659
LiH	level crossing	A ¹ Σ ⁺	dipole moment		660
LiH		A ¹ Σ ⁺	dipole moment		661
LiD	LIF	A ¹ Σ ⁺ –X ¹ Σ ⁺	test of <i>r</i> -centroid approximation		662a
			transition moment		662b
					663

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NaH	emission	$A^1\Sigma^+-X^1\Sigma^+$	extended analysis	potentials
NaH	quantum beats	$A^1\Sigma^+$	laser-induced Stark effect	dipole moments in ν'
NaH, NaD	LIF: hf discharge	$X^1\Sigma^+$		665
KH, KD				666
KH, KD	analysis	$A^1\Sigma^+-X^1\Sigma^+$	isotopic averaging	667
RbH	LIF	$A^1\Sigma^+-X^1\Sigma^+$		668
CsH		$A^1\Sigma^+-X^1\Sigma^+$		669
MgH, MgD	absorption	new $^2\Sigma^+$ state 2300—2350 Å		670
CaH	absorption	$C^2\Sigma^+, D^2\Sigma^+ (\nu = 13)$		671
CaH	analysis	$A^2\Pi$ perturbation		672
CaH	absorption	Rydberg states		673
CH	dissociative excitation	$A^2\Delta-X^2\Pi$	<i>e.g.</i> , Kr $^+$ (21 keV) + C ₂ H ₂ : CH has non-Boltzmann distribution over J levels	
CH		$A^2\Delta$	τ	675
CH	matrix isolation	$^2\Sigma^-, ^2\Delta-X^2\Pi$		676
CH ⁺	C ^{+(4P)} + H ₂ or D ₂	$b^3\Sigma^--a^3\Pi$	V	677
CH ⁺	laser ion beam Doppler tuned	predisociation	appearance of C ⁺ following absorption near 3500 Å	678
CH ⁺	electron-ion beam	CH ⁺ + e ⁻ → neutrals	absorption near 3500 Å and other ions, up to CH ₅ ⁺	
CH ⁺	CD ⁺	A ¹ P shape resonance	cross-section	679
SbH, SbD	LIF of trapped ions	A ¹ P-X ¹ P ⁺		680
OH, OD	absorption	B ² S ⁺ , C ² S ⁺		681 <i>a,b</i>
OH	flash discharge	$A^2\Sigma^+-X^2\Pi$	R, E	682
OH	electron impact			683
OH	analysis	$A^2\Sigma^+-X^2\Pi$		684
OH		$A^2\Sigma^+-X^2\Pi$		685
OH		$A^2\Sigma^+-X^2\Pi$		686
OH		$A^2\Sigma^+-X^2\Pi$	line widths: H ₂ O collision broadening	687
OH	analysis	$A^2\Sigma^+-X^2\Pi$	R, V, E	688

Table 11 (continued)

Molecule	Technique	States	Comments	Constants	Ref.
OH	quantum beats	$A^2\Sigma^+ - X^2\Pi$	$\Omega(1)$ beat frequencies to ~20 MHz at ~280 gauss	hf's	689
OH	high frequency deflection tabulation	$A^2\Sigma^+$	predisociation: $A^2\Sigma^+ \sim 4\Sigma^-$ line positions, strengths and intensities	τ	690
OH	LIF collisional excitation	$A^2\Sigma^+, v' = 0$ $X^2\Pi$	quenching transitions within ground state Λ -doublet ion rf trap	τ	691
OH	LIF of trapped ion <i>ab initio</i>	$A^1\Pi - X^1\Sigma$	Λ -doubling constants	693	692
CD ⁺	laser photodetachment	$X^1\Pi$	high resolution	V, R electron affinity	694
SH	laser photodetachment	ground states		electron affinity	695
SH ⁻ , SD ⁻	ion cyclotron resonance spectrometer				696a
SH	PES flash photolysis	Rydberg transitions		3rd IP	696b
SeH	(e, 2e)	valence orbitals of HF and HCl	(e, 2e) technique described	R, V, IP IP's	697
HF	HCl	Feshbach resonances,		dissociation attachment	698
HF	electron transmission	predisociation		cross-section	699
HF	electron impact	resonances 12.8—16.0 eV	mixing of parent Rydberg states		700
HF	HF-	7—46 eV Rydberg states	E		702
HF	analysis	shape and core excited resonances up to 14 eV	potentials calculated for resonant states of HF-HF ⁺ $X^2\Pi$, $A^2\Sigma^+$, $B^2\Sigma^+$		703
HF	(e, 2e)	photoionization	oscillator strengths, branching ratios		704
HF ⁺	analysis	$X^2\Pi$	direct summation of interaction Λ -doublings over vibrational levels		705
HCl		$C^1\Pi - X^1\Sigma^+$	f-values		706

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HCl	absorption	excited states	configurations; detailed analysis	R, V, E	707
HBr HI HBr DBr HBr DBr CoH He ₂	PES	21.2 eV	angular distribution	R	708
	absorption, synchrotron	1100—1200 Å	configurations; detailed analysis	R, V, E	709
	absorption	excited states	multichannel quantum defect analysis	R	710
	emission	4550 Å bands	structure 700—900 Å	R	711
		triplet levels: (1σ _g) ² (1σ _u) npλ	3000—11 000 Å	R	712
He ₂	pulsed discharge	3pπ 3Π _g –2sσ(a) 3Σ _u ⁺	4 ¹ He ₂ and ³ He ₂	R	713
He ₂		Rydberg states of high <i>n</i>	structure 700—900 Å	R	714
He ₂ ⁺		A ¹ Σ _u ⁺ → X ¹ Σ _g ⁺	3000—11 000 Å	potentials	715
He ₂ ⁺	absorption	a ³ Σ _u ⁺	3000—11 000 Å	potentials	716
Ne ₂ , Ar ₂	emission	1 _u (³ P ₂)			717
Kr ₂	glow discharges	0 _u ⁺ and 1 _u states	production and decay of excited states	τ	718
Kr ₂	synchrotron	1 _u 0 _u [−]			719
Xe ₂	synchrotron	1 _u 0 _u ⁺			720
Xc ₂	synchrotron	0 _u ⁺ (³ P ₁)	fluorescence at 172 nm		721
Xe ₂	collision pair absorption	Xe + Xe + hν(158 nm)			722
HeAr ⁺		B ² Σ ⁺ , A ² ₁ Π _{1/2} , X ² Σ ⁺			723a
Ar ₂	emission	82—86 nm			723b
Ar ₂ ⁺	emission	160—190 nm	kinetic study		724
ArKr, ArXe	scattering	He(2 ¹ S) + Na	penetration of Na(3p), orbital by He atom X ² Σ ⁺ ; is repulsive		725
HeNa	Na3s–3p profile	A ² Π	well-depth, <i>r</i> _e		726
HeNa			well-depth, <i>r</i> _e		727
NeNa	laser spectroscopy	A, B–X	long-range potential		728
NeNa	analysis	A ² Π, B ² Σ ⁺ –X ² Σ ⁺	coupling case		729
ArNa	analysis		spin-orbit coupling and Λ-doubling		730

Table 11 (continued)

Molecule	Technique	States	Comments	Constants	Ref.
NeCs to XeCs	absorption line profile	Cs($6S_{1/2}$ – $5D_{5/2, m=1/2}$)–rare gas	rare temperature dependence	potentials, oscillator strengths	731
HeCs	absorption	Cs($7S$ – $6D_{3/2}$)–He	molecular quantum defects	potentials	732
NeNa	MCD absorption	$^2\Sigma^+ - X^2\Sigma^+$ ($6P_{3/2}$ – $6S_{1/2}$) ($6S_{1/2}$ – $5D_{3/2}$)–Ar		potentials	733
ArCs		($6S_{1/2}$ – $5D_{3/2}$)–rare gas		potentials	734
ArCs		($6S_{1/2}$ – $5D_{3/2}$)–rare gas		potentials	735
ArCs					736
KrCs			nature of dissociating states three-body interaction and secondary satellites		737
XeCs			exciplexes populated by superradiant transitions		738
KrNa	multiphoton photolysis		near dissociation expansions	potential	739
KrCs				D_e	740
KrCs				potentials	741
XeRb	time-resolved spectroscopy	$^2\Sigma^+(7s) - 2\Sigma^+(6s)$		τ	742
XeCs	analysis	$A^2\Pi, X^2\Sigma^+$			743
ArBe ⁺	analysis	Hg 2537 Å			744
ArCa ⁺					745
KrHg					
ArCl	synchrotron excitation		state-to-state relaxation interpretation of bound-free spectra		746
KrCl			dissociation ionization: k.e. distribution of N ⁺		747
XeCl	emission	B, C	excitation predissociation	absolute transition probabilities	748
XeBr					749
XeI					750
N ₂	electron impact: tof	b ¹ Π _u , C ³ Π _u	N ₂ (C ³ Π _u and C ³ Π _g)	absolute transition probabilities	751
N ₂	electron impact				752
N ₂	afterglow emission				
N ₂	electron impact excitation by Ar ($P_{0,j}$)	C ³ Π _u	dissociative attachment propensity rules: anomalous population of Λ -doublets		

N_2	photoionization excitation	$N_2^+X^2\Sigma_g^+$	3 σ_g ; large departures from Franck-Condon branching ratios to $v = 0, 1 X^2\Sigma_g^+$	753 754
N_2	threshold energy electron collisions	Herman bands formed by energy pooling, $A^3\Sigma_u^+ + A^3\Sigma_u^+$ Rydberg states	maximum at $n \sim 29$	755
N_2	laser optogalvanic spectroscopy discharge LIF	$B^3\Pi_p - W^3\Delta_2$ Rydberg band ~590 nm	variations within autoionizing profiles model for laser lines	756
N_2	electron impact	$A^3\Sigma_u^+$ $b^1\Sigma_u^+ - X^2\Sigma_g^+$ $a^1\Pi_g - X^2\Sigma_g^+$	$X^1\Sigma_g^+ + 2h\nu_1 \rightarrow a^1\Pi_g$ $a^1\Pi_g + h\nu_2 \rightarrow b^1\Sigma_u^+$	757 758 759 760
N_2	emission: cooled glow discharge FTIR electron impact	$C^3\Pi_u$	interferometric recording	761
N_2	fluorescence: synchrotron radiation low-energy electron scattering LIF by MP excitation	$W^3\Delta_u - B^3\Pi_u$	RKR potential rotational excitation in supercooled N_2 complements electron impact	762 763 764
N_2	free jet expansion	$'\Pi_u$ and $'\Sigma_g^+$ states at 12.4—18.8 eV	E	765
N_2/N_2^+	<i>ab initio</i> (POL-CI)	$B^3\Pi_g$ $C^3\Pi_u - B^3\Pi_u$ $B^2\Sigma_u^+ - X^2\Sigma_g^+$ $B^2\Sigma_u^+ - X^2\Sigma_g^+$	interferometric line widths at low N	766 767
N_2^+	emission, hollow cathode PES electron impact s/s molecular beam LIF	lowest doublet and quartet states $A^2\Pi_u - X^2\Sigma_g^+$ $X^2\Sigma_g^+ - X^2\Sigma_g^+$ $B^2\Sigma_u^+ - X^2\Sigma_g^+$ $B^2\Sigma_u^+ - X^2\Sigma_g^+$	$N_2 + Ne^+$ charge transfer asymmetry parameter low rotational temperature	768 769 R, V, E 770 771 772 773, 681b

Table 11 (continued)

Molecule	Technique	States	Comments	Ref.
N_2^+/N_2	photoionization 450—660 Å	$\text{B}^2\Sigma_u^+$	fluorescence is partially polarized	774
N_2^+	afterglow of pulsed hf discharge	$\text{B}^2\Sigma_u^+-\text{X}^2\Sigma_g^+$ high vibrational levels	perturbations? $\text{A}^2\Pi_u \sim \text{B}^2\Sigma_u^+$ R, V	775
N_2^+	LIF of ion beam	$\text{B}^2\Sigma_u^+-\text{X}^2\Sigma_g^+$	internal state distribution: non-Boltzmann over rotational levels	776
N_2^+	photoelectron: 650—730 Å	$\text{B}^2\Sigma_u^+$ from Rydberg states of N_2^-	autoionization, angular distributions	777
N_2^+ N_2^-	PES electron impact	$\text{N}_2^- (\text{A}^2\Pi_u)$	$\text{N}_2^- \rightarrow \text{N}(\text{S}) + \text{N}^-(^3P)$ angular distributions	777a 778
N_2^-	electron impact	$\text{N}_2^- (\text{A}^2\Pi_u)$	decay to $\text{A}^3\Sigma_u^+$ and to $\text{X}'\Sigma_g^+$ in N_2^-	779
NO	2 and 3 photon	$\text{X}^2\Pi, \text{A}^2\Sigma, \text{M}^2\Pi$	third-order susceptibility enhancements	780
NO	emission PI/mol. beam analysis	$\text{B}^2\Pi-\text{X}^2\Pi$ 119—134 nm $\text{A}^2\Sigma^+-\text{X}^2\Pi$	$^4\Sigma^- \sim \text{B}^2\Pi$ interactions	781a 781b 782
NO	photoionization (tunable VUV laser)		R, V	783
NO	MPI PES	$\text{A}^2\Sigma^+-\text{X}^2\Pi_{1/2}$	resonantly enhanced	784a
NO	MPI, s/s beam	$4\text{f}-\text{F}^2\Delta$	AC Stark effect broadening	784b
NO	SISAM	$\text{b}^4\Sigma^--\text{a}^4\Pi$		785
NO	analysis	$\text{A}^2\Sigma^+$		786
NO	2 photon sub-Doppler analysis	5g—4f Rydberg-Rydberg $\text{D}^2\Sigma^+ \text{E}^2\Sigma^+ \text{B}'^2\Pi, \text{C}^2\Pi, \text{B}^2\Pi$	spin-rotation	787
NO	absorption and fluorescence synchrotron			788
NO	photoelectron (e, 2e)	states of NO^+	branching ratios	789
NO	analysis	Rydberg states		790
NO	emission FTIR	$\text{M}^2\Sigma^+-\text{E}^2\Sigma^+$		791
NO	fluorescence: synchrotron	$\text{C}^2\Pi, \text{D}^2\Sigma^+$	collision induced relaxation	792

NO	LIF: VUV partial photoionization X-sections	$B'^2\Delta$, $F^2\Delta$, $N^2\Delta$	lifetime discrepancies shape resonances	794 795
NO	MPI	through $A^2\Sigma^+$	MPI of molecules in selectively excited rovibrational states	796
NO		$A^2\Sigma^+$, $B^2\Pi$, $D^2\Sigma^+$ $A^2\Sigma^+ - X^2\Pi$	line-broadening: oscillator strength branching ratio: $I_{CA}/(I_{CA} + I_{CX})$ laser enhanced collisional broadening	797 798
NO	chemiluminescence	$A^2\Sigma^+$, $C^2\Pi$	perturbations	799a
NO	MPI, s/s beam	$A^2\Sigma^+ - X^2\Pi_{1/2}$	$A^1\Pi \sim e^3\Sigma^-$ effects of temperature and magnetic field excitation, ionization in discrete and continuous regions	799b
NO ⁺	laser photofragment spectroscopy	$2^3\Pi - b^3\Sigma^-$		800
O ₂	absorption: solid solution in N ₂	$b^1\Sigma_g^+ - X^3\Sigma_g^+$		801
O ₂	theory, electronic transitions			802
O ₂	UV PES	$O_2^+(^2\Phi_u) - O_2(^1\Delta_g)$	modulation technique transient species	803
O ₂	<i>ab initio</i>	Rydberg states		804
O ₂	FT	$b^1\Sigma_g^+ - X^3\Sigma_g^-$	electric quadrupole lines	805
O ₂		Rydberg states	Feshbach resonances	806
O ₂		Rydberg states		807
O ₂		$A'^1\Delta_u$		808
O ₂	UV afterglow FT	790–865 Å		809
O ₂		$a^1\Lambda_g^+ - X^3\Sigma_g^-$	predissociation line widths	810
O ₂	absorption of H, D Ly α	$B^3\Sigma_g^- - X^3\Sigma_g^-$	T 800–1700 K	811
O ₂ /O ₂ ⁺	PES: pulsed synchrotron tof	$b^4\Sigma_g^-$, $a^4\Pi_u$	dramatic deviation from F–C factors when resonance profiles excited	812
O ₂ /O ₂ ⁺	PES	X ² P _g , a ⁴ P _u	perturbations; nearby wide, near-repulsive state	813
				814

Table 11 (continued)

Molecule	Technique	States	Comments	Constants	Ref.
O_2/O_2^+	PI	$X^*\Sigma_g^-$ and $a' \Delta_g$, leading to $X^*\Pi_g^-$			815a
O_2	TPES	$a' \Pi_u A^2\Pi_u b^4\Sigma_g^-$	autoionization enhanced vibrational excitation		815b
O_2	PES	I and I' series	vibrational level populations in autoionization		815c
O_2^+	laser ion beam	$b^4\Sigma_g^- - a^4\Pi_u$			816
O_2^+	laser ion beam	$b^4\Sigma_g^-$	predissociation shape resonance		817a,b
O_2^+	laser ion beam	$f^3\Pi_g^+$	dissociative potential		818
O_2^+	laser ion beam	$f^3\Pi_u^+$	dissociative potential		819
O_2^+	emission: cooled hollow cathode	$A^2\Pi_u^- X^3\Pi_g^+$			820
O_2^+	PEPI analysis	$B^2\Sigma_g^-$	predissociation		821
O_2^+	photoionization	$a^4\Pi_u^-$	vibrational branching ratios: autoionization		822
O_2^+	PEPI coincidence laser ion beam	$B^2\Sigma_g^-$	competing predissociations		823
O_2^+	dissociative electron attachment	$b^4\Sigma_g^- - a^4\Pi_u$	predissociation		824
O_2^-	saturated absorption	$A^2\Pi_u^- X^3\Pi_g^+; b^4\Sigma_g^- - a^4\Pi_u$	autoionization		825
I_2		$2\Pi_u^2\Sigma_g^+; 2f^+_g$	$e^- + O_2(f^1\Delta_g)$		826
I_2		$B^3\Pi_{0-u}^- X^1\Sigma_g^+$	high resolution: good S/N with coherent trains of short light pulses		827
I_2		$B^3\Pi_{0-u}$	electric field induced predissociation		828
I_2^{127}	absorption		levels near dissociation limit: long-range potential		829
I_2^{129}	laser molecular beam analysis	$B^3\Pi_{0-u}^- X^1\Sigma_g^+$ $B^3\Pi_{0-u}^- X^1\Sigma_g^+$	FT spectra	R(15), P(13) 43-0 R, V, E	832 833 834

I ₂	LIF	$B^3\Pi_{0-u}-X^1\Sigma_g^+$	835
I ₂	molecular beam magnetic resonance	$X^1\Sigma_g^+$	836
I ₂	molecular beam emission, in argon	$X^1\Sigma_g^+, B^3\Pi_{0-u}$	837
I ₂	laser locked onto fluorescence by intracavity gain	ion pair states	838
I ₂	analysis	$X^1\Sigma_g^+, 1_g, 0_g^+, B^3\Pi_{0-u}$	839
I ₂	LIF at 193 nm	$B^3\Pi_{0-u}$	840
I ₂	LIF at 183 nm	D-X	841
I ₂	absorption	$A^3\Pi_{1u}-X^1\Sigma_g^+$	842
I ₂	absorption: FT spectrometry	$B0_u^{+-}-X^1\Sigma_g^+$	843
I ₂	LIF FT spectrometry	$B0_u^{+-}-X^1\Sigma_g^+$	844
I ₂	optogalvanic effects	$B0_u^{+-}-X^1\Sigma_g^+$	845
I ₂	MPI		846
I ₂	emission hf discharge in Ar	$1_g-A^3\Pi_{1u}$	847
I ₂	LIF	$B^3\Pi_{0-u}-X^1\Sigma_g^+;$ relative intensities	848
I ₂	optogalvanic		849
I ₂	2 photon sequential absorption		850
I ₂	MPI		851
I ₂	photodissociation	$^1\Pi_u, B^3\Pi_{0-u}-X^1\Sigma_g^+$	852
I ₂	photon echo		853
I ₂	FT	$A^3\Pi_{1u}-X^1\Sigma_g^+$	854
I ₂	absorption of 2 and 3 photons	405–610 nm	855
I ₂	intracavity absorption: s/s beam		856
I ₂			857
I ₂		UV and IR emission	858
I ₂			859

Table 11 (continued)

Molecule	Technique	States	Comments	Constants	Ref.
I ₂	saturation spectroscopy	B ³ Π _{0+u} –X ¹ Σ _g ⁺	laser locking to optical resonance: kHz accuracy sensitivity increased by high modulation frequency interference between different molecules	860	860
I ₂	sub-Doppler, frequency modulation			861	861
I ₂	resonant third harmonic generation: magnetic field effects	B ³ Π _{0+u} –X ¹ Σ _g ⁺ D ¹ Σ _u ⁺ B ³ Π _{0+u}	mixing of g and u states	863	863
I ₂	saturation spectroscopy LIF at 193 nm analysis		predisociation, hfs natural and magnetic calibration and assignments	864	864
I ₂	absorption	B ³ Π _{0+u} –X ¹ Σ _g ⁺	5915 Å	865	865
I ₂	LIF	B ³ Π _{0+u}	high <i>v</i> in B ³ Π _{0+u} hyperfine relaxation	866	866
I ₂ ¹³⁹ I ₂	photo-dissociation laser LIF saturated absorption	B ³ Π _{0+u} –X ¹ Σ _g ⁺ E[0 _g ⁺ –B(0 _u ⁺)–X ¹ Σ _g ⁺]	high <i>v</i> in B ³ Π _{0+u} hyperfine relaxation	867	867
I ₂	1 and 2 photon			868	868
I ₂	2 photon: polarization spectroscopy			869	869
I ₂	LIF: FT absorption	B0 _u ⁺ –a1 _g [–] , a0 _g ⁺	R, V	870	870
I ₂	pulsed frequency-modulation LIF	A1 _u ⁺ –a1 _g [–] , a0 _g ⁺	collision induced rotational transitions	871	871
I ₂	OODR (pulsed)	A ¹ Σ _u ⁺		872	872
I ₂	LIF	B ¹ Π _u [–] –X ¹ Σ _g ⁺		873	873
I ₂	OODR (pulsed)	G ¹ Π _g [–]		874	874
I ₂	OODR (pulsed)	E ¹ Σ _g ⁺ , F ¹ Σ _g ⁺		875	875
I ₂	OODR	C ¹ Π _u [–] –X ¹ Σ _g ⁺		876	876
I ₂	LIF			877	877
I ₂	photodissociation		reinterprets MPI spectra	878	878
Na ₂	LIF		polarization of atomic fluorescence	879	879
Na ₂	OODR			880	880
Na ₂		'Σ _g ⁺ , 'Π _g [–] , 'Δ _g	new bands	881	881
Na ₂			2-step polarization labelling	882	882
Na ₂				883, 884	883, 884

Na_2	<i>ab initio</i>	lower lying states	adiabatic potential energies lasing transition	885
Na_2	LIF		bound-continuum transitions	886
Na_2	LIF		RKR potential	887
Na_2	LIF		intensities	888
Na_2	LIF	$\text{A}^1\Sigma_u^+ - \text{X}^1\Sigma_g^+$	dipole strength function	889
Na_2	2-step photoionization	4 eV region	dependence on alignment	890
Na_2	2 photon absorption	450—850 nm	singlet and triplet absorption	891
Na_2	absorption: high pressure		high vibrational levels	893
Na_2	discharge		Rydberg series	894
Na_2	polarization	$\text{A}^1\Sigma_u^+$	line shapes near resonant	895
Na_2	polarization labelling	$^1\Sigma_g^+$ states	enhancement	
Na_2	2-photon			
Na_2^+	photoionization	$\text{B}'^1\Pi - \text{X}'^1\Sigma_g^+$		896
NaLi, NaK	LIF, s/s nozzle beam	lower-lying states	adiabatic potential energies	897
K_2	<i>ab initio</i>		$^3\Sigma$ states perturbation	885
K_2	LIF, s/s nozzle beam		pair excitation (2 g.s. atoms	897
Rb_2	radiative collision		simultaneously excited by	898
			absorption of one photon)	
Rb_2	LIF: s/s nozzle beam	$\text{C}'^1\Pi_u, \text{D}'^1\Pi_u$	predissociation	899
Rb_2	LIF: s/s nozzle beam	$\text{B}'^1\Pi_u - \text{X}'^1\Sigma_g^+$	$^3\Sigma$ states perturbation	900
Rb_2	LIF: s/s nozzle beam	$\text{C}'^1\Pi_u$	see Rb_2 , analysis of diffuse bands near	897
RbCs	radiative collision		610 nm	898
Cs_2	radiative collision		see Rb_2 , analysis of 480 nm band	902
Cs_2	laser photodissociation	758 nm	potential curves also energy loss spectrum, 4—10 eV	903
Cs_2	photodissociation			904
Na, K halides	electron scattering			905
CsCl	matrix isolation MCD	$^1\Pi_u - \text{X}^1\Sigma_g^+$	potentials	906
	LIF	$\text{A}^1\Sigma_u^+ - \text{X}^1\Sigma_g^+$	E, R, V, E	907
	matrix isolation MCD	$^1\Pi_u - \text{X}^1\Sigma_g^+$	E, V	908
	fluorescence, LIF	$\text{A}^1\Sigma_u^+ - \text{X}^1\Sigma_g^+$		

Table 11 (continued)

Molecule	Technique	States	Comments	Constants	Ref.
Sr ₂	matrix isolation MCD	$\Pi_u^-X^1\Sigma_g^+$			906
BeO	<i>ab initio</i>	X, A, B	SCF CI		909
MgO	chemiluminescence	d ¹ A-a ¹ Π, B ¹ Σ+-X ¹ Σ-			910
CaO	absorption, shock tube	B ¹ Σ+-A ¹ Π	transition moments	911	
SrO	LIF	C ¹ Σ+, B ¹ Π-X ¹ Σ+	R, V, E	912	
BaO	LIF	C ¹ Σ+-X ¹ Σ+	τ, transition moments	913	
BaO	ODDR sub-Doppler	C ¹ Σ+ and C-X, C-A, C-A', C-b, A-X, A'-X	rotational and translational relaxation	914	
BaO	ODDR sub-Doppler	A ¹ Σ+	collisional depolarization		
BaO	ODDR sub-Doppler	A ¹ Σ+(J, M _J) state-selected, C ¹ Σ+, D ¹ Σ ⁺ (also B ¹ Π, E ¹ Σ ⁺ , and C ³ Π _J)	cross-sections	915	
BaO	OODR sub-Doppler	low lying states: a ³ Σ+, A ¹ Σ+, b ¹ Π, A ¹ Π B ¹ Σ+, A ¹ Π-X ¹ Σ ⁺	R, V, E	916	
BaO	emission; arc	a ³ Σ+, A ¹ Π, A ¹ Π, A ¹ Σ ⁺	deperturbation	917	
BaS	LIF	A ² Π, A ¹ Π, A ¹ Σ ⁺	Λ-doubling		
BeF	<i>ab initio</i>	A ¹ Π-X ¹ Σ ⁺	R, V, E	918	
CaF	inter-modulated fluorescence	E ² Σ ⁺ , E ² Π	hfs: spin-rotation	919	
CaF	ODDR sub-Doppler	X ² Σ ⁺	R, V, E	920	
CaF	RFODR	A ² Π _{1/2} -X ² Σ ⁺	hfs, spin-rotation	921	
CaF	molecular beam: RFODR sub-Doppler	B ² Σ ⁺⁻ X ² Σ ⁺	spin-rotation hfs	922	
LIF	LIF	B ² Σ ⁺⁻ X ² Σ ⁺	variation of N, v	923	
CaCl	LIF: absorption	A ² Π-X ² Σ ⁺	variation of N, v	924	
CaCl	LIF	B ² Σ ⁺⁻ X ² Σ ⁺	V, R	925	
CaCl	analysis	X ² Σ ⁺	V, R	926	
CaCl	absorption	D ² Σ ⁺⁻ X ² Σ ⁺	V, R	927	
CaCl	analysis	A ² Π, B ² Σ ^{+(2Δ)}	E	928	
CaCl	analysis	X ² Σ ⁺ , A ² Π, B ² Σ ^{+, 2Δ}	τ, spin-orbit	929	
CaCl	molecular beam RFODR sub-Doppler	B ² Σ ⁺⁻ X ² Σ ⁺	line widths 15 MHz	930	
CaCl	inter-modulation spectroscopy	A ² Π-X ² Σ ⁺	cross-over signals	931	
CaCl				932	
CaCl				933	

CaBr	LIF analysis	$B^2\Sigma^+$, $A^2\Pi-X^2\Sigma^+$	934
CaBr	molecular beam LIF mol. beam, RFODR intermodulated fluorescence	$B^2\Sigma^+-X^2\Sigma^+$, $B^2\Sigma^+, A^2-X^2\Sigma^+$	935
CaBr	LIF	$B^2\Sigma^+$, $A^2\Pi-X^2\Sigma^+$	936
CaBr	intermodulated fluorescence	$B^2\Sigma^+, A^2\Pi-X^2\Sigma^+$	937
Cal	intermodulated fluorescence	$B^2\Sigma^+, A^2\Pi-X^2\Sigma^+$	938
Cal	molecular beam RFODR sub-Doppler analysis	$B^2\Sigma^+, A^2\Pi-X^2\Sigma^+$	939
SrF	OODR OODR LIF analysis	$B^2\Sigma^+, F^2\Pi$	939
SrF	emission, hollow cathode emission, discharge $BF_3 + He$	$C^2\Pi-X^2\Sigma^+$	940
BaF	emission, hollow cathode emission, hf discharge	$A^2\Pi_l-X^2\Sigma^+$	941
BaI	high frequency deflection intracavity laser	$A^2\Pi_l-X^2\Sigma^+$	942
BO	photodetachment	$B^2\Sigma^+-X^2\Sigma_g^+$	943
AlO	absorption	$\Sigma_u^+-\Sigma_g^+$	944
A1S	matrix isolation LIF	$B-X$, $D-X$, $C-A$	945
BF	laser vaporization	2 systems	946
GaBr	matrix isolation Raman matrix isolation: absorption, Raman analysis	$BO_u^+-XO_g^+$, $BO_u^+-XO_g^+$, XO_g^+ , $BO_u^+-XO_g^+$	947
Gal			948
C ₂			949
C ₂			950
C ₂ ⁻			951
Si ₂			952
Sn ₂			953
Sn ₂			954
Pb ₂			955
Pb ₂			956
Pb ₂			957
Pb ₂			958
CN			959
			960
			961

Table 11 (continued)

Molecule	Technique	States	Comments	Constants	Ref.
CO	electron impact	$d^3\Delta$ excitation and radiative decay	τ		962
CO	matrix isolation photoionization, tunable VUV laser	$a^3\Pi_r - X^1\Sigma^+$	calculation of cross-sections excitation of $A^1\Pi, v = 13$, followed by photoionization	quantum defects, IP E, V, R, dipole moments	963
CO	absorption: synchrotron <i>ab initio</i> SCF CI	Rydberg states $X^1\Sigma^+, B^1\Sigma^+, C^1\Sigma^+, (n-\pi^*)^1\Sigma^+, 1^1\Sigma^-$ and $A^1\Pi$	106—155 nm broad peak 19.5 eV	quantum yields	964
CO	absorption and fluorescence electron impact		shape resonances branching ratios for production of CO^+ in $v, X^2\Sigma^+$	cross-sections asymmetry parameters	965
CO	synchrotron photoionization		vibrational relaxation threshold photoelectron spectroscopy by electron attachment (TPSA)	τ	966
CO	LIF	$d^3\Delta - a^3\Pi_r$			967
CO	PES	$X^2\Sigma^+$			968a
CO	LIF	$A^1\Pi - X^1\Sigma^+$		branching ratios	969
CO ⁺	electron impact	$A^2\Pi, B^2\Sigma^+ - X^2\Sigma^+$		cross-sections: threshold to 500 eV	970
CO ⁺	electron impact	$A^2\Pi, B^2\Sigma^+ - X^2\Sigma^+$			971
PES	LIF, ion trap ion beam MODR	converging to $B^2\Sigma^+$ $A^2\Pi$			972
CO ⁺	LIF, electron impact emission, absorption	$A^2\Pi_r - X^2\Sigma^+$ $A^2\Pi_l$	perturbations with $X^2\Sigma^+$ dissociative attachment	τ	973
CO ⁺		$2\Sigma^+(v = 0 \text{ at } 10.04 \text{ eV})$	extensive deperturbation	R, V, E, interaction constants	974a
CO ⁻		$A^1\Pi, e^1\Sigma^-, d^3\Delta_r, a^3\Sigma^+, a^3\Pi$	deperturbation	R, V	974b
CS	emission: low pressure DC discharge	$d^3\Lambda_r - a^3\Pi_r$	perturbation enhanced quenching by O atoms		681b
CS	LIF	$A^1\Pi$			975
					976
					977
					978
					979
					980

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CS ⁺	B ² Σ ⁺	981
CSe	a ¹ $\Pi_{1,0}^+$ -X ¹ Σ ⁺	982
SiS	a ³ Σ ⁺ , b ³ $\Pi_{0,1}$	983
GeO	Rydberg states	984
GeS	a ³ Σ ⁺ , b ³ Π	985
GeS	A' ¹ Π -X ¹ Σ ⁺	986
SnO	b ³ $\Pi_{1,0}$, A' ¹ Π -X ¹ Σ ⁺	987
SnS	a ³ Ω , A ^{0,+} and other Ω states	988
PbO	LIF: time-resolved	989
PbS	LIF	990
PbS	chemiluminescence absorption	991
SiF	emission: hf discharge	992
SiCl	emission	993
SiCl	Penning ionization	994
SiCl ⁺	Penning ionization	995
GeCl ⁺	Penning ionization	996
SnCl ⁺	Penning ionization	997
PN	emission: hf discharge	998
PN ⁺	emission: Penning ionization	999
P ₂	absorption	1000
As ₂	absorption	1001
Sb ₂	LIF; heat pipe	1002
Sb ₂	matrix; absorption isolation	1003
Bi ₂	LIF	1004
Bi ₂	matrix isolation	1005
Bi ₂	LIF	1006
Bi ₂	matrix isolation	1007
Bi ₂	matrix isolation	1008
PO	B ² Σ ⁺ -X ² $\Pi_{1,0}$	1009
SbO ⁺	A' ¹ Π -X ¹ Σ ⁺	1010
NS	B ² Π -X ² Π , b ² Σ ⁺ , a ⁴ Π	1011
NCI	b ² Σ ⁺ , a ⁴ Δ -X ³ Σ ⁻	1012
NBr	b ² Σ ⁺ , a ⁴ Δ -X ³ Σ ⁻	1012

Table 11 (continued)

Molecule	Technique	States	Comments	Constants	Ref.
BiF	emission: hf discharge	B0 ⁺ -X0 ⁺	perturbations	R, V	1013
BiF	emission: hf discharge	A0 ⁺ -X0 ⁺	perturbations	R, V	1014
S ₂	<i>ab initio</i>	? ³ Σ _u ⁻ , ¹ Σ _g ⁺ , ³ Π _g ⁺ , ¹ Π _g ⁺ ; valence, ion-pair and Rydberg			1015
S ₂	matrix isolation	B ³ Σ _u ⁺ , B ¹ Π _u , A ¹ Σ _u ⁺ , A ¹ Δ _u , c ¹ Σ _u ⁻ , a ¹ Δ _g , B ³ Σ _u ⁻	predisociation, relaxation	E	1016
S ₂	LIF	X ³ Σ _g ⁻ , a ¹ Δ _g , b ¹ Σ _g ⁺		τ	1017
S ₂	<i>ab initio</i> : CI	B ³ Σ _u ⁻ -X ³ Σ _u ⁻		E, V	1018
S ₂	LIF	A ² Π _u -X ² Π _u		R	1019
S ₂ ⁺	Penning ionization	X ³ Σ _u ⁻ , a ¹ Δ _g , b ¹ Σ ⁺		E, V	1020
SO	<i>ab initio</i> : CI	B ³ Σ _u ⁻ -X ³ Σ _u ⁻ 190—235 nm		E, V	1018
SO	absorption cross-section emission; hf discharge	a ¹ Δ-X ² Σ ⁻		E, V	1021
SeO	chemiluminescence	b ¹ Σ ⁺ -X ³ Σ ⁻		E, V	1022
SeO	matrix isolation LIF	-X ³ Σ ⁻		E, V	1023
SeS	chemiluminescence	b ¹ Σ ⁺ -X ³ Σ ⁻		E, V	1024
SeS	chemiluminescence	b ¹ Σ ⁺ -X ³ Σ ⁻		E, V	1023
Se ₂	chemiluminescence	b ³ Σ _g ⁺ -X ³ Σ _g ⁻		E, V	1023
Se ₂	LIF: FT	B ³ Σ _u ⁻ -b ¹ Σ _g ⁺		R, V, E	1025
Se ₂	matrix isolation LIF	? ³ Σ _u ⁺		E, V	1026
Se ₂	matrix isolation LIF	? ³ Π _u ⁺ ; ? ³ Σ _u ⁺		E, V	1027
Se ₂	Zeeman quantum beats polarized laser fluorescence	B ³ Σ _u ⁻ -X ³ Σ _u ⁻ ; B ³ Π _u	perturbations	Landé g	1028
Se ₂	matrix isolation LIF	B ³ Σ _u ⁻ -X ³ Σ _u ⁻	collisions	1029	1029
TeSe	matrix isolation LIF	-X ³ Σ _u ⁻		E, V	1024
Te ₂	matrix isolation LIF	? A ³ Σ _u ⁺		E, V	1024
Te ₂	matrix isolation LIF	? A ³ Σ _u ⁺		E, V	1024
Te ₂	LIF: FT	B ³ Σ _u ⁻ -b ¹ Σ _g ⁺		R, V, E	1030
TeF	chemiluminescence	B ² Σ _g ⁺ , A ² Π ₁ -X ² Π ₁		V, E	1031
Cl ₂	LIF	B ³ Π _{0-u}		τ	1032
Cl ₂	LIF	B ³ Π _{0-u}		R, V, E	1033
Cl ₂	analysis	B ³ Π _{0-u} -X ¹ Σ _g ⁺	J dependent predissociation long-range potential, FC factors	R, V, E	1034

Cl ₂	absorption	states 69 100—81 800 cm ⁻¹ , ionic, Rydberg	perturbations	R, E	1035
Cl ₂	synchrotron: fluorescence	1354 Å excitation to $^1\Sigma_u^+$	2580 Å fluorescence	τ	1036
ClF	LIF	$B^3\Pi_0-$ $X^1\Sigma^+$	FC factors	τ	1037
ClF	LIF	$B^3\Pi_0-$	perturbations	τ	1038
Br ₂	LIF	$B^3\Pi_{0-u}$	coincidences with Kr laser lines	τ	1039
Br ₂	LIF	$B^3\Pi_{0-u}-X^1\Sigma_u^+$	fluorescence decay: predissociation	τ	1040
Br ₂	LIF	$B^3\Pi_{0-u}$	coincidences with Kr laser lines	τ	1041
Br ₂	analysis	$B^3\Pi_{0-u}, ^1\Pi_u$	predisociation potential for $^1\Pi_u$	1042	
Br ₂	LIF	$A^3\Pi_{1u}$		1043	
Br ₂	LIF	$B^3\Pi_{0-u}$		1044	
Br ₂	LIF	$B^3\Pi_{0-u}$		1045	
Br ₂	LIF: s/s beam	$B^3\Pi_{0-u}$	energy transfer	τ	1046
Br ₂	Zeeman quantum beats	$B^3\Pi_{0-u}$	relaxation	τ	1047
Br ₂	Tesla discharge	$D^1(2_g)-A^1(3\Pi_{2u})$	Rydberg states	Landé g	1048
Br ₂	2-photon resonant MPI emission in Ar	$D^1(2_g)-A^1(2_u)$	$D^1(2_g)-E-B, D^1-^1\Delta_{2u}$	R, V, E	1049
Br ₂	laser/molecular beam electron impact	$B^3\Pi_{0-u}-X^1\Sigma_u^+$	68 000—72 800 cm ⁻¹ ion-pair states	E, V	1050
Br ₂			electric quadrupole	V	
Br ₂			ionization: dissociative attachment: ion-pair formation	hfs	
BrF	LIF	$B^3\Pi_{0-u}$	rotationally dependent predissociation	τ	1053
BrF	chemiluminescence	$B^3\Pi_{0-u}-X^1\Sigma^+$		R, V	1054
IF	emission: electron beam absorption	? $E \rightarrow A^3\Pi_i$		τ	1055
ICl	emission: $I(^2P_{3/2}) + Cl(^2P_{1/2})$	$A^3\Pi_i-X^1\Sigma^+$	constants include absorption data	R, V, E	1056
ICl	photofragment spectroscopy	$A^3\Pi_i-X^1\Sigma^+$	curve crossings	R, V, E	1057
ICl	IBr	$X^1\Sigma^+$ and excited O^+ states	curve crossings	repulsive potential	1058
IBr	LIF	$B^3\Pi_{0-u}$	predissociation	τ	1059

Table 11 (continued)

Molecule	Technique	States	Comments	Constants	Ref.
I _{Br}	absorption 2-photon sequential LIF	B'(0 ⁺)–X'Σ ⁺ followed by E(?)0 ⁺ –B'(0 ⁺) B ³ Π ₀ –X'Σ ⁺ X'Σ ⁻ , 1Δ and 1Σ ⁺ of ion	line widths, predissociation	R, V, E	1060
I _{Br}	PES	A'Π–X'Π	predissociation	V, E	1061
FO	matrix isolation: absorption analysis	A'Π	revision of gas-phase analysis	E, V	1062
CIO	matrix isolation: absorption	A'Π–X'Π	Franck–Condon factors	E, V	1063
CIO	matrix isolation: absorption calculation	A'Π–X'Π		E, V	1062
BrO	matrix isolation absorption	A'Π _u –X'Σ _g ⁺		E, V	1064
IO	ab initio: CI	X'Σ _g ⁺	perturbations, pre-dissociation, new states	R, E	1065
Cu ₂	absorption 1890—2100 Å	–X'Σ ⁺	new low-lying states	E	1066
Cu ₂	LIF	A(Ω1)–X'Σ ⁺	R, (V)	E	1067
CuCl	emission, microwave discharge	A(Ω1), B(Ω1)–X'Σ ⁺		R, E	1068
CuBr	emission, hollow cathode	A(Ω1), C(0 ⁺)–X'Σ ⁺		E, V	1069
CuBr	emission	A(1), C(0 ⁺)–X'Σ ⁺		R, V	1070
CuI	LIF	A, X		R, V	1071
CuI	absorption 2470—2710 Å	C, E–X'Σ ⁺		R, V	1072
Ag ₂	matrix isolation		potentials, 1S ₀ –1S ₀ ⁺	E	1073
Ag ₂	absorption, 1849 Å; P, T variation		1P ₁ , m = +1 – 1S ₀ ⁺	1074	
Hg ₂	calculation		1P ₀ , m = 0 – 1S ₀	1075	
Hg ₂			Hg 6 ¹ S ₀ –Hg 6 ¹ P ₁ , long-range potential	1076	1077
HgCl			Rydberg states	E, V	1078
HgCl			B ² Σ ⁺ –X ² Σ ⁺	τ	1078
HgBr	photodissociation of HgCl ₂ by Xe ₂ laser	B ² Σ ⁺ –X ² Σ ⁺		τ	1078
HgBr	photodissociation of HgBr ₂ by ArF laser	B ² Σ ⁺ –X ² Σ ⁺	vibrational quenching of X ² Σ ⁺	1079	

HgI	photodissociation of HgI ₂ by Xe, laser	B ² Σ ⁺ -X ² Σ ⁺	τ	1078
ScX (X = F, Cl, Br, I)	LIF	-X ¹ Σ ⁺	E, V, τ	1081
YO	emission, hollow cathode	B ² Σ ⁺ -X ² Σ ⁺	perturbations	1081
YX (X = Cl, Br, I)	LIF	-X ¹ Σ ⁺	new states	1081
YCl	thermal emission	B ² Σ ⁺ -X ² Σ ⁺	new states	1082
YI	emission, microwave discharge, FT	-X ¹ Σ ⁺	V	1083
LaO	analysis	Π-X ¹ Σ ⁺	R, V	1084
LaF ⁺	emission: He + Ar discharge	C ² Π _r , B ² Σ ⁺ , A ² Π _r , A ² Δ _r	R, V	1085
Ti ₂	matrix isolation	X ² Σ ⁺	V	1086
TiN	absorption, pulsed discharge	B ² Σ, A ² Π-X ² Σ	R, V, E	1087
TiO	emission, microwave discharge	b ¹ Π-d ¹ Σ ⁺	R, V	1088
TiO	MCD, matrix isolation	B ³ Π-X ³ Δ; B ³ Π-X ¹ Σ ⁺	singlet-triplet separation	1089
ZrO	LIF	B ¹ Π-X ¹ Δ	E	1090
ZrO	emission: King furnace calculation	e ¹ Π-X ¹ Σ ⁺ ; ¹ Σ ⁺ -X ¹ Σ ⁺	R, V, E	1091
ZrO	LIF	B ¹ Π-A ¹ Δ; B ¹ Π-a ¹ Δ ₂	Franck-Condon factors	1092
ZrO ⁺	emission, arc	A ² Π-X ² Σ ⁺	E	1093
ZrCl	emission, hf discharge	² Π- ² Π	R	1094
V ₂	matrix isolation		FT spectrometry	1095
VO	emission, hf discharge: laser excitation	C ⁴ Σ-X ⁴ Σ-	R, V	1096
VO	emission, hf discharge: intermodulated fluorescence	C ⁴ Σ-X ⁴ Σ-	sub-Doppler	1097
VF	emission, microwave discharge	C ⁴ Σ-X ⁴ Σ-	hfs	1098
CrO	emission, microwave discharge LIF	A ⁵ Π-X ⁵ Π	perturbations	1099
CrO	equilibrium mass spectrometry	X ⁵ Π	D ₀ [⊕]	1100
Mn ₂	matrix isolation, e.s.r.		antiromagnetic ground state	1101

Table 11 (continued)

Molecule	Technique	States	Comments	Constants	Ref.
MnO	emission, microwave discharge	$A^6\Sigma^+ - X^6\Sigma^+$	perturbation	R, V, hfs	1102
FeO	emission, hollow cathode	-ground state		R, V	1103
FeO	emission, LIF intermodulated fluorescence	$-X^5\Delta_1$	sub-Doppler	R	1104
FeCl	emission, microwave discharge	$\Pi, ^6\Phi - X^6\Delta_1$		R	1105
NiF	emission, absorption, LIF	$B^3\Pi - X^3\Sigma^+$	low-lying states	R	1106
CeO	OODR			E	1107
CeO	LIF			E	1108
PrO	LIF		system XX	R, hfs	1109
PrO	LIF		low-lying states	R, hfs	1110
GdO	emission: arc			V	1111
TbO	thermal emission, absorption			R	1112
DyO	thermal emission, absorption			R	1112
HoO	thermal emission, absorption			R	1112
TaO	matrix isolation: MCD, absorption	low-lying states	assignments	E, g factors	1113
WO	flash photolysis		separated isotope	R, V	1114
ReO	emission, arc			R, V	1115

Table 12 Electronic spectroscopic studies of triatomic molecules. Molecules are listed in alphabetical order

Molecule	Technique	Comments	Ref.
ArKrCl	emission	emission in bands in UV	1116
ArKrF			
BO ₂	LIF	Π vibronic states of g.s., from $\tilde{\Lambda}^2\Pi_u - \tilde{X}^2\Pi_g$	1117
BO ₂	backscattering	sub-Doppler $\tilde{\Lambda}(0,0,0)^2\Pi_{3/2} - \tilde{X}(1,0,0)^2\Pi_{3/2}$	1118
BO ₂	LIF	lifetimes in (110), (2,0,0), and (1,0,0) of $\tilde{\Lambda}^2\Pi_u$	1119
BeOH	<i>ab initio</i>	structure and electronic properties	1120
BrCN ⁺	LIF, quadrupole trap	$\tilde{B}^2\Pi - \tilde{X}^2\Pi$; Fermi resonance, ν_1	1121
CF ₂	chemiluminescence, LIF	250–400 nm, mainly $\tilde{\Lambda}^1B_1 - \tilde{X}^1A_1$	1122
CFBr	LIF, argon matrix	excitation at 424 and 428 nm; fluorescence, origin 23 300 cm ⁻¹ , with progression in g.s. bend	1123
CFBr	LIF	$^1A'' - ^1A'$; FES 400–460 nm, $\tau = 1150 \pm 50$ ns	1124
C ₂ H	infrared absorption CCL	$^2\Pi - \tilde{X}^2\Sigma^-$	1125
CH ₂	<i>ab initio</i>	excitation energies, transition probabilities, frequency dependent polarizabilities	1126
CH ₂	<i>ab initio</i>	$^1B_1 - ^1A_1$, separation	1127
CH ₂	LIF, s/s jet	new vibronic bands $\tilde{b}^1B_1 - \tilde{a}^1A_1$	1128
C ^{1,3} H ₂	LIF	LIF of CD ₂ (\tilde{a}^1A_1); Renner–Teller in $C^{1,3}H_2$	1129
CH ₂ ⁻	photodetachment, laser PES	singlet-triplet splitting as before	1130
CHF	LIF	$\tilde{\Lambda}^1A'' - \tilde{X}^1A'$, $\tau_s \approx 2 \mu s$	1131
C ₂ O	LIF	$\tilde{\Lambda}^3\Pi_g - \tilde{X}^3\Sigma^-$, excitation and fluorescence	1132
CO ₂	matrix emission	$^3B_g - X^1\Sigma_g^+$; 350–550 nm continuum with $\tau = 570$ ns	1133
CO ₂	PI (synchrotron)	spin-polarized photoelectrons	1134
CO ₂	PES (synchrotron)	angle-resolved	1135
CO ₂	PES	s–o splitting, Renner–Teller effects in $^2\Pi$ bands	1136

1116 H. C. Brashears, jun., D. W. Setser and Y.-C. Yu, *J. Chem. Phys.*, 1981, **74**, 10.1117 K. G. Weyer, R. A. Beaudet, R. Straubinger, and H. Walther, *Chem. Phys.*, 1980, **47**, 171.1118 W. Schulz, K. G. Weyer, R. A. Beaudet, and H. Walther, *J. Chem. Phys.*, 1980, **72**, 589.1119 S. McIntosh, R. A. Beaudet, and D. A. Dows, *Chem. Phys. Lett.*, 1981, **78**, 270.1120 A. Hinchcliffe, *J. Mol. Struct.*, 1980, **64**, 289.1121 F. J. Grieman, B. H. Mahan, and A. O'Keefe, *J. Chem. Phys.*, 1981, **74**, 857.1122 T. Ishiguro, Y. Hamada, and M. Tsuboi, *Bull. Chem. Soc. Jpn.*, 1981, **54**, 367.1123 J. C. Miller and L. Andrews, *J. Phys. Chem.*, 1980, **84**, 401.1124 J. R. Purdy and B. A. Thrush, *Chem. Phys. Lett.*, 1980, **73**, 228.1125 P. G. Carrick, J. Pfeiffer, R. F. Curl, jun., E. Koester, F. K. Tittel, and J. V. V. Kasper, *J. Chem. Phys.*, 1982, **76**, 3336.1126 J. A. Nicholls and D. L. Yeager, *Chem. Phys. Lett.*, 1981, **84**, 77.1127 C. W. Bauschlicher, jun., *Chem. Phys. Lett.*, 1980, **74**, 273.1128 D. L. Monts, T. G. Dietz, M. A. Duncan, and R. E. Smalley, *Chem. Phys.*, 1980, **45**, 133.1129 M. N. R. Ashfold, M. A. Fullstone, G. Hancock, and G. Duxbury, *Mol. Phys.*, 1982, **45**, 887.1130 P. C. Engelking, R. R. Corderman, J. J. Wendeloski, G. B. Ellison, S. V. O'Neil, and W. C. Lineberger, *J. Chem. Phys.*, 1981, **74**, 5460.1131 M. N. R. Ashfold, F. Castano, G. Hancock, and G. W. Ketley, *Chem. Phys. Lett.*, 1980, **73**, 421.1132 W. M. Pitts, V. M. Donnelley, A. P. Baronavski, and J. R. McDonald, *Chem. Phys.*, 1981, **61**, 451.1133 H. H. Mohammed, J. Fournier, J. Deson, and C. Vermeil, *Chem. Phys. Lett.*, 1980, **73**, 315.1134 U. Heinemann, F. Schafers, and B. A. Hess, *Chem. Phys. Lett.*, 1980, **69**, 284.1135 F. A. Grimm, J. D. Allen, jun., T. A. Carlson, M. O. Krause, D. Mehaffy, P. R. Keller, and J. W. Taylor, *J. Chem. Phys.*, 1981, **75**, 92.1136 A. W. Potts and G. H. Fattahallah, *J. Phys. B*, 1980, **13**, 2545.

Table 12 (continued)

Molecule	Technique	Comments	Ref.
CO ₂	theory, cf. expt.	vibrational effects in shape-resonant photoionization	1137
CO ₂	electron impact	oscillator strengths etc., 8–75 eV; combined with (e, 2e) data	1138
CO ₂ ⁺	PES, angle-resolved	evidence for shape resonance in C ² Σ _g ⁺ band	1139
CO ₂ ⁺	PI calculation	nuclear motion effects; σ _u shape resonance at 19 eV	1140
^{12,13} CO ₂ ⁺	electron impact, low pressure discharge	Fermi resonance between (100) and (020) of X ² Π _g	1141
CO ₂ ⁺	PI	wavelength resolved fluorescence lifetimes, Ā–Ā̄ emission	1142
CO ₂ ⁺	PE-photon coincidence	quantum yields and lifetimes	1143
CO ₂ ⁺	electron impact/mol. beam	fluorescence A ² Σ _u → X ² Π _g	1144
CS ₂	LIF	¹ A ₂ , ¹ B ₂ states: magnetic field effect on fluorescence	1145
CS ₂	MCD	300–380 nm; zero field splittings in ³ A ₂	1146
CS ₂	mol. beam PI	absorption, photoionization efficiency 121.0–123.2, 107.5–113.0 nm	1147
CS ₂	mol. beam	¹ B ₂ absorption	1148
CS ₂	PES	s–o splitting of ² Π states	1136
CS ₂	LIF	a ³ A ₂ –X ¹ Σ _g ⁺ ("R"), ¹ A ₂ – ¹ Σ _g ⁺ ("T")	1149
CS ₂	LIF, s/s jet	'B ₂ ; strong coupling with low-lying triplets	1150
CS ₂	PES (synchrotron)	angle-resolved	1151
CS ₂	absorption, PI	oscillator strengths	1152
CS ₂	PES (variable wavelength)	branching in autoionization	1153
CS ₂	MPI	via 1st photon resonance, for $\tilde{\alpha}$ ³ A ₂ (361–375 nm)	1154
CS ₂	electron impact	forbidden transitions, 6–17 eV	1155
CS ₂	electron impact	new structure	1156

1137 J. R. Swanson, D. Dill, and J. L. Dehmer, *J. Phys. B*, 1981, **14**, L207.1138 A. P. Hitchcock, C. E. Brion, and M. J. van der Wiel, *Chem. Phys.*, 1980, **45**, 461.1139 T. A. Carlson, M. O. Krause, F. A. Grimm, J. D. Allen, jun., D. Mehaffy, P. R. Keller, and J. W. Taylor, *Phys. Rev. A*, 1981, **23**, 3316.1140 J. R. Swanson, D. Dill, and J. L. Dehmer, *J. Phys. B*, 1980, **13**, L231.1141 C. Larcher, D. Gauyacq, and J. Rostas, *J. Chim. Phys., Phys. Chim. Biol.*, 1980, **77**, 655.1142 R. C. Dunbar and D. W. Turner, *Chem. Phys.*, 1981, **57**, 377.1143 J. P. Maier and F. Thommen, *Chem. Phys.*, 1980, **51**, 319.1144 A. Carrington and R. P. Tuckett, *Chem. Phys. Lett.*, 1980, **74**, 19.1145 H. Oriita, H. Morita, and S. Nagakura, *Chem. Phys. Lett.*, 1981, **81**, 29.1146 G. Barth, R. E. Linder, E. Bunnenberg, C. Djerassi, L. Seamans, and A. Moscowitz, *J. Chem. Phys.*, 1980, **72**, 1423.1147 Y. On, S. H. Linn, H. F. Prest, M. E. Gress, and C. Y. Ng, *J. Chem. Phys.*, 1980, **73**, 2523.1148 V. Vaida and G. M. McClelland, *Chem. Phys. Lett.*, 1980, **71**, 436.1149 P. F. Bernath, M. Dulick, R. W. Field, and J. L. Hardwick, *J. Mol. Spectrosc.*, 1981, **86**, 275.1150 N. Mikami, H. Kasahara, and M. Ito, *Chem. Phys. Lett.*, 1981, **83**, 488.1151 T. A. Carlson, M. O. Krause, F. A. Grimm, J. D. Allen, jun., D. Mehaffy, P. R. Keeler, and J. W. Taylor, *J. Chem. Phys.*, 1981, **75**, 3288.1152 F. Carnovale, M. G. White, and C. E. Brion, *J. Electron Spectrosc.*, 1981, **24**, 63.1153 J. H. D. Eland, *Mol. Phys.*, 1980, **40**, 917.1154 R. Rianda, D. J. Moll, and A. Kupperman, *Chem. Phys. Lett.*, 1980, **73**, 469.1155 D. G. Wilden and J. Comer, *Chem. Phys.*, 1980, **53**, 77.1156 M. J. Hubin-Franskin, P. Marmet, and D. Huard, *Int. J. Mass Spectrom. Ion Phys.*, 1980, **33**, 311.

Table 12 (continued)

Molecule	Technique	Comments	Ref.
CS_2^+	Ne matrix	most strong vibronic $\tilde{\text{X}}^2\Pi_g \rightarrow \tilde{\text{A}}^2\Pi_u$ bands due to mixture of v_1 and v_2	1157
CS_2^+		see CO_2^+ , ref. 1142	
CS_2^+		see CO_2^+ , ref. 1143	
ClCN	absorption	Rydberg transition, $\pi \rightarrow 4s$	1158
ClCN	absorption	Rydberg states, 125—220 nm	1159
ClO_2	absorption	$\tilde{\text{A}}^2\text{A}_2 - \tilde{\text{X}}^2\text{B}_1$, long wavelength end	1160
ClO_2	absorption	$\tilde{\text{A}}^2\text{A}_2 - \tilde{\text{X}}^2\text{B}_1$; rotational state dependence of predissociation	1161
CuF_2	PES	3d orbitals have valence character (<i>c.f.</i> ZnF_2)	1162
CuF_2	PES	'pseudo-molecular beam'; also CuF	1163
FCO	chemiluminescence	max. intensity ~ 425 nm, some vib. assignments	1164
FCO	PES	first IP, extensive vibrational structure characteristic of FCO^+ deformation; ΔH_f^\ominus	1165
H_3	charge transfer/dissociation	fragment intensity varies with relative translational energy	1166
H_3	interpretation	refers to experiments of ref. 1166	1167
H_3	<i>ab initio</i>	properties of 15 lowest Rydberg states	1168
$^{1,2}\text{H}_3$	emission	560 and 602.5 nm parallel bands	1169
$^{1,2}\text{H}_3$	emission	710 nm perpendicular bands	1170
$^{1,2}\text{H}_3$	emission	discussion of \parallel and \perp bands	1171
$^{1,2}\text{H}_3$	emission	IR: $^2\text{A}'_1 - ^2\text{E}'$ excited states	1172
$^2\text{H}_3$	calculations	B_v constants for Rydberg states	1173
H_3^+	translational spectroscopy	H_3^+ is bound by 8.9 ± 3 eV w.r.t. $2\text{H}(1S) + \text{H}^+$	1174
HCF	combustion chemiluminescence	$\tilde{\text{A}}^1\text{A}'' - \tilde{\text{X}}^1\text{A}'$	1175
HCF	LIF	$\tilde{\text{A}}^1\text{A}'' - \tilde{\text{X}}^1\text{A}'$, 17188—17391 cm $^{-1}$	1176
^2HCF	LIF	as above	1177

¹¹⁵⁷ V. E. Bondybey and J. H. English, *J. Chem. Phys.*, 1980, **73**, 3098.¹¹⁵⁸ S. P. McGlynn, W. S. Felps, and G. L. Findley, *Chem. Phys. Lett.*, 1981, **78**, 89.¹¹⁵⁹ W. S. Felps, S. P. McGlynn, and G. L. Findley, *J. Mol. Spectrosc.*, 1981, **86**, 71.¹¹⁶⁰ Y. Hamada, A. J. Merer, S. Michielsen, and S. A. Rice, *J. Mol. Spectrosc.*, 1981, **86**, 499.¹¹⁶¹ S. Michielsen, A. J. Merer, S. A. Rice, F. A. Novak, K. F. Freed, and Y. Hamada, *J. Chem. Phys.*, 1981, **74**, 3089.¹¹⁶² J. M. Dyke, N. K. Fayad, G. D. Josland, and A. Morris, *J. Chem. Soc., Faraday Trans. 2*, 1980, **76**, 1672.¹¹⁶³ E. P. F. Lee and A. W. Potts, *Chem. Phys. Lett.*, 1980, **76**, 532.¹¹⁶⁴ S. Tobay and F. S. Tobay, *J. Phys. Chem.*, 1981, **85**, 4071.¹¹⁶⁵ J. M. Dyke, N. Jonathan, A. Morris, and M. J. Winter, *J. Chem. Soc., Faraday Trans. 2*, 1981, **77**, 667.¹¹⁶⁶ M. Vogler, *Phys. Rev. A*, 1979, **19**, 1.¹¹⁶⁷ J. K. G. Watson, *Phys. Rev. A*, 1980, **22**, 2279.¹¹⁶⁸ H. F. King and K. Morokuma, *J. Chem. Phys.*, 1979, **71**, 3213.¹¹⁶⁹ I. Dabrowski and G. Herzberg, *Can. J. Phys.*, 1980, **58**, 1238; erratum, 1980, **58**, 1524.¹¹⁷⁰ G. Herzberg and J. K. G. Watson, *Can. J. Phys.*, 1980, **58** 1250; erratum, 1980, **58**, 1524.¹¹⁷¹ G. Herzberg, *Faraday Discuss. Chem. Soc.*, 1981, **71**, 165.¹¹⁷² G. Herzberg, H. Lew, J. J. Sloan, and J. K. G. Watson, *Can. J. Phys.*, 1981, **59**, 428.¹¹⁷³ G. D. Carney, *J. Chem. Phys.*, 1981, **74**, 3077.¹¹⁷⁴ S. C. Goh and J. B. Swan, *Phys. Rev. A*, 1981, **24**, 1624.¹¹⁷⁵ R. I. Patel, G. W. Stewart, K. Casleton, J. L. Gole, and J. R. Lombardi, *Chem. Phys.*, 1980, **52**, 461.¹¹⁷⁶ M. Kakimoto, S. Saito, and E. Hirota, *J. Mol. Spectrosc.*, 1981, **88**, 300.¹¹⁷⁷ T. Suzuki, S. Saito, and E. Hirota, *J. Mol. Spectrosc.*, 1981, **90**, 447.

Table 12 (continued)

Molecule	Technique	Comments	Ref.
^{1,2} HCN	absorption	80—130 nm	1178
HCN	photofragment fluorescence polarization	excitation at Lyman α	1179
HCN	<i>ab initio</i>	intravalance triplet-triplet transition	1180
HCO	PES	first IP; adiabatic IP not directly observed; ΔH_f^\ominus	1181a
HCO	<i>ab initio</i>	lowest four doublet states	1181b
HCO	absorption (UV)	flash photolysis of $\text{H}_2\text{O}/\text{CO}$	1182
^{1,2} HCP ⁺	emission (electron beam excited)	$\text{A}^2\Sigma^+ \rightarrow \text{X}^2\Pi$; $\text{A}_0'', \nu_3'', \tau'$	1183
HNO	MODR	$\tilde{\text{A}}^1\text{A}''(100)$; a and b type transitions	1184
HNO	OODR	$\tilde{\text{A}}^1\text{A}''$, dipole moment	1185
HNO	LIF	magnetic and time-resolved studies; perturbations of $\tilde{\text{A}}^1\text{A}''$	1186
HNO	LIF	mechanism of predissociation of $\tilde{\text{A}}^1\text{A}''$	1187
HO_2^+	PES	progression in $\nu(\text{O}-\text{O})$ stretch IP, ΔH_f^\ominus	1188
^{1,2} H ₂ O	absorption	rotational structure of bands below 120 nm	1189
H ₂ O	TPES	ion fragmentation	1190
H ₂ O	photofragment fluorescence polarization	11.9—500 eV electrons	1191
H ₂ O	as above	9.3—500 eV electrons; fluorescence unpolarized for $E_i > 150$ eV	1192
^{1,2} H ₂ O	dissociative attachment	energy, angular dependence of ^{1,2} H ⁻ : most energy goes as translation	1193
H ₂ S	(e, 2e)	cf. CH ₄ , NH ₃ , PH ₃ , H ₂ O	1194
H ₂ S	absorption (synchrotron)	Rydberg transitions, 110—150 nm; <i>d</i> series to $n = 26$ gives IP; cf. H ₂ O	1195
H ₂ S	MPI	resonantly enhanced; multiple path model discussed	1196
H ₂ S ⁺	electron impact/drift tube	collision-induced dissociation, lifetimes	1197

1178 T. Nagata, T. Kondow, Y. Ozaki, and K. Kuchitsu, *Chem. Phys.*, 1981, **57**, 45.

1179 T. Nagata, T. Kondow, and K. Kuchitsu, *Chem. Phys. Lett.*, 1981, **81**, 391.

1180 W. D. Laidig and H. F. Schaeffer, III, *J. Chem. Phys.*, 1980, **73**, 1470.

1181 (a) J. M. Dyke, N. B. H. Jonathan, A. Morris, and M. J. Winter, *Mol. Phys.*, 1980, **39**, 629; (b) K. Tanaka and K. Takeshita, *Chem. Phys. Lett.*, 1982, **87**, 373.

1182 C. J. Hochanadel, T. J. Sworski, and P. J. Ogren, *J. Phys. Chem.*, 1980, **84**, 231.

1183 M. A. King, H. W. Kroto, J. F. Nixon, D. Klapstein, J. P. Maier, and O. Marthaler, *Chem. Phys. Lett.*, 1981, **82**, 543.

1184 K. Takagi, S. Saito, M. Kakimoto, and E. Hirota, *J. Chem. Phys.*, 1980, **73**, 2570.

1185 R. N. Dixon and M. Noble, *Chem. Phys.*, 1980, **50**, 331.

1186 R. N. Dixon, M. Noble, C. A. Taylor, and M. Delhoume, *Faraday Discuss. Chem. Soc.*, 1981, **71**, 125.

1187 R. N. Dixon, K. B. Jones, M. Noble, and S. Carter, *Mol. Phys.*, 1981, **42**, 455.

1188 J. M. Dyke, N. B. H. Jonathan, A. Morris, and M. J. Winter, *Mol. Phys.*, 1981, **44**, 1059.

1189 J. P. Connerade, M. A. Baig, S. P. McGlynn, and W. R. S. Garton, *J. Phys. B*, 1980, **13**, L705.

1190 R. Stockbauer, *J. Chem. Phys.*, 1980, **72**, 5277.

1191 K. Becker, B. Stumpf, and G. Schulz, *Chem. Phys.*, 1980, **53**, 31.

1192 K. Becker, B. Stumpf, and G. Schulz, *J. Phys. B*, 1981, **14**, L517.

1193 D. S. Belic, M. Landau, and R. I. Hall, *J. Phys. B*, 1981, **14**, 175.

1194 J. P. D. Cook, C. E. Brion, and A. Hamnett, *Chem. Phys.*, 1980, **45**, 1.

1195 M. A. Baig, J. Hormes, J. P. Connerade, and S. P. McGlynn, *J. Phys. B*, 1981, **14**, L725.

1196 T. E. Carney and T. Baer, *J. Chem. Phys.*, 1981, **75**, 4422; J. C. Miller, R. N. Compton, T. E. Carney, and T. Baer, *ibid.*, 1982, **76**, 5648; Y. Achiba, K. Sato, K. Shobatake, and K. Kimura, *ibid.*, 1982, **77**, 2709.

1197 S. K. Hindawi, V. Mercea, and A. Panula, *Int. J. Mass Spectrom. Ion Phys.*, 1980, **36**, 271.

Table 12 (continued)

Molecule	Technique	Comments	Ref.
H ₂ S ⁺	laser/ion beam	Ā ² A ₁ –Ā ² B ₁ ; monitor S ⁺ from pre-dissociation	1198
HSO	LIF	Ā ² A'(002)–Ā ² A''(000), 16 420–16 520 cm ⁻¹	1199
HSO	LIF	Ā ² A'–Ā ² A'', 570–700 nm; $\tau = 11.3 \mu\text{s}$; progression in SO stretch as ref. 1199	1200
² HSO			1201
HgBr ₂	photofragment fluorescence polarization	¹ S _g ⁺ (¹ A ₁) → ¹ B ₂ (¹ S _u ⁺)	1202
HgBr ₂ HgCl ₂	<i>ab initio</i>	low-lying excited states	1203
HgBr ₂ HgCl ₂	absorption	170–230 nm	1204
HgI ₂			
ICN	photofragment spectroscopy	branching ratios from Ā state photolysis	1205
KrXeBr			
KrXeCl	emission	bands in UV; no KrXeF emission found	1206
KrXeI			
Mg ₃	MCD	matrix spectra	1207
MgOH	<i>ab initio</i>	structure and electronic properties	1120
NH ₂	MODR	Ā ² A''; a-type rotational, and magnetic dipole, transitions	1208
NH ₂	PES	ionization to Ā ³ B ₁ , ¹ A ₁ , and ¹ B ₁ (<i>cf.</i> CH ₂)	1209
N ¹ H ² H	MODR	g.s. transitions in 4–12 GHz range; also ₁ ¹⁰ – ₁ ¹¹ near 73 GHz	1210
N ₂ O	absorption	172–197 nm; increasing structure at higher <i>T</i> , due to excited bending mode	1211
N ₂ O	PES	vibronic interaction and autoionization; X ² Π, A ² Σ ⁺ , C ² Σ ⁺	1212
N ₂ O	PES	spin polarization	1134
N ₂ O	PES	branching in autoionization see CO ₂ , ref. 1138	1153
N ₂ O ⁺	emission (electron beam excited)	τ_c of A ² Σ ⁺	1213
N ₂ O ⁺	laser/ion beam	rotationally resolved predissociation in near UV	1214

1198 C. P. Edwards, C. S. Maclean, and P. J. Sarre, *Chem. Phys. Lett.*, 1982, **87**, 11.1199 M. Kakimoto, S. Saito, and E. Hirota, *J. Mol. Spectrosc.*, 1980, **80**, 334.1200 M. Kawasaki, K. Kasatani, and H. Sato, *Chem. Phys. Lett.*, 1980, **75**, 128.1201 N. Ohashi, M. Kakimoto, S. Saito, and E. Hirota, *J. Mol. Spectrosc.*, 1980, **84**, 204.1202 J. Husain, J. R. Wiesenfeld, and R. N. Zare, *J. Chem. Phys.*, 1980, **72**, 2479.1203 W. R. Wadt, *J. Chem. Phys.*, 1980, **72**, 2469.1204 C. Roxio and A. Mandl, *J. Appl. Phys.*, 1980, **51**, 2969.1205 W. M. Pitts and A. P. Baronavski, *Chem. Phys. Lett.*, 1980, **71**, 395.1206 H. C. Brashears, jun., D. W. Setser, and Y.-C. Yu, *J. Chem. Phys.*, 1981, **74**, 10.1207 J. C. Miller, R. L. Mowery, E. R. Krausz, S. M. Jacobs, H. W. Kim, P. N. Schatz, and L. Andrews, *J. Chem. Phys.*, 1981, **74**, 6349.1208 T. C. Steimle, J. M. Brown, and R. F. Curl, jun., *J. Chem. Phys.*, 1980, **73**, 2552.1209 S. J. Dunlavy, J. M. Dyke, N. Jonathan, and A. Morris, *Mol. Phys.*, 1980, **39**, 1121.1210 J. M. Brown and T. C. Steimle, *Astrophys. J. Lett.*, 1980, **236**, L101.1211 G. S. Selwyn and H. S. Johnston, *J. Chem. Phys.*, 1981, **74**, 3791.1212 P. M. Dehmer, J. L. Dehmer, and W. A. Chupka, *J. Chem. Phys.*, 1980, **73**, 126.1213 D. Klapstein and J. P. Maier, *Chem. Phys. Lett.*, 1981, **83**, 590.1214 M. Larziliere, M. Carre, M. L. Gaillard, J. Rostas, M. Horani, and M. Velghe, *J. Chim. Phys., Phys. Chim. Biol.*, 1980, **77**, 689.

Table 12 (continued)

Molecule	Technique	Comments	Ref.
N_2O^+	PE-photon coincidence	quantum yields, lifetimes, for fluorescence	1143
NO_2	MODR	spin-rotation parameters in $\tilde{\text{X}}^2\text{A}_1$	1215
NO_2	LIF, s/s beam	sub-Doppler, analysis of ${}^1\text{B}_2 - \tilde{\text{X}}^2\text{A}_1$, 16 862—16 883 cm^{-1} , hfs	1216
NO_2	Hanle effect interpretation	two asymmetric equilibrium configurations of non-rigid NO_2	1217
NO_2	LIF, s/s beam	370—600 nm; onset of predissociation	1218
NO_2	polarization labelling	${}^2\text{B}_2 - {}^2\text{A}_1$	1219
NO_2	FT absorption, analysis	739 and 793.7 nm bands	1220
NO_2	MPI: 2 Torr, flow and mol. beam	420—520 nm: above 500 nm, 3 photon REMPI; below 500 nm, increasing fraction 2-photon dissociated to $\text{NO} + \text{O}$	1221
NO_2	LIF	excite at 532 nm, $T = 175$ —356 K; breakdown in ΔK selection rules	1222
NO_2	LIF	excite at 488 nm; anomalies in selection rules	1223
NO_2	LIF, s/s jet	445—460 nm; emission to $v_3 = 1$ observed	1224
NO_2	level crossing, beam and bulb	$\tau_{\text{R}}/\tau_{\text{Hanle}}$ discussed	1225
NO_2	level crossing; RFODR	irregular g-factor in ${}^2\text{B}_2$	1226
$^{15}\text{NO}_2$	absorption	249 nm band: predissociated rotational structure	1227
NO_2^-	photodetachment	435—540 nm, 260—355 nm	1228
O_3	photodissociation	$\text{O}(^1\text{S})$ yield from dissociation 170—240 nm	1229
O_3	PES	double breakdown of Koopman's theorem in HeII PES	1230
OCS	absorption, PI	oscillator strengths 5—50 eV	1231
OCS		see CO_2 , ref. 1136	
OCS	electron impact	5—17 eV, 30 meV resolution	1232
OCS	mol. beam PI	PI efficiency for ${}^2\Pi_{3/2}$ and ${}^2\Pi_{1/2}$, ≈11 eV	1233
OCS	TPES	11—19 eV; autoionization 12—16 eV; $\tilde{\text{X}}$, $\tilde{\text{A}}$, $\tilde{\text{B}}$, $\tilde{\text{C}}$ ionic states	1234
OCS		see CS_2 , ref. 1151	

1215 J. M. Brown, T. C. Steinle, M. E. Coles, and R. F. Curl, jun., *J. Chem. Phys.*, 1981, **74**, 3668.1216 H. J. Foth, H. J. Vedder, and W. Demtröder, *J. Mol. Spectrosc.*, 1981, **88**, 109.1217 H. G. Weber, *J. Mol. Struct.*, 1980, **61**, 141.1218 C. H. Chen, D. W. Clark, M. G. Payne, and S. D. Kramer, *Opt. Commun.*, 1980, **32**, 391.1219 J. C. D. Brand, K. J. Goss, and N. P. Ernsting, *Chem. Phys.*, 1981, **59**, 405.1220 A. Perrin, C. Camy-Peyret, J.-M. Fland, and P. Luc, *J. Mol. Spectrosc.*, 1981, **88**, 237.1221 R. J. S. Morrison, B. H. Rockney, and E. R. Grant, *J. Chem. Phys.*, 1981, **75**, 2643.1222 D. G. Keil, V. M. Donnelly, and F. Kaufman, *J. Chem. Phys.*, 1980, **73**, 1514.1223 M. J. Armstrong, J. C. D. Brand, and C. di Lauro, *Can. J. Phys.*, 1981, **59**, 559.1224 I. Raitt, A. M. Griffiths, and P. A. Freedham, *Chem. Phys. Lett.*, 1981, **77**, 433.1225 F. Bylicki and H. G. Weber, *Chem. Phys. Lett.*, 1981, **79**, 355; *Phys. Lett. A*, 1981, **82**, 456.1226 F. Bylicki and H. G. Weber, *Chem. Phys. Lett.*, 1981, **79**, 517; 1982, **88**, 142.1227 A. S.-C. Cheung and A. J. Merer, *J. Mol. Spectrosc.*, 1980, **80**, 23.1228 S. B. Woo, E. M. Helmy, P. H. Mank, and A. P. Paszek, *Phys. Rev. A*, 1981, **24**, 1380.1229 L. C. Lee, G. Black, R. L. Sharpless, and T. G. Slanger, *J. Chem. Phys.*, 1980, **73**, 256.1230 N. Kosugi, H. Kuroda, and S. Iwata, *Chem. Phys.*, 1981, **58**, 267.1231 M. G. White, K. T. Leung, and C. E. Brion, *J. Electron Spectrosc.*, 1981, **23**, 127.1232 B. Leclerc, A., Poulin, D. Roy, M.-J. Hubin-Franskin, and J. Delwiche, *J. Chem. Phys.*, 1981, **75**, 5329.1233 Y. Ono, E. A. Osuch, and C. Y. Ng, *J. Chem. Phys.*, 1981, **74**, 1645.1234 J. Delwiche, M.-J. Hubin-Franskin, P.-M. Guyon, and I. Nenner, *J. Chem. Phys.*, 1981, **74**, 4219.

Table 12 (continued)

Molecule	Technique	Comments	Ref.
OCS	PES	s-o components of A ² Π; autoionizing Rydberg state around 73.7 nm	1235
OCS	electron impact	Rydberg levels converging to A ² Π, B ² Σ ⁺ , and C ² Σ ⁺	1156
OCS ⁺		see CO ₂ ⁺ , ref. 1143	
OCS ⁺	high frequency deflection	A ² Π _{3/2} , $\tau = 103 \pm 3$ ns A ² Π _{1/2} , $\tau = 77 \pm 3$ ns	1236
OCS ⁺		see N ₂ O ⁺ , ref 1213	
OCSe	fluorescence excitation	Se (‘S → ‘P) laser [Φ Se(‘S) ~0.6, 160–180 nm]	1237
SO ₂	LIF	294–328 nm; interaction of ‘B ₁ and ¹ A ₂	1239
SO ₂	LIF	Ā ¹ A ₂ , 304.3 nm (‘E) band; $\tau = 13.4 \pm 1.3$ μs	1240
SO ₂	LIF	Ā ¹ A ₂ , collision-induced rotational transitions, propensity rules	1241
SO ₂	MPI, beam and bulb; thermal lensing	³ B ₁ – ¹ A ₁ single photon region (360–390 nm)	1242
SO ₂	LIF, s/s beam	Ā state lifetime	1243
SO ₂	absorption	cross-sections 290–317 nm	1244
SO ₂	emission	magnetic quenching of fluorescence and phosphorescence	1245
SO ₂	absorption (and dye laser)	linewidth 2×10^{-6} nm; absorption coefficients of 200 nm band, <i>T</i> dependence	1246
SO ₂	2 photon	Ā ¹ B ₂ , mechanism of photodissociation	1247
SO ₂	quantum beats (s/s beam)	Ā ¹ B ₂ , ‘resonance limit’	1248
SO ₂	IRMPPE	inverse electronic relaxation; luminescence (270–470 nm) from SO ₂	1249
SO ₂	electron impact	undetected triplets, 4–11 eV; optical measurements 50–320 nm	1250
SO ₂	absorption, fluorescence excitation	17.5–76 nm, dissociative ion states	1251
SO ₂	mol. beam PI	60–106 nm	1252
S ₂ O	absorption	190–230 nm: bands assigned to S ₂ O seem to arise from SO ₂	1253

¹²³⁵ J. Delwiche, M.-J. Hubin-Franskin, G. Caprace, P. Natalis, and D. Roy, *J. Electron Spectrosc.*, 1980, **21**, 193.

¹²³⁶ P. Erman and M. Larsson, *Phys. Scr.*, 1981, **23**, 1052.

¹²³⁷ W. M. Trott, J. R. Woodworth, J. K. Rice, and C. K. Miller, *J. Appl. Phys.*, 1981, **52**, 5811.

¹²³⁸ R. J. Shaw, J. E. Kent, and M. F. O'Dwyer, *J. Mol. Spectrosc.*, 1980, **82**, 1.

¹²³⁹ D. L. Holtermann, E. K. C. Lee, and R. Nanes, *Chem. Phys. Lett.*, 1980, **75**, 91.

¹²⁴⁰ D. L. Holtermann, E. K. C. Lee, and R. Nanes, *Chem. Phys. Lett.*, 1980, **75**, 249.

¹²⁴¹ S. D. Colson, W. Y. Cheung, J. H. Glowina, and S. J. Riley, *Chem. Phys. Lett.*, 1980, **76**, 515.

¹²⁴² H. Watanabe, Y. Hyodo, S. Tsuchiya, and S. Koda, *Chem. Phys. Lett.*, 1981, **81**, 439.

¹²⁴³ D. J. Brassington, *Appl. Opt.*, 1981, **20**, 3774.

¹²⁴⁴ V. I. Makarov, N. L. Lavrik, G. I. Skubnevskaya, and N. M. Bazhin, *Opt. Spectrosc.*, 1981, **50**, 154.

¹²⁴⁵ B. R. Marx, K. P. Birch, R. C. Felton, B. W. Jolliffe, W. R. C. Rawley, and P. T. Woods, *Opt. Commun.*, 1980, **33**, 287.

¹²⁴⁶ R. Vasudev and W. M. McClain, *J. Mol. Spectrosc.*, 1981, **89**, 125.

¹²⁴⁷ W. Sharfin, M. Ivanco, and S. C. Wallace, *J. Chem. Phys.*, 1982, **76**, 2095.

¹²⁴⁸ G. L. Wolk, R. E. Weston, jun., and G. W. Flynn, *J. Chem. Phys.*, 1980, **73**, 1649.

¹²⁴⁹ L. Vuskovic and S. Trajmar, *J. Raman Spectrosc.*, 1981, **10**, 136.

¹²⁵⁰ C. Y. Wu and D. L. Judge, *J. Chem. Phys.*, 1981, **74**, 3805.

¹²⁵¹ J. Erickson and C. Y. Ng, *J. Chem. Phys.*, 1981, **75**, 1650.

¹²⁵² P. C. Sung and C. L. Chiu, *J. Mol. Spectrosc.*, 1980, **80**, 459.

Table 12 (continued)

Molecule	Technique	Comments	Ref.
TeBr_2	PES interpretation	effects of relativity	1254
TeCl_2			
Xe_3	PEPI, s/s jet	Xe_3 , cf. Xe_2	1255
XeF_2	polarized photofragment fluorescence	193 nm: Σ_u^+ symmetry for XeF_2	1256
YBr_2	LIF, chemiluminescence	chemiluminescence from dihalides, not monohalides, as earlier thought; also ScBr_2 , ScCl_2	1257
YCl_2			
ZnCl_2	PES	resolution 30 meV	1258
ZnF_2	PES	3d orbitals of core character, cf. CuF_2	1162

Table 13 Electronic spectroscopic studies of tetra-atomic molecules. Molecules are listed in alphabetical order.

Molecule	Technique	Comments	Ref.
BrN_3	PES	cf. ab initio and semi-empirical calculations; reassessments for parent acids HN_3 and HNCO in high energy region	1259
BrNCO			
CH_3	MPI	npe' (E') and $npa_2(^2\text{A}_2'')$ Rydberg states	1260
CH_3	MPI	$^2\text{A}_1'$, $^2\text{E}'$, and $^2\text{A}_1''$ states (β , γ , and δ series)	1261
C_2H_2	laser intracavity	weak bands $\Pi_u^- - \Sigma_g^+$, 9366.6 and 9407.7 cm^{-1}	1262
C_2H_2	PES (synchrotron)	energy dependence of satellite line intensity	1263
C_2H_2	PI	cross-sections, angular distributions 12—50 eV	1264
C_2H_2	PES	'perfluoro effect' investigated	1265
C_2HF			
C_2F_2			
$\text{C}_2^{1,2}\text{H}_2$	absorption	126—137 nm: confirms presence of $\tilde{\text{D}}$, $\tilde{\text{E}}$, and $\tilde{\text{F}}$ Rydberg states	1267
C_2H_2	PES	angular distributions: $\pi\beta$ parameter lower than for double bond in C_2H_4	1267
C_2H_2^+	PES (synchrotron)	effect of a resonance on vibrational structure, $h\nu \sim 14 \text{ eV}$	1268

1254 G. Jonkers, C. A. de Lange, and J. G. Snijders, *Chem. Phys.*, 1980, **50**, 11.1255 E. D. Poliakoff, P. M. Dehrer, J. L. Dehrer, and R. Stockbauer, *J. Chem. Phys.*, 1981, **75**, 1568.1256 G. W. Loge and J. R. Wiesenfeld, *Chem. Phys. Lett.*, 1981, **78**, 32.1257 H. C. Braynan, D. R. Fischell, and T. A. Cool, *J. Chem. Phys.*, 1980, **73**, 4247.1258 G. M. Bancroft, D. J. Bristow, and L. L. Coatsworth, *Chem. Phys. Lett.*, 1981, **81**, 344.1259 D. C. Frost, C. B. MacDonald, C. A. McDowell, and N. P. C. Westwood, *Chem. Phys.*, 1980, **47**, 111.1260 T. G. Di Giuseppe, J. W. Hudgens, and M. C. Lin, *J. Chem. Phys.*, 1982, **76**, 3337.1261 T. G. Di Giuseppe, J. W. Hudgens, and M. C. Lin, *J. Phys. Chem.*, 1982, **86**, 36.1262 L. N. Sinitsa, *J. Mol. Spectrosc.*, 1980, **84**, 57.1263 A. M. Bradshaw, W. Eberhardt, H. J. Levinson, W. Domcke, and L. S. Cederbaum, *Chem. Phys. Lett.*, 1980, **70**, 36.1264 J. Kreile, A. Schweig, and W. Thiel, *Chem. Phys. Lett.*, 1981, **79**, 547.1265 G. Bieri, A. Schmelzer, L. Åsbrink, and M. Jonsson, *Chem. Phys.*, 1980, **49**, 213.1266 M. Herman and R. Colin, *J. Mol. Spectrosc.*, 1981, **85**, 449.1267 J. Kreile and A. Schweig, *Chem. Phys. Lett.*, 1980, **69**, 71.1268 R. Unwin, I. Khan, N. V. Richardson, A. M. Bradshaw, L. S. Cederbaum, and W. Domcke, *Chem. Phys. Lett.*, 1981, **77**, 242.

Table 13 (continued)

Molecule	Technique	Comments	Ref.
$\text{C}_2^{1,2}\text{HBr}$	absorption	intermediate coupling analysis of low energy $\pi \rightarrow \sigma$ Rydberg transitions	1269
$\text{C}_2^{1,2}\text{HCl}^+$	emission (electron beam excited)	radiationless transitions, multiexponential decays, hot ground states	1270
Cl_2CS	absorption	$\tilde{\text{B}}^1\text{A}_1 - \tilde{\text{X}}^1\text{A}_1$	1271
Cl_2CS	two-photon (sequential)	delayed fluorescence from energy pooling	1272
Cl_2CS	LIF, s/s jet	$2S_1 \rightarrow S_0 + S_0$	1273
Cl_2CS	LIF, magnetic rotation	$\tilde{\text{A}}^1\text{A}_2 - \tilde{\text{X}}^1\text{A}_1$, hot bands identified, assignments adjusted	1274
Cl_2CS	LIF	$\tilde{\text{B}}^1\text{A}_1$	1275
Cl_2CS	LIF	$\tilde{\text{B}}^1\text{A}_1$, lifetimes	1276
ClFCS	absorption	260–283 nm, analysis: $\tilde{\text{B}}^1\text{A}' - \tilde{\text{X}}^1\text{A}'$	1277
ClFCS	LIF	$\tilde{\text{B}}^1\text{A}' - \text{X}^1\text{A}'$	1278
Cl_3N_3		see BrN_3 , ref. 1259	
H_2CO	LIF	$S_1, 4_1^1$ band; electric field dependence of SRL lifetimes; S_0 resonances $\sim 28\ 000\ \text{cm}^{-1}$	1279
$^{1,2}\text{H}_2\text{CO}$	LIF	4^1 (4^3 in D_2CO); electric field and vibrational state dependence of SRL lifetimes	1280
H_2CO	LIF	v_3 in S_1	1281
H_2CO	LIF	4_0^1 ; measures 'absorption coefficients'	1282
$^{2}\text{H}_2\text{CO}$	LIF	4^1 ; rotational relaxation (4_2^1 emission)	1283
H_2CO	LIF	4^1 ; rotational relaxation, pressure dependence of Φ_{f_1}	1284
$^{2}\text{H}_2\text{CO}, ^1\text{H}_2\text{HCO}$	IRUVDR	CO_2 laser, then $S_0 - S_1$ excited	1285
$^{2}\text{H}_2\text{CO}$	IRUVDR	as above: v_4 , then 4_1^1 , gives fluorescence at $\sim 420\ \text{nm}$	1286
$^{2}\text{H}_2\text{CO}$	IRUVDR	as above: rotational relaxation cross-sections up to 5 times gas kinetic	1287

1269 W. S. Felps, G. L. Findley, and S. P. McGlynn, *Chem. Phys. Lett.*, 1981, **81**, 491.1270 G. Dujardin, S. Leach, G. Taieb, J. P. Maier, and W. M. Gelbart, *J. Chem. Phys.*, 1980, **73**, 4987.1271 R. H. Judge and D. C. Moule, *J. Mol. Spectrosc.*, 1980, **80**, 363.1272 D. J. Clouthier, A. R. Knight, R. P. Steer, and P. A. Hackett, *J. Chem. Phys.*, 1980, **72**, 1561.1273 R. Vasudev, Y. Hirata, E. C. Lim, and W. M. McClain, *Chem. Phys. Lett.*, 1980, **76**, 249.1274 D. J. Clouthier and D. C. Moule, *J. Mol. Spectrosc.*, 1981, **87**, 471.1275 D. J. Clouthier, A. R. Knight, R. P. Steer, and P. A. Hackett, *Chem. Phys.*, 1980, **48**, 1.1276 D. J. Clouthier, A. R. Knight, R. P. Steer, and P. A. Hackett, *Chem. Phys. Lett.*, 1980, **70**, 89.1277 D. J. Clouthier, A. R. Knight, R. P. Steer, R. H. Judge, and D. C. Moule, *J. Mol. Spectrosc.*, 1980, **83**, 148.1278 D. J. Clouthier, A. R. Knight, R. P. Steer, and P. A. Hackett, *Chem. Phys.*, 1980, **48**, 13.1279 J. C. Weisshaar and C. B. Moore, *J. Chem. Phys.*, 1980, **72**, 2875.1280 J. C. Weisshaar and C. B. Moore, *J. Chem. Phys.*, 1980, **72**, 5415.1281 C. M. L. Kerr and D. A. Ramsay, *J. Mol. Spectrosc.*, 1981, **87**, 575.1282 P. W. Fairchild, N. L. Garland, W. E. Howard, III, and E. K. C. Lee, *J. Chem. Phys.*, 1981, **73**, 3046; erratum, **74**, 5928.1283 P. W. Fairchild and E. K. C. Lee, *J. Phys. Chem.*, 1980, **84**, 3346.1284 P. W. Fairchild, K. Shibuya, and E. K. C. Lee, *J. Chem. Phys.*, 1981, **75**, 3407.1285 B. J. Orr and G. F. Nutt, *J. Mol. Spectrosc.*, 1980, **84**, 272.1286 B. J. Orr and G. F. Nutt, *Opt. Lett.*, 1980, **5**, 12.1287 B. J. Orr, J. G. Haub, G. F. Nutt, J. L. Steward, and O. Vozzo, *Chem. Phys. Lett.*, 1981, **78**, 621.

Table 13 (continued)

Molecule	Technique	Comments	Ref.
$^2\text{H}_2\text{CO}$	LIF	$4^0, 4^1$; magnetic field effects (oscillation)	1288
$^{1,2}\text{H}_2\text{CO}$	LIF	4^1 ; SRL radiative and non-radiative decay rates, Φ_{fl}	1289
H_2CO	LIF, s/s jet absorption	$4_0^1, 4_0^3$; dependence on J, K	1290
H_2^{13}CO		300—360 nm: $4_0^1, 4_0^3, 2_0^1 4_0^1$ (Type B); $4_0^2 6_0^2$ (Type C); perturbations	1291
HC_2S	absorption	thiophene flash photolysed; absorption 377—417 nm; tentatively linear $^2\Pi(b)-^2\Pi(b)$	1292
H_2CS	absorption	$\tilde{\alpha}^3\text{A}_2-\tilde{\chi}^1\text{A}_1$, analysis	1293
H_2CS	LIF	SRL, $v_2'', v_2'' + v_3''$, $\tilde{\chi}^1\text{A}_2-\tilde{\chi}^1\text{A}_1$ see BrN ₃ , ref. 1259	1294
INCO			
Li_4	<i>ab initio</i>	rhombic (singlet) and bent square (triplet) most stable; spin coupling important	1295
Mg_4	<i>ab initio</i>	chemical bonding originating from electron correlation effects alone	1296
NH_3	MPI, s/s jet	300—500 nm; quantitative analysis of rotational intensities; C' characterization confirmed	1297
NH_3	MPI, s/s jet	MPI, cf. VUV; new state assignments 5.7—9.3 eV	1298
NH_3	band shape calculation	continuum under $\tilde{\alpha}-\tilde{\chi}$ transition arises from overlapping tails of vibronic line shapes	1299
NH_3	MPI	analysis of vibronic intensities and rotational line strengths for 3-photon spectrum	1300
NH_3	IRUVDR	$n \rightarrow 3s$; hot band spectra, optical density transients	1301
Na_4		see Li_4 , ref. 1295	
ONCN	PES	molecule as loosely bound ON and CN fragments	1302
PbF_3^-	matrix isolation	300—600 nm, with Cs^+ in ion pair	1303

1288 H. Orita, H. Morita, and S. Nagakura, *Chem. Phys. Lett.*, 1981, **81**, 409.1289 K. Shibuya, P. W. Fairchild, and E. K. C. Lee, *J. Chem. Phys.*, 1981, **75**, 3397.1290 W. E. Henke, H. L. Selze, T. R. Hays, E. W. Schlag, and S. H. Lin, *J. Chem. Phys.*, 1982, **76**, 1327.1291 F. W. Birss, R. M. Gordon, D. A. Ramsay, and S. M. Till, *Can. J. Phys.*, 1980, **57**, 1676.1292 S. L. N. G. Krishnamachari and D. A. Ramsay, *Faraday Discuss. Chem. Soc.*, 1981, **71**, 205.1293 R. H. Judge, D. C. Moule, and G. W. King, *J. Mol. Spectrosc.*, 1980, **81**, 37.1294 D. J. Clouthier, C. M. L. Kerr, and D. A. Ramsay, *Chem. Phys.*, 1981, **56**, 73.1295 H.-O. Beckmann, J. Kontecky, and V. Bonacic-Konetzky, *J. Chem. Phys.*, 1980, **73**, 5183.1296 R. A. Chiles, C. E. Dykstra, and K. D. Jordan, *J. Chem. Phys.*, 1981, **75**, 1044.1297 J. H. Glownia, S. J. Riley, S. D. Colson, and G. C. Nieman, *J. Chem. Phys.*, 1980, **72**, 5998.1298 J. H. Glownia, S. J. Riley, S. D. Colson, and G. C. Nieman, *J. Chem. Phys.*, 1980, **73**, 4297.1299 Ph. Avowis, A. R. Rossi, and A. C. Albrecht, *J. Chem. Phys.*, 1981, **74**, 5516.1300 G. C. Nieman, *J. Chem. Phys.*, 1981, **75**, 584.1301 M. B. Robin and N. A. Kuebler, *Chem. Phys. Lett.*, 1981, **80**, 512.1302 G. Jonkers, R. Mooyman, and C. A. de Lange, *Chem. Phys.*, 1981, **57**, 97.1303 B. S. Ault, *J. Chem. Phys.*, 1981, **85**, 3083.

Table 14 Electronic spectroscopic studies of polyatomic molecules. Molecules are listed with increasing number of carbon atoms. For molecules containing carbon, listing is then with increasing number of hydrogen atoms. Listing is otherwise alphabetical

Molecule	Technique	Comments	Ref.
OsO ₄	2 photon	state below first strong 1 photon state (T_1 , electronic origin $27\ 295\ \text{cm}^{-1}$)	1304
NH ₄	emission	Rydberg states	1171
SO ₂ F	LIF		1305
SO ₃ F	LIF	band origin components at $19\ 383$ and $19\ 354\ \text{cm}^{-1}$; evidence that g.s. is not C_{3v}	1306
UF ₆	LIF	$\tilde{\Lambda}-\tilde{X}$: Arrhenius-type T dependence	1307
CCl ₄ CCl ₃ Br CF ₃ Br CF ₃ I CF ₄ ⁺	absorption	170—230 nm	1204
CFCl ₃ ⁺ CF ₃ NO	PEPI photodissociation (2 photon NO fluorescence)	\tilde{B}^2E ; does not relax by emission of photons, between 200 and 900 nm \tilde{D}^2E ; as above predissociation 600—800 nm	1308 1309
CF ₃ NO	LIF	$S_1 \rightarrow S_0$: promoting mode is a torsion (first example)	1310
CF ₃ NO CF ₃ NO CH ₂ FBr ⁺ CH ₂ FCl ⁺ CH ₂ FI ⁺	LIF, s/s jet LIF, s/s jet absorption	$\tilde{\Lambda}\Lambda'' \leftarrow \tilde{\Lambda}\Lambda'$: eclipsed g.s. FES solid Ar; photochemistry	1311 1312 1313
CH ₂ I ₂ CH ₃ Br	photodissociation MCD	$\Phi I(^2P_{1/2})$, 248—340 nm 5500—61 000 cm^{-1} ; s-Rydberg states	1314 1315
CH ₃ Br	PES	unpolarized radiation produces spin polarized photoelectrons	1316
C ^{1,2} H ₃ Br	absorption	intermediate coupling analysis, $\pi \rightarrow \sigma$ Rydberg transition	1269

1304 K. M. Swift and E. R. Bernstein, *J. Chem. Phys.*, 1981, **74**, 5981.

1305 C. H. Warren, *J. Mol. Spectrosc.*, 1980, **83**, 451.

1306 C. H. Warren, *J. Mol. Spectrosc.*, 1980, **84**, 102.

1307 W. W. Rice, R. C. Oldenborg, P. J. Wantuck, J. J. Tiee, and F. B. Wampler, *J. Chem. Phys.*, 1980, **73**, 3560.

1308 J. P. Maier and F. Thommen, *Chem. Phys. Lett.*, 1981, **78**, 54.

1309 M. P. Roellig, P. L. Houston, M. Asscher, and Y. Haas, *J. Chem. Phys.*, 1980, **73**, 5081.

1310 K. G. Spears and L. D. Hoffland, *J. Chem. Phys.*, 1981, **74**, 4765.

1311 B. M. De Koven, K. H. Fung, D. H. Levy, L. D. Hoffland, and K. G. Spears, *J. Chem. Phys.*, 1981, **74**, 4755.

1312 B. M. De Koven and D. H. Levy, *J. Chem. Phys.*, 1981, **74**, 1515.

1313 F. T. Prochaska and L. Andrews, *J. Chem. Phys.*, 1980, **73**, 2651.

1314 J. B. Koffend and S. R. Leone, *Chem. Phys. Lett.*, 1981, **81**, 136.

1315 S. P. McGlynn, J. D. Scott, W. S. Felps, and G. L. Findley, *J. Chem. Phys.*, 1980, **72**, 421.

1316 U. Heinzmann, B. Osterheld, F. Schafers, and G. Schonhense, *J. Phys. B*, 1981, **14**, L79.

Table 14 (continued)

Molecule	Technique	Comment	Ref.
CH_3I	absorption (synchrotron)	113—180 nm; ns , np and nd converging on $^2\text{E}_{3/2}$ and $^2\text{E}_{1/2}$ of ion; high n values	1317
$\text{C}^{1,2}\text{H}_3\text{I}$	absorption	massive vibronic coupling (dynamic Jahn-Teller) effect observed in 1st s -Rydberg of CD_3I	1318
$\text{C}^{1,2}\text{H}_3\text{I}$	2 photon MPI	49 000—55 000 cm^{-1} ; $1\ 5p\pi$ electron excited to 6s molecular Rydberg orbital	1319
$\text{C}^{1,2}\text{H}_3\text{I}^+$	photodissociation mass spectrometry	vibrational frequencies, $\tilde{\Lambda}$ state	1320
CH_3NO (and CX_3NO , X = Br, Cl, F)	PES	Koopman breakdown; strong lone pair interactions in nitroso group	1321
CH_3NO_2	electron impact (variable angle)	new triplet feature near 3.8 eV, other new features, 7—12 eV	1322
CH_3O	LIF, s/s jet	$\tilde{\Lambda}^2\text{A}_1-\tilde{\chi}^2\text{E}$	1323
CH_3O	LIF	$\tilde{\Lambda}^2\text{A}_1-\tilde{\chi}^2\text{E}$	1324
CH_3O	emission	$\tilde{\Lambda}^2\text{A}_1-\tilde{\chi}^2\text{E}$	1325a
CH_4	PES, angle resolved	threshold to 30 eV	1325b
C_2Cl_4	electron transmission	evidence for both Σ and Π temporary anion states	1326
C_2ClF_3	electron impact	optically forbidden valence shell transitions ~8.5 eV	1327
C_2F_4	PES	analysis by Green's function method	1328
$\text{C}_2\text{N}_2\text{S}_2$ (thiocyanogen)	PES	disulphide structure, dihedral angle 87.8°	1329a
C_2HCl_3		see C_2Cl_4 , ref. 1326	
C_2HF_3		see C_2F_4 , ref. 1328	
$\text{C}_2\text{H}_2\text{Cl}_2$ (<i>cis</i> , <i>trans</i> and 1,1-)		see C_2Cl_4 , ref. 1326	
$\text{C}_2\text{H}_2\text{F}_2$ (1,1-)		see C_2ClF_3 , ref. 1327	
$\text{C}_2\text{H}_2\text{F}_4$ (<i>cis</i> and <i>trans</i>)		see C_2F_4 , ref. 1328	
$\text{C}_2^{1,2}\text{H}_2\text{N}_4$ (s-tetrazine)	absorption	$\tilde{\Lambda}^1\text{B}_{3u}-\tilde{\chi}^1\text{A}_g$, 1D F-C analysis	1329b
$\text{C}_2^{1,2}\text{H}_2\text{N}_4$	LIF	$\tilde{\Lambda}^1\text{B}_{3u}$; vibrational relaxation non-statistical in early stages	1330

1317 M. A. Baig, J. P. Connerade, J. Dagata, and S. P. McGlynn, *J. Phys. B*, 1981, **14**, L25.1318 S. P. McGlynn, W. S. Felps, J. D. Scott, and G. L. Findley, *J. Chem. Phys.*, 1980, **73**, 4925.1319 D. H. Parker, R. Pandolfi, P. R. Stannard, and M. A. El-Sayed, *Chem. Phys.*, 1980, **45**, 27.1320 S. P. Goss, D. C. McGilvery, J. D. Morrison, and D. L. Smith, *J. Chem. Phys.*, 1981, 1820.1321 N. P. Ernsting, J. Pfab, J. C. Green, and J. Romalt, *J. Chem. Soc., Faraday Trans. 2*, 1980, **76**, 844.1322 W. M. Plicker, O. A. Mosher, and A. Kupperman, *J. Chem. Phys.*, 1980, **72**, 2789.1323 D. E. Powers, J. B. Hopkins, and R. E. Smalley, *J. Phys. Chem.*, 1981, **85**, 2711.1324 G. Inoue, H. Akimoto, and M. Okuda, *J. Chem. Phys.*, 1980, **72**, 1769.1325 (a) M. Sutoh, N. Washida, H. Akimoto, M. Nakamura, and M. Okuda, *J. Chem. Phys.*, 1980, **73**, 591; (b) G. V. Marr and R. A. Holmes, *J. Phys. B*, 1980, **13**, 939.1326 P. D. Burrow, A. Modelli, N. S. Chiu, and K. D. Jordan, *Chem. Phys. Lett.*, 1981, **82**, 270.1327 G. J. Verhaar and H. H. Brongersma, *Chem. Phys.*, 1980, **52**, 431.1328 G. Bieri, W. von Niessen, L. Åsbrink, and A. Svensson, *Chem. Phys.*, 1981, **60**, 61.1329 (a) D. C. Frost, C. Kirby, W. M. Lan, C. B. MacDonald, C. A. McDowell, and N. P. C. Westwood, *Chem. Phys. Lett.*, 1980, **69**, 1; (b) K. K. Innes, D. V. Brumbaugh, and L. A. Franks, *Chem. Phys.*, 1981, **59**, 439.1330 D. V. Brumbaugh and K. K. Innes, *Chem. Phys.*, 1981, **59**, 413.

Table 14 (continued)

Molecule	Technique	Comment	Ref.
C ₂ H ₂ O ₂ (glyoxal)	LIF, s/s jet	collision induced ISC; (0 ₀ , 2 ₀ ¹) ¹ A _u ← ¹ A _g excited, fluorescence and phosphorescence observed	1331
C ₂ H ₂ O ₂	anticrossing, RFODR	single-triplet coupling (weak coupling limit)	1332
C ₂ H ₂ O ₂	LIF	³ A _u ~ ¹ A _g ; spin-rotation decoupling in magnetic field	1333
C ₂ H ₂ O ₂	anticrossing	theory of positions of double resonances near S-T anticrossing	1334
C ₂ H ₂ O ₂ C ₂ H ₂ O ₂	anticrossing electron impact	theory of widths and intensities triplet n → π*, π → π* transitions; several triplet states located	1335 1336
C ₂ H ₂ O ₂	optoacoustic	T ₁ quenched by S ₀ to form long-lived intermediate M, which produces heat via M + M	1337
C ₂ H ₂ O ₂	LIF	predisociation in S ₁ zero-point level? product analysis suggests S ₁ initially decays to an intermediate	1338
C ₂ H ₂ O ₂ C ₂ H ₂ O ₂	LIF, s/s jet dissociation, product analysis	¹ A _u - ¹ A _g FES S ₁ dissociation via an intermediate	1339 1340
C ₂ H ₂ O ₂	LIF, photolysis (solid Ar)	S ₁ fluorescence, products from S ₂	1341
C ₂ H ₃	absorption	long-lived transient, 140—157 nm? see C ₂ Cl ₄ , ref. 1326	1342
C ₂ H ₃ Cl		see C ₂ ClF ₃ , ref. 1327	
C ₂ H ₃ F		see C ₂ F ₄ , ref. 1328	
C ₂ H ₃ F		$\tau = 0.8 \mu\text{s}$	
C ₂ ^{1,2} H ₃ O	LIF	see C ₂ Cl ₄ , ref. 1326	1343
C ₂ H ₄		see C ₂ ClF ₃ , ref. 1327	
C ₂ H ₄		lowest Rydberg state; 2 photon resonant at n → 3s	
C ₂ H ₄ O (CH ₃ CHO)	MPI	2 photon polarization ratio of n → 3s transition	1344
C ₂ H ₄ O	MPI		1345

1331 C. Jouvet and B. Soep, *J. Chem. Phys.*, 1980, **73**, 4127.1332 M. Lombardi, R. Jost, C. Michel, and A. Tramer, *Chem. Phys.*, 1980, **46**, 273.1333 C. Michel and C. Tric, *Chem. Phys.*, 1980, **50**, 341.1334 M. Lombardi, R. Jost, J. Michel, and A. Tramer, *Chem. Phys.*, 1981, **57**, 341.1335 M. Lombardi, R. Jost, C. Michel, and A. Tramer, *Chem. Phys.*, 1981, **57**, 355.1336 G. J. Verhaart and H. H. Brongersma, *Chem. Phys. Lett.*, 1980, **72**, 176.1337 M. B. Robin, N. A. Kuebler, K. Kaya, and G. J. Diebold, *Chem. Phys. Lett.*, 1980, **70**, 93.1338 G. W. Loge, C. S. Parmenter, and B. F. Rordorf, *Chem. Phys. Lett.*, 1980, **74**, 309.1339 M. Gurnick, J. Chaiken, T. Benson, and J. D. McDonald, *J. Chem. Phys.*, 1981, **74**, 99.1340 G. W. Loge and C. S. Parmenter, *J. Phys. Chem.*, 1981, **85**, 1653.1341 M. Diem, B. G. MacDonald, and E. K. C. Lee, *J. Phys. Chem.*, 1981, **85**, 2227.1342 A. H. Laufer, *J. Chem. Phys.*, 1980, **73**, 49.1343 G. Inoue and H. Akimoto, *J. Chem. Phys.*, 1981, **74**, 425.1344 B. A. Heath, M. B. Robin, N. A. Kuebler, G. J. Fisanick, and T. S. Eichelberger, IV, *J. Chem. Phys.*, 1980, **72**, 5565 and 5571.1345 B. A. Heath, G. J. Fisanick, M. B. Robin, and T. S. Eichelberger, IV, *J. Chem. Phys.*, 1980, **72**, 5991.

Table 14 (continued)

Molecule	Technique	Comment	Ref.
C ₂ H ₄ O	MPI beam and bulb	molecule remains planar in 2 photon resonant state; evidence for saturation	1346
C ₂ H ₄ O	emission	³ A'' phosphorescence	1347
C ₂ H ₄ S (thiirane)	electric dichroism	Rydberg absorptions	1348
C ₂ H ₄ Br	absorption	doubling of bands in first s- and p-Rydberg excitations due to vibronic coupling	1349
C ₂ H ₄ Br		see CH ₃ Br, ref. 1269	
C ₂ H ₄ I		see CH ₃ I, ref. 1319	
C ₂ H ₄ I ⁺		see CH ₃ I ⁺ , ref. 1320	
C ₂ H ₄ O	LIF	$\tilde{\Lambda}-\tilde{\chi}$; (0, 0) at 342.4 nm	1350
C ₂ H ₄ S (CH ₃ SCH ₃)		see C ₂ H ₄ S, ref. 1348	
C ₃ ^{1,2} HOCl (propiolyl chloride)	absorption	$n \rightarrow \pi^*$, 270—360 nm	1351
C ₃ ^{1,2} HOF (propiolyl fluoride)	absorption	$n \rightarrow \pi^*$, 260—303 nm; all bands rotationally diffuse	1352
C ₃ H ₃ N ₃ (s-triazine)	1- and 2-photon	¹ E'', vibronic assignments and coupling	1353
C ₃ H ₃ N ₃	LIF, s/s jet	$\tilde{\Lambda}^1E''-\tilde{\chi}^1A'$	1354
C ₃ H ₃ N ₃	LIF	$6_0^1, 6_0^2$ absorption bands; rotational effects on Φ and τ for slow fluorescence	1355
C ₃ H ₄ O ₂ (malonaldehyde)	absorption	¹ B ₁ - ¹ A ₁ ; 0 ⁺ /0 ⁻ tunnelling splitting suggests ¹ B ₁ less tightly H-bonded	1356
C ₃ H ₄ O (methyl glyoxal)		see C ₂ H ₂ O ₂ , ref. 1339	
C ₃ H ₄ O ₂	quantum beats	S-T coupling	1357
C ₃ H ₄ O ₂	LIF	magnetic field effect on two fluorescence components	1358
C ₃ H ₇	<i>ab initio</i>	comparison of 7 different configurations	1359
C ₃ H ₇ Br		see CH ₃ Br, ref. 1269	
C ₃ H ₇ Br		see C ₂ H ₅ Br, ref. 1349	
C ₃ H ₇ I		see CH ₃ I, ref. 1319	
C ₃ H ₇ I ⁺		see CH ₃ I ⁺ , ref. 1320	
C ₃ H ₈ N (trimethylamine)	2 photon	450—530 nm: vibrationally induced transitions, umbrella inversion at longer λ	1360

1346 T. S. Eichelberger, IV, and G. J. Fisanick, *J. Chem. Phys.*, 1981, **74**, 5962.1347 W. F. Beck, M. D. Schuh, and I. R. Williams, *Chem. Phys. Lett.*, 1981, **81**, 435.1348 D. D. Altenloh and B. R. Russell, *Chem. Phys. Lett.*, 1981, **77**, 217.1349 W. S. Felps, J. D. Scott, G. L. Findley, and S. P. McGlynn, *J. Chem. Phys.*, 1981, **74**, 4832.1350 G. Inoue, M. Okuda, and H. Akimoto, *J. Chem. Phys.*, 1981, **75**, 2060.1351 W. J. Balfour and S. Visaisouk, *J. Mol. Spectrosc.*, 1980, **80**, 117.1352 W. J. Balfour and S. Visaisouk, *J. Mol. Spectrosc.*, 1980, **80**, 109.1353 J. D. Webb, K. M. Swift, and E. R. Bernstein, *J. Chem. Phys.*, 1980, **73**, 4891.1354 M. Heaven, T. Sears, V. E. Bondybey, and T. A. Miller, *J. Chem. Phys.*, 1981, **75**, 5271.1355 N. Ohta and H. Baba, *Chem. Phys. Lett.*, 1981, **84**, 308.1356 C. J. Seliskar and R. E. Hoffmann, *J. Mol. Spectrosc.*, 1981, **88**, 30.1357 J. Chaiken, M. Gurnick, and J. D. McDonald, *J. Chem. Phys.*, 1981, **74**, 106.1358 K. Hashimoto, S. Nagakura, J. Nakamura, and S. Iwata, *Chem. Phys. Lett.*, 1980, **74**, 228.1359 J. Pacansky and M. Dupuis, *J. Chem. Phys.*, 1980, **73**, 1867.1360 K. Kasatani, M. Kawasaki, H. Sato, Y. Murasawa, K. Obi, and I. Tanaka, *J. Chem. Phys.*, 1981, **74**, 3164.

Table 14 (continued)

Molecule	Technique	Comment	Ref.
$C_4Cl_2^+$	emission, LIF and PE-photon coincidence	$\tilde{A}^2\Pi_{\Omega u}-X^2\Pi_{\Omega g}$	1361
C_4F_2 , C_4HCl^+ , C_4HF }	PES	'perfluro-effect' investigated see $C_4Cl_2^+$, ref. 1361	1265
C_4H_2 }		see C_4F_2 , ref. 1265	
$C_4^{1,2}H_4N_2$ (pyrazine)	LIF, absorption	$^1B_{3u}$; may be some lowering of molecular symmetry	1362
$C_4H_4N_2$	LIF, s/s jet	$^1B_{3u}$; rotational state dependence of non-radiative rate leading to biexponential decay	1363
$C_4H_4N_2$	LIF, absorption	Fermi resonance, Duschinski effect	1364
$C_4H_4N_2$	quantum beats	nuclear spin effects	1365
$C_4H_4N_2$ (pyrazine and pyrimidine)	LIF, absorption	rotational dependence of S-T coupling	1366
$C_4H_4N_2$	LIF, bulb and beam	effect of cooling on biexponential decay	1367
$C_4H_4N_2$	quantum beats	intermediate case	1368
$C_4H_4N_2$ (pyrimidine)	laser excitation	non-radiative decay, FC effects on ISC	1369
C_4H_6 (<i>trans</i> -1,3-butadiene)	electron impact	analysis of valence and Rydberg transitions	1370
C_4H_6	MPI	also methyl-substituted butadienes studied, leading to reassignment of spectra; little core/Rydberg mixing observed	1371
C_4H_6	MPI	615–675 nm; 4-photon resonant bound-bound excimer transition	1372
$C_4H_6N_4$ (dimethyl tetrazine)	emission	see $C_2H_2O_2$, ref. 1336	1373
$C_4H_6O_2$ (biacetyl)	quantum beats	strong variations in weak magnetic fields	1374
$C_4H_6O_2$		see $C_2H_2O_2$, ref. 1339	
$C_4H_6N_4$ (dimethyl-s-tetrazine)	LIF, absorption	see $C_2H_2O_2$, ref. 1357	1375
		$\tilde{A}^1B_{3u}-\tilde{X}^1A_g$	

1361 J. P. Maier, O. Marthaler, L. Misev, and F. Thommen, *Faraday Discuss. Chem. Soc.*, 1981, **71**, 181.1362 Y. Udagawa, M. Ito, and I. Suzuka, *Chem. Phys.*, 1980, **46**, 237.1363 G. ter Horst, D. W. Pratt, and J. Kommandeur, *J. Chem. Phys.*, 1981, **74**, 3616.1364 D. B. McDonald and S. A. Rice, *J. Chem. Phys.*, 1981, **74**, 4893.1365 B. J. van der Meer, H. T. Jonkman, G. M. ter Horst, and J. Kommandeur, *J. Chem. Phys.*, 1982, **76**, 2099.1366 H. Baba, M. Fujita, and K. Uchida, *Chem. Phys. Lett.*, 1980, **73**, 425.1367 A. K. Jameson, S. Okajima, and E. C. Lim, *J. Chem. Phys.*, 1981, **75**, 480.1368 S. Okajima, H. Saigusa, and E. C. Lim, *J. Chem. Phys.*, 1982, **76**, 2096.1369 A. K. Jameson and E. C. Lim, *Chem. Phys. Lett.*, 1981, **79**, 326.1370 J. P. Doering and R. McDiarmid, *J. Chem. Phys.*, 1980, **73**, 3617; erratum, 1981, **75**, 500.1371 L. J. Rothberg, D. P. Gerrity, and V. Vaida, *J. Chem. Phys.*, 1980, **73**, 5508.1372 R. McDiarmid and A. Auerbach, *Chem. Phys. Lett.*, 1980, **76**, 520.1373 D. V. Brumbaugh, C. A. Haynam, and D. H. Levy, *J. Chem. Phys.*, 1980, **73**, 5380.1374 W. Henke, H. L. Selzle, T. R. Hays, S. H. Lin, and E. W. Schlag, *Chem. Phys. Lett.*, 1981, **77**, 448.1375 G. G. Asmuth, K. K. Innes, and V. A. Job, *J. Mol. Spectrosc.*, 1980, **83**, 266.

Table 14 (continued)

Molecule	Technique	Comment	Ref.
C ₄ H ₆ O (cyclobutanone)	electric dichroism	186—206 nm, 2nd-excited singlet, B ₂ —A ₁ , 3sa ₁ ← nb ₂ see CH ₃ I, ref. 1319	1376
C ₄ H ₉ J	PES	see CH ₃ NO, ref. 1321	
C ₄ H ₉ NO		7—11 eV, primarily Fe 3d ionizations, to ² E' (clear Jahn-Teller distortion) and ² E'' (much less so)	1377
C ₅ O ₃ Fe (iron pentacarbonyl)		A(π ⁻¹)—X(π ⁻¹)	
C ₅ H ₄ ⁺ (methyl diacetylene)	emission (electron beam excited)		1378
C ₅ H ₄ ⁺	LIF	Ā ² E—X ² E, and d ₃	1379
C ₅ H ₄ ⁺	PE-photon coincidence	Ā ² E, Φ _{f1} and τ	1380
C ₅ ^{1,2} H ₅ N (pyridine)	LIF	S ₁ , Duschinski effect	1381
C ₅ H ₈ (<i>trans</i> -piperylene, isoprene)		see C ₄ H ₆ , ref. 1371	
C ₅ H ₈ O (cyclopentanone)	PES	see C ₄ H ₆ O, ref. 1376	
C ₅ H ₈ O ₂ (2,3 pentanedione)		see C ₂ H ₂ O ₂ , ref. 1339	
C ₅ H ₈ (cyclopentyl)		thermal decomposition	1382
C ₆ Br ₂ F ₄ ⁺ , s-C ₆ Br ₃ F ₃ ⁺ (benzene derivatives)	emission	670 nm, 830 nm, B(π ⁻¹) → Ā(π ⁻¹), X(π ⁻¹)	1383
s-C ₆ Br ₃ F ₃	Ne matrix	vibrational structure of B ² A _g '' similar to parent compound	1384
s-C ₆ Cl ₃ F ₃	LIF, matrix	Jahn-Teller distortions	1385
C ₆ F ₆ ⁺	LIF, absorption	B ² A _{2u} —X ² E _{1g} , dispersed fluorescence	1386
C ₆ F ₆ ⁺	analysis, modelling	Jahn-Teller effect	1387
C ₆ F ₆ ⁺	LIF, matrix	B—Ā, and substituted fluoro- and chlorofluoro-benzene cations	1388
C ₆ F ₆ ⁺	electron beam, s/s beam	B—X, Jahn-Teller	1389
C ₆ F ₆ ⁺	LIF	B ² A _{2u} —X ¹ E _{1g} , dispersed fluorescence	1390
C ₆ F ₆ ⁺ (and other fluorobenzenes)	electron beam, s/s jet	B—X	1391

1376 G. C. Causley and B. R. Russell, *J. Chem. Phys.*, 1980, **72**, 2623.1377 J. L. Hubbard and D. L. Lichtenberger, *J. Chem. Phys.*, 1981, **75**, 2560.1378 J. P. Maier, O. Marthaler, and E. Kloster-Jensen, *J. Chem. Phys.*, 1980, **72**, 701.1379 J. P. Maier and L. Misev, *Chem. Phys.*, 1980, **51**, 311.1380 P. Forster, J. P. Maier, and F. Thommen, *Chem. Phys.*, 1981, **59**, 85.1381 Y. Mochizuki, K. Kaya, and M. Ito, *Chem. Phys.*, 1981, **54**, 375.1382 F. A. Houle and J. L. Beauchamp, *J. Phys. Chem.*, 1981, **85**, 3456.1383 J. P. Maier, O. Marthaler, M. Mohraz, and R. H. Shiley, *Chem. Phys.*, 1980, **47**, 307.1384 V. E. Bondybey, T. J. Sears, T. A. Miller, C. Vaughn, J. H. English, and R. H. Shiley, *Chem. Phys.*, 1981, **61**, 9.1385 T. J. Sears, T. A. Miller, and V. E. Bondybey, *Faraday Discuss. Chem. Soc.*, 1981, **71**, 175.1386 V. E. Bondybey and T. A. Miller, *J. Chem. Phys.*, 1980, **73**, 3053.1387 T. J. Sears, T. A. Miller, and V. E. Bondybey, *J. Chem. Phys.*, 1981, **74**, 3240.1388 V. E. Bondybey, C. R. Vaughn, T. A. Miller, J. H. English, and R. H. Shiley, *J. Chem. Phys.*, 1981, **74**, 6584.1389 R. P. Tuckett, *Chem. Phys.*, 1981, **58**, 151.1390 T. Sears, T. A. Miller, and V. E. Bondybey, *J. Am. Chem. Soc.*, 1981, **103**, 326.1391 T. A. Miller, B. R. Zegarski, T. J. Sears, and V. E. Bondybey, *J. Phys. Chem.*, 1980, **84**, 3154.

Table 14 (continued)

Molecule	Technique	Comment	Ref.
$C_6F_6^+$	photoion/photon coincidence	$\tilde{B}-\tilde{X}$, $\tilde{B}-\tilde{A}$; Φ_{f1} and τ	1392
$C_6H_aCl_bF_c$ (17 cations)	emission, electron beam excited	$\tilde{B}(\pi^{-1}) \rightarrow \tilde{A}(\pi^{-1}), \tilde{X}(\pi^{-1})$; τ in \tilde{B} states	1393
$C_6H_aF_b^+$ (11 cations)	PEPI	\tilde{B} and \tilde{C} states, Φ_{f1} and τ ; $\tilde{C} \leftrightarrow \tilde{B}$ and fast vibrational redistribution precedes $\tilde{B} \rightarrow \tilde{A}, \tilde{X}$	1394
$C_6HF_5^+$	LIF, s/s jet	see $C_6F_6^+$, ref. 1392	1395
$C_6HF_5^+ \quad n = 3-6$		LIF follows laser ionization	
$C_6HF_5O^+$ (perfluorophenol)	absorption and LIF, 4K	no evidence of perturbation by low-lying \tilde{A} state	1396
$C_6HF_5O^+$	emission, electron beam excited	$\tilde{B}(\pi^{-1})-\tilde{X}(\pi^{-1})$	1397
$C_6H_2F_4^+$		see $C_6F_6^+$, ref. 1392	
$C_6H_3Cl_3^+$	theory	Jahn-Teller theory reviewed	1398
$C_6H_3F_3^+$		wavelength-resolved, $\tilde{B}^2A_2''-\tilde{X}^2E''$	1399
$C_6H_3Cl_3^+$	emission		
$C_6H_3Cl_3^+$	matrix and low T gas phase	\tilde{B} state fluorescence	1400
$C_6H_3F_3^+$			
$C_6H_3ClF_2^+$		see $C_6F_6^+$, ref. 1388	
$C_6H_3Cl_2F^+(1,3,5-)$			
$C_6H_3F_3^+(1,2,4-)$		see $C_6F_6^+$, ref. 1392	
$C_6H_3F_3^+(1,2,4-, 1,3,5-)$	gas phase, Ne matrix	\tilde{B}^2A_2 ; considerable geometry change on excitation	1401
$C_6H_3F_3^+(1,2,3-)$	LIF	<200 cm ⁻¹ splitting between \tilde{X} and \tilde{A} states	1402
$C_6H_3F_3^+(1,2,3-)$	low T gas phase and Ne matrix		
$C_6H_4F_2^+(1,3-)$		see $C_6F_6^+$, ref. 1392	
$C_6H_4F_2^+(1,4-)$	LIF	S_1 intramolecular vibrational energy redistribution	1403
$C_6H_4F_2$		as above	1404
$C_6H_4F_2$	LIF	$S_1(^1B_{2u})-S_0(^1A_{1g})$ assignments; S_1 non-planar, several strong Fermi resonances	1405

1392 G. Dujardin, S. Leach, and G. Taieb, *Chem. Phys.*, 1980, **46**, 407.1393 J. P. Maier, O. Marthaler, M. Mohraz, and R. H. Shiley, *Chem. Phys.*, 1980, **47**, 295.1394 J. P. Maier and F. Thommen, *Chem. Phys.*, 1981, **57**, 319.1395 M. C. Heaven, T. A. Miller, and V. E. Bondybey, *J. Chem. Phys.*, 1982, **76**, 3831.1396 V. E. Bondybey, J. H. English, T. A. Miller, and C. B. Vaughn, *J. Phys. Chem.*, 1981, **85**, 1667.1397 J. P. Maier, O. Marthaler, M. Mohraz, and R. H. Shiley, *J. Electron Spectrosc.*, 1980, **19**, 11.1398 T. Sears, T. A. Miller, and V. E. Bondybey, *J. Chem. Phys.*, 1980, **72**, 6070.1399 T. Sears, T. A. Miller, and V. E. Bondybey, *J. Chem. Phys.*, 1980, **72**, 6749.1400 V. E. Bondybey, T. J. Sears, J. H. English, and T. A. Miller, *J. Chem. Phys.*, 1980, **73**, 2063.1401 V. E. Bondybey, J. H. English, and T. A. Miller, *J. Mol. Spectrosc.*, 1980, **84**, 124.1402 V. E. Bondybey, J. H. English, and T. A. Miller, *J. Mol. Spectrosc.*, 1981, **90**, 592.1403 R. A. Coveleskie, D. A. Dolson, and C. S. Parmenter, *J. Chem. Phys.*, 1980, **72**, 5774.1404 N. Halberstadt and A. Tramer, *J. Chem. Phys.*, 1980, **73**, 6343.1405 R. A. Coveleskie and C. S. Parmenter, *J. Mol. Spectrosc.*, 1981, **86**, 86.

Table 14 (continued)

Molecule	Technique	Comment	Ref.
C ₆ H ₄ X ₂ (1,4; X = Br, Cl, I)	PES	extensive vibrational structure for ionization from π and lone pair orbitals	1406
C ₆ H ₅ Br	MPI	2-photon spectra, $^1\text{B}_2(L_b) \leftarrow ^1\text{A}_1(\text{A})$	1407
C ₆ H ₅ Br	MPI, s/s beam	resonance enhanced, $^1\text{B}_2 \leftarrow ^1\text{A}_1$	1408
C ₆ H ₅ X (X = Cl, Br, I)	MPI, s/s beam	see C ₆ H ₄ X ₂ , ref. 1406	
C ₆ H ₅ Cl	MPI, s/s beam	2-photon resonant 4-photon ionization	1409
C ₆ H ₅ Cl C ₆ H ₅ F	absorption	see C ₆ H ₅ Br, ref. 1407	
C ₆ H ₅ F	absorption	see C ₆ H ₅ Cl, ref. 1409	
C ₆ ^{1,2} H ₅ F	absorption	264.4 nm system, cold and hot bands	1410
C ₆ H ₅ I	absorption	see C ₆ H ₅ Br, ref. 1408	
C ₆ H ₆ (benzene)	absorption	$S_n \leftarrow S_1$; transient absorption 210—930 nm, 248 nm excitation; selective quenching	1411
C ₆ ^{1,2} H ₆	2 photon	$^1\text{B}_{2u} \leftarrow ^1\text{A}_{1g}$; Duschinski rotation	1412
C ₆ H ₆	MPI, s/s beam	see C ₆ H ₅ Cl, ref. 1409	
C ₆ H ₆	flash-sensitized phosphorescence	$^1\text{B}_{2u} \leftarrow ^1\text{A}_{1g}$; channel 3	1413
C ₆ ^{1,2} H ₆ (and 15 alkyl benzenes)	flash-sensitized phosphorescence	see C ₆ H ₅ Br, ref. 1407	
C ₆ H ₆	MCD	triplet state lifetimes	1414
C ₆ H ₆	2 photon, CW	assignment of Rydberg transitions 136—190 nm	1415
C ₆ H ₆	MPI	Doppler-free; benzene S_1 is a symmetrical rotor	1416
C ₆ H ₆	MPI, s/s beam	two ladders to fragmentation	1417
C ₆ H ₆	MPI	2 colour; broad autoionization as well as direct process	1418
C ₆ H ₆	(e,2e)	$^1\text{B}_{1u}(S_2) \tau \approx 20$ ps; mass spectrum	1419
C ₆ H ₆	electron impact	valence orbitals	1420
C ₆ H ₆	PI, s/s beam	4.5—9.5 eV, cf. fluorobenzenes	1421
		$^3\text{C}_6\text{H}_6 \leftarrow 6^1\text{S}_1$, then photoionized at 193 nm. $\tau_{\text{triplet}} = 470 \pm 50$ ns	1422

¹⁴⁰⁶ A. W. Potts, M. L. Lyus, E. P. F. Lee, and G. H. Fattahallah, *J. Chem. Soc., Faraday Trans. 2*, 1980, **76**, 556.

¹⁴⁰⁷ L. Goodman and R. P. Rava, *J. Chem. Phys.*, 1981, **74**, 4826.

¹⁴⁰⁸ T. G. Dietz, M. A. Duncan, M. G. Liverman, and R. E. Smalley, *J. Chem. Phys.*, 1980, **73**, 4817.

¹⁴⁰⁹ J. Murakami, K. Kaya, and M. Ito, *J. Chem. Phys.*, 1980, **72**, 3263.

¹⁴¹⁰ E. D. Lipp and C. J. Seliskar, *J. Mol. Spectrosc.*, 1981, **87**, 242, 255.

¹⁴¹¹ N. Nakashima, H. Inoue, M. Sumitani, and K. Yoshihara, *J. Chem. Phys.*, 1980, **73**, 5977.

¹⁴¹² R. P. Rava, L. Goodman, and K. Krogh-Jespersen, *J. Chem. Phys.*, 1981, **74**, 273.

¹⁴¹³ K. Aron, C. Otis, R. E. Demaray, and P. Johnson, *J. Chem. Phys.*, 1980, **73**, 4167.

¹⁴¹⁴ K. W. Holtzclaw and M. D. Schuh, *Chem. Phys.*, 1981, **56**, 219.

¹⁴¹⁵ P. A. Snyder, P. A. Lund, P. N. Schatz, and E. M. Rowe, *Chem. Phys. Lett.*, 1981, **82**, 546.

¹⁴¹⁶ E. Riedle, H. J. Neusser, and E. W. Schlag, *J. Chem. Phys.*, 1981, **75**, 4231.

¹⁴¹⁷ U. Boesl, H. J. Neusser, and E. W. Schlag, *J. Chem. Phys.*, 1980, **72**, 4327.

¹⁴¹⁸ M. A. Duncan, T. G. Dietz, and R. E. Smalley, *J. Chem. Phys.*, 1981, **75**, 2118.

¹⁴¹⁹ J. P. Reilly and K. L. Kompa, *J. Chem. Phys.*, 1980, **73**, 5468.

¹⁴²⁰ I. Fuss, I. E. McCarthy, A. Minchinton, E. Weigold, and F. P. Larkins, *Chem. Phys.*, 1981, **63**, 19.

¹⁴²¹ J. Philis, A. Bolovinos, G. Andritsopoulos, E. Pantos, and P. Tsekleris, *J. Phys. B*, 1981, **14**, 3621.

¹⁴²² M. A. Duncan, T. G. Dietz, M. G. Liverman, and R. E. Smalley, *J. Phys. Chem.*, 1981, **85**, 7.

Table 14 (continued)

Molecule	Technique	Comment	Ref.
C ₆ H ₆	MPI	electron time of flight distributions	1423
C ₆ H ₆ ⁺	Ar matrix, photolysis, PI	cation absorption	1424
C ₆ H ₆ ⁺		see C ₆ F ₆ ⁺ , ref. 1388	
C ₆ H ₆ (2,4-hexadiyne)	MPI	long wavelength dependence of mass spectrum; dissociation through ionic states	1425
C ₆ H ₆ ⁺		see C ₃ H ₄ ⁺ , refs. 1378—1380	
C ₆ H ₆ ⁺	emission, s/s jet	$\bar{A}^1E_u \rightarrow \bar{X}^3E_g$, vibrational frequencies	1426
C ₆ H ₆ O (phenol)	LIF, s/s jet	also phenoxyalkanes, FES and dispersed fluorescence; large anharmonic coupling, cf. alkylbenzenes	1427
C ₆ H ₇ N (aniline)	LIF, s/s jet	double minimum potential for inversion in S ₁	1428
C ₆ H ₇ N	MPI, s/s jet	exciting S ₀ \rightarrow S ₁ produces parent ion with near 100% efficiency, even at flux of 2×10^7 W cm ⁻²	1429
C ₆ H ₇ N	LIF, s/s jet	also p-alkylanilines, ¹ B ₂ ($\pi\pi^*$) \rightarrow ¹ A ₁ ; intramolecular relaxation into chain modes in <1 ns	1430
C ₆ H ₇ N	2 photon ionization, s/s beam	isotopic shift of vibronic band origin smaller than rotational bandwidth	1431
C ₆ H ₇ N	absorption in s/s jet	planar expansion	1432
C ₆ H ₈ (1,2,5-hexatriene)	emission (electron beam excited) and PEPI	see C ₆ H ₅ Br, ref. 1407	1433
C ₆ H ₈ ⁺	photodissociation (ion cyclotron resonance)	$\bar{A}(\pi^-)\rightarrow\bar{X}(\pi^-)$	
C ₆ H ₈ (1,4-cyclohexadiene)	electron impact	cis and trans spectra identical within 10 ms of formation	1434
C ₆ H ₁₀ (trans-2,3-dimethylbutadiene)		variable angle, impact energy	1435
C ₆ H ₁₀ O (cyclohexanone)		see C ₄ H ₆ O, ref. 1376	
C ₆ H ₁₁ (cyclohexyl)		see C ₅ H ₉ , ref. 1382	
C ₆ H ₁₂ N ₂ (triethylene diamine)	MPI	fragmentation pattern depends on 2-photon resonance ('doorway state') selected	1436

1423 J. T. Meek, R. K. Jones, and J. P. Reilly, *J. Chem. Phys.*, 1980, **73**, 3503.1424 J. H. Miller, L. Andrews, P. A. Lund, and P. N. Schatz, *J. Chem. Phys.*, 1980, **73**, 4933.1425 T. Carney and T. Baer, *J. Chem. Phys.*, 1981, **75**, 477.1426 D. Klapstein, S. Lentwyler, and J. P. Maier, *Chem. Phys. Lett.*, 1981, **84**, 534.1427 J. B. Hopkins, D. E. Powers, and R. E. Smalley, *J. Chem. Phys.*, 1981, **74**, 6986.1428 N. Mikami, A. Hiraya, I. Fujiwara, and M. Ito, *Chem. Phys. Lett.*, 1980, **74**, 531.1429 T. G. Dietz, M. A. Duncan, M. G. Liverman, and R. E. Smalley, *Chem. Phys. Lett.*, 1980, **70**, 246.1430 D. E. Powers, J. B. Hopkins, and R. E. Smalley, *J. Chem. Phys.*, 1980, **72**, 5721.1431 S. Lentwyler and U. Even, *Chem. Phys. Lett.*, 1981, **81**, 578.1432 A. Amirav, U. Even, and J. Jortner, *Chem. Phys. Lett.*, 1981, **83**, 1.1433 M. Allan, J. Dannacher, and J. P. Maier, *J. Chem. Phys.*, 1980, **73**, 3114.1434 L. N. Morgensthaler and J. R. Eyler, *J. Chem. Phys.*, 1981, **74**, 4356.1435 R. McDiarmid and J. P. Doering, *J. Chem. Phys.*, 1981, **75**, 2687.1436 D. A. Lichtin, S. Dalta-Ghosh, K. R. Newton, and R. B. Bernstein, *Chem. Phys. Lett.*, 1980, **75**, 214.

Table 14 (continued)

Molecule	Technique	Comment	Ref.
C ₆ H ₁₅ N (triethylamine)		see C ₃ H ₈ N, ref. 1360	
C ₇ ^{1,2} H ₅ FO (benzoyl fluoride)	absorption	260—290 nm; barriers to rotation in upper and lower states	1437
C ₆ H ₅ F ₃ ⁺ (1,3,5 trifluorotoluene)	LIF, absorption	also several other methyl and fluorine substituted benzenes	1439
C ₆ H ₆ O (benzaldehyde)	spectrofluorimetry	220—540 nm phosphorescence: S ₁ —T ₁ (ISC) dominates at low to moderate excess energy, but S ₁ —S ₀ (IC) becomes important for higher energy	1438
C ₆ H ₆ O	absorption in s/s jet	2nd π → π*: most prominent bands associated with substituents (in contrast to 1st π → π*)	1440
C ₆ H ₇ (benzyl)	absorption, solid Ar	310.5 and 449.6 nm	1441
C ₆ H ₇ ⁺	absorption		1442
C ₆ ^{1,2} H ₇	LIF	1 ² A ₂ —1 ² B ₂ , 2 ² B ₂ —1 ² B ₂ rearrangements	1443
C ₆ H ₇ ⁺ (benzyl and tropylum)	absorption, solid Ar		1444
C ₆ H ₅ Cl ⁺	matrix PI		
C ₆ H ₅ F ⁺ (halotoluenes, halobenzenes)			
C ₆ H ₅ F (p-fluorotoluene)	LIF	intramolecular vibrational redistribution in S ₁ with ε _{vib} = 1988 cm ⁻¹ observed throughout first 50 ps see C ₆ H ₅ Br, ref. 1407	1445
C ₆ H ₈ (toluene)	MPI, s/s jet	internal rotation, strongly coupled with electronic motion	1447
C ₆ H ₈ ⁺	LIF, s/s jet	FES, dispersed fluorescence, for 1 ² B ₂ (ππ*)—1A ₁ of alkyl benzenes	1448
C ₆ H ₈	MPI	3p Rydberg transitions, 1A ₁ , 1B ₂	1449
C ₆ H ₈ ⁺	absorption, solid Ar	430 nm	1441
C ₆ H ₈ (norbornadiene)	electron impact	forbidden and allowed valence transitions, Rydberg transitions to 1st and 2nd IP's	1450
C ₆ H ₈ O (phenoxy methane)		see C ₆ H ₆ O, ref. 1427	

1437 W. J. Balfour, *J. Mol. Spectrosc.*, 1980, **84**, 60.1438 Y. Hirata and E. C. Lim, *J. Chem. Phys.*, 1980, **72**, 5505.1439 V. E. Bondybey, C. Vaughn, T. A. Miller, J. H. English, and R. H. Shiley, *J. Am. Chem. Soc.*, 1981, **103**, 6303.1440 D. G. Leopold, R. J. Hemley, V. Vaida, and J. L. Roebber, *J. Chem. Phys.*, 1981, **75**, 4758.1441 L. Andrews, J. H. Miller, and B. W. Keelan, *Chem. Phys. Lett.*, 1980, **71**, 207.1442 F. Bayrakceken, *Chem. Phys. Lett.*, 1980, **74**, 298.1443 T. Okamura, T. R. Charlton, and B. A. Thrush, *Chem. Phys. Lett.*, 1982, **88**, 369.1444 L. Andrews and B. W. Keelan, *J. Am. Chem. Soc.*, 1981, **103**, 99.1445 B. W. Keelan and L. Andrews, *J. Am. Chem. Soc.*, 1981, **103**, 822 and 829.1446 D. A. Dolson, C. S. Parmenter, and B. M. Stone, *Chem. Phys. Lett.*, 1981, **81**, 360.1447 J. Murakami, M. Ito, and K. Kaya, *Chem. Phys. Lett.*, 1981, **80**, 203.1448 J. B. Hopkins, D. E. Powers, and R. E. Smalley, *J. Chem. Phys.*, 1980, **72**, 5039 and 5049.1449 G. O. Uneberg, P. A. Campo, and P. Johnson, *J. Chem. Phys.*, 1980, **73**, 1110.1450 J. P. Doering and R. McDiarmid, *J. Chem. Phys.*, 1981, **75**, 87.

Table 14 (continued)

Molecule	Technique	Comment	Ref.
C ₆ H ₇ N (methylaniline)		see C ₆ H ₇ N, ref. 1430	
C ₆ H ₁₂ O (cycloheptanone)		see C ₆ H ₆ O, ref. 1376	
C ₈ H ₉ ON (benzoyl cyanide)	MPD	CN(B) emission	1451
C ₈ H ₆ (phenylethyne)	LIF, s/s jet	FES and dispersed fluorescence, $^1\text{B}_2(\pi\pi^*) \leftarrow ^1\text{A}_1$; vibrational relaxation sub-nanosecond	1452
C ₈ H ₆		see C ₇ H ₆ O, ref. 1440	
C ₈ H ₈ N ₂ (1,5 naphthyridine)	absorption	vibronic coupling predicted to have severe and complex consequences	1453
C ₈ ^{1,2} H ₆ N ₂	absorption	$^1\text{B}_g \leftarrow ^1\text{A}_g$; 2 origins, magnetic dipole allowed, and electronic dipole (vibronically) allowed	1454
C ₈ H ₈ (styrene)	absorption in s/s jet	S_2 , 220–260 nm	1455
C ₈ H ₈	LIF	288 nm band, $\bar{\Lambda}^1\text{A}' - \bar{\chi}^1\text{A}'$; CH ₂ group is not \perp to molecular plane	1456
C ₈ H ₈		see C ₇ H ₆ O, ref. 1440	
C ₈ H ₈ ⁺	absorption, matrix PI, solid Ar	α, β -methyl styrene, β -ethyl styrene, allyl benzene and cyclopropyl benzene cations	1457
C ₈ H ₈ O (acetophenone)	laser excitation	$T_1 \rightarrow S_0$ as indicator of vibrational energy redistribution	1458
C ₈ H ₈ O		see C ₇ H ₆ O, ref. 1440	
C ₈ H ₁₀ (ethyl benzene)	LIF, s/s jet	erratum to <i>J. Chem. Phys.</i> , 1979, 71, 3886	1459
C ₈ H ₁₀		see C ₇ H ₈ , ref. 1448	
C ₈ H ₁₀ (<i>p</i> -xylene)		see C ₇ H ₈ , ref. 1449	
C ₈ H ₁₀ (<i>trans, trans</i> - 1,3,5,7-octatetraene)	LIF, s/s jet	$S_2 - S_0$ ($^1\text{B}_u \rightarrow ^1\text{A}_g$), FES 265–298 nm; significant narrowing in jet, in contrast to 1,3-butadiene	1460
C ₈ H ₁₀ ⁺ (diethyldiacetylene)		see C ₅ H ₄ ⁺ , ref. 1378	
C ₈ H ₁₀ O (phenoxyethane)		see C ₆ H ₆ O, ref. 1427	
C ₈ H ₁₁ N (<i>p</i> -ethylaniline)		see C ₆ H ₇ N, ref. 1430	
C ₈ H ₁₂ (1,5-cyclo- octadiene)		see C ₆ H ₈ ref. 1435	
C ₉ H ₇ N (isoquinoline)	LIF, s/s jet	$S_2 - S_1$ coupling, non-exponential fluorescence	1461
C ₉ H ₈ (1-phenylpropane)		see C ₈ H ₆ , ref. 1452	
C ₉ H ₈ O (1-indanone)		see C ₈ H ₈ O, ref. 1458	
C ₉ H ₁₂ (n-propylbenzene)		see C ₈ H ₁₀ , ref. 1459	

¹⁴⁵¹ J. B. Lurie and M. A. El-Sayed, *Chem. Phys. Lett.*, 1980, **70**, 251.¹⁴⁵² D. E. Powers, J. B. Hopkins, and R. E. Smalley, *J. Chem. Phys.*, 1981, **74**, 5971.¹⁴⁵³ P. J. Chappell, G. Fischer, J. R. Reimers, and I. G. Roso, *J. Mol. Spectrosc.*, 1981, **87**, 316.¹⁴⁵⁴ G. Fischer and I. G. Ross, *J. Mol. Spectrosc.*, 1981, **87**, 331.¹⁴⁵⁵ R. J. Hemley, D. G. Leopold, V. Vaida, and J. L. Roebber, *J. Phys. Chem.*, 1981, **85**, 134.¹⁴⁵⁶ J. M. Hollas and T. Ridley, *J. Mol. Spectrosc.*, 1981, **89**, 232.¹⁴⁵⁷ L. Andrews, J. A. Harvey, B. J. Kelsall, and D. C. Duffy, *J. Am. Chem. Soc.*, 1981, **103**, 6415.¹⁴⁵⁸ Y. Hirata and E. C. Lim, *Chem. Phys. Lett.*, 1980, **71**, 167.¹⁴⁵⁹ J. B. Hopkins, D. E. Powers, and R. E. Smalley, *J. Chem. Phys.*, 1980, **72**, 2905.¹⁴⁶⁰ L. A. Heinbrook, J. E. Kenny, B. E. Kohler, and G. W. Scott, *J. Chem. Phys.*, 1981, **75**, 4338.¹⁴⁶¹ A. K. Jameson, S. Okajima, H. Saigusa, and E. C. Lim, *J. Chem. Phys.*, 1981, **75**, 4729.

Table 14 (continued)

Molecule	Technique	Comment	Ref.
C ₉ H ₁₂ (n-, isopropyl-benzene)		see C ₇ H ₈ , ref. 1448	
C ₉ H ₁₃ N (p-, n-, isopropyl-aniline)		see C ₆ H ₇ N, ref. 1430	
C ₉ H ₂₁ N (tri-n-propylamine)		see C ₃ H ₉ N, ref. 1360	
C ₁₀ H ₈ (naphthalene, azulene)	MPI	also two-colour	1462
C ₁₀ ^{1,2} H ₈ (naphthalene)	absorption, s/s jet	32 000—38 000 cm ⁻¹ ; d _g line profiles 50% wider	1463
C ₁₀ H ₈	LIF, s/s jet	¹ B _{3u} (ππ*) ← ¹ A _g ; intramolecular vibrational energy redistribution	1464
C ₁₀ ^{1,2} H ₈	LIF, s/s jet	ISC, similar to benzene	1465
C ₁₀ H ₈	LIF, cold and warm	vibrational assignments and frequencies; spectroscopy reviewed	1466
C ₁₀ H ₈		direct ionization: see C ₆ H ₆ , ref. 1418	
C ₁₀ H ₈ ⁺	MPD, ion cyclotron resonance	2-photon (240—350 nm) and 4-photon (600—670 nm) processes	1467
C ₁₀ ^{1,2} H ₈ ⁺	matrix PI		1468
C ₁₀ H ₁₀ (1-phenyl-1-butyne)	LIF, s/s jet	FES and dispersed fluorescence, ¹ B ₂ (ππ*) ← ¹ A ₁ , vibrational relaxation	1469
C ₁₀ H ₁₄ (n-butyl benzene)		see C ₈ H ₁₀ , ref. 1459	
C ₁₀ H ₁₄ (n, t-butyl benzene)		see C ₇ H ₈ , ref. 1448	
C ₁₀ H ₁₄ O (phenoxybutane)		see C ₆ H ₆ O, ref. 1427	
C ₁₀ H ₁₅ N (p-n-butyl aniline)		see C ₆ H ₇ N, ref. 1430	
C ₁₁ H ₁₆ (n-pentyl benzene)		see C ₈ H ₁₀ , ref. 1459	
C ₁₁ H ₁₆		see C ₇ H ₈ , ref. 1448	
C ₁₁ H ₁₆	LIF, s/s jet	nanosecond time evolution	1470
C ₁₂ H ₆ O ₂ (naphthoquinone)	LIF	S ₁ (nπ*) and S ₂ (ππ*) excited; prompt fluorescence (fast and slow), and phosphorescence observed (reversible ISC, S ₁ /T)	1471
C ₁₂ H ₈ (biphenylene)	LIF	S ₁ emits even when S ₂ excited	1472
C ₁₂ H ₁₄ (1-phenyl-1-hexyne)		see C ₈ H ₆ , ref. 1452	

1462 D. M. Lubman, R. Naaman, and R. N. Zare, *J. Chem. Phys.*, 1980, **72**, 3034.1463 S. M. Beck, D. E. Powers, J. B. Hopkins, and R. E. Smalley, *J. Chem. Phys.*, 1980, **73**, 2019.1464 S. M. Beck, J. B. Hopkins, D. E. Powers, and R. E. Smalley, *J. Chem. Phys.*, 1981, **74**, 43.1465 F. M. Behlen and S. A. Rice, *J. Chem. Phys.*, 1981, **75**, 5672.1466 F. M. Behlen, D. B. McDonald, V. Sethuraman, and S. A. Rice, *J. Chem. Phys.*, 1981, **75**, 5685.1467 M. S. Kim and R. C. Dunbar, *J. Chem. Phys.*, 1980, **72**, 4405.1468 L. Andrews and T. A. Blankenship, *J. Am. Chem. Soc.*, 1981, **103**, 5977.1469 D. E. Powers, J. B. Hopkins, and R. E. Smalley, *J. Chem. Phys.*, 1981, **74**, 5971.1470 J. B. Hopkins, D. E. Powers, and R. E. Smalley, *J. Chem. Phys.*, 1980, **73**, 683.1471 T. Itoh and H. Baba, *Chem. Phys.*, 1980, **51**, 179.1472 N. Ohta, M. Fujita, H. Baba, and H. Shizuka, *Chem. Phys.*, 1980, **47**, 389.

Table 14 (continued)

Molecule	Technique	Comment	Ref.
C ₁₂ H ₁₈ (n-hexyl benzene)		see C ₁₁ H ₁₆ , ref. 1470	
C ₁₂ H ₂₇ N (tri-n-butylamine)		see C ₃ H ₉ N, ref. 1360	
C ₁₃ H ₈ O ₂ (methyl naphthoquinone)		see C ₁₂ H ₆ O ₂ , ref. 1471	
C ₁₃ H ₁₀ (fluorene)	2 photon, s/s jet	pulsed planar expansion	1473
C ₁₃ H ₂₀ (n-heptyl benzene)	quantum beats	see C ₁₁ H ₁₆ , ref. 1470	
C ₁₄ H ₁₀ (anthracene)	quantum beats	coherent preparation of a few levels in S ₁ manifold?	1474
C ₁₅ H ₉ N } C ₁₆ H ₈ N ₂ } (9-cyano, and 9,10-dicyanoanthracene)	spectrofluorimetry	Φ_{fl} and τ_{fl} variation, 185—295 °C	1475
C ₁₆ H ₁₀ (pyrene)	matrix absorption	analysis, deperturbation	1476
C ₁₆ H ₁₀	emission, FES	flame temperatures; inverse electronic relaxation	1477
C ₁₇ H ₁₃ N (9-cyano-10-ethyl anthracene)		see C ₁₅ H ₉ N, ref. 1475	
C ₁₈ H ₁₂ (tetracene)	LIF, s/s jet	onset of quasicontinuum: when vibrational level structure in cold molecules gets congested	1478
C ₁₈ H ₁₂	LIF, s/s jet	FES, dispersed fluorescence	1479
C ₂₁ H ₁₃ N (9-cyano-10-phenylanthracene)	LIF, s/s jet	S ₁ intramolecular dynamics see C ₁₅ H ₉ N, ref. 1475	1480
C ₂₂ H ₁₄ (pentacene)	LIF, s/s jet	S ₁ (¹ B _{2u}) quasi-planar; butterfly motion	1481
C ₂₂ H ₁₄ C ₃₂ H ₁₄ (ovalene) C ₃₂ H ₁₄	LIF, s/s jet	see C ₁₈ H ₁₂ , ref. 1478 FES and dispersed fluorescence; coupling between S ₂ and S ₁ (origins separated by 1800 cm ⁻¹)	1482
C ₃₂ H ₁₄ C ₃₂ H ₁₈ N ₈ (phthalocyanine)	LIF, s/s jet	as above S ₁ , S ₂ ; resolved vibrational structure	1483
C ₃₂ H ₁₈ N ₈	LIF, s/s jet	intramolecular vibrational relaxation	1484

1473 A. Amirav, U. Even, and J. Jortner, *J. Chem. Phys.*, 1981, **75**, 3151.1474 W. R. Lambert, P. M. Felker, and A. H. Zewail, *J. Chem. Phys.*, 1981, **75**, 5958.1475 S. Hirayama, *J. Am. Chem. Soc.*, 1981, **103**, 2934.1476 C. A. Langhoff and S. Mahajan, *J. Mol. Spectrosc.*, 1980, **84**, 94.1477 D. S. Coe and J. I. Steinfeld, *Chem. Phys. Lett.*, 1980, **76**, 485.1478 A. Amirav, U. Even, and J. Jortner, *Opt. Commun.*, 1980, **32**, 266.1479 A. Amirav, U. Even, and J. Jortner, *J. Chem. Phys.*, 1981, **75**, 2489.1480 A. Amirav, U. Even, and J. Jortner, *J. Chem. Phys.*, 1981, **75**, 3770.1481 A. Amirav, U. Even, and J. Jortner, *Chem. Phys. Lett.*, 1980, **72**, 21.1482 A. Amirav, U. Even, and J. Jortner, *Chem. Phys. Lett.*, 1980, **69**, 14.1483 A. Amirav, U. Even, and J. Jortner, *J. Chem. Phys.*, 1981, **74**, 3745.1484 P. S. H. Fitch, C. A. Haynam, and D. H. Levy, *J. Chem. Phys.*, 1980, **73**, 1064.1485 P. S. H. Fitch, C. A. Haynam, and D. H. Levy, *J. Chem. Phys.*, 1981, **74**, 6612.

Table 15 Electronic spectroscopic studies of loosely bound complexes. Molecules are listed in alphabetical order (Diatomic molecules are listed in Table 11)

Molecule	Technique	Comments	Ref.
(CF ₃ NO) ₂	LIF, s/s jet	CF ₃ NOHe + CF ₃ NO → (CF ₃ NO) ₂ + He	1312
(CS ₂) _n ⁺ (n = 2—5)	absorption in mol. beam	photoionization efficiency 65—113 nm	1147
CH ₃ O · Ar	LIF, s/s jet	Ar at O end, on 3-fold axis	1323
C ₂ H ₂ O ₂ · He	LIF, s/s jet	ISC in ¹ A _u state to ³ A _u (non-fluorescent)	1486
C ₂ H ₂ O ₂ · Ar _n (glyoxal)	LIF, s/s jet		
(C ₆ F ₅ H ⁺) · Ar _n	LIF, s/s jet	2 photon ionization preceding LIF	1395
(C ₆ H ₆) ₂ ⁺	Ar matrix absorption		1424
(C ₆ H ₆) _n	transient absorption	laser-induced cluster formation	1487
(C ₆ H ₆) _n	LIF, s/s jet	¹ B _{2u} ← ¹ A _{1g} , UV spectra; n = 1—4 show sharp structure in fluorescence, larger clusters broad band	1488
C ₆ H ₆ · Ar	MPI	2-colour 2-photon ionization; IP shifted 21.2. meV to red of benzene	1489a
C ₁₄ H ₁₀ · Ar _n	LIF, s/s jet	lifetimes	1489b
C ₁₄ H ₂₀ · Ar _n	LIF, s/s jet	predissociation: laser excitation initially localized in ring	1490
C ₁₄ H ₂₀ · N ₂ {n-(t-octylbenzene)}	LIF, s/s jet	S ₀ → S ₁ , microscopic solvation effects	1479
(C ₁₈ H ₁₂) _n Ar _a , Kr _b , Xe _c (tetracene)	LIF, s/s jet	some features attributed to tetracene-Ar stretch (ν = 36.5 ± 2 cm ⁻¹)	1491
C ₁₈ H ₁₂ · Ar _n	LIF, s/s jet	competition between autoionization and vibrational predissociation of vibrationally excited (H ₂) ₂ ; no evidence for (H ₂) ₂ ⁺	1492
(H ₂) ₂	PI, mol. beam	ionization thresholds do not correlate as 1/n	1493
(H ₂ S) _n (n = 1—7)	PI, mol. beam	I ₂ B(v' = 13—26) → X(v'' = 0) dispersed fluorescence	1494
I ₂ Ne _a He _b	LIF, s/s jet	I ₂ * product state distribution used to measure D ₀ for I ₂ X*	1495
I ₂ He, Ne, Ar	LIF, s/s jet	intermolecular potentials, vibrational predissociation lifetimes	1496
I ₂ ^{1,2} H ₂ (o- and p-)	LIF, s/s jet		

1486 C. Jouvet and B. Soep, *J. Chem. Phys.*, 1981, **75**, 1661.1487 N. Nakashima, H. Inoue, M. Sumitani, and K. Yoshihara, *J. Chem. Phys.*, 1980, **73**, 4793.1488 P. R. R. Langridge-Smith, D. V. Brumbaugh, C. A. Haynam, and D. H. Levy, *J. Phys. Chem.*, 1981, **85**, 3742.1489 (a) K. H. Fung, W. E. Henke, T. R. Hays, H. L. Selzle, and E. W. Schlag, *J. Phys. Chem.*, 1981, **85**, 3560; (b) T. R. Hays, W. E. Henke, H. L. Selzle, and E. W. Schlag, *Chem. Phys. Lett.*, 1981, **77**, 19.1490 J. B. Hopkins, D. E. Powers, and R. E. Smalley, *J. Chem. Phys.*, 1981, **74**, 745; *Chem. Phys. Lett.*, 1981, **80**, 225.1491 A. M. Griffiths and P. A. Freedman, *Chem. Phys.*, 1981, **63**, 469.1492 S. L. Anderson, T. Hirooka, P. W. Tiedermann, B. H. Mahan, and Y. T. Lee, *J. Chem. Phys.*, 1980, **73**, 4779.1493 E. A. Walters and N. C. Blais, *J. Chem. Phys.*, 1981, **75**, 4208.1494 J. E. Kenny, K. E. Johnson, W. Sharfin, and D. H. Levy, *J. Chem. Phys.*, 1980, **72**, 1109.1495 J. A. Blazy, B. M. De Koven, T. D. Russell, and D. H. Levy, *J. Chem. Phys.*, 1980, **72**, 2439.1496 J. E. Kenny, T. D. Russell, and D. H. Levy, *J. Chem. Phys.*, 1980, **73**, 3607.

Table 15 (continued)

Molecule	Technique	Comments	Ref.
I ₂ Ar _a He _b	LIF, s/s jet	band shift rule (complex's spectral feature moved from I ₂ feature by Aa + Bb)	1497
I ₂ N ₂ , I ₂ N ₂ He	LIF, s/s jet	dispersed fluorescence	1498
I ₂ Ar, N ₂ , C ₆ H ₆ , C ₅ -C ₈ n-alkanes and others	LIF, s/s jet	blue shift in 'solvent complexes'	1499
(O ₂) _n n = 1—5	PI, mol. beam	(O ₂) ₂ ⁺ bound by 0.26 ± 0.02 eV, higher clusters less tightly (as expected from charge induced dipole interaction)	1492
NO, Ar (NaF) ₂	LIF, s/s jet PES, pseudo-mol. beam	A ^{2Σ} state: direct photodissociation possibly also (CsF) ₂	1500 1501
(SO ₂) ₂	PI, mol. beam	PI and dissociative ionization, 60—106 nm	1252

Developments in Technique, and Some Interesting New Experiments.—Sources and Detectors. We cannot begin to document all the improvements and modifications of lasers relevant to their performance as spectroscopic sources, although we did consider laser sources in some detail in Part 1.¹ A ring dye laser system has been described which provides single frequency (extremely narrow bandwidth) output over the whole visible region (407—887 nm); when pumped with a 24 W argon ion laser, 5.6 W stable and frequency scanned single mode power is obtained at the peak of the R6G* tuning curve.¹⁵⁰³

Advances continue towards shorter wavelengths[†] and shorter pulse lengths. Intracavity second harmonic generation has been reported in a synchronously mode-locked cw dye laser (the second harmonic wave can be generated efficiently inside the mode-locked dye laser cavity) operating on R6G. Pumping with an argon ion laser of average power ~800 mW produced ~0.13 mW of the second harmonic, with a pulse duration of ~3 ps.¹⁵⁰⁴ Pulses shorter than 70 fs have been generated with a synchronously-pumped cw dye laser. However, Heisenberg and frequency chirping conspire to produce a bandwidth of 100 Å.¹⁵⁰⁵

An optically pumped cw molecular iodine laser has been used to investigate collisional relaxation from highly excited vibrational levels of I₂X^{1Σ_g⁺ state. These}

* Rhodamine 6G. Laser dye synonyms can sometimes cause confusion, but Kauffman has tabulated them with their trade names and structures.¹⁵⁰²

† The use of laser sources for spectroscopy in the vacuum ultraviolet are considered on p. 363.

1497 K. E. Johnson, W. Sharfin, and D. H. Levy, *J. Chem. Phys.*, 1981, **74**, 163.

1498 K. E. Johnson and D. H. Levy, *J. Chem. Phys.*, 1981, **74**, 1506.

1499 K. L. Saenger, G. M. McClelland, and D. R. Herschbach, *J. Chem. Phys.*, 1981, **85**, 3333.

1500 P. R. R. Langridge-Smith, E. Carrasquillo, M., and D. H. Levy, *J. Chem. Phys.*, 1981, **74**, 6513.

1501 E. P. F. Lee and A. W. Potts, *J. Chem. Soc., Faraday Trans. 2*, 1980, **76**, 1523.

1502 J. M. Kauffman, *Appl. Opt.*, 1980, **19**, 3431.

1503 T. J. Johnson, jun., R. H. Brady, and W. Proffitt, *Appl. Opt.*, 1982, **21**, 2307.

1504 M. Yamashita, W. Sibbett, D. Welford, and D. J. Bradley, *J. Appl. Phys.*, 1980, **51**, 3559.

1505 G. A. Mourou and T. Sizer, jun., *Opt. Commun.*, 1982, **41**, 47.

levels are the lower levels of lasing transitions, and so the technique permits depopulation of no-fluorescing states to be detected by observing the variation in spontaneous emission with and without laser oscillation.⁸³⁶

A colour centre laser has been used to measure transitions between excited bending vibrational levels of the $\tilde{X}^2\Sigma^-$ and the low lying $A^2\Pi$ electronic states of the C_2H radical.¹¹²⁵ Using the magnetic rotation technique (see p. 263) four Q-branch series were found near 3772, 3780, 4000, and 4100 cm^{-1} . The 3772 cm^{-1} band is the most irregular, and the \tilde{A} state is presumed perturbed by vibrationally excited levels of the ground state. The radicals were generated in an electrical discharge, and the laser beam traversed an effective path length (multipass) of 80 m. (A sensitivity for OH of 10^9 molecule cm^{-3} is reported for this experimental system.)

Coleman^{1506a} has reviewed imaging detectors for the middle and far ultraviolet. He discusses luminescent phosphors (such as tetraphenyl butadiene compared to sodium salicylate), semi-transparent and opaque photocathodes, mesh-based photocathodes (which can have a quantum efficiency of ~35% at Lyman- α), micro-channel plates, and solid-state devices. Photon-counting techniques for the UV have been discussed by Heroux.^{1506b} Talmi and Simpson¹⁵⁰⁷ have considered the self-scanned linear photodiode (SPD) array with particular regard to its use by research spectroscopists ('an economically uninteresting, eccentric, and rare group of scientists') as a multichannel detector. It has a quantum efficiency of over 70% in the red, and 50% at 200 nm. It was still high at 190 nm, and was expected to respond throughout the VUV. Sources of noise, and other response characteristics, are considered.

The pressure, density, and velocity distributions in a spectroscopic heat pipe have been analysed,¹⁵⁰⁸ and the operating conditions for such devices have been discussed.¹⁵⁰⁹

Detection Techniques. Dye laser spectroscopy has for some time been used to probe the concentration of species involved in combustion systems.¹⁵¹⁰ Harris and Weiner⁹⁵² have described how the tomography of the C_2 radical in an oxyacetylene flame was determined using a cw intracavity absorption technique. The output from the laser was dispersed by a 1.5 m monochromator onto an optical multichannel analyser. Concentration profiles were built up by translating the flame across the laser beam. Dyer and Crosley¹⁵¹¹ have pointed out the desirability of measuring radical concentrations at different points simultaneously, to obtain an instantaneous distribution rather than one which is time-averaged. Such a capability would be particularly valuable when operating under conditions of turbulence. Its feasibility has been demonstrated in a stable flame by performing two-dimensional imaging laser-induced fluorescence on OH. Using a cylindrical lens, the laser output beam was formed into a sheet which crossed the flame, exciting fluorescence which was monitored on a 2D (500 × 500 channel) array detector. Problems remain in relating

¹⁵⁰⁶ (a) C. I. Coleman, *Appl. Opt.*, 1981, **20**, 3693; (b) L. Heroux, 'Absolute photon counting in the ultraviolet', in 'Spectrometric Techniques,' Vol. II, ed. G. A. Vanasse, Academic Press, New York, 1981, p. 239.

¹⁵⁰⁷ Y. Talmi and R. W. Simpson, *Appl. Opt.*, 1980, **19**, 1401.

¹⁵⁰⁸ R. W. Boyd and J. G. Dodd, *J. Appl. Phys.*, 1980, **51**, 6058.

¹⁵⁰⁹ L. A. Metton and P. H. Wire, *J. Appl. Phys.*, 1980, **51**, 4059.

¹⁵¹⁰ D. R. Crosley, 'Laser Probes for Combustion Chemistry', ACS Symposium Series, No. 134, American Chemical Society, Washington DC, 1980.

¹⁵¹¹ M. J. Dyer and D. R. Crosley, *Opt. Commun.*, to be published.

LIF intensity to concentration, however, one of which is that of spatially inhomogeneous quenching.

In Section 2 we discussed a number of 'indirect' methods of spectroscopic detection. Another such method exploits the optogalvanic effect.¹⁵¹² Experiments with this technique have usually involved using a tunable dye laser to study electronic transitions, although Begemann and Saykally¹⁵¹³ have used a colour centre IR laser to perform optogalvanic spectroscopy of various atomic Rydberg states, and Webster¹⁵¹⁴ has reported laser optogalvanic (LOG) spectra of NO₂ at 6.2 μm and NH₃ at 9.5 μm achieved with a tunable diode laser.

An optogalvanic spectrum arises from the variation in impedance of a gaseous discharge following the absorption of radiation by a species present. This variation may be due to a change in collisional ionization efficiency on excitation, or in some circumstances may result principally from heating of the discharge gas.^{1514, 1515}

Schenck *et al.*¹⁵¹⁶ first used a tunable dye laser to obtain molecular LOG spectra of ScO, YO, and LaO in a flame; Feldman¹⁵¹⁷ observed molecular species including the free radical NH₂ in a DC discharge. The latter experiments were repeated by Dembynck and Destombes,⁸⁴⁸ who saw in addition the I₂-B-X system. In a study of this system by Rettner *et al.*,⁸⁵² both transverse and longitudinal excitation geometries (of the laser beam with respect to the discharge) were used; LOG signals were still obtained when the irradiating beam was well displaced from the DC discharge. Transverse excitation away from the discharge enhanced the measured current; this was attributed to pressure variations being caused within the discharge region, by local increase in pressure resulting from the dissociation of I₂ molecules, and by dissipation of electronic energy as heat. The strongest LOG signals, appearing as a *reduction* in discharge current, occurred on transverse excitation of the region between the positive column and the cathode. This was thought to be associated with collisional dissociation of B state I₂ within the discharge, resulting in a lowering of its current carrying capability. A comparison of LOG and LIF spectra should thus reveal any differences in the variation with wavelength of collisional and radiative decay rates, although a measurable effect was neither expected nor observed in this case because of the great facility of the collisional process. This study illustrated that the effects giving rise to LOG signals may depend on species, manner of excitation, and cell geometry,

LOG spectra of molecular species have also been obtained using electrodeless rf discharges, which have operational advantages. Suzuki⁷⁵⁸ has observed a new Rydberg band of N₂ ($c_s'{}^1\Sigma_u^+ \leftarrow a''{}^1\Sigma_g^+$) in such a discharge at ~590 nm. Signal may be detected by monitoring changes in the reflected rf field, or by measuring the rf current using a pick-up coil. Stanciulescu *et al.*¹⁵¹⁸ have described a technique where signals appear as perturbations of an rf oscillator, but the oscillator is operated at a power below that needed to excite a discharge. This experiment has so far been performed on atomic caesium vapour.

¹⁵¹² J. E. M. Goldsmith and J. E. Lawler, *Contemp. Phys.*, 1981, **22**, 235.

¹⁵¹³ M. H. Begemann and R. J. Saykally, *Opt. Commun.*, 1982, **40**, 277.

¹⁵¹⁴ C. R. Webster, *Appl. Opt.*, 1982, **21**, 2299.

¹⁵¹⁵ *Laser Focus*, October 1982, p. 14.

¹⁵¹⁶ P. K. Schenck, W. G. Maillard, J. C. Travis, and K. C. Smyth, *J. Chem. Phys.*, 1978, **69**, 5147.

¹⁵¹⁷ D. Feldmann, *Opt. Commun.*, 1979, **29**, 67.

¹⁵¹⁸ C. Stanciulescu, R. C. Bobulescu, A. Surmeian, D. Popescu, I. Popescu, and C. B. Collins, *Appl. Phys. Lett.*, 1980, **37**, 888.

The predissociated $\tilde{\Lambda}$ state of HCO, which has eluded study by $\tilde{\Lambda}-\tilde{X}$ laser induced fluorescence because of low emission probability, has been observed in an rf discharge with LOG spectroscopy.¹⁵¹⁹ By associating measured LOG linewidths with lifetimes, a strong dependence of predissociation rate upon rotational quantum number was found. The operation of this technique required a quantity of precursor (acetaldehyde) five orders of magnitude smaller than that needed for conventional flash-photolysis/absorption experiments. Other sophisticated optogalvanic spectroscopy experiments may be expected: optical-optical double resonance with optogalvanic detection has, for example, already been performed on atomic systems,¹⁵²⁰ and found to give signal enhancements of up to two orders of magnitude compared to the one-photon case (principally, it is thought, as a result of the general shift in population to higher excited states).

Spectroscopy in Supersonic Expansions. The study of the spectroscopy of cold gas-phase molecules has itself undergone a near supersonic expansion in the last few years,^{632a} and we shall see some more evidence of this later. Amirav *et al.*¹⁵²¹ have investigated the effect of changing the diluent gas on the degree of vibrational and rotational cooling in expansions of several large molecules, and have demonstrated laser spectroscopy of such molecules in high-flow seeded supersonic beams in an experimental system which is only mechanically pumped.

The low average energy of molecules in supersonic expansions has allowed many weakly bound species, particular so called van de Waals molecules, to be studied, as was mentioned, for example, on p. 279. This technique has also allowed the observation of bound-bound transitions in an excimer, the dimethyltetrazine dimer, which is bound in its excited state but conventionally unbound in the ground state.¹³⁷³ Hydrocarbon excimers are well known in solution, but by comparison the dimethyltetrazine excimer is not strongly bound in its excited state, and the corresponding spectral shift in fluorescence is much less than is observed in hydrocarbon cases. With hydrocarbons, bonding is thought to rely on $\pi \rightarrow \pi^*$ charge transfer, whereas in dimethyltetrazine the transition is $n \rightarrow \pi^*$, which, because of lone pair localization, might be expected to be less susceptible to charge transfer. Because in addition excimers in solutions are usually identified by a large spectral shift in fluorescence, it is suggested that this weaker bonding may be the reason why $n \rightarrow \pi^*$ excimers have not previously been observed.

Although most of the studies of electronic spectroscopy in supersonic expansions have relied on the observation of fluorescence, there have now been a number of cases where absorption spectra (true absorption spectra, as opposed to laser induced fluorescence excitation spectra) have been measured. Such experiments were first performed in the infrared with conventional¹⁵²² and laser^{1551, 1523} sources. Ultraviolet absorption experiments on molecules from a nozzle expansion were reported by Vaida and McLelland¹¹⁴⁸ for *trans*-butadiene and also CS₂. They found that the broadness of the absorption spectrum (${}^1\text{B}_{1u} \leftarrow \text{X}$) of *trans*-butadiene is not reduced on cooling, and

¹⁵¹⁹ R. Vasudev and R. N. Zare, *J. Chem. Phys.*, 1982, **76**, 5267.

¹⁵²⁰ R. Shuker, A. Ben-Amar, and G. Erez, *Opt. Commun.*, 1981, **39**, 51.

¹⁵²¹ A. Amirav, U. Even, and J. Jortner, *Chem. Phys.*, 1980, **51**, 31.

¹⁵²² R. J. Jensen, J. G. Marizuzzi, C. P. Robinson, and S. D. Rockwood, *Laser Focus*, 1976, May, p. 51.

¹⁵²³ D. N. Travis, J. C. McGurk, D. McKeown, and R. G. Denning, *Chem. Phys. Lett.*, 1977, **45**, 287.

thus inferred that it was the result of very rapid radiationless relaxation rather than congestion of the spectrum.

This technique, besides having the obvious advantage of permitting the study of non- or weakly-fluorescing states, also measures true absorption intensities, rather than absorption intensities multiplied by fluorescence quantum yield (important because branching ratios for various relaxation pathways may vary with wavelength). It has allowed the investigation of the second $\pi \rightarrow \pi^*$ absorption bands of phenylacetylene, benzaldehyde, acetophenone,¹⁴⁴⁵ and styrene.^{1445,1455} The most important vibronic bands were attributed to modes associated with the substituents, in contrast to the first $\pi - \pi^*$ bands which are dominated by ring-localized mode structure.

The disadvantage of absorption compared with laser induced fluorescence is of course its much lower sensitivity. Arranging for absorption to occur within the laser cavity, thus modifying the laser output, may increase sensitivity greatly.^{656,1524} Lambert *et al.*⁸⁵⁹ have performed intracavity absorption (ICA) spectroscopy on dimethyl-s-tetrazine and molecular iodine in molecular beams, obtaining large enhancements of signal over extracavity experiments. Lineshapes obtained using this technique are not natural lineshapes, however, and the spectra require careful interpretation. Amirav *et al.*¹⁴³² have taken a more direct approach to improving sensitivity in absorption by increasing the path length. Using a pulsed, seeded, planar jet, expanded through a slit 35 mm long and 0.2 mm wide, they recorded absorption spectra of aniline, 9,10-dichloroanthracene, and 9-methylanthracene. Having gained three orders of magnitude in sensitivity over absorption experiments with a conventional nozzle source, they were able to compare absorption and fluorescence excitation spectra.

High Resolution, Double Resonance and Two-photon Techniques. Varieties of source modulation are often used in all branches of spectroscopy to improve signal-to-noise ratios, and heterodyne techniques (involving mixing with a local oscillator to produce beats, see also Part I¹), widely applied at low frequencies, have been used in the optical region. Bjorklund¹⁵²⁵ has described a new type of wavelength modulation spectroscopy, FM spectroscopy, which uses a single mode dye laser and an external phase modulator driven at radiofrequencies that are large compared to the spectral width of the feature of interest. Because they are thus widely separated, a single isolated frequency modulated sideband can probe the feature. This produces a distortion of the rf heterodyne beat signal, and by measuring the phase and amplitude of this signal, absorption and dispersion can be separately determined. I₂ absorption lines have been studied in this way. A modification of the technique⁸⁷³ uses very short pulses of light, and can build up absorption data quickly with very little exposure of the sample to the interrogating light, which may be important if the sample is particularly light sensitive. A further modification⁸⁶¹ splits the laser beam into pump and probe, and so by saturation spectroscopy allows investigation within the Doppler width. Similar experiments have been described by Hall *et al.*⁸⁶⁰ One reason why the signal-to-noise ratio is in all these cases very good (see, for example, Figure 12) is that the dye laser is relatively noise free at the modulation frequencies employed. The technique permits locking to optical resonances, promising laser stabilization to kilohertz accuracy.⁸⁶⁰

Some methods of sub-Doppler spectroscopy were described in Part I,¹ and have

¹⁵²⁴ S. J. Harris and A. M. Weiner, *J. Chem. Phys.*, 1981, **74**, 3673.

¹⁵²⁵ G. C. Bjorklund, *Opt. Lett.*, 1980, **5**, 15.

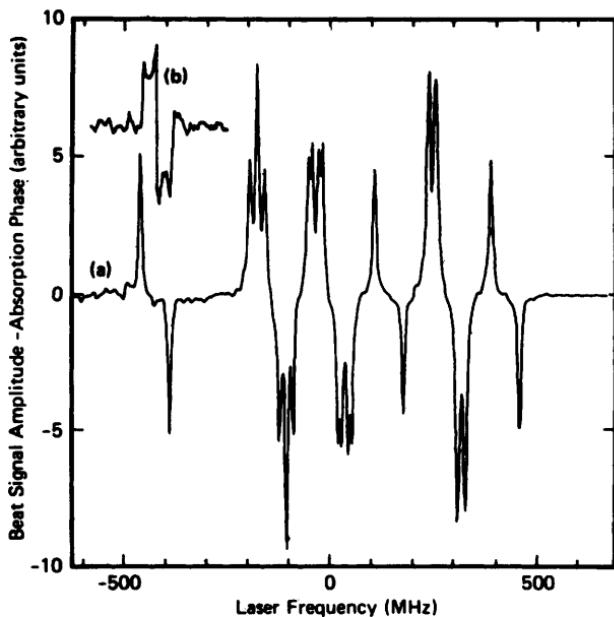


Figure 12 (a) Hyperfine splitting of a single rovibronic line of I_2 resolved by FM saturation spectroscopy, with the absorption phase detected. The modulation frequency was 71 MHz. Either the positive-going or negative-going peaks reproduce the hyperfine spectrum. (b) Dispersion-phase line shape due to the lowest-frequency hyperfine component.

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been discussed by, amongst others, Liao and Bjorkholm.¹⁵²⁶ They have involved using very narrow bandwidth lasers to saturate transitions in one velocity sub-group of molecules, then probing only these velocity-selected molecules. Couillaud *et al.*⁸²⁹ have demonstrated a technique which uses signal from several velocity sub-groups, since it employs counter-propagating trains of short light pulses from a mode-locked laser (*i.e.*, one with many oscillating modes, each ~ 1.6 MHz wide). Each mode interacts with a different sub-group, and from the resulting fringe pattern, they derive Doppler-free spectra, with improved signal-to-noise because of the increased fraction of molecules contributing. The experiment also promises a precise method for measuring line separations.

A number of other reports of interesting sub-Doppler experiments have appeared. Line-narrowing in backscattered fluorescence from BO_2 ($\bar{A}^2\Pi_u - \bar{X}^2\Pi_g$) has been observed, and the theoretical interpretation of this phenomenon discussed.¹¹¹⁸ The technique requires only one laser beam, which interacts with a velocity sub-group of molecules as usual, and uses a Fabry-Perot interferometer to analyse fluorescence; provided that the molecules fluoresce before being collisionally perturbed, the fluorescence will be narrower than the Doppler width. Similar considerations permit

¹⁵²⁶ P. F. Liao and J. E. Bjorkholm, 'Doppler-free laser spectroscopy', in 'Methods of Experimental Physics,' Vol. 15, Part B, ed. C. L. Tang, Academic Press, New York, 1979, p. 232.

sub-Doppler Fourier transform spectroscopy,* analysing either forward or backward scattered fluorescence.⁸³⁵

Polarization spectroscopy, described in Part 1,¹ is a sub-Doppler technique employing polarized pump and probe laser beams. By analysing with crossed polarizers, very small signals may be detected as a change in polarization of the probe beam, and this approach has been used to increase the sensitivity of saturated absorption experiments. Population labelling spectroscopy is a sub-Doppler optical-optical double resonance (OODR) technique; a pump beam is used to saturate a particular transition, and thus 'label' the participating levels. If a probe beam (generally now of a different frequency) is tuned to a second transition which shares a common level with the first, then when the first is pumped, the absorption of the probe beam will be modified. When polarization and population labelling spectroscopy are combined, the result is a method of spectral simplification with high sensitivity and sub-Doppler resolution.

This combination has been called two-step polarization labelling, and has been applied by Carlson *et al.*⁸⁸⁴ to study excited states of Na₂. In their experiment, the probe beam excitation was out of the upper level of the labelled transition, thus reaching Rydberg states (see Figure 13). Twenty-four new ¹Σ_g⁺, ¹Π_g and ¹Δ_g states were observed, and assigned as *n* = 3 to 14 members of several Rydberg series; it was possible to extrapolate to obtain constants for the ground state of this ion (Na₂⁺, X²Σ_g⁺). A later study⁸⁹⁴ considers the ¹Σ_g⁺ states of Na₂ in more detail, exploiting the accessibility of these states *via* this two-photon process denied to one-photon spectroscopy by inversion symmetry. Brand *et al.*⁸⁷² have used this approach to study

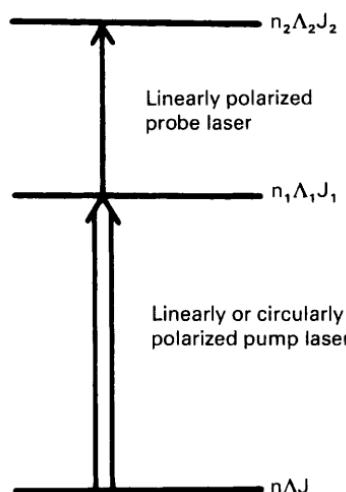


Figure 13 Two-step polarization labelling, examining higher excited states
(Reproduced by permission from *Phys. Rev.*, 1981, **24**, 822)

* Technical details of Fourier transform spectroscopy may be found in 'Spectrometric Techniques', Vols. I and II, ed. G. A. Vanasse, Academic Press, New York, 1977 and 1981.

the E state of I_2 , exciting $E(0_g^+) \leftarrow B(0_u^+) \leftarrow (X0_g^+)$, and carried out rotational analysis of the $v = 0$ —15 levels of the E state.

Optical-optical double resonance population labelling experiments in which detection is by the monitoring of fluorescence are well established, as we saw in Part 1,¹ and a number of variations on this theme have appeared. Johnson *et al.*⁹⁴³ have studied the C-X system of BaI, sampling from the already narrow velocity distribution of a molecular beam. Signals could appear as an increase or decrease in fluorescence intensity, as Figure 14 shows. Related experiments on CeO in a Broida oven have been

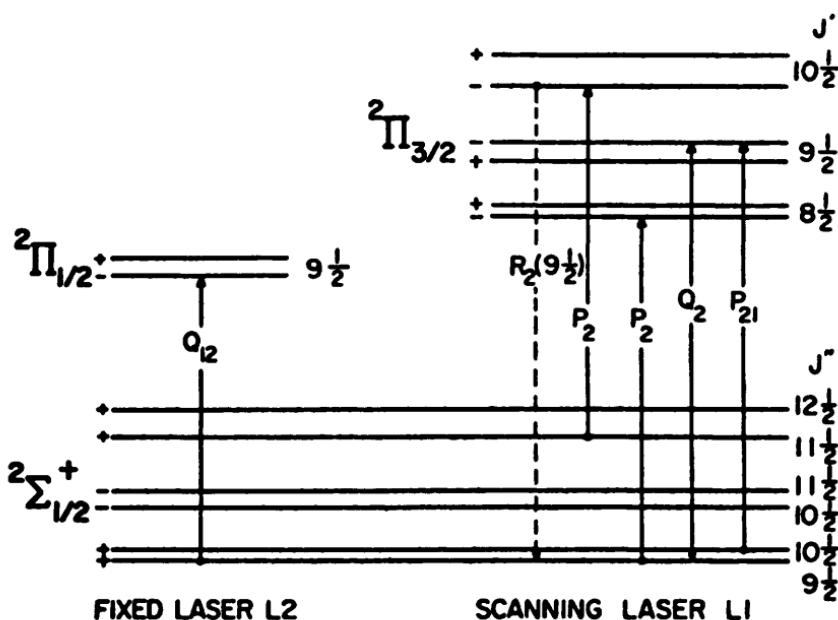


Figure 14 Energy level diagram for double resonance transitions. A double resonance signal results from a population change in the labelled level (in this case, $J'' = 9\frac{1}{2}$) probed by laser L2. Negative signals result when lasers L1 and L2 excite transitions with the same lower level, e.g., $P_2(9\frac{1}{2})$, $Q_2(9\frac{1}{2})$. Positive signals occur when L1 excites a transition terminating on an upper level optically connected to the labelled level, e.g., pump $P_2(11\frac{1}{2})$ and populate $J'' = 9\frac{1}{2}$ through fluorescence via $R_2(9\frac{1}{2})$

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carried out by Linton and Dulick,¹¹⁰⁸ in which the lower level of a transition being excited to give laser induced fluorescence was depopulated by a second laser, leading to reduced intensity of fluorescence.

Double resonance techniques are well suited to relaxation studies, because double resonance signals can arise when transitions are coupled by collisions, as well as when they are directly coupled. Gottscho *et al.*⁹¹⁴ have applied sub-Doppler OODR spectroscopy to study rotational and translational relaxation of BaO ($A^1\Sigma^+$) by Ar or CO₂ in a Ba + CO₂ + Ar flame (Broida oven). These two forms of relaxation were found to be strongly correlated, with small changes in J occurring with small centre of mass deflection angles, and being associated with the long range part of the

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intermolecular potential. The short range part of the potential was thought responsible for the larger changes in J , which were accompanied by large deflection angles. The technique has also been used to investigate collisional depolarization (changes in M_J).⁹¹⁵

Another related experiment is that of selective vibrational excitation by stimulated emission pumping (SEP),¹⁵²⁷ which uses two lasers called 'pump' and 'dump'. 'Pump' populates an intermediate electrically excited state. 'Dump' stimulates emission from the intermediate state down to high vibrational levels of the ground state. (This stimulated emission step contrasts with the second absorption step of conventional OODR.) As a method for the preparation of highly vibrationally excited molecules, SEP is much more state-selective than infrared multiphoton excitation, and can access a wider range of vibrational levels than can the direct excitation of overtones. The initial application populated high vibrational levels of I_2 via the B state.¹⁵²⁷ Subsequent experiments have been carried out on H_2CO ¹⁵²⁸ and *p*-difluorobenzene,¹⁵²⁹ and for the latter molecule vibrational relaxation from selectively populated levels has been observed.¹⁵³⁰

Related to SEP, and also to polarization labelling, is SEEPOL, stimulated emission enhanced polarization labelling.¹⁵³¹ As in SEP, there is pumping to an electronically excited state and a second laser field stimulating emission to high vibrational ground state levels. The sample is located within the cavity of the second (probe) laser, and so the signal (from emission to the vibrationally excited ground state levels) grows exponentially on propagation through the medium. Crossed polarizers suppress background light and only allow the probe beam to reach the detector when there is 'double resonance', so the technique is sensitive and bright line signals are observed. SEEPOL spectroscopy has been carried out on I_2 and NO_2 .

Experiments on $CaBr$ and CaF radicals have used a technique involving a molecular beam which is intersected normally by a pump laser beam, passes through a radiofrequency field, then is intersected, again normally, by a probe beam (split from the pump). The first beam, in exciting a fluorescent electronic state, severely depletes one hyperfine level of the ground state. The second beam, exciting the same transition, will only produce significant fluorescence if the depleted hyperfine level has been repopulated by the time molecules reach it. Repopulation can be achieved if the rf field is tuned to transfer molecules from neighbouring ground state hyperfine levels, and when this occurs a double resonance signal arises. This technique permits high precision measurements of spin-rotation and hyperfine interactions.^{923, 924, 936, 937} It has also been applied to SrF .⁹⁴⁰

Sub-Doppler resolution has been achieved in infrared-optical double resonance (IRODR) spectroscopy, which was used to investigate vibration-rotation transitions in the excited $\tilde{\Lambda}^1A_1$ state of the NH_2 radical.¹⁵³² A ring dye laser and either a CO_2 or an N_2O laser were employed. The sample cell could be placed either inside or outside the

¹⁵²⁷ C. Kittrell, E. Abramson, J. L. Kinsey, S. A. McDonald, D. E. Reisner, R. W. Field, and D. H. Katayama, *J. Chem. Phys.*, 1981, **75**, 2056.

¹⁵²⁸ D. E. Reisner, P. H. Vaccaro, C. Kittrell, R. W. Field, J. L. Kinsey, and H.-L. Dai, *J. Chem. Phys.*, 1982, **77**, 573.

¹⁵²⁹ W. D. Lawrance and A. E. W. Knight, *J. Chem. Phys.*, 1982, **76**, 5637.

¹⁵³⁰ W. D. Lawrance and A. E. W. Knight, *J. Chem. Phys.*, 1982, **77**, 570.

¹⁵³¹ J. C. D. Brand, K. J. Cross, N. P. Ernsting, and A. B. Yamashita, *Opt. Commun.*, 1981, **37**, 178.

¹⁵³² T. Amano, K. Kawaguchi, M. Kakimoto, S. Saito, and E. Hirota, *J. Chem. Phys.*, 1982, **77**, 159.

IR laser cavity, and each laser could be used as pump or probe. Detection involved the observation of \tilde{A} state fluorescence modulated, at double resonance, by the effect of the chopped infrared laser. Transitions were brought into resonance with an IR laser line by application of a magnetic field, and so the experiment combined IRODR with LMR. Some transitions were observed to a highly excited vibrational level of the ground state, assigned as a rotational level in \tilde{X} (2, 8, 0), but the measured spin-splitting did not agree with the value for \tilde{X} (0, 8, 0) earlier calculated by Jungen *et al.*¹⁵³³

The double resonance types of two-photon process we have so far discussed involve at least three real states. Two-photon absorption does not of course have to proceed *via* a real intermediate state. Electronically excited states of many molecules have been investigated by direct two-photon spectroscopy, which involves simultaneous rather than sequential absorption. Friedrich and McClain¹⁵³⁴ have collected together work in this area reported in the period 1973—79. Wirth, Koskelo, and Sanders¹⁵³⁵ have presented a tutorial discussion of the theoretical basis of two-photon spectroscopy, considering selection rules (different from those for the one-photon process, thus different states are populated) and in particular describing how excited state symmetry information may be acquired through the use of polarized laser beams.

Two-photon transitions in Na₂ have been investigated with a technique which analyses the response of a medium to elliptically polarized radiation (ELLIPSA – elliptical polarization state alteration).¹⁵³⁶ ELLIPSA probes the non-linear susceptibility of the sample. Polarizers and retarders are placed at either end of the sample, and are adjusted to give a null transmission value at low laser intensity. As the laser intensity is increased transmission can occur because of optically non-linear processes in the sample. Comparison of ELLIPSA with conventional two-photon excitation spectra showed that typically linewidths were similar but ELLIPSA line density was twice as great. Exceptional features, which were very broad and intense, appear in the ELLIPSA spectrum at 568—569 nm. These were ascribed to hybrid molecular atomic resonances associated with the 4d–3p atomic transition.

Many rotational lines are usually hidden within the Doppler profile of a molecule such as benzene, but two-photon spectroscopy with high resolution cw lasers has been used to excite individual lines in a sample of the gas at room temperature.¹⁴¹⁶ In this the first example of such an experiment benzene in the S₁ state was found to be well described as a symmetric top. Two-photon spectroscopy has also been carried out (using a pulsed laser) in a planar supersonic expansion of the type described earlier, where transitions in the molecule fluorene were observed.¹⁴⁷³

Developments in Theory and Data Interpretation.—An appreciation of the various ways in which angular momenta can couple is central to the interpretation of much of electronic spectroscopy. Hund distinguished a number of different cases of such coupling¹⁵³⁷ but these are of course limiting cases: electronic molecular spectroscopy, even of diatomics, is rarely simple, and spectra arising from coupling of an inter-

¹⁵³³ Ch. Jungen, K. E. J. Hallin, and A. J. Merer, *Mol. Phys.*, 1980, **40**, 65.

¹⁵³⁴ D. M. Friedrich and W. M. McClain, *Annu. Rev. Phys. Chem.*, 1980, **31**, 559.

¹⁵³⁵ M. J. Wirth, A. Koskelo, and M. J. Sanders, *Appl. Spectrosc.*, 1981, **35**, 14.

¹⁵³⁶ R. Vasudev, T. M. Stachelek, W. M. McClain, and J. P. Woodman, *Opt. Commun.*, 1981, **38**, 149.

¹⁵³⁷ G. Herzberg, 'Molecular Spectra and Molecular Structure. I. Spectra of Diatomic Molecules', Van Nostrand, New Jersey, 1950.

mediate type are frequently encountered. It may be possible to consider such spectra on the basis of a pure coupling case by introducing perturbations (off-diagonal terms in the chosen basis). It may further be possible, however, to perform a deperturbation and recover the (diagonal) parameters of the basis state. Perturbations are generally manifested as irregularities in spectroscopic observations, but these irregularities may be 'removed' on deperturbation.

As the number of mutually perturbing states increases, so naturally do the difficulties, in the gathering of sufficient data as well as in the deperturbation of the results. A spectroscopic *tour de force* in this area is the study by Bergemann and Cossart of the lower excited states of CS,⁹⁷⁸ the report of which occupies over seventy pages of the *Journal of Molecular Spectroscopy*, and which brings together experimental results in the ultraviolet and the infrared recorded in four laboratories over a number of years. Although limiting cases are quite good descriptions of coupling in the valence states of CS [case (b) for Σ states], there are 'incipient case (c) effects', whereby the spin-orbit operator tends to couple all levels of the same Ω [Ω is the total angular momentum along the internuclear axis: L and S are not defined in pure case (c) because their mutual interaction is stronger than their individual coupling to the internuclear axis]. The spin-orbit coupling elements vary with vibronic levels, so it is necessary to have a substantial amount of information on each electronic state, and then to analyse all levels and interactions, in order to extract deperturbed parameters for any one of the states involved.

An iterative process was used to obtain deperturbed vibration and rotation parameters for the $A^1\Pi$, $a^3\Pi$, $a'^3\Sigma^+$, $e^3\Sigma^-$, and $d^3\Delta_i$ states of CS. The $G(v)$ and $B(v)$ parameters so derived were found in general to vary smoothly with v , and RKR potential curves were calculated. Studies such as this are not only of fundamental importance, but should for example allow the calculation of more accurate Franck-Condon factors, and may improve the understanding of spectra observed when the molecule is produced as an excited photofragment.

Other recent interesting deperturbation analyses include that of Gottscho *et al.*⁷²⁹ of the $A^2\Pi-X^2\Sigma^+$ and $B^2\Sigma^+-X^2\Sigma^+$ exciplex bands of NaNe [the molecule exhibits a transition from *atomic* (Na) Hund's case (c) near the dissociation limit where the Na-Ne interaction is weak, to Hund's case (a) as the interatomic distance decreases] and the analysis by Vergès *et al.*¹⁵³⁸ of the Fourier transform data on Te_2 .

Orbital angular momentum in triatomic molecules has been considered in a series of papers by Jungen, Merer, and Hallin. A matrix treatment is described of orbital angular momentum effects in Born-Oppenheimer states that become degenerate in the limit of a linear configuration.¹⁵³⁹ Essentially it extends Renner's treatment of linear molecules to bent molecules, and includes the effects of large amplitude bending motions as perturbations of a linear molecule. Applications are described to NH_2 and H_2O^+ ($\tilde{A}^2A_1-\tilde{X}^2B_1$)¹⁵⁴⁰ and $C_3(\tilde{A}^1\Pi_u)$.¹⁵⁴¹ (Vibronic corrections and anharmonic effects in linear molecules have also been considered.¹⁵⁴²) Duxbury and Dixon¹⁵⁴³ have

¹⁵³⁸ J. Verges, C. Effantin, O. Babaky, J. d'Incan, S. J. Prosser, and R. F. Barrow, *Phys. Scr.*, 1982, **25**, 338.

¹⁵³⁹ Ch. Jungen and A. J. Merer, *Mol. Phys.*, 1980, **40**, 1; 41, 383.

¹⁵⁴⁰ Ch. Jungen, K.-E. J. Hallin, and A. J. Merer, *Mol. Phys.*, 1980, **40**, 25 and 65.

¹⁵⁴¹ Ch. Jungen, K.-E. J. Hallin, and A. J. Merer, *Mol. Phys.*, 1980, **40**, 95.

¹⁵⁴² D. Gaujacq and Ch. Jungen, *Mol. Phys.*, 1980, **41**, 383.

¹⁵⁴³ G. Duxbury and R. N. Dixon, *Mol. Phys.*, 1981, **43**, 255.

treated this problem adiabatically using a bent molecule approach, and have shown that, whilst the two methods are numerically equivalent, there are occasions when each is computationally more appropriate. Application to CH₂ and CD₂ has been described.¹¹²⁹

Reliable estimates of Franck–Condon factors are often needed when information sufficient for their accurate calculation is not available. Nicholls¹⁵⁴⁴ has presented simple approximate analytic expressions which may be used to calculate Franck–Condon arrays when only ω_e , r_e and reduced mass values are known. Applications to CeO, CoH, CrH, CrO, CuH, GeH, LaO, NiH, SnH, and ZnH are tabulated.

Whiting *et al.*¹⁵⁴⁵ have attempted to resolve the confusion in diatomic spectroscopy in the relationship between electronic transition moments and rotational line intensity factors. Applying the definition of line strength for atomic lines directly to rotational lines,

$$S_{J'J''} = \sum_{M'M''} | \langle \psi_M | \mu | \psi_{M''} \rangle |^2$$

they propose that the following equation

$$S_{J'J''} = q_{v'v''} |R_e|^2 S_{J'J''}$$

should define the relationship between $S_{J'J''}$ (the rotational line intensity factor) and R_e (the electronic transition moment) where $q_{v'v''}$ is the Franck–Condon factor. It is to apply to a *single* rotational line, and not, for example, to both rotational lines in a lambda doublet. They further recommend that the electronic transition moment operator for perpendicular transitions be defined as $(\frac{1}{2})(\mu_x \pm i\mu_y)$. This leads to consistency of the sum rules for rotational line intensity factors for parallel and perpendicular transitions.

Hutson¹⁵⁴⁶ has presented an improved computational method for the calculation of centrifugal distortion constants for diatomic molecules. It solves perturbation equations directly, without expansion of the solution in terms of unperturbed eigenfunctions, and so avoids summations over vibrational states. Such an approach is useful particularly when high vibrational levels are involved, as it is more economical in computer time, and is more accurate because it does not neglect contributions from continuum states.

The behaviour of diatomic molecules near the dissociation limit has long been of interest, not least because of its importance to the determination of dissociation energies. A good estimate of the dissociation energy may be obtained from the area under a correctly extrapolated curve of $\Delta G_{v+\frac{1}{2}}$ versus v , as pointed out by Birge and Sponer, but there is no reason why the extrapolation should be linear, and so considerable uncertainty may be associated with the use of this approach.

An alternative approach has been proposed by LeRoy and Lam.⁷⁴² A molecule near the dissociation limit spends most of its time around the outer turning point. Its properties thus depend mainly on that particular part of the potential energy curve, which has an inverse power form [$V(r) \simeq D - C_n/r^n$], and simple analytic expressions derived from this equation have been shown to describe quantitatively behaviour in this

¹⁵⁴⁴ R. W. Nicholls, *Astrophys. J. Suppl.*, 1981, **47**, 279.

¹⁵⁴⁵ E. E. Whiting, A. Schadee, J. B. Tatum, J. T. Hougen, and R. W. Nicholls, *J. Mol. Spectrosc.*, 1980, **80**, 249.

¹⁵⁴⁶ J. M. Hutson, *J. Phys. B*, 1981, **14**, 851.

region (see, for example, the data of King *et al.*⁸³¹ on $^{129}\text{I}_2$, which extends to within 2 cm^{-1} of the dissociation limit). LeRoy and Lam have incorporated this description in an empirical 'near-dissociation expansion', and so the unsure extrapolation becomes an *interpolation* between known properties lower down the potential and known limiting near-dissociation behaviour. Application of this method to BeAr^+ produced markedly different values for D_e , and the total number of bound levels, than had previously been estimated.

LeRoy⁸⁴² has further considered *deviations* from limiting near dissociation behaviour. He finds that for strongly bound species, deviations are associated with higher inverse power terms than C_n/r^n contributing to the long range potential, and indeed that the leading term C_n/r^n may only be responsible for a fraction of the strength of the potential at the outer turning points. Nevertheless, it seems that vibrational energies should often *still* obey the limiting near-dissociation equation (in other words, it works better than is should at first sight). B_v values are more sensitive to the deviations, and their measurement, when this is possible, may provide a route to the determination of the coefficients of the higher order terms in the potential.

Increasingly, experiments are being designed to probe behaviour near the dissociation limit. In the laser induced fluorescence experiments of Verma *et al.*⁸⁸⁷ on Na_2 , transitions are seen not only to bound vibrational levels of the entire potential well, but also to the continuum. Bacis *et al.*⁸⁴¹ have used LIF/FTS to measure hyperfine parameters eQq in the X, 1_g and 0_g^+ states of I_2 , and have obtained eQq as a function of vibrational energy from the bottom of the potential well to close to the dissociation limit. They interpreted the results using LCAO eigenfunctions at short internuclear distances and a separated atom basis near the limit, and could observe the transition between the two basis sets. From this study, they propose that eQq may be considered as an indicator of the appropriateness of a particular molecular eigenfunction. The saturated absorption results of Bordé *et al.*⁸⁶³ on the hyperfine spectroscopy of $^{127}\text{I}_2$ show a variation in hyperfine constants near the dissociation limit which is interpreted as indicating a mixing of u and g states.

(We shall not discuss *ab initio* calculations as these are outside the scope of this report, but we draw attention to the books by Carsky and Urban¹⁵⁴⁷ which describes the methods and applications of such calculations, and by Mulliken and Ermel¹⁵⁴⁸ which reviews the results of *ab initio* calculations on polyatomic molecules reported up to and including 1979.)

Excited State Dynamics.—Here we discuss the large and complex subject of the relaxation of molecules in electronically excited states. It is difficult to draw a line to separate spectroscopy from kinetics and molecular dynamics, since the interpretation of the former is often bound up in the latter, and again we have to be brief in our treatment. However, some parts of this field have prompted the writing of many review articles, and we shall first mention some of these.

If articles on radiationless processes often seem daunting, then an introduction which is slightly more friendly than usual may be found in the report of a NATO

¹⁵⁴⁷ P. Carsky and M. Urban, 'Ab initio Calculations: Methods and Applications in Chemistry' (Lecture notes in Chemistry, 1980, Vol. 16.)

¹⁵⁴⁸ R. S. Mulliken and W. C. Ermler, Polyatomic Molecules: Results of *ab initio* Calculation', Academic Press, New York, 1981.

summer school held in 1979,¹⁵⁴⁹ which includes accounts of present trends in theory,¹⁵⁵⁰ basic theory,¹⁵⁵¹ and spectroscopy and radiationless decay in simple¹⁵⁵² and large molecules¹⁵⁵³ (although the treatments are not in general restricted to the gas phase). A notable book at the research level which has appeared is the compilation 'Radiationless Transitions',¹⁵⁵⁴ containing articles about rotational effects on radiationless processes,^{1555,1556} intramolecular vibrational relaxation¹⁵⁵⁷ and experimental measurements of state-selected relaxation in small polyatomic molecules.¹⁵⁵⁸ Another considerable collection of relevant reviews may be found in the 'Photoselective Chemistry' volume of *Advances in Chemical Physics*.¹⁵⁵⁹ Some of these reviews we have referred to in Section 2; others concern excitation and relaxation processes,¹⁵⁶⁰ photofragment spectroscopy,^{1561,1562} and collision-induced relaxation.^{1563,1565} Studies of collision-induced intersystem crossing and radiationless transitions using time-resolved techniques have been discussed by Erman.¹⁵⁶⁶ Schlag, Henke, and Lin have reviewed the photophysics of molecules in single rovibronic states.¹⁵⁶⁷ Volume 4 of 'Excited States' has appeared since our last Report,¹ and contains articles on luminescence from molecules in magnetic fields¹⁵⁶⁸ and time-resolved spectroscopic studies.¹⁵⁶⁹

Diatomic Molecules. A 'lifetime-separated' spectroscopic study of the a-X system of PbO has been carried out by Brom and Beattie.⁹⁸⁹ The a state is expected to be long-lived, based on a $^3\Sigma^+(1)$ assignment, but confirmation of the Hund's case (c) $\Omega = 1$

- ¹⁵⁴⁹ B. di Bartolo, ed. 'Radiationless Processes', Plenum Press, New York, 1980.
- ¹⁵⁵⁰ F. Williams, D. E. Berry, and J. E. Bernard, 'Present Trends in the Theory of Radiationless Processes' in 'Radiationless Processes', ed. B. di Bartolo, Plenum Press, New York, 1980, p. 1.
- ¹⁵⁵¹ B. di Bartolo, 'Spectroscopy and Radiationless Deactivation', in 'Radiationless Processes', ed. B. di Bartolo, Plenum, New York, 1980, p. 39.
- ¹⁵⁵² 'Spectroscopy and Radiationless Processes in Simple Molecules.' in 'Radiationless Processes', ed. B. di Bartolo, Plenum Press, New York, 1980, p. 89.
- ¹⁵⁵³ J. Jortner, 'Electronic Relaxation in Large Molecules', in 'Radiationless Processes', ed. B. di Bartolo, Plenum Press, New York, 1980, p. 103.
- ¹⁵⁵⁴ S. H. Lin, ed., 'Radiationless Transitions', Academic Press, New York, 1980.
- ¹⁵⁵⁵ W. E. Howard and E. W. Schlag, 'Rotational Fine Structure in Radiationless Transitions', in 'Radiationless Transitions', ed. S. H. Lin, Academic Press, New York, 1980, p. 81.
- ¹⁵⁵⁶ F. A. Novak, S. A. Rice, M. D. Morse, and K. F. Freed, 'On Rotational Effects in Radiationless Processes in Polyatomic Molecules', in 'Relationless Transitions', ed. S. H. Lin. Academic Press, New York, p. 135.
- ¹⁵⁵⁷ R. P. H. Reitnschnick, 'Vibrational Relaxation of Isolated Molecules', in 'Radiationless Transitions', ed. S. H. Lin, Academic Press, New York, 1980, p. 185.
- ¹⁵⁵⁸ E. K. C. Lee and G. L. Loper, 'Experimental Measurement of Electronic Relaxation of Isolated Small Polyatomic Molecules from Selected States', in 'Radiationless Transitions', ed. S. H. Lin, Academic Press, New York, 1980, p. 1.
- ¹⁵⁵⁹ J. Jortner, R. D. Levine and S. A. Rice, ed., 'Photoselective Chemistry' (*Advances in Chemical Physics*, Vol. 47, Parts 1 and 2) Wiley-Interscience, New York, 1981.
- ¹⁵⁶⁰ J. Jortner and R. D. Levine, *Adv. Chem. Phys.*, 1981, **47** (Part 1), 1.
- ¹⁵⁶¹ A. Baronavski, M. E. Umstead, and M. C. Lin, *Adv. Chem. Phys.*, 1981, **47**, 85.
- ¹⁵⁶² K. H. Welge and R. Schmiedl, *Adv. Chem. Phys.*, 1981, **47**, 133.
- ¹⁵⁶³ S. A. Rice, *Adv. Chem. Phys.*, 1981, **47** (Part 2), 237.
- ¹⁵⁶⁴ K. F. Freed, *Adv. Chem. Phys.*, 1981, **47** (Part 2), 291.
- ¹⁵⁶⁵ A. Tramer and A. Nitzan, *Adv. Chem. Phys.*, 1981, **47** (Part 2), 337; see also K. F. Freed, *ibid.*, 1980, **42**, 207.
- ¹⁵⁶⁶ P. Erman, *Phys. Scr.*, 1982, **25**, 365.
- ¹⁵⁶⁷ E. W. Schlag, W. E. Henke, and S. H. Lin, *Int. Rev. Phys. Chem.*, 1982, **2**, 43.
- ¹⁵⁶⁸ S. H. Lin and Y. Fujimura, 'Effect of Magnetic Field on Molecular Luminescence', in 'Excited States', Vol. 4. ed. E. C. Lim, Academic Press, New York, 1979.
- ¹⁵⁶⁹ A. Tramer and R. Voltz, 'Time-resolved Studies of Excited Molecules', in 'Excited States', Vol. 4 ed. E. C. Lim, Academic Press, New York. 1979.

nature of the state required rotational analysis. A laser excitation spectrum was taken, and by careful choice of delay and gate widths, it was possible to eliminate A–X fluorescence, which occurs in the same region but has a much shorter radiative lifetime. A rotational analysis could thus be carried out, and the nature of the state was confirmed.

Predissociation of the halogens and interhalogens continues to be of interest; despite the radiationless pathway, laser induced fluorescence can often still be observed, and the rovibrational dependence of the predissociation may thus be studied (e.g. ref. 1033). A strong state dependence of predissociation rate is often found. As we saw in Part 1,¹ for the $B^3\Pi(0_u^+)$ state of Br_2 the lifetime results could be fitted to an expression:

$$\Gamma_0 = \Gamma_r + K_{v'}(J' + 1)J'$$

where $\Gamma = 1/\tau$, Γ_r is the lifetime free from predissociation, and k_v is a vibronically dependent constant. This predissociation is heterogeneous, and occurs because the bound (B state) potential curve is crossed by the repulsive curve of the $\Pi(1_u)$ state. The continuum wavefunction is expected to be of the form of an Airy function, rising sharply near the crossing point and extending outwards in a series of fluctuations. There can thus be variations in the bound–free overlap integrals and hence in the predissociation rate. Child¹⁰⁴² has derived an analytical procedure whereby the period of the variations can be related to the rate of divergence of the bound and repulsive potential curves. It involves expressing the Franck–Condon factors in terms of an energy dependent phase integral, which can be inverted to allow an RKR type determination of the repulsive potential curve. The problem in this particular case was that the rate of variation was slow, with few maxima; it was shown that this occurs when the inner limb of the bound state is roughly parallel with the repulsive state and that it is associated with a change of phase integral of π between successive vibrational levels. This was turned to advantage, since it allowed simplified expressions to be derived for the recovery of the repulsive potential curve.

Clyne *et al.*¹⁵⁷⁰ have treated this problem numerically, rather than analytically, calculating overlap integrals and varying the form of the repulsive potential to reproduce the experimental results, within some constraints imposed by an analysis of continuum absorption results pertaining to the $^1\Pi_u$ state. There is excellent agreement between the two approaches (even though in Child's case the results are not constrained to connect with the curve derived from the continuum absorption profile). The semi-classical treatment of Child has also been shown to be successful when applied to predissociation linewidth data on the $B'0^+-X\Sigma^+$ system of IBr .¹⁰⁶¹

The predissociation of the $B^3\Pi_{0+u}$ of I_2 has been discussed in a series of three papers by Vigué, Broyer, and Lehmann, which incorporate all current work and review results past and present.⁸⁶⁵ The first paper establishes the theory, and the second considers experiments on natural and hyperfine predissociation: predissociation of the B state of I_2 differs from that of Br_2 not only by being much slower, but by having a measurable *hyperfine* predissociation, suggested by the apparent predissociation of $J' = 0$, and confirmed by the detectable difference in lifetime between *ortho* and *para* rotational states. This more recent work confirms the picture of hyperfine and gyroscopic predissociation, paying attention to interference terms, and includes in its calculations

¹⁵⁷⁰ M. A. A. Clyne, M. C. Heaven, and J. Tellinghuisen, *J. Chem. Phys.*, 1982, **76**, 5341.

the J dependence of the Franck–Condon density (achieved *via* the Child approach) which significantly improves data interpretation.

The third paper in the series is concerned with experiments on magnetic predissociation, where interpretation is complicated further by interference by hyperfine and gyroscopic predissociation. Parameters relating to magnetic, natural, and hyperfine predissociation, and radiative decay, are deduced. These papers certainly represent the most comprehensive study carried out on such a complicated predissociation.

Triatomic Molecules. Predissociation in the $\tilde{\text{A}}^2\text{A}_2$ state of ClO_2 has been studied by the classical method of measuring absorption linewidths, in this case for the $\tilde{\text{A}}^2\text{A}_2 \leftarrow \tilde{\text{X}}^2\text{B}_1$ transition. Either a single pass or a White cell was used in conjunction with a 7 m spectrograph. The predissociation is indirect, proceeding *via* an intermediate manifold. The rate was found to be independent of the rotational state initially excited; a model prediction is that this should be so if the prepared and intermediate states have very similar geometry. The dominant interaction between the prepared and intermediate states is thought to be spin–orbit coupling. There also appears to be spin–rotation interaction leading to a mixing of spin states, and a dependence of rate on the spin state prepared.¹¹⁶¹

Predissociation and excited state dynamics in HNO $\tilde{\text{A}}^1\text{A}''$ have been studied using cw and time-resolved laser induced fluorescence spectroscopy^{1186, 1187} (and the excited state dipole moment measured by an OODR Stark sub-Doppler technique.¹¹⁸⁵ Breaking off of rotational structure was observed in several branches, and this was taken to indicate the onset of predissociation, which was shown to occur at threshold by crossing to the $\tilde{\text{X}}$ state. Spectroscopic and thermochemical data, and quantum calculations, were used to construct potential surfaces for the $\tilde{\text{X}}^1\text{A}'$, $\tilde{\text{a}}^3\text{A}''$, and $\tilde{\text{A}}^1\text{A}''$ states to aid in interpretation of the predissociation mechanisms. The breaking off energy was J' dependent, and this dependence could be fitted quantitatively, which led to an improved estimate of the ground-state dissociation energy.¹¹⁸⁷ Many apparently unperturbed levels of the $\tilde{\text{A}}$ state exhibited weak magnetic character, too large to be associated with a pure singlet state, but too small to be caused by interaction with a pure triplet state. Mixing of $\tilde{\text{A}}$ state and $\tilde{\text{X}}$ state levels, by orbital–rotational interaction, was thought to be responsible for this magnetic effect, because $\tilde{\text{X}}$ state levels are mixed by spin–orbit coupling to $\tilde{\text{a}}$ state levels, and thus the wavefunctions become contaminated with triplet character.¹¹⁸⁶

In Part 1,¹ we reported on unusual observations in the spectroscopy of NO_2 ,* where initially there appeared to be a large discrepancy between coherence lifetime (τ_c) in the excited state determined by Hanle effect measurements, and radiative lifetime. A suggested rationalization was as follows. In the excited state, NO_2 is asymmetrically distorted, and thus has two identical nuclei occupying two non-equivalent sites. Tunnelling can occur, and this causes a ‘bunch’ structure of close lying states. Thus if the molecule were prepared initially in a state which was non-stationary because of the bunch structure, internal relaxation (dephasing) could occur on a time-scale short compared with the fluorescence lifetime. In support of this rationalization, a broad resonance detected by radiofrequency-optical double resonance spectroscopy was ascribed to such a non-stationary state.

* Electronic relaxation in NO_2 is reviewed in ref. 1558.

However, we saw at the time that quantum beat experiments appeared to show that $\tau_c \sim \tau_r$, and subsequent RFODR experiments¹²²⁵ revealed that the ‘non-stationary state’ resonance structure was due instead to optical-radiofrequency two-photon transitions. Other magnetic field and level crossing experiments confirmed the removal of the experimental discrepancy between τ_c and τ_r .^{1217, 1225, 1226}

The explanation for these results appears to lie with the pressure dependence of the linewidth in the Hanle experiments. The Hanle width is linearly dependent on pressure above 0.5 μ bar (the lower limit of static gas experiments), but it transpires that linear extrapolation to zero pressure to obtain τ_c is invalid, and the zero pressure linewidth is narrower than had been estimated; this was demonstrated by molecular beam experiments. So the molecule is initially excited into levels belonging to one bunch, but the internal relaxation which causes the apparent shortening of τ_c must be a *collision-induced* process, and it does not arise through the spontaneous evolution of a non-stationary state.

Polyatomic Molecules. Formaldehyde is a small, stable polyatomic molecule with a sharp, rotationally resolvable spectrum; it has been very extensively studied. Its excited state dynamics are frequently reviewed and discussed,^{1558, 1571} most recently with specific reference to rotational fine structure.¹⁵⁶⁷ It is the rotational dependence of the fluorescence lifetime, and the implicit information about radiationless processes, which have been attracting most attention recently. Should there be a systematic rotational effect, and is it there?

There is evidence to suggest that H₂CO predissociates by a sequential mechanism via a ‘lumpy’ continuum ($S_1 \rightarrow S_0 \rightarrow H_2 + CO$): the ‘lumpiness’ of the continuum results in certain levels being resonantly predisposed towards the radiationless transition, so variations in lifetime might be expected. Experiments to Stark shift the $S_1 - S_0$ level spacings have shown that the continuum of S_0 levels coupled to S_1 near the S_1 origin is not particularly continuous,^{1279, 1280} and some lifetime variations have been found, although they were not generally thought to be systematic with J' , K' , or E_{rot} .^{1279, 1280, 1289, 1588}

Schlag and co-workers however^{1290, 1567, 1572} have extended earlier theoretical work^{1555, 1556, 1573} to allow the study of the effect of the rotational energy gap on the non-radiative single rotational level rate constant, as well as the effects of vibration–rotation coupling (through change in moment of inertia, and Coriolis interaction), intermolecular dephasing, and electric fields. The theory predicts a *systematic J and K dependence*, and such an effect is demonstrated for formaldehyde in the near-collisionless environment of a hypersonic jet.¹²⁹⁰ It is also suggested that trends may be present in other workers’ data, although they were not recognized as such at the time.¹⁵⁶⁷

The actual dissociation process in formaldehyde has also received experimental and theoretical attention.^{1574–1576} Crossed laser-molecular beam experiments^{1577a} have

¹⁵⁷¹ E. K. C. Lee and R. S. Lewis, *Adv. Photochem.*, 1980, **12**, 1.

¹⁵⁷² W. Henke, H. L. Selzle, T. R. Hays, E. W. Schlag, and S. H. Lin, *J. Chem. Phys.*, 1982, **76**, 1335.

¹⁵⁷³ F. A. Novak and S. A. Rice, *J. Chem. Phys.*, 1980, **73**, 858.

¹⁵⁷⁴ W. M. Gelbart, M. L. Elert, and D. F. Heller, *Chem. Rev.*, 1980, **80**, 403.

¹⁵⁷⁵ J. D. Goddard, Y. Yamaguchi, and H. F. Schaeffer, III, *J. Chem. Phys.*, 1981, **75**, 3459.

¹⁵⁷⁶ S. K. Gray, W. H. Miller, Y. Yamaguchi, and H. F. Schaeffer, III, *J. Am. Chem. Soc.*, 1981, **103**, 1900.

¹⁵⁷⁷ (a) P. Ho, D. J. Bamford, R. J. Buss, Y. T. Lee, and C. B. Moore, *J. Chem. Phys.*, 1982, **76**, 3630; (b) P. Ho and A. V. Smith, *Chem. Phys. Lett.*, 1982, **90**, 407.

demonstrated that formaldehyde definitely does dissociate without collisions following excitation near the S_1 origin. In agreement, LIF of CO following 355 nm dissociation of H₂CO shows it to be formed promptly in rotationally excited states ($J = 25-63$) and not by way of an intermediate.^{1577b}

Radiationless processes in glyoxal and related molecules have been studied.¹⁵⁵⁸ Level anticrossing spectroscopy has been used to probe singlet-triplet coupling for single rovibronic levels (SRL's) of the vibrationless 1A_u state,¹³³² and has confirmed that singlet-triplet interaction occurs at the weak coupling limit (*i.e.*, singlet-triplet relaxation does not occur in isolated molecules). The results were analysed in detail to give information on the coupling, the fine and hyperfine parameters of the triplet,¹³³⁴ and relaxation processes.¹³³⁵ Collision-induced relaxation has also been studied in a supersonic expansion, by monitoring fluorescence and phosphorescence following laser excitation ($0_0^0, 2_0^{1,1}A_u \leftarrow ^1A_g$).¹³³¹

Again, the dissociation process is of interest, since it seems that it does not have to proceed *via* the triplet. SRL excitation of glyoxal at low ('collision-free') pressures suggests that ' S_1 photochemistry' proceeds *via* an intermediate species, possibly vibrationally hot S_0 or an isomer.^{1338,1340} An intermediate also appears to be formed at higher pressures (where $S_1 \rightarrow T_1$), as revealed by the unusual variation of phase angle ϕ (between the light and pressure-train waves) in the optoacoustic S_1-S_0 spectrum. ϕ is usually constant or monotonically varying across an electronic transition, but not so here, where ϕ at fixed wavelength is intensity dependent, and at fixed intensity is wavelength dependent. This behaviour is attributed to quenching of T_1 by S_0 to form M, a long-lived intermediate, which produces heat (and products) *via* M + M.¹³³⁷

An important aspect of excited-state dynamics is vibrational energy redistribution, which can have a vital influence on the appearance of molecular spectra. We cannot consider adequately collisionally induced vibrational relaxation here, and refer the reader to recent reviews by Rice¹⁵⁷⁸ and by Parmenter.¹⁵⁷⁹

Parmenter¹⁵⁷⁹ also deals thoroughly with recent work on collision-free intramolecular vibrational (energy) redistribution (IVR). This may occur on a time-scale much shorter than the lifetime of the electronic state itself. IVR may be associated with the loss of sharp rotational structure (given that spectral congestion does not obscure the effect: if this is a problem, it can often be overcome by jet-cooling) and lifetimes with respect to IVR may be estimated from linewidths. From absorption spectra, Dunn¹⁵⁸⁰ has estimated level widths in *p*-difluorobenzene S_1 corresponding to lifetimes varying from tens of picoseconds at energies where broadening begins to appear, to picoseconds or less for levels above 3000 cm⁻¹. This compares with the collision-free lifetime of 12 nanoseconds (zero energy), falling to ~5 ns near 3300 cm⁻¹.¹⁵⁷⁹ Similar results were obtained from a study of fluorescence from jet-cooled naphthalene,¹⁴⁶⁴ where IVR occurred on a time-scale much shorter than that for fluorescence at a vibrational energy of 2570 cm⁻¹.

Smalley and co-workers have investigated a large number of jet-cooled alkyl benzenes,^{1448, 1459, 1470} phenylalkynes,¹⁴⁵² phenoxyalkanes¹⁴²⁷ and *p*-alkylanilines,¹⁴³⁰ finding extensive evidence of fast IVR, usually by pumping ring modes and observing redistribution into side-chain modes; in the case of the *p*-alkylanilines, even energy

¹⁵⁷⁸ S. A. Rice, *Adv. Chem. Phys.*, 1981, **47** Part 2, 237.

¹⁵⁷⁹ C. S. Parmenter, *J. Phys. Chem.*, 1982, **86**, 1735.

¹⁵⁸⁰ T. M. Dunn, unpublished, reported in ref. 1579.

deposited in the $-\text{NH}_2$ inversion mode found its way into the chain modes on the other side of the benzene ring within a nanosecond.

There have now been a number of observations of quantum beats in polyatomic molecules, such as SO_2 ,¹²⁴⁸ methyl glyoxal,¹³⁵⁷ biacetyl,^{1357, 1374} anthracene,¹⁴⁷⁴ pyrazine,^{1365, 1368, 1581} and pyrimidine,¹³⁶⁸ and whilst it is difficult to identify coupled levels, it is hoped that this type of spectroscopy may yield useful information on intramolecular relaxation processes, such as densities of interacting states, and average coupling energies,¹³⁵⁷ or rates of dephasing.^{1579*}

Photofragment Spectroscopy. In many of the examples we have considered so far in this sub-section, molecules have been excited to states where rotational structure, or at least vibrational structure, is resolvable, even though the molecule may be relaxed nonradiatively or even dissociatively. It is often the case, however, that spectra of molecules undergoing fast predissociation or direct dissociation reveal little information about the nature or dynamics of the excited state. The spectra may be broad, and may be further complicated if states overlap. Under these circumstances, it may be possible to recover information about the molecular excited states and dynamics by observing spectroscopically the distributions over energy or space of fragments produced in the dissociation.

A long standing problem approached in this way is the identification of excited states in the so-called A state continuum region in ICN, above 200 nm. Experiments have investigated product state distributions in both the I atom and the CN fragment, and measurements of I^* (5^2P_1) quantum yields suggest that at least three electronic states contribute to the absorption spectrum in the 240—280 nm region.¹²⁰⁵ For CH_2I_2 variation in the quantum yield for I^* (5^2P_1) production (248—340 nm) implies the operation of a curve-crossing mechanism in the dissociation,⁸⁵⁵ and $\text{I}(2^2P_1/2^2P_{3/2})$ branching ratio measurements following dissociation of I_2 (425—498 nm) have permitted deconvolution of the continuous I_2 absorption spectrum into contributions from the transitions $\text{B}^3\Pi_{0+u} \leftarrow \text{X}^1\Sigma_g^+$ and $\text{^1\Pi}_{1u} \leftarrow \text{X}^1\Sigma_g^+$.¹³¹⁴

Angular distributions of photofragments can reveal information about the nature of the dissociating state. By directly measuring such distributions following dissociation of sodium and potassium iodides and bromides, and thus measuring the ratios of parallel to perpendicular transitions in the 'first' excited state (there are two nearby excited states, of angular momentum $\Omega = 0$ and 1), van Veem *et al.*⁹⁰⁴ were able to construct potential curves for the Franck–Condon region. Measurement of the Doppler profiles of departing photofragments can also provide information on angular distributions,¹⁵⁸² combined with that on energy distributions.¹⁵⁸³ Angular momentum in the excited state may be investigated by observing the polarization of fragment fluorescence.¹⁵⁸⁴ A number of examples of this technique have recently been reported,^{1179, 1191, 1192, 1202, 1256} and the theory has been extended to allow for delayed predissociation,¹⁵⁸⁵ and the specific effects of electron impact excitation.¹⁵⁸⁶ All these

* We have not included here measurements of magnetic⁶⁸⁹ or electric⁶⁶⁵ field induced quantum beats, which have already allowed measurements of energy level splittings⁶⁸⁹ and dipole moments.⁶⁶⁵

¹⁵⁸¹ P. M. Felker, W. R. Lambert, and A. H. Zewail, *Chem. Phys. Lett.*, 1982, **89**, 309.

¹⁵⁸² J. A. Serri, J. L. Kinsey, and D. E. Pritchard, *J. Chem. Phys.*, 1981, **75**, 663.

¹⁵⁸³ K. H. Welge and R. Schmiedl, *Adv. Chem. Phys.*, 1981, **47**, Part 2, 133.

¹⁵⁸⁴ M. T. Macpherson, J. P. Simons, and R. N. Zare, *Mol. Phys.*, 1979, **38**, 2049.

¹⁵⁸⁵ G. W. Loge and R. N. Zare, *Mol. Phys.*, 1981, **43**, 1419.

¹⁵⁸⁶ H. W. Dassen and J. W. McConkey, *J. Phys. B.*, 1981, **14**, 3777.

examples have been of *molecular* photofragment polarized fluorescence. Such an effect, however, was first predicted many years ago for the *atomic* case,¹⁵⁸⁷ but only recently has the prediction been experimentally borne out, in the emission of polarized radiation by Na(²P_{3/2}) following dissociation of Na₂B(¹Π_u).⁸⁸¹

Ions.—Many fluoro- and chloro-substituted benzene radical cations, when excited into the B state, have a high quantum yield for fluorescence. They have been studied under various circumstances, such as by LIF following Penning ionization at room temperature, at low temperature, and in matrices,* and some examples were discussed in Part 1.¹ A good example is C₆F₆⁺; the B state is ²A_{2u}, and the ground state X²E_{1g}, and so fluorescence spectra exhibit effects of Jahn-Teller distortions in the ground state. Sears *et al.*¹³⁸⁷ have assembled the experimental data (which show that all four e_{2g} modes are Jahn-Teller active) and interpreted it using a model Hamiltonian which incorporates quadratic as well as linear Jahn-Teller coupling, and also mixing between the active modes. Level positions and transition intensities were successfully predicted by matrices of order ~7000 × 7000, and the distorted ion geometry at the potential minimum was determined.

Experiments on asymmetrically substituted halogenated benzene radical cations (LIF in neon matrices) have studied the asymmetry splitting of the doubly degenerate ground state (of C₆F₆⁺ or C₆H₆⁺) to form a non-degenerate ground state and a low-lying A state, with which there may be strong vibronic interactions. B → A emission was observed, and fluorescence polarization analysed.¹³⁸⁸

Radiative decay in radical cations has now been investigated in a large number of species, particularly substituted acetylenes and substituted benzenes, and radiative lifetimes have been measured. Maier^{1591–1593} has reviewed this field.† Many ions have been observed in emission in effusive molecular beams following excitation by a low energy electron beam.¹⁵⁹³ This technique, and the complementary techniques of LIF following Penning ionization, and photoelectron-photon coincidence spectroscopy, are illustrated in a study of chlorodiacetylene and dichlorodiacetylene.¹³⁶¹ (In photoelectron-photon coincidence spectroscopy,^{1143, 1592, 1593} an ion is generated by monochromatic radiation, the photoelectron is detected, then a photon is detected in ‘delayed coincidence’. If the ion decays radiatively, the signal will consist of a decay curve (of true coincidences) superimposed on a background of random coincidences. Furthermore, fluorescence quantum yields can be measured if the rate of collection of true electrons is known, and the electron collection efficiency can be established as a function of wavelength using internal standards.) A photoelectron-photon coincidence study of the Č state of fluorobenzene cations revealed that a Č ~ B radiationless step, and fast vibrational redistribution, precede the radiative relaxation (B → A, X).¹²⁹⁴

* We do not intend particularly to discuss the spectroscopy of ions in matrices. This field has been reviewed.^{1588, 1590}

† Studies to 1979 are tabulated in ref. 1591.

¹⁵⁸⁷ R. J. van Brunt and R. N. Zare, *J. Chem. Phys.*, 1968, **48**, 4304.

¹⁵⁸⁸ V. E. Bondybey and L. E. Brus, *Adv. Chem. Phys.*, 1980, **41**, 269.

¹⁵⁸⁹ V. E. Bondybey, *Adv. Chem. Phys.*, 1981, **47**, 521.

¹⁵⁹⁰ L. E. Brus and V. E. Bondybey, ‘Spectroscopic and Time Resolved Studies of Small Molecule Relaxation in the Condensed Phase’ in ‘Radiation Processes’, ed. S. H. Lin, Academic Press, New York, 1980, p. 259.

¹⁵⁹¹ J. P. Maier, *Chimia*, 1980, **34**, 219.

¹⁵⁹² J. P. Maier, *Angew. Chem., Int. Ed. Engl.*, 1981, **20**, 638.

¹⁵⁹³ J. P. Maier, *Acc. Chem. Res.*, 1982, **15**, 18.

Radiative decay and quantum yield information has been obtained for fluorobenzene cations¹³⁹² by the related technique of photoion–photon coincidence spectroscopy,^{1392, 1594} in which the photoions are accelerated to a detector, and photons are detected in coincidence as a function of delay to yield a decay trace. Emission from the $\tilde{\text{B}}$ state to the $\tilde{\text{A}}$ and $\tilde{\text{X}}$ states was observed, and some results were interpreted in terms of parent ion predissociation.

Several reports have now appeared of emission spectra recorded following electron impact excitation of species in supersonic molecular beams, which possess the usual properties of higher molecular densities and lower internal temperatures compared with effusive sources. First observed were $\text{N}_2^+(\text{B}^1\Sigma_u^+ \rightarrow \text{X}^2\Sigma_g^+)$, $\text{N}_2\text{O}^+(\text{A}^2\Sigma_u^+ \rightarrow \text{X}^2\Pi)$ and $\text{CO}_2^+(\text{A}^2\Pi_u \rightarrow \text{X}^2\Pi_g)$ by Carrington and Tuckett.⁷⁷² Fluorobenzene cations^{1389, 1391} have been studied in this way, as has the 2,4-hexadiyne cation, for which accurate excited state vibrational frequencies are reported.¹⁴²⁶ This technique has also been used to study the electron-molecule collision process leading to the formation of $\text{N}_2^+\text{B}^2\Sigma_u^+$ by observing the rotationally resolved emission spectrum as a function of incident electron energy. It was proposed that if the ejected electron leaves slowly (and there may be a significant probability for this even at high incident electron energies), there may be interactions between the ejected electron and the new N_2^+ ion; this could account for the observed (optically forbidden) large changes in ΔN ($\Delta N = 3, 5, 7 \dots$) which the spectra suggest are occurring.⁷⁶⁴

Fast ion beam photofragment spectroscopy has been reviewed by Moseley and Durup.¹⁵⁹⁵ A mass-selected ion beam interacts with a laser beam (intracavity or extracavity), and if dissociation occurs, any fragments produced may be detected with high sensitivity by another mass spectrometer. Fixed-frequency or tunable cw lasers may be used, and if laser and ion beam are coaxial, the system may additionally be Doppler tuned (by varying the ions' velocity), and sub-Doppler resolution may be obtained (because the absolute energy spread of the ion beam remains the same when the beam is accelerated from perhaps 1 eV to several keV; the velocity spread then corresponds to a temperature of less than 1 K). Using dye laser irradiation of NO^+ between 565 and 660 nm, 20 vibrational transitions tentatively identified as $2^3\Pi(v' = 0-19) \leftarrow b^3\Sigma^-(v'' = 8-10)$ were detected by production of N^+ or O^+ photofragments. The weakly bound $2^3\Pi$ state is homogeneously perturbed, and predissociated by the $a^4\Sigma^+$ state.⁸⁰⁰ Rotational lines have been observed in the $\tilde{\text{A}}^2\text{A}_1 - \tilde{\text{X}}^2\text{B}_1$ system of H_2S^+ , where predissociation was detected by the monitoring of S^+ ions.¹¹⁹⁸

Nuclear hyperfine structure has been observed using the fast ion beam photofragment technique in NH^+ , PH^+ , and SH^+ .¹⁵⁹⁶ The upper states involved were only weakly predissociated, but the experiment is very sensitive, and N^+ , P^+ , and S^+ were detected. The hyperfine structure could be resolved because of the reduction of the Doppler width, as discussed above, on acceleration; in this case the width was 40 MHz.

Optical-optical double resonance of molecular ions has been performed in an extension of this technique.¹⁵⁹⁷ The experiment is represented in Figure 15, and the apparatus is shown schematically in Figure 16. A probe laser labels a bound molecular

¹⁵⁹⁴ J. H. D. Eland, M. Devoret, and S. Leach, *Chem. Phys. Lett.*, 1976, **43**, 97.

¹⁵⁹⁵ J. Moseley and J. Durup, *Annu. Rev. Phys. Chem.*, 1981, **32**, 53.

¹⁵⁹⁶ C. P. Edwards, C. S. Maclean, and P. J. Sarre, *J. Chem. Phys.*, 1982, **76**, 3829.

¹⁵⁹⁷ P. C. Cosby and H. Helm, *J. Chem. Phys.*, 1982, **76**, 4720.

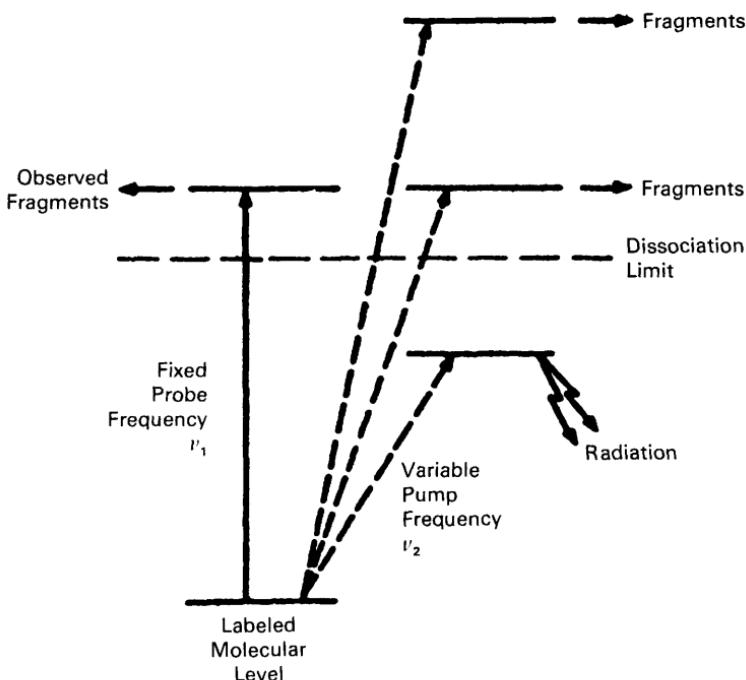


Figure 15 Schematic representation of the three-level double-resonance technique in photofragment spectroscopy

(Reproduced by permission from *J. Chem. Phys.*, 1982, **76**, 4720)

ion state (v'' , J'' , Ω'') by exciting it into a discrete predissociating state; the intensity of the photofragments so produced is a measure of the population of the labelled state. Upstream of the probe laser region, another laser beam interacts with the ion beam. If it is tuned to transitions originating from the labelled level, then the probe photofragment signal will drop. It does not matter whether these transitions are radiative or dissociative, so not only is the usual OODR advantage of spectral simplification conferred, but it becomes possible to use the photofragment technique to observe transitions between bound states. This technique has been applied to $O_2^+ b^4\Sigma_g^- (v' = 4) \leftarrow a^4\Pi_u (v'' = 5)$ and $f^4\Pi_g (v' = 1, 2, 3) \leftarrow a^4\Pi_u (v'' = 5); v' = 4, N' = 7$ of the b state and $v' = 1$ of the f state are not predissociated. The observations here support earlier proposals on vibrational numbering in the f state, and predissociation by the $E^2\Sigma_g^+$ state.⁸²⁰ (Other studies of b state predissociation have also appeared,^{816, 817, 826} and data relating to the $a^4\Pi_u$ state has been reconsidered using a modified Hamiltonian.⁸²³)

Laser induced fluorescence of CO^+ in a fast ion beam was reported in Part 1.¹ N_2^+ has also been detected in this way, and the internal state distribution of the ions in the beam has been measured.⁷⁷⁶ Laser induced fluorescence has further been observed from ions contained in a mass-selective quadrupole ion trap under collision-free conditions. Species studied include CH^+ and CD^+ , produced by electron impact on

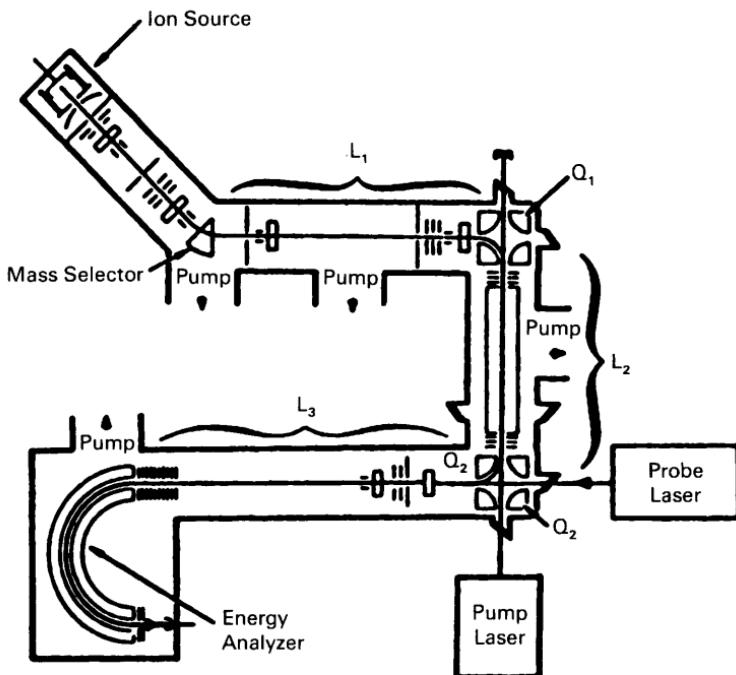


Figure 16 Schematic view of the laser-ion beam spectrometer in the configuration used for the double-resonance experiments. The scanned pump laser is coaxial with the molecular ion beam in region L₂. The fixed probe laser is coaxial with the molecular ion beam in L₃. Photofragments produced by the probe laser that are transmitted through the energy analyzer and detected, serve to monitor the population in the labelled lower state level

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CH(D)₄ or C₂H(D)₂, and observed spectra correspond to nascent internal energy distributions of the fragments.⁶⁸¹ Laser induced fluorescence spectra of supersonic jet-cooled molecular ions and ion-inert gas clusters have also been observed;¹³⁹⁵ we shall discuss this in the next sub-section.

Loosely Bound Complexes.—The spectroscopy and photochemistry of van der Waals molecules have been summarized by Levy.¹³⁹⁸ A number of recent studies, both experimental and theoretical, have been directed towards an understanding of the dynamics and predissociation processes which occur on electronic excitation, and many of these are discussed in the review by Beswick and Jortner.¹³⁹⁹

In experiments similar to those on alkylbenzenes and related molecules described on p. 354, Hopkins *et al.*¹⁴⁹⁰ have studied intramolecular vibrational relaxation (IVR) in van der Waals complexes of alkylbenzenes (up to n-octylbenzene) with Ar and N₂. If on electronic excitation the ring modes receive energy in vibration greater than the

¹³⁹⁸ D. H. Levy, *Adv. Chem. Phys.*, 1981, **47**, Part 1, 323.

¹³⁹⁹ J. A. Beswick and J. Jortner, *Adv. Chem. Phys.*, 1981, **47**, Part 1, 363.

dissociation energy of the complex, vibrational predissociation can occur. When Ar-alkylbenzene complexes are excited in the $6b$ ring distortion mode of the ${}^1\text{B}_{2u} S_1$ electronic state (529 cm^{-1}), they predissociate much faster than the fluorescence decay rate of about $1.3 \times 10^7 \text{ s}^{-1}$. This is indicated by the fluorescence spectrum, which is significantly narrower for the complex than for the free alkyl benzene (the free alkyl benzene spectrum is broadened by vibrational randomization, whereas in the complex energy finds its way into the dissociative mode and the complex falls apart before randomization can occur). With N₂-alkylbenzene complexes, however, the time scale for vibrational randomization is faster, and the complex and free molecule spectra have similar widths. IVR into the alkyl chain modes thus proceeds at a rate lying between those for dissociation of the argon and nitrogen complexes. From linewidth measurements, predissociation in the argon complex following $6b_0^1$ excitation cannot be faster than $2 \times 10^{11} \text{ s}^{-1}$, and an upper limit to IVR is placed at about 10^{10} s^{-1} .

A related experiment, which again essentially forms the van der Waals complex in order to study the free molecules, has used the internal competition between the vibrational predissociation of the complex (chromyl chloride -He) and a non-radiative decay channel to detect a mode selective non-radiative process in chromyl chloride.¹⁶⁰⁰

A number of studies have involved I₂ van der Waals complexes. Observation of dispersed I₂* emission following dissociation of iodine-rare gas molecules has been used to estimate the binding energies of the complexes. D_0 for I₂He* is $13.6-14.8 \text{ cm}^{-1}$, for I₂Ne* $65-67 \text{ cm}^{-1}$, and for I₂Ar $220-226 \text{ cm}^{-1}$.¹⁴⁹⁵ Complexes of I₂ with *ortho* and *para*-H₂ and D₂ have been studied in a supersonic expansion sample (supersonic expansions were used in all the experiments discussed in this sub-section) by fluorescence excitation and wavelength-resolved emission spectroscopy.¹⁴⁹⁶ Many spectral features could be accounted for by an isotropic Morse potential with parameters $D_e = 122 \text{ cm}^{-1}$, $\omega_e = 106 \text{ cm}^{-1}$. However, differing absorption frequencies for *o*- and *p*-H₂ and D₂ complexes, and differing product state distributions following vibrational predissociation of *o*- and *p*-H₂I₂*, indicated some anisotropy in the potential. From linewidth measurements, vibrational predissociation lifetimes were estimated; the lifetime of *o*-H₂I₂* was thought to be as short as 18 ps, due to the similarity of the van der Waals stretching frequency (relatively high at $\omega_e \approx 100 \text{ cm}^{-1}$), and the stretching frequency of I₂* ($\omega_e \approx 128 \text{ cm}^{-1}$).

A one-dimensional cage effect is thought to hinder the dissociation of I₂Ar at 488 nm, which is 448 cm^{-1} above the I₂ B state dissociation limit and about 434 cm^{-1} above the B state dissociation limit for I₂Ar. Despite this excitation energy, I₂B → X fluorescence is observed, with a prominent (v' , 0) progression from $v' = 49$ to $v' = 23$. Termolecular recombination is excluded as an explanation because of the low gas density in the jet, and the observed pressure dependence. Instead it is proposed that impulsive transfer of kinetic energy occurs from an iodine atom fragment to the argon atom before separation of the atomic fragments is appreciable.¹⁶⁰¹

Langridge-Smith *et al.*¹⁵⁰⁰ have pointed to the long list of van der Waals molecules excited electronically for which the strength of the $\Delta v = 0$ transitions have indicated little change in the van der Waals potential on excitation. They have found an exception to this behaviour with the molecule NO-Ar, where there is a shift outwards of the excited state potential. Excitation is thus to the repulsive part of the potential,

¹⁶⁰⁰ J. A. Blazy and D. H. Levy, *J. Chem. Phys.*, 1982, **76**, 4328.

¹⁶⁰¹ J. J. Valentini and J. B. Goss, *J. Chem. Phys.*, 1982, **77**, 572.

and they observe direct dissociation (as opposed to the more usual vibrational predissociation) manifested as a broad, weak feature in the fluorescence excitation spectrum.

Larger complexes have been studied. Spectral features of I_2 with Ne and He, and with Ar and He, have been found to obey a band shift rule, *i.e.*, the displacement $\nu - \nu_0$ of a spectral feature in say $I_2Ar_aHe_b$ is given by:

$$\nu - \nu_0 = Aa + Bb \quad (\text{up to } a + b \approx 5)$$

where ν and ν_0 represent the frequencies of the feature in the complexed and uncomplexed I_2 , respectively, and A and B are shift frequencies. Thus the change in the binding energy appears simply related to the number of atoms complexed.^{1494, 1497}

Much larger complexes involving I_2 , with partners now described as 'solvent' species [Ar, N₂, benzene, n-alkenes (C_5 — C_8), cyclohexanone, diethylether, dimethyl-sulphide] have been observed by Saenger *et al.*¹⁴⁹⁹ The fluorescence excitation spectra 0—1400 cm⁻¹ above the dissociation limit of free I_2 were structureless. The fluorescence resulted, it was thought, from blue-shifted absorption of complexed I_2 , causing dissociation of the complex and emission from free I_2 . The absorption spectra of the complexes were seen to resemble liquid-phase spectra, and the presence of a fluorescence excitation spectrum at energies above the I_2 dissociation threshold suggests a hindering of the dissociation by a cage-effect process as discussed for I_2Ar .

Studies have also been made of large molecules bound in complexes with inert gases.¹⁶⁰² The tetracene (four fused rings) molecule has been observed bound to argon,^{1479, 1491} krypton and xenon¹⁴⁷⁹ atoms. Amirav *et al.*¹⁴⁷⁹ identify the molecules TAr_n ($n \leq 7$), TKr_n ($n \leq 4$), and TXe_n ($n \leq 2$), but report that spectral features do not obey a band shift rule with increasing n , in contrast to the observation of I_2 complexes. They suggest that successive rare gas atoms occupy geometrically inequivalent sites. Freedman and co-workers however,¹⁴⁹¹ studying tetracene–Ar complexes, see the spectral lines as series which can be fitted to a band shift rule, of the form:

$$\omega = \omega_0 + An + Bn^2$$

where A and B are frequencies of about -48 cm^{-1} and $+2\text{ cm}^{-1}$, respectively.

Ion-neutral interactions may be investigated by measuring photoionization efficiencies of van der Waals molecules in free jet expansions. This is illustrated in a study of carbon disulphide dimers and clusters.¹¹⁴⁷ Light from a discharge source is focused onto the molecular beam target with a vacuum monochromator, and ions are detected with a quadrupole mass spectrometer. Ionization energies were measured for $(CS_2)_n$, $n = 1$ —5, and the binding energy of $CS_2^{+} \cdot CS_2$ was deduced to be $17.5 \pm \text{kcal mol}^{-1}$.

Doubly ionized van der Waals dimers have been observed following electron beam impact on a supersonic expansion. A consideration of first and second atomic ionization potentials suggest that these species should exist below the dissociation limit, and NeX^{++} and $ArXe^{++}$ have been observed.¹⁶⁰³

As we mentioned earlier, laser induced fluorescence spectra of ions and ion–inert gas clusters have been observed.¹³⁹⁵ (After expansion through a nozzle, the parent molecules are ionized in a two-photon process by an ArF laser.) Species studied

¹⁶⁰² U. Even, A. Amirav, S. Leutwyler, M. J. Ondrechen, Z. Berkovitch-Yellin, and J. Jortner, *Faraday Discuss. Chem. Soc.*, 1982, 73.

¹⁶⁰³ H. Helm, K. Stephan, T. D. Mark, and D. L. Huestis, *J. Chem. Phys.*, 1981, 74, 3844.

include various halogen-substituted benzenes, and dimethyl diacetylene; linewidths of the uncomplexed ions were often instrument limited (1 cm^{-1}), contrasting with the $20\text{--}40\text{ cm}^{-1}$ linewidths observed at room temperature. Figure 17 shows the low frequency part of the excitation spectrum of $\text{C}_6\text{F}_5\text{H}^+$ at various stagnation pressures. In (a), the sharp structure corresponds to the free ion. In (b), the sharp lines remain but broad ($\sim 50\text{ cm}^{-1}$) features appear to the red. In (c), the sharp lines have disappeared, but the other features have broadened further and shifted to slightly lower frequency. At higher pressures still, only a continuous background is observed. The red shifted features are believed to be associated with $\text{C}_6\text{F}_5\text{H}^+$ clustered with several argon atoms.

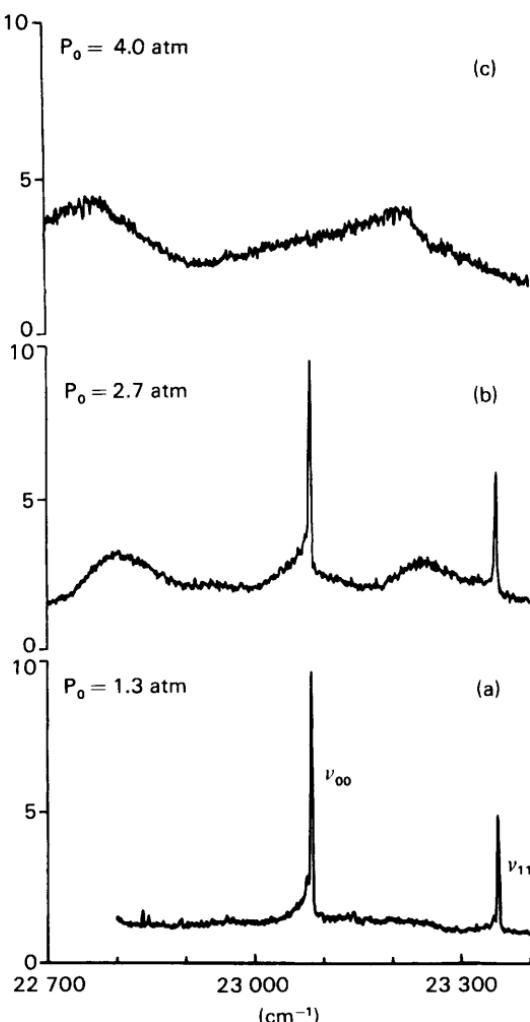


Figure 17 Laser excitation spectrum of $\text{C}_6\text{F}_5\text{H}^+$ expanded in a mixture of 10% Ar in He. The relevant stagnation pressure (P_0) is indicated on each trace
(Reproduced by permission from *J. Chem. Phys.*, 1982, **76**, 3831)

The shift in frequency corresponds well with that observed for $C_6F_5H^+$ in a solid argon matrix, but the features in the matrix are very much *sharper*. This may be because the large clusters are not extremely cold, despite collisional cooling in the expansion, because of heating which occurs on complex formation.

ArF laser photolysis of a species (methyl benzoate) in a supersonic expansion has been used to produce CH_3O radicals and the van der Waals complex $CH_3O \cdot Ar$. Laser induced fluorescence ($\bar{A}^2A_1 - \bar{X}^2E$) was excited, and rotational analysis showed the argon atom to lie on the three-fold symmetry axis at the oxygen end of the methoxy.¹³²³

(Some interesting *ab initio* calculations have been carried out on bonding in the Mg_4 cluster. This bonding was found to originate entirely from the effects of electron correlation. 'In general, if Hartree-Fock calculations yield little or no bonding, it has been concluded that the species is at best a van der Waals complex. The results for Mg_4 contradict this notion.'¹²⁹⁶)

Spectroscopy at Higher Frequencies.—This sub-section will be concerned with species and states produced at energies corresponding to one-photon excitation in the vacuum and extreme ultraviolet, although multiple photon processes will also be considered here.

One-photon Laser Spectroscopy. The desirability of intense, tunable one-photon sources at high frequencies remains very strong, if anything heightened by the glimpses of interesting spectroscopy provided by multiphoton ionization studies.* Raman-shifted sources have been used, particularly at the very low energy end of the region. Coherent VUV sources involving harmonic generation or frequency mixing have been known for some time, but until recently have usually remained the property of laser physicists rather than spectroscopists. Whilst molecular spectroscopic studies with such sources have been carried out, they remain sufficiently rare to warrant separate discussion.

A general review of this area has been given by Wallace.¹⁶⁰⁴ Coherent sources have now been demonstrated for wide regions of the high frequency spectrum; Hilbig and Wallenstein^{1605a} have shown that narrowband continuously tunable VUV radiation may be generated between 110 and 210 nm by non-resonant sum- and difference-frequency mixing in xenon and krypton. The second harmonic, ω_{UV} , of a Nd:YAG pumped dye laser is mixed with either the fundamental of the dye, ω_L , ($\omega_{VUV} = 2\omega_{UV} \pm \omega_L$) or of the Nd:YAG, ω_{IR} ($\omega_{VUV} = 2\omega_{UV} - \omega_{IR}$). With the narrow bandwidth dye laser used ($\Delta\nu \leq 120$ MHz), VUV output of narrow spectral width was obtained ($\Delta\lambda \leq 3 \times 10^{-5}$ nm at $\lambda_{VUV} = 121.6$ nm, although somewhat broader if the IR fundamental was mixed in). (See also ref. 1605b.) At yet higher frequencies, frequency mixing and harmonic generation have provided line sources down to 38 nm (7 \times fourth harmonic of Nd:YAG).¹⁶⁰⁶ All these sources have been pulsed, but cw coherent radiation (10⁷ photons s⁻¹ near 170 nm, using fundamental beams of less than 1 W power), produced by four-wave sum frequency generation in strontium vapour, has been reported.^{1607a}

Molecular hydrogen has been probed with coherent radiation in the extreme

* One and multiphoton experiments can be complementary, as we shall see later.

¹⁶⁰⁴ S. C. Wallace, *Adv. Chem. Phys.*, 1981, **47**, 153.

¹⁶⁰⁵ (a) R. Hilbig and R. Wallenstein, *Appl. Opt.*, 1982, **21**, 913; (b) J. Hager and S. C. Wallace, *Chem. Phys. Lett.*, 1982, **90**, 472.

¹⁶⁰⁶ J. Reintjes, *Appl. Opt.*, 1980, **19**, 3889.

¹⁶⁰⁷ (a) R. R. Freeman, G. C. Bjorklund, N. P. Economou, P. F. Liao, and J. E. Bjorkholm, *Appl. Phys. Lett.*, 1978, **33**, 779; (b) G. L. Wolk and I. W. Rich, *Chem. Phys. Lett.*, 1982, **87**, 117.

ultraviolet, around 83 nm.⁶⁵¹ 497 nm radiation from a cw dye laser was pulse amplified in a chain of four dye cuvettes pumped by a xenon fluoride laser. This blue radiation was then frequency doubled, and amplified in a single pass KrF exciplex cavity, to produce a 60 mJ, 15 ns pulse at 248 nm, with a bandwidth of ~150 MHz and a divergence of ~50 μrad (the elaborate arrangement being necessary to produce a high power, narrow bandwidth beam). This output was frequency tripled by focusing into ~10 Torr of xenon, with an efficiency of ~10⁻¹⁰ (a hundred-fold improvement occurs at 249.6 nm, coincident with a two photon resonance in xenon). The source is continuously tunable from 120 000 to 120 800 cm⁻¹, with a bandwidth of ≈0.1 cm⁻¹.

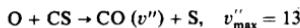
A number of excited states of hydrogen occur around 83 nm, some of which are predissociated. Whilst studies of this spectroscopy may be carried out over a wider spectral range with incoherent sources, such as a helium discharge,⁶⁴² or a synchrotron (with which fluorescence excitation spectra have been obtained),⁶⁴⁴ predissociation linewidths an order of magnitude narrower than previously possible have been measured with the coherent source. The D(3pπ)¹Π_u, D''(5pπ)¹Π_u, and B''(4pσ)¹Σ_u⁺ states in H₂, HD, and D₂ were studied, and line profile analyses based on Fano theory were performed to assess the importance of various factors in determining lineshape. In particular, it was seen that overlap integrals could vary linewidths by a factor of 2 or 3 over an energy range of ≈100 cm⁻¹. Mixing occurred at near resonances between weakly and strongly predissociated states, causing large changes in line shape and width, and these effects varied with isotopic species.

Zacharias *et al.*⁹⁶⁵ have photoionized CO with tunable VUV laser radiation. Nd:YAG pumped dye laser output (565 nm) was mixed with the IR laser fundamental to produce radiation around 370 nm, which was frequency tripled on focusing into 13–16 mbar of krypton. The transition (A¹Π, v' = 13 ← X¹Σ⁺, v'' = 0) was excited, and fluorescence could be observed* or ionization effected by the fourth harmonic of the Nd:YAG. NO was also photoionized directly with the VUV laser (NO⁺, X¹Σ⁺ ← NO, X²Π, v'' = 0).

By four wave sum mixing the output of two dye lasers in a heat pipe containing magnesium vapour, tunable coherent radiation in the range 145–174 nm may be obtained. Banic *et al.*⁷⁹⁴ have used such radiation to measure radiative lifetimes in the B²Δ state (v'' = 0 to 8) of NO. The resolution (~0.1 cm⁻¹) and intensity of the source permitted SRL excitation; some decays were single exponentials, and some double exponentials because of F²Δ and N²Δ perturbations. B²Δ state lifetimes obtained were about 220 ns, twice as long as those earlier determined by the high-frequency deflection electron excitation method.

Whilst some of the sophisticated laser experiments described above may require

* The production of A state fluorescence from CO (X¹Σ⁺, v'' = 0) requires VUV radiation. Hancock and Zacharias, however,⁹⁷² have excited such fluorescence from electronic ground state CO using Raman-shifted laser radiation between 213 and 230 nm. This was achieved by starting well up the potential curve, using vibrationally excited CO produced in the reaction:



Since virtually no CO is produced in low vibrational levels, electronic excitation creates a population inversion between levels of the A state and the low ground state levels. It is thus proposed that the excess energy of a chemical reaction may be used to convert UV to VUV laser radiation. Wolk and Rich^{1607b} have also performed LIF on CO using a doubled dye laser, first creating a highly non-equilibrium vibrational population of CO(X¹Σ⁺) in levels up to v'' = 40 by optical pumping and V-V energy transfer.

resources greater than those found in the average laboratory, Miller *et al.*^{1608a} have demonstrated that VUV spectroscopy may be performed with coherent light produced when the output of a commercial N₂-pumped dye laser is focused into a rare gas, and thus frequency tripled. Whilst third harmonic generation THG will only occur in regions of anomalous dispersion particular to individual non-linear media, tuning ranges with krypton and xenon are 140.3—146.9 nm, 125.0—129.6 nm, 120.3—123.5 nm, and 110.0—116.5 nm (the last requires an exciplex-pumped or frequency-doubled dye laser), and the bandwidth is ~0.05 Å. Demonstrations of the technique include the one-photon absorption spectrum of CO around 144 nm (see also ref. 1609), the one-photon photoionization threshold region in iodobenzene around 141 nm, and a comparison of the two-photon (one VUV + one blue) photoionization and one-photon absorption spectrum of NO around 145 nm. CO itself is a promising medium for THG, which has been observed in competition with 6-photon MPI.^{1608b}

Multiphoton Ionization. One reason why spectroscopy in the vacuum ultraviolet region is more difficult than at higher wavelengths is that it is rarely possible to monitor fluorescence, because the highly excited states produced at these energies are subject to other faster internal relaxation processes. These states are quite close to the ionization limit, however, and could be detected electrically (and sensitively) by exciting them beyond that limit.

There remains the problem of raising preferably a large number of molecules to highly excited states. We have seen that sources of coherent vacuum ultraviolet radiation are not yet widely available, but laser sources for the UV and visible are. Reaching the VUV is plainly going to need more than one photon from such a source, and whilst the cross-sections for the simultaneous absorption of two or three photons are very small (typically 10⁻⁵⁰ cm⁴ s and 10⁻⁸² cm⁶ s², respectively,¹⁶⁰⁹ focused, pulsed dye lasers provide such an instantaneously high flux (routinely 10²⁸ photons cm⁻² s⁻¹), that the transition probability σI^n becomes appreciable, and multiphoton ionization practical.

A typical multiphoton ionization (MPI) experiment might involve the excitation of a state (A) which lies below the ionization limit by a non-linear process not involving a real intermediate state, and the ionization of the molecules by one further photon from the same source. It can essentially be a simple experiment, requiring in addition to the laser a means of collecting charged particles (this might only be a pair of parallel plates) and a sensitive device for measuring current.

The non-linear process is generally rate-limiting, since when the intensity is sufficient for it to proceed at a moderate rate, the subsequent step to the ionization continuum occurs very quickly. The MPI spectrum recorded as a function of wavelength is thus the spectrum of the $A \xleftarrow{h\nu} X$ transition. Several resonant excited states may be involved as the wavelength is scanned, and the appearance of the MPI spectrum may be quite different from the one-photon absorption spectrum, not only because different selection rules may be operating for the multiphoton transition, but because of the dynamics of the excited states. Intravalance transitions excited at vacuum ultraviolet wavelengths usually involve the promotion of an electron to an antibonding orbital causing fast

¹⁶⁰⁸ (a) J. C. Miller, R. N. Compton, and C. D. Cooper, *J. Chem. Phys.*, 1982, **76**, 3967; (b) J. H. Gownia and R. K. Sander, *Appl. Phys. Lett.*, 1982, **40**, 648.

¹⁶⁰⁹ P. M. Johnson and C. E. Otis, *Annu. Rev. Phys. Chem.*, 1981, **32**, 139.

dissociation or decay and an associated broad spectral feature. At the same frequency there might be a state involving electron promotion to a molecular Rydberg (non-bonding) orbital. In a normal absorption spectrum the transition to this state might be hidden in the stronger intravalance system. However, the Rydberg state will often have the longer lifetime and it is also likely to have a similar geometry to that of the ion. Ionization from the Rydberg state may then be favoured and thus the MPI spectrum may contain sharp Rydberg features not seen in the one-photon absorption spectrum.

MPI spectra may be much more complicated than one-photon spectra because of the number of different multiphoton processes which can occur. If an experiment consisted of exciting a three-photon absorption to a resonant state, followed by one photon ionization ($3 + 1$ resonance enhanced multiphoton ionization, REMPI) then on scanning to shorter wavelength, the $2 + 1$ process would become energetically possible, and would be more probable; three-photon ionization (not resonance enhanced, but direct to a state in the ionization continuum) might also be observed.

Johnson¹⁶¹⁰ has presented a very readable introduction to MPI spectroscopy, and with Otis¹⁶⁰⁹ has reviewed techniques and results. Another branch of this subject is concerned with the fragmentation which may occur following MPI, and also its possible application as an analytical technique,^{1611, 1612} although we will not deal with this branch here.

We saw earlier (p. 277) the limiting effect of the optical Stark effect on ultimate resolution in CARS spectra. An AC Stark effect has been observed in the ($2 + 2$) MPI spectrum of NO in a supersonic molecular beam, where it is thought to be principally responsible for the asymmetric line broadening.^{784b} Under the influence of an intense coherent field, a shifting and broadening of levels takes place.^{1613, 1614} It can be quite significant ($\sim 2 \text{ cm}^{-1} \text{ GW}^{-1} \text{ cm}^{-2}$)¹⁶⁰⁹ at moderate powers, and appears as asymmetry rather than a shift because of intensity variations within a laser pulse. It can also have a dramatic effect near a resonance, where for example with increasing laser intensity, the increasing (optical) electric field could pull the transition towards resonance; a log-log plot of intensity *versus* signal at a given point in the spectrum could thus have a gradient much larger than the number of photons involved in the ionization. The effect diminishes with reducing laser intensity, and with increasing NO pressure; in a bulb experiment, lines were found to be laser linewidth limited.^{784b, 799b}

The NO molecule has received a certain amount of attention recently *via* MPI spectroscopy; this work is summarized in a discussion by Dressler and Miescher⁷⁹¹ of perturbations of highly excited states of this molecule.

An extensive study has been made of the higher excited states of ammonia, involving beam and bulb MPI, and VUV (one-photon) absorption spectroscopy.^{1297, 1298} We mentioned in Part 1¹ that the $\tilde{\text{C}}'$ state had been revealed by MPI, nearly isoenergetic with the $\tilde{\text{C}}$ state apparent in the VUV spectrum. The $\tilde{\text{C}}'$ state was assigned to the promotion $2\text{pa}_2'' \rightarrow 3\text{pa}_2''$; the rotational analysis possible with simplified jet-cooled spectra has confirmed the assignment. A number of new states have been identified in the 5.7—9.3 eV energy range, and some reassessments have been made; the studies

¹⁶¹⁰ P. M. Johnson, *Acc. Chem. Res.*, 1980, **13**, 20.

¹⁶¹¹ M. B. Robin, *Appl. Opt.*, 1980, **19**, 3941.

¹⁶¹² V. S. Antonov and V. S. Letokhov, *Appl. Phys.*, 1981, **24**, 89.

¹⁶¹³ Y. Gontier and M. Trahin, *Phys. Rev. A*, 1973, **7**, 1899.

¹⁶¹⁴ M. Morellec, D. Normand, and G. Petite, *Phys. Rev. A*, 1976, **14**, 300; *J. Phys. (Paris)*, 1979, **40**, 115.

show the importance of electron promotions to *d* orbitals in ammonia. Further, vibronic intensities and rotational line strength factors are calculated for the three-photon absorption spectrum; cases considered are for three different photons, two identical photons and one different, and three identical photons (which corresponds to the experiment), and the absorption ratios for circularly *versus* linearly polarized light are calculated. Experimental and calculated spectra for the $\tilde{\text{B}}$ and $\tilde{\text{C}}'$ systems at 45 K agree well.¹³⁰⁰

Polarization ratios for the simultaneous absorption of 2, 3 and 4 photons have been calculated,¹⁶¹⁵ and if experimental polarizations are well behaved, they may provide useful information in MPI as in two-photon absorption spectroscopy. They seem dependable in the ammonia case, and for the ($^1\text{B}_{2u} \leftarrow ^1\text{A}_{1g}$) transition in benzene,¹⁶⁰⁹ although Heath *et al.*¹³⁴⁵ found polarization measurements unreliable for the $n \rightarrow 3s$ transition in acetaldehyde, varying with pressure and laser flux; this may be because of the proximity of a one-photon resonance.¹⁶⁰⁹

Marinero *et al.*¹⁶¹⁶ have reported the three-photon (2 + 1) ionization of H_2 . The experiment, employing Raman shifted lines from a doubled dye laser, was principally designed to detect ground state H_2 molecules in individual (v'', J'') levels. It also probes the electronic spectroscopy of the interesting E , $\text{F}'\Sigma_g^+$ state, which has a double minimum.

CH_3 and CD_3 radicals have been observed using the technique of mass-selected MPI, where a laser beam was focused into the ionization region of a quadrupole mass spectrometer containing radicals produced by an oven. The quadrupole signal at the radical mass was recorded as a function of laser wavelength. The first experiments¹²⁶¹ detected the one-photon allowed $^2\text{A}_1'(\beta)$ and $^2\text{E}''(\gamma)$ states as three-photon resonances, and vibrational frequencies in the $^2\text{E}''$ state were reported. A subsequent study¹²⁶⁰ observed new states assigned as $npe'(^2\text{E}')$, and $npa_2(^2\text{A}_2'')$, although confirmation of these symmetries awaits polarization studies. CH_3 has also been detected by two photon (1 + 1) ionization, at 215 nm (using Raman shifted radiation from a doubled YAG pumped dye laser) following MPI of CH_3I .¹⁶¹⁷

There may be advantages in using two lasers of different frequency in performing MPI. If, for example, two bound states are simultaneously populated by two- and three-photon resonances, two-colour excitation may simplify the spectrum considerably.¹⁶⁰⁹ If a variable delay can be introduced between the two laser pulses, then the evolution of excited states may be followed. This has been done in a modification of the very sensitive resonance enhanced two-photon ionization (R2PI) technique, where decays of triplet benzene¹⁴²² and triplet toluene¹⁶¹⁸ have been observed.

Ion dip spectroscopy⁸⁴⁹ combines the sensitivity of R2PI with the high resolution of stimulated emission spectroscopy described earlier. The principle is shown schematically in Figure 18(a) and the experimental arrangement in Figure 18(b). Two photons of frequency ω_1 ionize efficiently because of resonance enhancement through state $|1\rangle$. A laser field of high intensity, and frequency $\omega_2 < \omega_1$, is applied. When $(\omega_1 - \omega_2)$ is equal to a suitable vibrational frequency of the ground state, emission to level $|v\rangle$ is stimulated (provided there is a population inversion), in competition with

¹⁶¹⁵ D. L. Andrews and W. A. Ghoul, *J. Chem. Phys.*, 1981, **75**, 531.

¹⁶¹⁶ E. E. Marinero, C. T. Rettner, and R. N. Zare, *Phys. Rev. Lett.*, 1982, **48**, 1323.

¹⁶¹⁷ J. Danon, H. Zacharias, H. Rottke, and K. H. Welge, *J. Chem. Phys.*, 1982, **76**, 2399.

¹⁶¹⁸ T. G. Dietz, M. A. Duncan, and R. E. Smalley, *J. Chem. Phys.*, 1982, **76**, 1227.

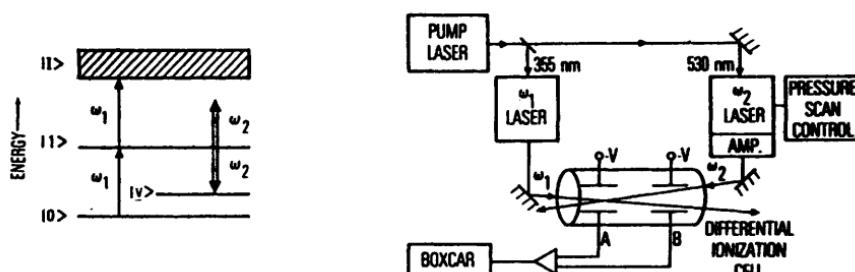


Figure 18 (a) Simplified energy-level diagram for ion dip spectroscopy. The scheme is appropriate for two-photon near-ionization of polyatomic molecules. For I_2 , the B state resonance corresponds to $|12\rangle$, and higher state resonances have been omitted from the diagram; (b) Experimental set-up with differential detection to reduce noise associated with pulse-to-pulse variations in laser excitation efficiency
(Reproduced by permission from *Phys. Rev. Lett.*, 1981, **46**, 324)

ionization, producing a dip in the ionization signal. Dips may also occur if level $|v'\rangle$ is at a higher energy than $|11\rangle$. Although the diagram shows a two-photon ionization, the experiment has been performed on iodine, using five ω_1 photons, and one ω_2 photon. With ω_1 set to the peak of the MPI spectrum, at $18\ 393.9\text{ cm}^{-1}$, scanning a ω_2 caused sharp dips ($\Delta\omega < 0.2\text{ cm}^{-1}$) in the ionization current at 14941.5 cm^{-1} and 14938.1 cm^{-1} , which were assigned to $R(23)$ and $P(25)$ of B ($v' = 26 \rightarrow X(v'' = 17)$), thus identifying the intermediate state in the ionization process. Other dips were observed, and simplicity of the ion dip spectra implied that only one rovibronic level in the B state was involved in each MPI peak.

(Selective rovibrational ground-state levels of NO have been detected in a double resonance type of experiment using a tunable IR laser coupled with MPI detection.⁷⁹⁶ Also for NO, a similar technique has been used to measure absolute collisional relaxation rates between spin-orbit states and rotational states.¹⁶¹⁹)

Optical Studies of Rydberg States. Synchrotron sources are being used to obtain high quality optical spectra in the vacuum ultraviolet region and beyond, as illustrated in the study by Baig *et al.*¹³¹⁷ of the Rydberg states of CH_3I , in which spectra were recorded between 113 and 180 nm with a resolution of $\pm 3 \times 10^{-4}\text{ nm}$. VUV spectra may be complex and states may be difficult to identify; the dichroic behaviour of transitions under the influence of magnetic¹³¹⁵ and electric^{1348, 1376} fields has been used to aid assignment.

Spectroscopy in this region is very much concerned with Rydberg states, their mutual interaction, and their interaction with intravalence states. The nature of molecular Rydberg states has been discussed by McGlynn and Findley,¹⁶²⁰ who categorize a Rydberg state operationally as one which is defined with respect to an asymptotically hydrogenic Hamiltonian. They consider molecular Rydberg states in terms of a double well potential with a centrifugal barrier such that bound states may be approximate eigenstates of either well. The barrier controls the finite number of such states supported by the inner well; the outer well potential can sustain an infinite

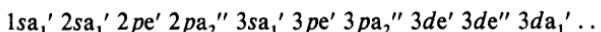
¹⁶¹⁹ A. S. Sudbo and M. M. T. Loy, *Chem. Phys. Lett.*, 1981, **82**, 135.

¹⁶²⁰ S. P. McGlynn and G. L. Findley, *J. Photochem.*, 1981, **17**, 461.

number of Rydberg states and is asymptotically hydrogenic. Differing characteristics of Rydberg series can be associated with levels possessing differing degrees of bimodality (inner and outer well character).

Rather than probing Rydberg states spectroscopically from the ground state, it may be advantageous to create large populations of molecules in excited states, for example in a discharge, and then study Rydberg states by observing relatively low frequency transitions. The Rydberg states of H₃ and NH₄ have been studied in this way.

Molecules such as H₂, NH₃ have high proton affinities so that the ions H₃⁺, NH₄⁺ are stable. A consequence is that Rydberg states of the neutral species H₃, NH₄ (and for example H₃O and CH₅), are also stable to dissociation. The study of the electronic spectra of H₃ and of D₃, noted briefly in our last report,¹ has been greatly extended,^{1169–1172} and details of the analyses have now been published, the technique used in the production of the spectra involving a cooled hollow-cathode discharge has been described, and a summary of the results has been given. The spectra arise from transitions between states with $n = 3$ and states with $n = 2$, and from transitions within the $n = 3$ manifold. The lowest MO's in D_{3h} symmetry are:



In all states two of the electrons occupy the lowest orbital, 1s_{a'}, while the third electron can occupy any of the other orbitals. The lowest state, 2p²E', is repulsive, and dissociates to H ($n = 1$) + H₂ (${}^1\Sigma_g^+$). The other states correlate with higher lying products and all are stable, with substantial energies of dissociation. Observed transitions, some of which remain to be investigated in detail, are illustrated in Figure 19. The levels with $n = 2$, 2s²A'₁ and 2p²A'₂ are predissociated by 2p²E', more strongly in the case of 2s²A'₁ than for 2p²A'₂, when the predissociation is vibronically forbidden and occurs only on account of rovibronic interaction. Molecular constants show that the structure of these Rydberg states is as expected very similar to that of the molecular ion, although the 3p²E' orbital appears to be somewhat anti-bonding. The rotational structure of the 3p²E' state shows the effects of a small Jahn-Teller splitting in the double potential surface associated with the v_2 mode. The minimum of the Jahn-Teller distorted potential function is found to be 87 cm⁻¹ below the undistorted energy, corresponding to a shift of the equilibrium position by 0.026 Å from the undistorted configuration.

The H₃ molecule has been produced by charge-transfer collisions of a fast beam (10 keV) of H₃⁺ ions with H₂. The subsequent dissociation of H₃ into H₂ + H was studied by a coincidence method and the fragment intensity was found to vary with the relative translational energies of the fragments, forming a spectrum of peaks on a falling continuous background.¹¹⁶⁶ This structure is interpreted¹¹⁶⁷ as arising from predissociation of the 2s²A'₁ state of H₃ to H, 1s + H₂, X¹ Σ_g^+ (v, J). According to this interpretation, the process H₃(2s²A'₁, $v = 0$) → H₂(X¹ Σ_g^+ , $v = 0, J = 0$) + H(1s²S_{1/2}) is exothermic by 5.52 eV.

Two bands have now been assigned¹¹⁷¹ to transitions between Rydberg states of the ammonium radical, NH₄⁺. Both occur in discharges through ammonia; the Schuster band, first described in 1872 and the Schüler band, which predominates at high pressure. The Schuster band as excited in NH₃ consists of a broad diffuse continuum with maxima at 5639 and 5672 Å. The corresponding band excited in ND₃ is shifted to the red by about 440 cm⁻¹, and shows a clear fine structure. Experiments with partly

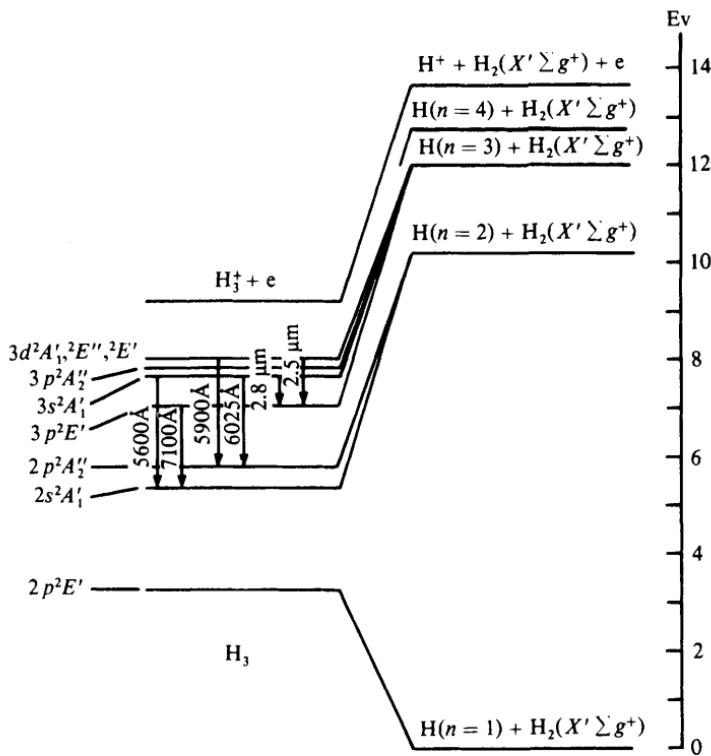


Figure 19 Observed electronic states of H_3 at left and of the dissociation products at right. The excited states of H_2 are not included; the lowest of these would be at 11.18 eV
(Reproduced by permission from *Faraday Discuss. Chem. Soc.*, 1981, **71**, 165)

deuteriated ammonia reveal three bands between those arising from discharges in NH_3 and in ND_3 , while a 50:50 mixture of $^{14}\text{ND}_3$ and $^{15}\text{ND}_3$ gives only a superposition of the two bands obtained with pure $^{14}\text{ND}_3$ and pure $^{15}\text{ND}_3$. Thus the emitter contains one nitrogen atom and four hydrogen atoms. The suggestion is made that the Schuster bands arise from a transition $3d^2\text{F}_2 - 3s^2\text{A}_1$ when the lower state is the weakly bound ground state of tetrahedral NH_4 (T_d).

The Schüller bands consist of double headed bands shaded to shorter wavelengths (with heads at 6636.77 and 6634.72 Å for NH_4 and 6749.41 and 6746.57 Å for ND_4). The NH_4 band is diffuse but there is extensive sharp structure in ND_4 : analysis will demand a treatment of the problem of the spin-rotation interaction in tetrahedral molecules. Meanwhile the transition is assigned tentatively to $3d^2\text{D} - 3p^2\text{F}_2$.

A strong emission feature at 4 μm observed¹⁶²¹ in arcs in air at $T \sim 5700$ K and in shock tubes at higher temperatures has now been recognized⁷⁸⁸ as a transition between 5g and 4f Rydberg complexes in NO. With increasing rotation, the complexes assume patterns of levels according to Hund's case-d, in which l of the Rydberg electron couples to the axis of molecular rotation with components $L = -l, \dots, 0, \dots, +l$. The L

¹⁶²¹ K. L. Wray and R. L. Taylor, *J. Quant. Spectrosc. Radiat. Transfer*, 1969, **9**, 1317.

structure of the levels is given by $-a_{nl}L^2$, and analysis of the absorption spectrum^{1622, 1623} gives values of a_{4f} (1.80 cm^{-1}) and of a_{5f} (0.99 cm^{-1}), independent of the vibrational and rotational state of the molecular ion core. The band represents a novel type of molecular spectrum in which vibrational and rotational structures have disappeared, with $\Delta v = 0$ and $\Delta R = 0$, for all states of the complexes have identical vibrational and rotational constants, equal to those of the ground state of the NO^+ ion.

The 4f complex is the upper state of an emission system at $1.71\text{ }\mu\text{m}$ whose lower state is $\text{F}^2\Delta$: a rotational analysis of this system, recorded on a SISAM spectrometer, has been given.⁷⁸⁵

Photoionization and Photoelectron Spectroscopy. Classical photoelectron spectroscopy (PES) excites with monoenergetic photons and analyses the kinetic energy of ejected electrons. Alternative techniques may involve the detection of 'zero energy' (or fixed energy^{815c}) electrons as the excitation wavelength is scanned. Classical PES of valence states has been reviewed by Price, principally with reference to the structure of simple molecules.¹⁶²⁴ A 'Handbook of HeI Photoelectron Spectra of Fundamental Organic Molecules' has been compiled by Kimura *et al.*,¹⁶²⁵ which also contains results of *ab initio* calculations, and valence electronic structures. Heilbronner has described it as a 'dignified successor' to Turner, Baker, Baker, and Brundle's 'Molecular Photoelectron Spectroscopy'. A data bank of HeII photoelectron spectra of organic molecules has also begun.^{1625b}

The photoionization process has been considered in the book 'Photoabsorption, Photoionization and Photoelectron Spectroscopy', by Berkowitz,¹⁶²⁶ which also discusses extensively experimental measurements of total cross sections, partial cross sections (for producing selected ionic states), and photoelectron angular distributions.

Angular distributions of ejected photoelectrons are intimately connected with the nature of the excitation process, and their importance has long been recognized.¹⁶²⁷ They are usually discussed in terms of the asymmetry parameter β , defined in the expression for the differential cross section, following excitation with plane polarized light, as

$$\frac{d\sigma}{d\Omega} = \frac{\sigma_{\text{total}}}{4\pi} \left[1 + \beta P_2(\cos \theta) \right]$$

where $P_2(\cos \theta) = (3 \cos^2 \theta - 1)/2$. With the availability of synchrotron radiation it has been possible to measure photoelectron angular distributions as a function of exciting wavelength for diatomic (e.g., ref. 633) and polyatomic^{1135, 1151, 1325b} molecules. Measurements of β for OCS and CS₂ were made at energies from near the ionization threshold to 29 eV in order to test how well current X_α multiple scattering

¹⁶²² Ch. Jungen and E. Miescher, *Can. J. Phys.*, 1969, **47**, 1769.

¹⁶²³ E. Miescher, *Can. J. Phys.*, 1976, **54**, 2074.

¹⁶²⁴ W. C. Price, *Int. Rev. Phys. Chem.*, 1981, **1**, 1.

¹⁶²⁵ (a) K. Kimura, S. Katsumata, Y. Achiba, T. Yamazaki, and S. Iwata, 'Handbook of HeI Photoelectron Spectra of Fundamental Organic Molecules. Ionization Energies, Ab Initio Assignments, and Valence Electronic Structure for 200 Molecules', Japan Scientific Societies Press, Tokyo and Halsted Press, New York, 1980; (b) G. Bieri and L. Åsbrink, *J. Electron Spectrosc.*, 1980, **20**, 149; **21**, 93.

¹⁶²⁶ J. Berkowitz, Photoabsorption, Photoionization and Photoelectron Spectroscopy, Academic Press, New York, 1979.

¹⁶²⁷ J. Cooper and R. N. Zare, *J. Chem. Phys.*, 1968, **48**, 942; Lectures in Theoretical Physics, 1969, **XIC**, 317.

calculations can predict differential photoelectron cross-sections. Good agreement was obtained with the least tightly bound orbitals of CS_2 , although with orbitals more tightly bound, and with the (polar) molecules OCS, some problems were encountered. However, a combined consideration of these results and earlier work on CO_2^{1135} suggested that the multiple scattering method will be useful in interpreting variable excitation energy electron angular distributions.¹¹⁵¹

The behaviour of β may be very sensitive to the presence of resonances in the photoionization spectrum, as these may involve a breakdown of the Born–Oppenheimer approximation. Franck–Condon factors may also differ markedly on and off resonance.

Autoionization is a common phenomenon in photoionization, and may be the major relaxation process for molecules in high n Rydberg states.¹⁶²⁸ It involves dissociation to a molecular ion plus an electron following excitation to a quasidiscrete state above the ionization energy, and is analogous to predissociation. Studies of N_2^{777} ⁷⁷⁷ CO^{969} and O_2^{824} have shown partial cross-sections and photoelectron angular distributions (measured as a function of wavelength) to be vibrational state dependent, because of the presence of autoionizing resonances. Theoretical interpretation of such effects has been presented for H_2 .⁶³⁴

Vibrational state dependence of these observables can also arise through the presence of shape resonances.¹⁶²⁹ A shape resonance is associated with a centrifugal barrier in the potential energy curve through which an electron in an excited state tunnels to the continuum. Thus again there will be a breakdown of the Franck–Condon separation in the region of the resonance (which may be very broad), with the dipole transition amplitude being a rapidly varying function of internuclear separation. A number of experimental observations have been attributed to shape resonances.¹⁶²⁹ Angle resolved PES of CO_2 found a sharp drop in the value of β near 42 eV (incident photon energy), corresponding well with theoretical predictions of a shape resonance.¹¹³⁹ Non-Franck–Condon vibrational intensities have been observed over 25 eV of the $3\sigma_g$ photoionization continuum of N_2 , in qualitative agreement with theoretically predicted shape-resonance enhanced coupling of nuclear and electronic motion.⁷⁵³

Photodetachment spectroscopy is essentially photoelectron spectroscopy of negative ions. Because of low electron affinities of neutral molecules, the energy for detachment can be provided by a tunable dye laser. Investigation of C_2^- in the range 1.75–2.5 eV revealed sharp resonances due to autodetachment at incident photoenergies corresponding to transitions between high vibrational levels of the $\text{C}_2^- \text{X}^2\Sigma_g^+$ and $\text{B}^2\Sigma_u^+$ states. There was insufficient energy for configuration interaction to be responsible for coupling of the bound state to the continuum; it was concluded that the coupling was due to the nuclear kinetic energy operator, ignored in the Born–Oppenheimer approximation.⁹⁵³

More detail of the photoionization process, further dissecting the photoionization cross-section, may be obtained by measuring the spin polarization of photoelectrons.¹⁶³⁰ Spin polarization may occur because of spin–orbit interaction in the ground, ionic, or continuum states, and has been observed with CO_2 and N_2O .

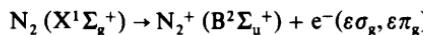
¹⁶²⁸ J. P. Connerade, M. A. Baig, and S. P. McGlynn, *J. Phys. B*, 1981, **14**, L67.

¹⁶²⁹ P.-M. Guyon and I. Nenner, *Appl. Opt.*, 1980, **19**, 4068.

¹⁶³⁰ U. Heinzmann, *Appl. Opt.*, 1980, **19**, 4087.

following excitation with circularly polarized synchrotron radiation;¹¹³⁴ it has been demonstrated also for CH₃Br with polarized and unpolarized exciting light.¹³¹⁶

Fluorescence from molecular ions following photoionization has been shown to be polarized. Poliakoff *et al.*⁷⁷⁴ studied the photoionization of N₂:



proceeding *via* parallel (σ_g) and perpendicular (π_g) transition dipoles. They showed that, under most circumstances, the degree of fluorescence polarization depends only on the dipole strength ratio D_{π}^2/D_{σ}^2 . This technique can thus measure the ratio of dipole strengths for degenerate ionization channels; it provides information on the alignment of ions following photoionization independently of the relative phases of the ionization channels, because it does not require measurement of the photoelectron angular distribution.

Dyke *et al.* have reviewed VUV photoelectron spectroscopy of transient species.^{1631, 1632} The HCO¹¹⁸¹ and FCO¹¹⁶⁵ radicals have been studied recently; these molecules are bent in the ground state of the neutrals, whereas the ions are linear, and the first photoelectron bands show vibrational structure attributed to the deformation mode. HO₂ has also been observed,¹¹⁸⁸ the one band seen in the spectrum showing a vibrational progression in the O — O stretching mode of the HO₂⁺ (X³A'') state.

A high resolution supersonic molecular beam sampling photoelectron spectrometer has been described.¹⁶³³ An efficient electron collection system, with a multichannel detector based on dual microchannel plates, was necessary to allow a high resolution signal to be obtained from the relatively low density of molecules in a molecular beam. Use of the beam greatly reduces Doppler and rotational broadening. Photoelectron spectra of C₂H₄¹⁶³³ and n-H₂, p-H₂, HD, and D₂¹⁶³⁴ have been recorded. The room temperature Doppler linewidth for H₂⁺ ($v = 0$) with HeI α light is 20 meV. The spectra recorded with this technique were at a resolution of 11 meV fwhm, allowing some Q-branch features to be resolved for the first time; a typical spectrum is shown in Figure 20. ω_e , ω_ex_e , ω_ey_e , ω_ez_e , B_e , and σ_e were determined for all isotopic species.

A problem in performing photoelectron spectroscopy of *clustered* species lies in the difficulty of selectively probing a cluster of a particular size. This problem has been overcome in a study of Xe₃ in a supersonic expansion, where the ion mass was detected in coincidence with the photoelectron. Stagnation conditions could be varied to produce Xe₂, Xe₃, and larger clusters. The Xe₃ coincidence spectrum was much broader than that of Xe₂, probably because of the overlapping of excited states, and the predicted change in geometry from triangular (neutral) to linear (ionic ground state). Spectra were also recorded under conditions where larger clusters were formed to ensure that post-ionization fragmentation of such species did not contribute to the Xe₃ coincidence signal.¹²⁵⁵

Molecular photoelectron spectra have been recorded following resonance enhanced

¹⁶³¹ J. M. Dyke, N. Jonathon, and A. Morris, 'Vacuum Ultraviolet Photoelectron Spectroscopy of Transient Species', in Electron Spectroscopy, Vol. 3, ed. C. R. Brundle and A. D. Baker, Academic Press, London, 1979.

¹⁶³² J. M. Dyke, N. Jonathon, and A. Morris, *Int. Rev. Phys. Chem.*, 1982, **2**, 3.

¹⁶³³ J. E. Pollard, D. J. Trevor, Y. T. Lee, and D. A. Shirley, *Rev. Sci. Instrum.*, 1981, **52**, 1837.

¹⁶³⁴ J. E. Pollard, D. J. Trevor, J. E. Reutt, Y. T. Lee, and D. A. Shirley, *J. Chem. Phys.*, 1982, **77**, 34.

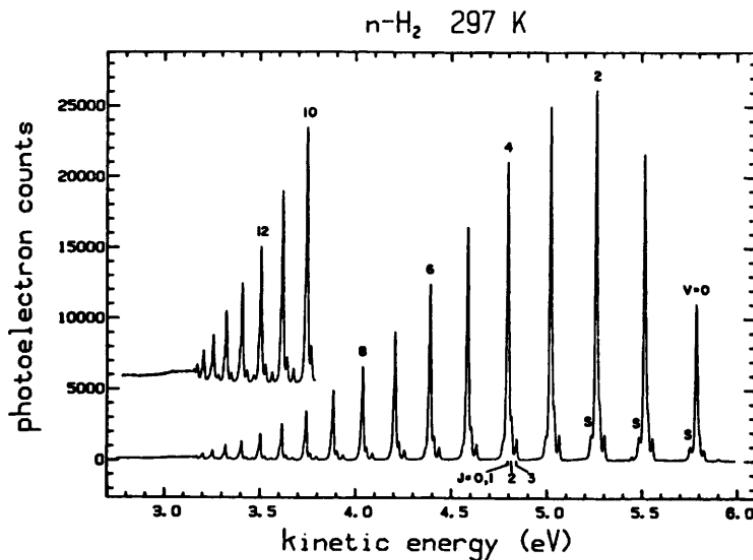
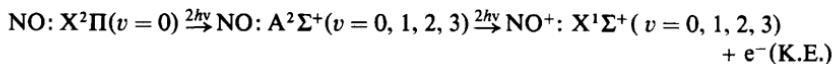


Figure 20 The 584 Å photoelectron spectrum of n-H₂ expanded from 800 Torr at 297 K. The ionic vibrational states and the rotational quantum numbers of a typical Q branch are indicated in the figure. The S branch is also labelled for the first three states
(Reproduced by permission from *J. Chem. Phys.*, 1982, **77**, 34)

multiphoton ionization.⁷⁸⁴ First studied was the (2 + 2) ionization of NO in an effusive molecular beam:



On tuning the laser to each resonant vibrational state, two electron energy peaks were detected, the higher energy peak corresponding to direct ionization, and the lower, near zero energy peak to some as yet unidentified channel (possibly autoionization or internal conversion). Direct ionization prepared the ion in a single vibrational state, of the same *v* as the initially excited Rydberg state; this is because of the structural similarity between Rydberg and ionic states, and the predisposition of MPI to proceed *via* Rydberg states, as we discussed earlier. If direct ionization were the only process occurring to a significant degree, state-selected ions could be prepared in this way. This is not the case for A state enhanced ionization, but has been achieved with C state enhancement. The (3 + 1) ionization of NH₃ has also been studied, and again zero energy electrons were detected following ionization *via* all but one of the initial Rydberg states excited, probably because of vibrational autoionization.¹⁶³⁵ REMPI-PES is presented as a convenient alternative to synchrotron PES, and will become more powerful when developed as a two-colour technique.

Electron Impact Spectroscopy. In this Report, we have restricted our discussion to optical spectroscopy. We will briefly consider, however, the complementary infor-

¹⁶³⁵ J. H. Głownia, S. J. Riley, S. D. Colson, J. C. Miller, and R. N. Compton, *J. Chem. Phys.*, 1982, **77**, 68.

mation which can be obtained from electron impact spectroscopy. Electron impact excitation can extend from the far infrared to the *X*-ray region, and whilst attainable resolution does not become comparable with that of optical spectroscopy until very high energies, transitions are not subject to optical selection rules.

An introduction to electron impact spectroscopy has been provided by Trajmar,¹⁶³⁶ and low energy^{1637, 1638} and high energy¹⁶³⁹ aspects have been reviewed. In an electron impact experiment, a beam of nearly monoenergetic electrons collides with a target gas, and scattered electrons are detected as a function of energy and geometry. Low and intermediate energy electrons interact most strongly with the valence shell, and may cause electron promotion or excitation of nuclear motion, with possible consequences of ionization or dissociation. There is high probability for the occurrence of spin and symmetry forbidden transitions, in addition to those which are optically allowed. Optically allowed transitions are favoured at narrow scattering angles and high energies, but optically forbidden transitions become comparable or greater in strength at wide angles and low energies. 'Spin-forbidden' transitions, which can occur through spin-exchange between incident and molecular electrons, require short-range interactions and result in an isotropic electron distribution, whereas parity forbidden transitions have zero cross-sections for forward and backward scattering. Scattering characteristics can thus be very useful diagnostics.

Wilden and Comer¹¹⁵⁵ have used such characteristics to study spin and symmetry forbidden transitions in CS₂ in the energy loss range 6—17 eV, obtaining information complementary to the optical absorption spectrum, and offering improved assignments of Rydberg states.

Electron impact spectroscopy may of course also reveal electron molecule resonances. In a study of N₂, the A²Π_u of N₂⁺, a core-excited shape resonance, was detected; its parent, to which it is strongly coupled by a one-electron transition, is A³Σ_u⁺, and its width is ~1 eV. It decays to A³Σ_u⁺ and to X¹Σ_g⁺ ($v \leq 25$) with about equal probability.⁷⁷⁹

The impact of an electron on a target may result in the ejection of two electrons. This is exploited in the (e, 2e) technique, where the electrons are detected in coincidence. If the energies of the electrons are measured, separation or binding energies of the ejected electrons may be determined. If the momenta are measured, this information can be related to the momentum distribution of electrons in the target. The (e, 2e) cross-section is sensitive to the properties of valence electrons. Further details of this technique may be found in a report of a study on HF and HC1.⁷⁰¹

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¹⁶³⁶ S. Trajmar, *Acc. Chem. Res.*, 1980, **13**, 14.

¹⁶³⁷ R. J. Celotta and R. H. Huebner, 'Electron Impact Spectroscopy: An Overview of the Low Energy Aspects', in 'Electron Spectroscopy,' Vol. 3, ed. C. R. Brundle and A. D. Baker, Academic Press, London, 1979.

¹⁶³⁸ N. F. Lane, *Rev. Mod. Phys.*, 1980, **52**, 29.

¹⁶³⁹ R. A. Bonham, 'High-energy Electron Impact Spectroscopy', in 'Electron Spectroscopy,' Vol. 3, ed. C. R. Brundle and A. D. Baker, Academic Press, London, 1979.

Appendix

Abbreviations used in Tables

β	asymmetry parameter
CARS	coherent anti-Stokes Raman scattering/spectroscopy
CI	configuration interaction
DFS	difference frequency spectrometer
DR	double-resonance (usually preceded, as in <i>e.g.</i> , MODR, microwave-optical double resonance)
FC	Franck–Condon
FES	fluorescence excitation spectrum (total undispersed fluorescence observed as a function of wavelength)
FIR	far infrared
FT	Fourier transform (as in, <i>e.g.</i> , FTIR)
hfs	hyperfine structure (usually means some constants, <i>e.g.</i> , quadrupole coupling constants, measured)
IP	ionization potential
LIF	laser induced fluorescence (may indicate any fluorescence arising from laser excitation, either at a single excitation frequency or as a function of frequency, with or without the dispersal of the fluorescence)
LMR	laser magnetic resonance
MBER	molecular beam electric resonance
MBMR	molecular beam magnetic resonance
MCD	magnetic circular dichroism
MCQD	multichannel quantum defect theory
MMW	millimetre wave
MP	multiphoton, multiple photon (not distinguished here)
MPD	multiphoton dissociation
MPE	multiphoton excitation
MPI	multiphoton ionization
OPO	optical parametric oscillator
PE	photoelectron
PEPI	photoelectron–photoion coincidence
PES	photoelectron spectrum/spectroscopy
PI	photoionization
Φ	quantum yield
r_s, r_o, r_e	structural parameters, types of determined structure (see text, p. 243 ff.)
r_m, r_z	
RAD	radiospectrometer with acoustic detection
RR	resonance Raman
SCF	self-consistent field
SMMW	sub-millimetre wave
SRS	stimulated Raman scattering
s/s	supersonic
tof	time-of-flight
TPES	threshold photoelectron spectroscopy