

Pressure broadening of the HCO^+ $J=0-1$ transition by hydrogen

Thomas G. Anderson, Christopher S. Gudeman, Thomas A. Dixon, and R. Claude Woods

Citation: *The Journal of Chemical Physics* **72**, 1332 (1980); doi: 10.1063/1.439196

View online: <http://dx.doi.org/10.1063/1.439196>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jcp/72/2?ver=pdfcov>

Published by the AIP Publishing

Articles you may be interested in

Rotational relaxation rates for the OCS $J=0-1$ pure rotational transition broadened by argon and helium
J. Chem. Phys. **80**, 3544 (1984); 10.1063/1.447199

Pressure dependence of rotational relaxation times T_1 and T_2 in the $J=0-1$ transition of OCS
J. Chem. Phys. **63**, 5145 (1975); 10.1063/1.431296

VibrationHindered Rotation Interactions in Methyl Alcohol. The $J=0 \rightarrow 1$ Transition
J. Chem. Phys. **26**, 48 (1957); 10.1063/1.1743263

Erratum: $J=0 \rightarrow 1$ Rotational Transition of Trifluoroiodomethane
J. Chem. Phys. **23**, 762 (1955); 10.1063/1.1742113

$J = 0 \rightarrow 1$ Rotational Transition of Trifluoroiodomethane
J. Chem. Phys. **22**, 2094 (1954); 10.1063/1.1740013



Pressure broadening of the HCO^+ $J=0-1$ transition by hydrogen^{a)}

Thomas G. Anderson,^{b)} Christopher S. Gudeman, Thomas A. Dixon,^{c)} and R. Claude Woods

Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706
(Received 27 August 1979; accepted 24 September 1979)

Measurements have been made of the broadening of the HCO^+ $J=0-1$ microwave absorption line by hydrogen. The linewidths ($\Delta\nu$, half-width at half-intensity) were obtained from a nonlinear least squares analysis of the individual spectra, taken over the pressure range of 4–40 mTorr. The pressure dependence of the linewidth $d\Delta\nu/dP$ was determined to be 29.6 ± 3 MHz/Torr for the HCO^+ transition broadened by H_2 near 100°K. This corresponds to a collisional cross section of 182 ± 20 Å² for HCO^+-H_2 . Also, a new and more reliable measurement is reported for broadening of the $J=7-8$ transition of ^{18}OCS , which gives $d\Delta\nu/dP = 7.11 \pm 0.15$ MHz/Torr for self-broadening at 296°K.

I. INTRODUCTION

The pressure broadened linewidths in the microwave spectra of molecular ions are of considerable interest from several standpoints. They enter in a crucial way into the estimation of the feasibility of detection of ionic spectra, they are closely related to collisional relaxation cross sections used in the interpretation of radio astronomical data, and they can potentially serve as a probe in the intermolecular forces between the ion and a colliding neutral perturber molecule. Prior to the first observations of molecular ion spectra, estimations of the magnitude of linewidths to be expected varied over a considerable range. The more pessimistic view^{1,2} held that the widths would be 20 or 30 times as large as that for similarly polar neutral molecules due to the very long-range nature of the monopole-dipole or monopole-quadrupole forces. Had this view been correct, observations of the microwave spectra of CO^+ , HCO^+ , and HN_2^+ (Ref. 3) made in this laboratory would not have been possible. The design of the experiments and the optimism that they would succeed, on the other hand, were based on a contrasting prediction that the ion linewidths would be similar to those for similar neutrals or only somewhat larger.⁴ This position was supported by a semiclassical argument that the monopole-dipole force, while of long range, does not exert any torque on the ionic collision partner and, therefore, is not very effective in changing its rotational state. Using different arguments and detailed numerical computations, Green⁵ predicted that rotational excitation rates and cross sections of molecular ions would be only a few times larger than those for similar neutrals. The early experiments appeared to support the idea that linewidths of ions were at most a few times larger than those for neutrals.

In this paper we report the results of studies on pressure broadening of the $J=0-1$ rotational transition

of HCO^+ (at 89 188.5 MHz). The resulting linewidth versus pressure data allowed determination of the pressure broadening parameter, $d\Delta\nu/dP$, for the HCO^+ transition broadened by hydrogen. As a test of both the spectrometer and the data analysis procedure, pressure broadening data was also obtained for the $J=7-8$ transition of ^{18}OCS (at 91 278 MHz). The present paper then provides the first quantitative measurement of the pressure broadening parameter for a molecular ion. Although we hope to report more accurate and extensive measurements of such parameters at a later time, it is felt that the general magnitude is reliably established by the present result, and it is hoped that the experimental value will stimulate consideration of the theory involved, leading ultimately to a quantitative interpretation of such data in terms of intermolecular forces.

II. EXPERIMENTAL

The frequency modulated microwave spectrometer with a liquid-nitrogen-cooled, glow discharge absorption cell has been described in detail in previous papers.³ Data collection and signal averaging were computer controlled with a marker synchronized, but non-phase-locked, sweep; all spectra were stored on magnetic tape for analysis as described in Sec. III. The major change in operating procedure was the use of faster frequency sweeps (about 0.3 sec for 1000 data points) and a correspondingly lower time constant (1 msec) for the lock-in amplifier. The faster sweep minimized the effects of klystron instabilities and resulted in smaller uncertainties in the frequency marker position. Pressures were measured with a capacitance manometer (MKS Baratron) which was connected to the grounded cathode of the discharge cell. This gauge has good stability, with typical drifts of about 0.5 mTorr over a 12-h period. For both the HCO^+ and OCS spectra, uncertainties in the pressure are between ± 0.5 and ± 1 mTorr.

The HCO^+ spectra were obtained from a slow continuous flow of a mixture of hydrogen and carbon monoxide through a liquid-nitrogen-cooled glow discharge. The input flow of CO was set to give a pressure in the cell of about 3–4 mTorr with a 200 mA discharge current (this pressure decreases at higher current). Addition of a small amount of hydrogen causes the discharge

^{a)}This work was supported by the National Science Foundation under Grant CHE76-07374.

^{b)}Present address: Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Mass. 02139.

^{c)}Present address: Department of Chemistry, Harvard University, Cambridge, Mass. 02138.

pressure to decrease, probably due to the formation of condensable species by reactions in the discharge. As even more hydrogen is added, the pressure begins to increase, and it is under these conditions that the series of HCO^+ spectra were recorded. Only the hydrogen input was changed to adjust the pressure in the absorption cell. Although these conditions do not maximize the HCO^+ signal, this method produces a discharge in which hydrogen is presumably the major species responsible for broadening the HCO^+ transition. Even under these conditions, the discharge pressure was somewhat dependent on the current. As a precaution, a complete set of data was obtained at currents of 20C and 400 mA. However, the linewidths show no significant dependence on the discharge current at constant pressure, and both sets of data were combined for the determination of the pressure broadening parameter of HCO^+ . For the ^{18}OCS spectra, the only differences in experimental conditions were that the absorption cell was at ambient temperature (296 °K) and that the glow discharge was not used.

III. DATA ANALYSIS

To obtain linewidths from the spectra, a FORTRAN program was written to perform a nonlinear least-squares analysis using an appropriate line-shape model.⁶ All the spectra could be adequately described by the sum of the three-parameter Lorentzian profiles and a three-parameter quadratic base line. The fitting parameters are the peak intensities (I_i), the half-width at half-maximum ($\Delta\nu_i$), the center frequencies (ν_{0i}) for each line in the spectrum, and the base-line parameters. Although almost all the fits converged, some data was rejected due to high correlations, which produced parameters that did not adequately describe the spectra. As a final check, superimposed plots of both experimental and calculated spectra were obtained. For the source modulated (bipolar square wave) spectrum of a single transition, one should obtain the main absorption line with a satellite line on each side. The splittings of these lines will depend on the magnitude of the excursions of the bipolar square wave, and the modulation sensitivity and sweep linearity of the microwave source. Ideally, the relative intensities will have the ratios $-1:2:-1$, and the linewidths will be equal.⁷ It was found that trying to fit all twelve of the resulting parameters (three line-shape profiles and the base line) would often produce poor results or no convergence. However, since some of the parameters are in principle related, they may be fixed relative to the main absorption line. For the analysis, two combinations of fixed parameters were used. (i) the integrated intensities, $I_i\Delta\nu_i$ of the satellite lines were fixed to $-\frac{1}{2}$ of the value for the main line. (ii) the satellite linewidths were fixed equal to the main line and the satellite peak intensities fixed to $-\frac{1}{2}$ of the main line. Analysis of the spectra obtained of the ^{18}OCS $J=7-8$ transition provided a check on the reliability of these assumptions. The linewidths obtained from the two combinations of fixed parameters agreed to within the 95% confidence limits. However, the linewidths from the second fixed parameter combination (which places a more stringent limita-

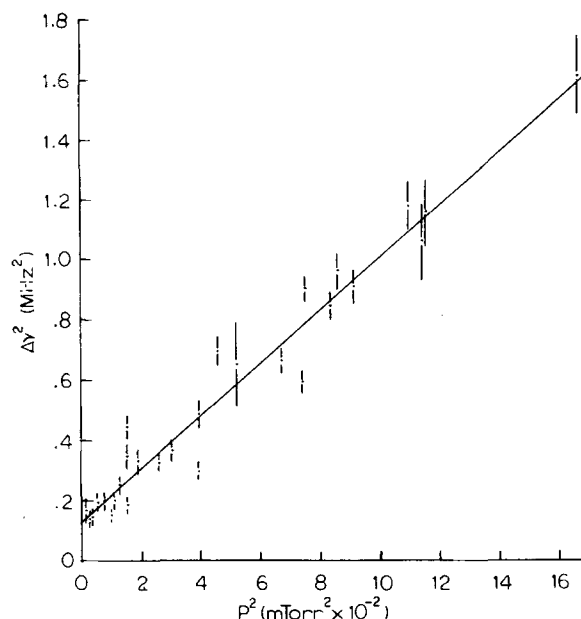


FIG. 1. $\Delta\nu^2$ vs P^2 for the $J=0-1$ HCO^+ transition. Spectra were obtained by flowing a mixture containing a small amount of carbon monoxide and an excess of hydrogen through a liquid-nitrogen-cooled glow discharge. The bars represent the uncertainties in $\Delta\nu^2$ and the solid line is the result of a least-squares fit of the data using Eq. (1).

tion on the model) were usually 2–5 kHz smaller. In an attempt to push the measurements to as high a pressure as possible, the inevitable overlapping of the lines and resultant correlations of the several parameters at high pressure were partially mitigated by using the fact that the line center positions are pressure independent to a good approximation. Analysis of lower pressure spectra with well-resolved satellite lines allowed determination of the satellite splittings, which could then be fixed in the least-squares fits for some of the higher pressure data. However, at pressures above 200 mTorr (linewidths above about 1.3 MHz), the main line and satellites overlapped to such an extent that reliable parameters could not be obtained. Further increase of the modulation amplitude was not practical because of the resultant poor base line.

The plots of linewidth versus pressure for both the HCO^+ $J=0-1$ and the ^{18}OCS $J=7-8$ transitions show a linear region due to pressure broadening and a curvature in the low pressure region due to non-pressure-dependent effects. This can be accounted for by the approximate relationship⁸

$$\Delta\nu^2 = \left(\frac{d\Delta\nu}{dP}\right)^2 P^2 + \Delta\nu_d^2, \quad (1)$$

where $\Delta\nu$ is the observed linewidth, $d\Delta\nu/dP$ gives the pressure dependence in the linear collisional broadening region, and $\Delta\nu_d$ is the Doppler limited or other non-pressure-related linewidth. Figures 1 and 2 show plots of $\Delta\nu^2$ versus P^2 for the HCO^+ and ^{18}OCS transitions, respectively. The vertical bars show 95% confidence limits in the square of the linewidth. Using Eq. (1), a linear least-squares fit of the linewidth versus pressure data gives $d\Delta\nu/dP = 29.6 \pm 0.6$ MHz/Torr and $\Delta\nu_d$

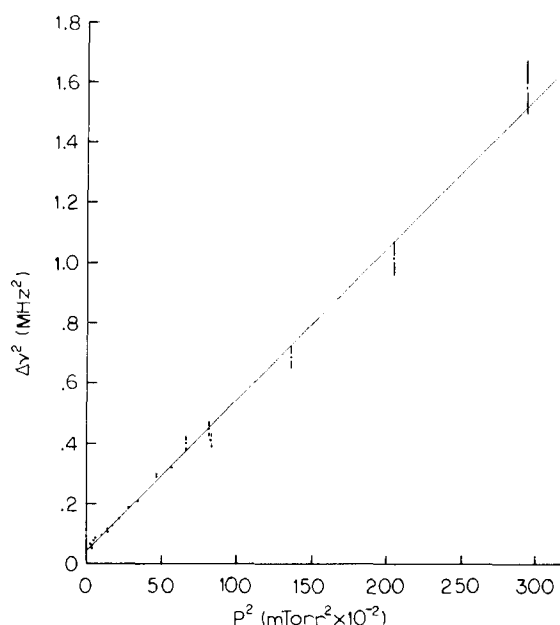


FIG. 2. $\Delta\nu^2$ vs P^2 for the $J=7-8$ transition of ^{18}OCS . The spectra were observed in natural abundance, using a static absorption cell at room temperature and without the glow discharge. The bars show the uncertainties in $\Delta\nu^2$ and the solid line is the result of the least-squares fit of the data.

$\approx 363 \pm 32$ kHz for the $\text{HCO}^+ J=0-1$ transition; and for the $^{18}\text{OCS} J=7-8$ transition, $d\Delta\nu/dP = 7.11 \pm 0.05$ MHz/Torr and $\Delta\nu_d = 201 \pm 14$ kHz (see Table I). The uncertainties given here are one standard deviation in the fitted parameters. The solid lines in Figs. 1 and 2 show the calculated curve from the least-squares fit.

IV. DISCUSSION

The linewidth of a microwave absorption lines is related to the average time between effective collisions, τ , by $2\pi\Delta\nu = 1/\tau$. This then defines an effective cross section and interaction diameter,

$$2\pi\Delta\nu = N\bar{v}\sigma = N\bar{v}\pi b^2, \quad (2)$$

where N is the density of molecules, \bar{v} is the mean relative velocity, and σ is the collision cross section. The collisional cross section calculated from the linewidth parameter of the $\text{HCO}^+ J=0-1$ transition broadened by

hydrogen is $182 \pm 20 \text{ \AA}^2$. This value was obtained using a temperature of 100°K in the calculation of the relative velocity, an assumption that required some further comment. Although the walls of the discharge tube are cooled by liquid nitrogen, the plasma need not be in equilibrium with the walls or even with itself. Various kinds of experience, e.g., Doppler widths of probe molecules at low enough pressure or pressure changes with current for pure gases in a closed constant volume system combined with the ideal gas law, lead us to believe 100°K is a good estimate for the translational temperature of the predominate neutral gas (including H_2) part of the discharge. The kinetic temperature of the ions may be considerably higher, but no value is directly available for these conditions at present. Fortunately, due to the fact that H_2 is much lighter than HCO^+ , the relative velocity is quite insensitive to the HCO^+ temperature. Raising it from 100 to 4500°K would be required to double the mean relative velocity.

Although there is no other experimental linewidth data for molecular ions, some useful comparisons can be made with the experimental^{9,10} and theoretical¹¹ collisional cross sections of the isoelectronic neutral HCN (also listed in Table I), which has a similarly large dipole moment, and with the calculated collisional excitation rates⁵ for the molecular ion HNN^+ . Since there are no experimental or theoretical data for $\text{HCN}-\text{H}_2$ collisions, it becomes necessary to make some qualitative estimates. Experimental linewidth studies on OCS ,^{12,13} formaldehyde,¹⁴ formic acid,¹⁵ and ammonia⁸ show that collisional cross sections with H_2 are larger than those for He by a factor of 1.5–2.3. Such an increase is also predicted by Green and Thaddeus,¹¹ due to the long-range dipole-quadrupole interaction with hydrogen. Since there is good agreement between the experimental and theoretical cross sections for $\text{HCN}-\text{He}$ at 300°K , the theoretical result¹¹ at 100°K ($\sigma = 34.4 \text{ \AA}^2$) can be combined with the experimentally observed trend mentioned above to predict a cross section of $52-79 \text{ \AA}^2$ for $\text{HCN}-\text{H}_2$ at 100°K . This would correspond to a pressure broadening parameter of 8–13 MHz/Torr. In comparison, our experimental linewidth and collisional cross section for HCO^+-H_2 (29.6 MHz/Torr and 182 \AA^2) are about three times larger than the predicted parameters for $\text{HCN}-\text{H}_2$. This result is consistent with the conclusions of Woods *et al.*⁴ Also, calculations by Green⁵

TABLE I. Pressure broadening parameters of HCO^+ , HCN, and ^{18}OCS .

Absorber	Transition	Perturber and temperature ($^\circ\text{K}$)	$d\Delta\nu/dP$ (MHz/Torr)	$\Delta\nu_d$ (kHz)	σ (\AA^2)	b (\AA)	Ref.
HCO^+	$J=0-1$	$\text{H}_2/100$	29.6 ± 3	363 ± 32	182 ± 20	7.62 ± 0.84	This work
HCN	$J=6, 7, 8, 10$ (I -doublets)	HCN/300	40		1570	22	9
		He/300	1.6		23	2.7	
		Ar/300	2.1		67	4.6	
		Xe/300	2.2		76.5	5.0	
HCN	$J=0-1$	He/300			29 ± 6		10
HCN	$J=0-1$	He/300			27.0 (Theor.)		11
		He/100			34.4		
^{18}OCS	$J=7-8$	$\text{OCS}/296$	7.11 ± 0.15	201 ± 14	302 ± 2	9.80 ± 0.06	This work

on rotational excitation of HNN^+ by collisions with helium indicated that the total rate of collisional excitation out of the lowest level would be about four times greater than for the HCN-He system.

The parameters obtained for $J=7-8$ transition of ^{18}OCS are also summarized in Table I. The linewidth which we obtain, 7.11 MHz/Torr, is in reasonable agreement with the calculated J dependence of the OCS linewidths (Murphy and Boggs¹⁶), but is not in agreement with experimental work on higher J transitions (Anderson¹⁷ obtains 9.5 ± 1.6 MHz/Torr for the $J=7-8$ transition). However, as pointed out by Murphy and Boggs,¹⁶ there is serious doubt as to the reliability of this earlier experimental work. Unfortunately, the linewidths of these transitions have not been remeasured, and our study appears to be the only reliable data available for a high J transition of OCS.

The intercepts in Figs. 1 and 2 lead to linewidths at zero pressure of 201 kHz for ^{18}OCS and 363 kHz for HCO^+ . For the former, this is clearly an instrumental limit due to the frequency instabilities of the free running klystron, since the Doppler width and other expected contributions to broadening are far below 201 kHz. In the HCO^+ case, the situation is much less clear. The large value could be due to Doppler width at a high ion kinetic temperature, or it could be just additional source broadening, since noise from the discharge may degrade the klystron stability. In future experiments, we expect to carry out the linewidth measurements with a phase locked and digitally programmed microwave source, so that source broadening will be essentially eliminated. In addition to generally improving the precision of the pressure broadening data, this will allow the ion temperature to be quantitatively determined, at least at the low pressure limit, from Doppler widths. As mentioned before the ion temperatures may be elevated in the discharge plasma.¹⁸ Also there exists a Doppler shift of the HCO^+ line frequency due to the unidirectional shift of the ions in the dc discharge.¹⁹ No attempt was made to measure this for the gas mixtures utilized in this study, but future linewidth measurements with digital frequency programming will simultaneously yield this shift, and thus the ion mobilities.

Several points should be mentioned in connection with the reliability of the present value of $d\Delta\nu/dP$ for HCO^+ by H_2 and the general problems associated with obtaining this parameter in a glow discharge apparatus. First, there is clearly more scatter in the data of Fig. 1 than in that of Fig. 2, but the former set of points is nevertheless adequate to determine the slope rather well. More precise values of the linewidths will clearly be obtained later, but will not change $d\Delta\nu/dP$ very much. Another possible problem is the nonuniformity of the pressure due to the flow system. This we believe is negligible because of the large discharge tube diameter, the small pump-out port diameter, and the slow flow rate. The really serious problems are the uncertainties in temperature and gas composition. In addition to the nonequilibrium nature of the plasma discussed earlier, there is a possibility that the "temperature" is

spatially nonuniform or that it varies with pressure. Parts of the discharge tube (the anode and cathode regions) are at room temperature, but these are thought to make negligible contributions to the absorption, since no signal is detected when the whole tube is at room temperature. Variations of temperature with pressure should show up as a deviation from linearity in Fig. 1, which is not apparent, but more precise data points would be helpful in looking for such a deviation. We are, of course, using total pressure rather than partial pressure of H_2 , and the linewidth could have contributions arising from other more polar molecules as collision partners. The cryogenic wall surface is helpful here though, since reaction byproducts like formaldehyde, which even in small concentration might make a large contribution, are efficiently removed from the gas soon after they are formed. Any error of this kind would probably make the reported value too high, since most other molecules would cause more broadening than hydrogen. At any rate, the H_2 is thought to be greatly in excess, especially at the high pressures, CO itself is not very polar, and it seems unlikely that any polar molecule would increase in concentration in proportion to the overall pressure, thus changing the slope of $d\Delta\nu/dP$. Nevertheless, we plan to use a quadrupole mass spectrometer system to directly measure the various partial pressures in future experiments. Such precautions will clearly be more important in similar measurements in discharges where the liquid-nitrogen cooling is absent, or wherever the chemistry is more difficult to predict. Yet another uncertainty associated with the nonequilibrium nature of the plasma is that of vibrational distribution. The nature of the experiment dictates that the HCO^+ observed is in the ground vibrational level, but the H_2 is in an unknown vibrational distribution, in which we expect $v=0$, however, to be greatly preponderant. Taking account of all these potential systematic errors as best we can, we have increased the statistical error in the linewidth (one standard deviation = 0.6 (MHz/Torr) by a factor of 5 for a final result $d\Delta\nu/dP = 29.6 \pm 3$ MHz/Torr. For the OCS, a 3σ error seems more appropriate, (7.11 \pm 0.15 MHz/Torr). In future work, in order to sharpen the comparison of the HCO^+-H_2 broadening with that of HCN-H_2 , we hope to measure the latter directly, in a liquid-nitrogen-cooled discharge tube.

¹E. Herbst and W. Klemperer, *Astrophys. J.* **188**, 255 (1974).

²B. E. Turner, *Astrophys. J.* **193**, L83 (1974).

³T. A. Dixon and R. C. Woods, *Phys. Rev. Lett.* **34**, 61 (1975); R. C. Woods, T. A. Dixon, R. J. Saykally, and P. G. Szanto, *ibid.* **35**, 1269 (1975); R. J. Saykally, T. A. Dixon, T. G. Anderson, P. G. Szanto, and R. C. Woods, *Astrophys. J.* **205**, L101 (1976).

⁴R. C. Woods, P. R. Certain, and R. B. Bernstein, Theoretical Chemistry Institute Report, WIS-TCI-503 (Madison, Wisconsin, 1974).

⁵S. Green, *Astrophys. J.* **201**, 366 (1975).

⁶R. C. Woods and T. A. Dixon, *Rev. Sci. Instrum.* **45**, 1122 (1974).

⁷J. F. Verdick and C. D. Cornwell, *Rev. Sci. Instrum.* **32**, 1383 (1961).

⁸C. H. Townes and A. L. Schawlow, *Microwave Spectroscopy*

- (McGraw-Hill, New York, 1955).
- ⁹J. B. Cohen and E. B. Wilson, *J. Chem. Phys.* **58**, 442 (1973).
- ¹⁰R. B. Nerf (private communication), reported in Ref. 11.
- ¹¹S. Green and P. Thaddeus, *Astrophys. J.* **191**, 653 (1974).
- ¹²B. T. Berendts, Ph.D. thesis, Catholic University of Nijmegen, The Netherlands, 1966.
- ¹³F. A. Liuima, A. V. Bushkovitch, and A. G. Rouse, *Phys. Rev.* **96**, 434 (1954).
- ¹⁴A. C. Venkatachar and J. A. Roberts, *J. Mol. Spectrosc.* **57**, 166 (1975).
- ¹⁵A. C. Venkatachar and J. A. Roberts, *J. Chem. Phys.* **62**, 3364 (1975).
- ¹⁶J. S. Murphy and J. E. Boggs, *J. Chem. Phys.* **49**, 3333 (1968).
- ¹⁷R. S. Anderson, *Phys. Rev.* **97**, 1654 (1955).
- ¹⁸A. von Engel, *Ionized Gases* (Oxford University, London, 1965), Chap. 4.
- ¹⁹R. C. Woods, R. J. Saykally, T. G. Anderson, P. G. Szanto, and T. A. Dixon (to be published).