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Prof. J. N. Murrell (*University of Sussex*) said: The existence of a clear boundary between quasi-periodic and stochastic motion, and the implications of this for a well defined separatrix is well established for two-dimensional motion. In Prof. Rice's paper he states that it is not obvious how to extend the method to systems having more degrees of freedom. The question is whether even the concepts are useful. How far might one have to go before traditional statistical theories apply? Could it be that two dimensions is very special?

Prof. S. A. Rice (*University of Chicago, USA*) said: Prof. Murrell has raised a very important issue. Some of our new knowledge of non-linear dynamics is general enough to apply to systems with many degrees of freedom, for example, the Kolmogoroff–Arnold–Moser theorem on the stability of quasiperiodic motion. On the other hand, a much larger part of our new knowledge of non-linear dynamics is derived from studies of systems with only two degrees of freedom, and even from the mathematical characteristics of non-linear mappings in a finite two-dimensional domain. There may be many surprises when we learn how to study the details of the dynamics of systems with more than two degrees of freedom. Nevertheless, I remain optimistic that the theory described in our paper, or variants of it, will prove useful for the description of unimolecular reactions of real molecules.

It must be remembered that the very successful RRKM statistical theory of the reaction rate constant is, in effect, an analysis which describes the system as having only one important degree of freedom, the reaction coordinate. Our analysis shows that there are circumstances for which the non-linear coupling between two degrees of freedom qualitatively alters the dynamics of the system and thereby influences the rate of reaction. Although our analysis has been illustrated for models with two degrees of freedom, and draws on particular features of mappings of two-dimensional Hamiltonian flow in phase space, I believe all of the qualitative features of the dynamics we find to influence the reaction rate will also be important in systems with more than two degrees of freedom, at least to the extent that it is a good approximation to single out two dominant coupled motions in such systems.

Consider the case that it is possible to identify two strongly coupled motions in the molecule. If these motions are slow relative to those characteristic of the other degrees of freedom, the latter define an effective two-dimensional potential-energy surface for the former. If the motions of the selected pair of degrees of freedom are rapid relative to all other motions, the latter adiabatically follow the former, again defining an effective two-dimensional potential-energy surface. In both limits it is possible to define a reaction path Hamiltonian with only two effective degrees of freedom. I do not expect this reaction path Hamiltonian to generate qualitatively different dynamics from those characteristic of the 'pure' two-degree-of-freedom systems studied to date.

There is another way of thinking about the extension of our analysis to larger systems. Suppose the coupling between the pair of motions selected to describe the reaction and all other degrees of freedom of the molecule is weak. Then the principal role played by these other degrees of freedom is as a reservoir which feeds in and absorbs energy from the subsystem of interest. If the modulation of the energy of the subsystem does not greatly perturb the local phases of the component motions, it is plausible that the qualitative features of the dynamics are not greatly altered from the dynamics of the 'pure' two-degree-of-freedom systems studied to date.

Of course, the cases cited above have not yet been studied in detail, so my expectations remain to be verified. To answer the first of your specific questions, I believe the use

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of a zero-order separatrix to define the transition state for unimolecular reaction, as well as the other concepts we employ, will be useful for many systems, particularly when the properties of the system potential-energy surface make intramolecular energy transfer difficult. As to your second question, there are many different ways of averaging, or otherwise reducing, the level of a description of the molecular dynamics so as to generate a statistical analysis of the dynamics. However, even in very large molecules it is possible to have local, *e.g.* group-specific, chemistry which requires more than a one-dimensional reaction coordinate description. Much depends on the level of description needed. Some aspects of reactions of very small molecules are well described using only a statistical approach, neglecting all dynamical characteristics of the system. On the other hand, description of the rate of the malonaldehyde tautomerization reaction requires use of a reaction-path Hamiltonian with two degrees of freedom.[1] As experimental data relevant to the dynamics of reactions improve I suspect we will increasingly want to go beyond the predictions of a fully statistical theory of the processes involved.

1 T. Carrington Jr and W. H. Miller, *J. Chem. Phys.*, 1986, **84**, 4364.

Dr M. S. Child (*Oxford University*) said: The elegant new theory described in the paper proves remarkably successful even at the approximate level, for a system with two degrees of freedom.

I wonder whether Prof. Rice can indicate how practicable the method might prove in more realistic situations. Will it be equally easy to find an approximate separatrix for example? Secondly, can one see how the theory will go over to the RRKM limit in appropriate systems.

Prof. S. A. Rice (*University of Chicago, USA*) said: At present we have insufficient experience with applications of the new theory to provide a good answer to your first question. We have studied the fragmentation of T-shaped HeI_2 in the $J = 0$ state,[1] *i.e.* with the I_2 angular momentum and the orbital angular momentum constrained to sum to zero. It is relatively easy to find a zero-order separatrix in this system but, for the particular choice of zero-order system made, the accuracy of the theory is less than in the similar fragmentation without any rotation. I am optimistic that, with common sense and some experience, it will prove possible to define tractable zero-order systems, even for large molecules, which yield accurate approximations for the unimolecular fragmentation rate constant.

Your second question is harder to answer; the answer may depend on the kind of system studied. For example, we have studied isomerization using the equivalent double-well DeLeon–Berne model.[2,3] For an energy barely above the barrier, our theory and RRKM theory, suitably corrected for the quasiperiodic behaviour present at that energy, give equivalent results. On the other hand, when the system energy is considerably higher, our theory and RRKM theory give different results. Actually, in this case our theory yields a new conceptualization of the isomerization process, which is different from the RRKM conceptualization at all energies.

In general, if the projection of the two- or higher-dimensional reaction-path Hamiltonian for a system onto a one-dimensional reaction path leads to a configuration-space definition of the transition state which has the property that flux through the separatrix in the full phase space maps one-to-one into flux through the transition state so defined, and if intramolecular energy transfer is very much faster than reaction, then our theory should reduce to RRKM theory. The mapping referred to may exist for some molecular systems and not others.

1 S. K. Gray, S. A. Rice and M. J. Davis, *J. Phys. Chem.*, 1986, **90**, 3470.
2 S. K. Gray and S. A. Rice, *J. Chem. Phys.*, submitted for publication.
3 N. DeLeon and B. J. Berne, *J. Chem. Phys.*, 1981, **75**, 3495.

Prof. M. Quack (*ETH Zürich*) said: Can you give us a hint as to how one could generalize your most interesting theory to a quantum treatment? Would it not also be worthwhile to start out the opposite way, searching for generalised quantum-statistical theories of unimolecular reactions and then obtain the classical limit of these theories?

Prof. S. A. Rice (*University of Chicago, USA*) said: There are several levels at which your question can be answered. The theory, as developed to date, makes extensive use of concepts from classical mechanics that have no direct analogues in quantum mechanics. The problem, then, is how to translate the insights obtained from the classical mechanics into a quantum-mechanical description.

At the purely formal level, Nordholm and Rice[1] developed a description of unimolecular fragmentation based on dividing the system Hilbert space into a subspace of bound states and a complementary subspace of free fragment states. This subdivision of the Hilbert space is, in a free-association sense, related to focussing attention on the importance of the separatrix, but in fact it is more subtle. The amplitudes of the system wavefunction in the bound state and free-state subspaces satisfy a pair of coupled integral equations which involve the 'memory' of the evolution of the amplitude under the projected Hamiltonians corresponding to the defined subspaces. This solution of the problem is exact but intractable. The formalism suggests various routes to obtaining useful approximate theories of fragmentation, but only one crude approximation has been explored to date.[1] However, even that crude approximation reveals an influence of the rate of intramolecular energy transfer on the fragmentation dynamics; the analogue of competition between the rate of crossing the intramolecular bottleneck (the cantorus) and the intermolecular bottleneck (the separatrix). It is my opinion that the Nordholm–Rice formal analysis is worthy of further study and may yet provide a vehicle for development of an accurate quantum-mechanical theory of unimolecular fragmentation.

At the level of semiclassical quantization, it is possible to use the conventional relation between area in phase space and number of quantum states supportable to transform our approximate formula for the rate constant to a quantum-mechanical equivalent. This analysis is quick and easily understood, and it leads to a 'sensible' result. On the other hand, it is not easy to see how to include competition between intramolecular energy transfer and fragmentation, nor how to improve the analysis.

As you suggest, it is possible to start with any one of a number of exact quantum-mechanical formulations of the unimolecular fragmentation process. Of course, all of these exact analyses are merely transcriptions of the original N-body problem into another form. We cannot solve the N-body problem in any representation, so the value of the transcriptions is that they suggest new kinds of approximations to reduce the description to a tractable form. But how are we to choose these approximations? I view the classical mechanical theory as one of the most powerful tools for providing insight into the choice of approximations in the quantum-mechanical theory. I certainly support the view that it is essential to develop a quantum-mechanical theory of unimolecular fragmentation (and isomerization), and I am open to any approach that leads to an accurate and useful formulation.

1 S. Nordholm and S. A. Rice, *J. Chem. Phys.*, 1975, **62**, 157.

Mr A. C. Peet, Dr D. C. Clary and **Dr J. M. Hutson** (*University of Cambridge*) (*communicated*). The calculations presented in our paper are concerned with predissociation from the lowest rovibrational van der Waals states of the ethylene dimer correlating with the ν_7 excited monomer vibration. However, highly excited van der Waals states based on the lower-lying ν_{10} monomer vibration also exist in this region and the density of these states has been shown by Beswick[1] to be very large. A formalism for a situation

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such as this has been given by Bixon and Jortner.[2] Each of the states correlating with the ν_{10} vibration has a small amount of ν_7 character mixed in by the intermolecular potential and thereby gains some intensity in the spectrum. The intensity of a given transition depends upon the degree of mixing and this is largest for states which lie closest in energy to the zeroth-order ν_7 level. If the spacing between the ν_{10} states is much less than the matrix element coupling them to the ν_7 state, the ν_7 character becomes spread out over many ν_{10} states and the envelope of the spectral lines becomes a Lorentzian whose width depends upon the coupling matrix element.

Gentry[3] has used Bixon and Jortner's formalism[2] to interpret the broad spectra seen in the low-resolution experiments in terms of intramolecular vibrational relaxation (IVR) with a lifetime of *ca.* 0.5 ps. However, it should be noted that the model described in the previous paragraph does not require time-dependence to explain the broad Lorentzian envelope. An important consequence of the model is that it identifies the fine structure observed by Snels *et al.*[4] with transitions to states which are largely ν_{10} in character. At the energy of importance, states correlating with the ν_{10} excited mode can have a large component of hindered monomer rotation and should predissociate efficiently to give highly rotationally excited fragments. We have calculated the width of a resonance corresponding to a ν_{10} state of the appropriate energy, using the AVCC-IOS approximation as described in our paper. The width obtained was 1.3×10^{-3} cm^{-1}, which is substantially wider than the ν_7 resonances and is in better agreement with the experiments of Snels *et al.*

It is also possible to attain the energy of the ν_7 mode by exciting van der Waals vibrational and hindered rotational modes without exciting any monomer vibrations. The large quantum numbers required for the van der Waals modes ensure that coupling to the ν_7 levels is small and that infrared transitions to states correlating with the monomer ground vibrational state are very weak. An interesting property of these states, however, is that they undergo rapid rotational predissociation, so that the spectral lines associated with them are broad. The lines are likely to overlap, forming a continuous, but weak, background and such a background is indeed observed experimentally.[5]

1 J. A. Beswick, personal communication.
2 M. Bixon and J. Jortner, *J. Chem. Phys.*, 1968, **48**, 715.
3 W. R. Gentry, in *Resonances in Electron–Molecule Scattering, van der Waals Complexes, and Reactive Chemical Dynamics*, ed. D. G. Truhlar (ACS Symp. Ser., No. 263), (American Chemical Society, Washington, 1984).
4 M. Snels, R. Fantoni, M. Zen, S. Stolte and J. Reuss, *Chem. Phys. Lett.*, 1986, **124**, 1.
5 J. Reuss, personal communication.

Dr D. S. King (*NBS Gaithersburg, USA*) said: Dr Hutson described the results of AVCC-IOS calculations for the vibrational predissociation of the ethylene dimer excited to the $v = 1$ level of the ethylene-like ν_7 mode at 950 cm^{-1}. In earlier work,[1] these same calculations were applied to the dissociation of Ne–ethylene(ν_7) and Ar–ethylene(ν_7). The preferred final-state distributions were found to be those that minimized momentum transfer. Specifically, for the ethylene dimer where only *ca.* 550 cm^{-1} of excess energy is available for fragment excitations, rotational excitation of the ethylene fragment was found to be favoured; for the dissociation of the vibrationally excited Ne–ethylene complexes, >850 cm^{-1} of energy is available and reaction channels resulting in vibrationally excited ethylene(ν_{10}) were favoured.

We have performed measurements of the distributions of energy in the fragments following ν_7 and $\nu_7 + \nu_8$ excitations of the NO–ethylene dimer. The experiments were similar to those reported in our paper at this Discussion.[2] Since the bond energy of this complex is *ca.* 400 cm^{-1}, there is an interesting analogy between these experiments and the theoretical predictions of Hutson and colleagues: following NO–ethylene($\nu_7 + \nu_8$) excitation there is sufficient excess energy to result in vibrationally excited fragments, but following NO–ethylene(ν_7) excitation the vibrationally excited fragment channel is

closed. In these experiments we directly determined the internal energy and kinetic energy distributions of the NO fragments by laser-excited fluorescence techniques including Doppler-profile measurements, and the kinetic energies of the ethylene fragments through conservation of linear momentum. Although we do not determine the internal energy distribution of the ethylene fragments, we do obtain the average internal energy of these fragments from conservation of energy arguments.

Dissociation of NO–ethylene(ν_7) results in little kinetic energy release and little rotational excitation of the NO fragments.[3] The observed Doppler profiles for these NO fragments were independent of pump–probe laser geometry and were approximately Gaussian with f.w.h.m. $2\Delta\nu_D = 0.060$ cm^{-1}, consistent with an isotropic flux distribution and an average kinetic energy of *ca.* 105 cm^{-1} per fragment. The average internal energy of the NO fragments was 52 cm^{-1}. Assuming a van der Waals bond energy of *ca.* 400 cm^{-1}, the average internal energy of the ethylene fragments must be *ca.* 300 cm^{-1}. This excitation is most probably involved in rotational motion about the ethylene *a*-axis ($A = 4.8$ cm^{-1}) since this amount of rotational energy release would require excitation to levels of very large J for rotation about the other molecular axes ($B = 1.0$ cm^{-1} and $C = 0.83$ cm^{-1}).

Excitation of the $\nu_7 + \nu_8$ combination band at 1899 cm^{-1} provides the fragments with *ca.* 1500 cm^{-1} of energy, an amount nearly three times that available following ν_7 excitation. The observed Doppler profiles for the resulting NO fragments were narrower, exhibiting 0.045 cm^{-1} f.w.h.m., and the rotational temperature of the NO fragments was slightly colder. In essence, 1330 of the *ca.* 1500 cm^{-1} of energy available, nearly 90%, must go into internal excitations of the ethylene fragment. It seems unreasonable to expect all this energy to have been absorbed by rotational excitation of the ethylene in light of the minimal rotational excitation and kinetic energy release in the NO fragment. It seems most likely that all ethylene fragments are created vibrationally excited, in $v = 1$ levels of either ν_7 or ν_8.

In summary, we have experimental evidence for the preferred fragmentation channels of ethylene–NO complexes excited to initial levels from which the formation of vibrationally excited fragments are either energetically possible ($\nu_7 + \nu_8$ excitation) or not possible (ν_7). The observed results closely parallel the theoretical predictions for ethylene dimer and Ne–ethylene(ν_7) predissociation.

1 J. M. Hutson, D. C. Clary and J. A. Beswick, *J. Chem. Phys.*, 1984, **81**, 4474.
2 D. S. King, M. P. Casassa and J. C. Stephenson, *Faraday Discuss. Chem. Soc.*, 1986, **82**, 251.
3 D. S. King and J. C. Stephenson, *J. Chem. Phys.*, 1985, **82**, 5286.

Mr A. C. Peet (*University of Cambridge*) said: Apart from resolving fine structure in the ethylene dimer spectrum Snels *et al.*[1] also observed broad structure consisting of two peaks one on either side of the main peak. They assigned this broad structure to sum and difference bands of a van der Waals mode with the ν_7 monomer vibration, but were unable to specify the van der Waals mode involved.

We have calculated an approximate spectrum which helps to assign the peaks.[2] The AVCC-IOS approximation has been applied to the dynamics, restricting the van der Waals bending modes to those involving motion of the ethylene monomers about their C—C axes. Energy levels, obtained by solution of the appropriate coupled-channel equations, indicate that the bending motion is hindered to an extent where it can be considered as a vibration of frequency *ca.* 40 cm^{-1}.

Approximate intensities have been evaluated for transitions involving the different azimuthal bending states by evaluating the matrix element

$$|\langle\psi_i|\mu_{AC}|\psi_f\rangle|^2$$

where the initial and final wavefunctions, ψ_i and ψ_f, respectively, are taken to be
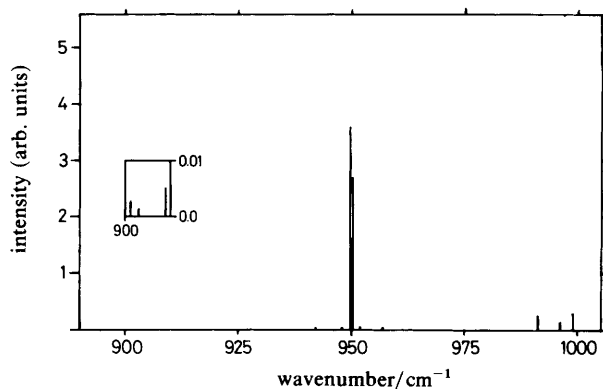
Fig. 1. Photodissociation spectrum for the ethylene dimer. The peak at 905 cm^{-1} is shown as an inset with an expanded vertical scale.

rovibrational functions calculated at one value of the intermolecular distance. The dipole moment operator μ_{AC} is assumed to be independent of intermolecular distance and is taken to be due solely to the ν_7 vibration of one of the monomers.

The calculated spectrum is shown in fig. 1. The selection rules $\Delta J = 0$ and $\Delta K = 0$, where J is the total angular momentum of the complex and K is its projection along the intermolecular vector, have been imposed and this is one reason for the sparse nature of the spectrum. Structure which is similar to that observed by Snels *et al.* is predicted and so it seems likely that the van der Waals mode which produces the satellite peaks is the azimuthal bending mode of the ethylene monomers about their C—C axes. Bending modes associated with the angles θ_A, θ_B and ξ which were fixed in the calculation could produce peaks in the spectrum but as the rotational constant for these motions is small it is likely that they would be much closer to 950 cm^{-1} than the observed peaks. Transitions involving the van der Waals stretching mode could produce peaks close to those present in the experimental spectrum. However, such peaks would be observed in the existing experiments only if the transition dipole moment operator were to have a strong dependence upon the intermolecular distance, and this seems unlikely.

1 M. Snels, R. Fantoni, M. Zen, S. Stolte and J. Reuss, *Chem. Phys. Lett.*, 1986, **124**, 1.
2 A. C. Peet, *Chem. Phys. Lett.*, in press.

Prof. N. Sheppard (*University of East Anglia*) said to Mr Peet: You have stated your preference for assigning the satellites to the ν_7 infrared band of the ethylene dimer to quasi-rotational motions about CC axes within the dimer, but I wonder if you have not too readily rejected the inter-monomer vibrational mode as a candidate for giving rise to these features. It seems to me not at all unlikely that a reasonable degree of modulation of the vibrational dipole change associated with the out-of-plane CH deformation mode, *i.e.* ν_7, should occur as a result of the inter-monomer mode. In this connection may I ask what is the evidence for the relative orientations of the two ethylene molecules within the dimer?

Mr A. C. Peet (*University of Cambridge*) said: The transition dipole moment of the ethylene dimer can be divided into one part which is present in the monomer and another which is induced in one molecule by the presence of the other. The leading term in the monomer expansion is the transition dipole for the ν_7 vibration. This term couples the ground and ν_7 states of the dimer directly giving rise to intense features in

the spectrum. Apart from the main peak it is also responsible for the excitation of hindered rotational motion of the monomers.

The monomer transition dipole moment is independent of intermolecular distance and so in the absence of bend/stretch coupling it does not excite the van der Waals stretching mode. However, such transitions can occur as a result of the induced dipole, which is dependent upon the intermolecular distance. The leading term in the expansion of the induced dipole is a dipole-induced quadrupole term, and this is expected to be small compared to the monomer term making transitions caused by it weak. It thus seems likely that the satellite peaks seen by Snels *et al.* are due to hindered rotational motion of the monomers rather than the van der Waals stretching motion.

Evidence for the structure of the ethylene dimer comes from both experiment and theory. The structure inferred from experimental data uses mainly solid-state[1] and matrix-isolated dimer[2] studies. Theoretical studies on the ethylene dimer structure have used self-consistent field calculations on the monomer and then used perturbation theory to calculate the interaction between the monomers.[3,4]

1 G. J. H. van Nes and A. Vos, *Acta Crystallogr., Sect. B*, 1977, **33**, 1653.
2 E. Rytter and G. M. Gruen, *Spectrochim. Acta, Part A*, 1979, **35**, 199.
3 T. Waisutynski, A. van der Avoird and R. M. Berns, *J. Chem. Phys.*, 1978, **69**, 5288.
4 A. van der Avoird, *Top. Curr. Chem.*, 1980, **93**, 1.

Ms K. von Puttkamer and **Prof. M. Quack** (*ETH Zürich*) replied: Peet *et al.* have presented interesting calculations on the predissociation lifetimes of the ethylene dimer.[1] Other theoretical calculations at this conference include the work of Gray and Rice[2] and Balint-Kurti and Kidd.[3] There is also clearly a need to obtain more experimental data on systems which are of fundamental interest and could serve as test cases for theory (see also the work of King *et al.*[4]). We have investigated with this aim the $(HF)_2$ hydrogen-bonded system,[5] which is one of the simplest and may also serve as a model for the first step of condensation in hydrogen-bonded liquids. We have recorded the rovibrational spectra for this molecule in the entire range between the far-infrared and the visible on our BOMEM DA 002 interferometric Fourier-transform spectrometer system, allowing for a maximum apodized resolution of $0.004\ cm^{-1}$. The $(HF)_2$ was created under equilibrium conditions between 250 and 300 K and pressures between 1 and 750 kPa in home-made thermostatted cells with optical path lengths of 4 and 10 m.

Fig. 2 shows the vibrationally adiabatic potentials of the ground state and the first and second excited state of the HF stretching vibration. The energy of the HF stretching fundamental already largely exceeds the hydrogen-bond dissociation energy $\Delta U_0^0 \approx (hc)$ $1800\ cm^{-1}$. Pine *et al.*[6] have inferred a predissociation lifetime of 800 ps from the linewidths of the hydrogen-bond HF stretching fundamental spectrum. We have reproduced and extended their data in this range. We have also measured overtone spectra covering up to eight times the dissociation energy. There is evidence for some fine structure and thus long lifetimes for all the overtone spectra, which are, however, still subject to pressure-broadening.

Fig. 3(*a*) shows an overview of the first overtone region of the HF dimer. The large features are due to HF monomer absorption. The broad bathochromically shifted absorption arises from various polymers mainly from hexamers. The hardly visible substructure between the monomer P and R lines arises from the dimer. Fig. 3(*b*) shows a part of the dimer spectrum in more detail. A first estimate from our preliminary assignment places the $2\nu_2$ near $7542\ cm^{-1}$ and the $2\nu_1$ near $7679\ cm^{-1}$. The most significant result is the observation of fine structure with pressure-broadening-limited widths of the order of $0.1\ cm^{-1}$. This implies dissociation lifetimes >40 ps.

Fig. 4 shows an overview of the region of the second overtone of the ν_1 and ν_2 HF stretching vibrations. The large features are due to HF monomer absorption. The broad

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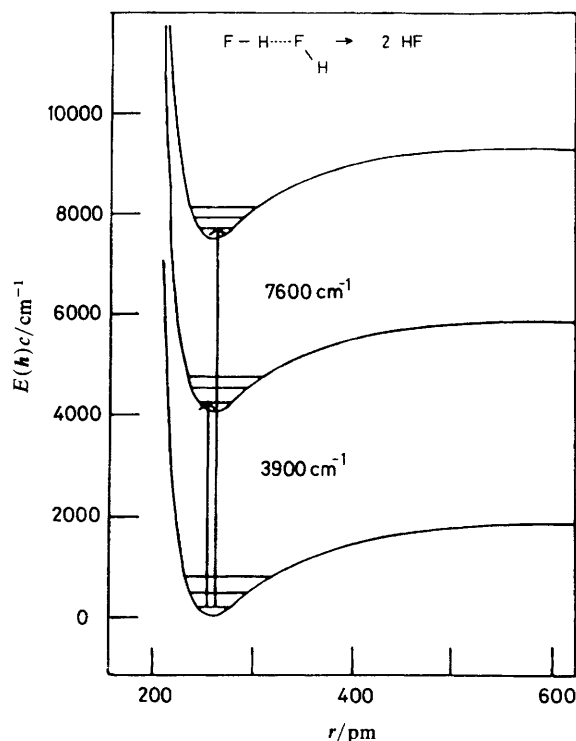**Fig. 2.** Schematic drawing of vibrationally adiabatic $(HF)_2$ channel potentials showing quasibound states and the fundamental and overtone transitions of the HF stretching vibrations. Predissociation occurs by transferring HF stretching energy into the low-frequency modes including the reaction coordinate.

bathochromically shifted absorption arises from various polymers, including hexamers. The small substructure between the monomer P and R lines arises from the dimer. The harmonic frequency and anharmonicity constants obtained from the first and second excited HF stretching vibrational states would place the $3\nu_1$ band centre at 11 247 cm^{-1} and the $3\nu_2$ at 11 019 cm^{-1}, which seem to be good preliminary estimates. For these vibrational states lying six times above the dissociation threshold we find average pressure-broadening-limited linewidths of 1 cm^{-1}. Thus the minimum lifetime of the dimer is still at least 4 ps. We also measured structured spectra at energies up to eight times above the dissociation threshold.

For the theoretical understanding of the dissociation it is also important to have reliable values for the low-frequency fundamentals of the dimer. These have been calculated in numerous *ab initio* investigations, but no gas-phase spectrum at high resolution has been reported. We have started an investigation of the far-i.r. spectrum, aiming at the observation of all low-frequency fundamentals.

We wish to report here the first successful analysis of a vibrational state near 400 cm^{-1}, which we could assign to the $K = 1 \leftarrow 0$ sub-band. Fig. 5 is an overview over the sub-band showing clearly the red shaded Q-branches hiding somewhat the P-branches of the two tunnelling components. These results allow us to place the centre of $\tilde{\nu}_-$ ($K = 0 \rightarrow 1$) at 400.755 cm^{-1} with $B_- = 0.2103$ cm^{-1} and $\tilde{\nu}_+$ ($K = 0 \rightarrow 1$) at 399.783 cm^{-1} with $B_+ = 0.2106$ cm^{-1} for the two tunnelling components of internal rotation, respectively. The vibrational band centre is then estimated to be at *ca.* 370 cm^{-1}, which may
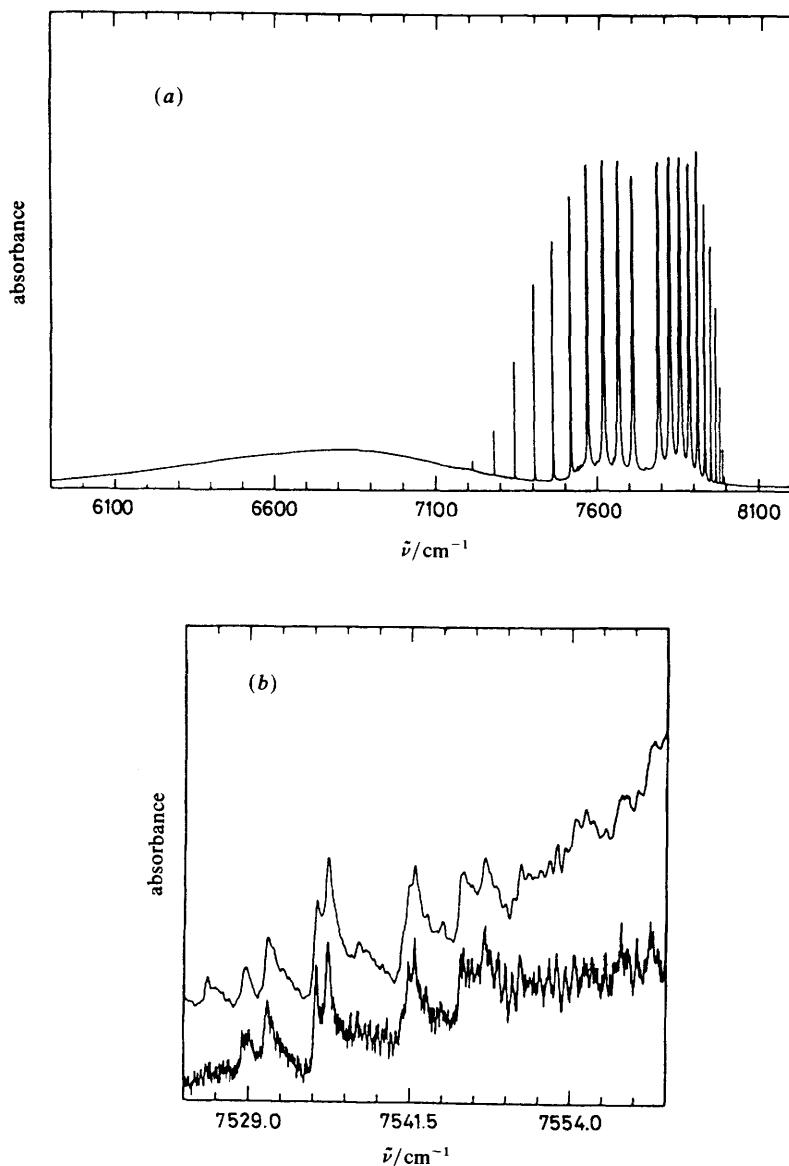
Fig. 3. (*a*) Overview spectrum in the first overtone region of HF polymers ($p = 37$ kPa, $l = 4$ m, room temperature). (*b*) Fine structure in the 7500 cm^{-1} region at two resolutions [upper trace as in fig. 3(*a*), lower trace: $p = 14$ kPa, $l = 10$ m, $T = 265$ K, resolution $= 0.025$ cm^{-1}].

be compared with *ab initio* results ranging from 442 to 623 cm^{-1}, depending also upon possible assignments (see below).

Work is in progress to analyse further bands in the far-infrared and to provide a theoretical interpretation for the observation of highly excited, long-lived states. We may note at present that a straightforward statistical model (say, RRKM theory or the statistical adiabatic channel model[7]) is in clear contradiction to our results. This does not exclude extensions of statistical models to be potentially useful, and such extensions are under study in our laboratory. In this context the work of Gray and Rice[2] is
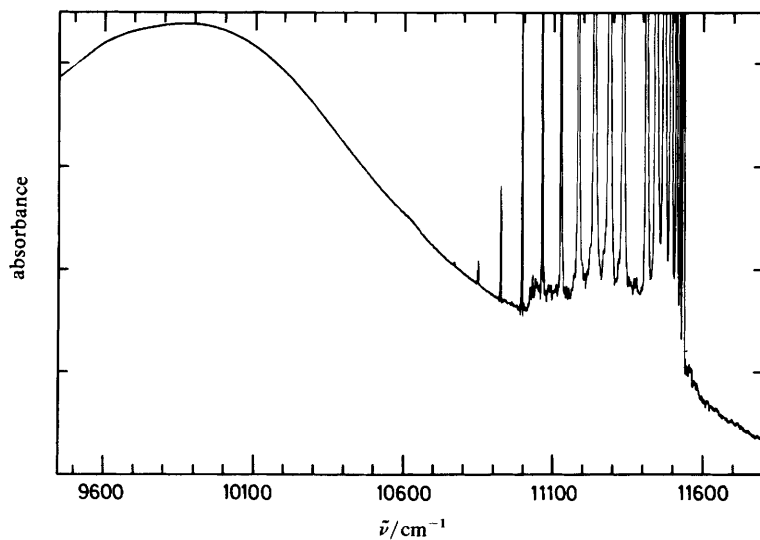
Fig. 4. Overview spectrum in the second overtone region of HF polymers ($p = 70$ kPa, $l = 10$ m, room temperature).
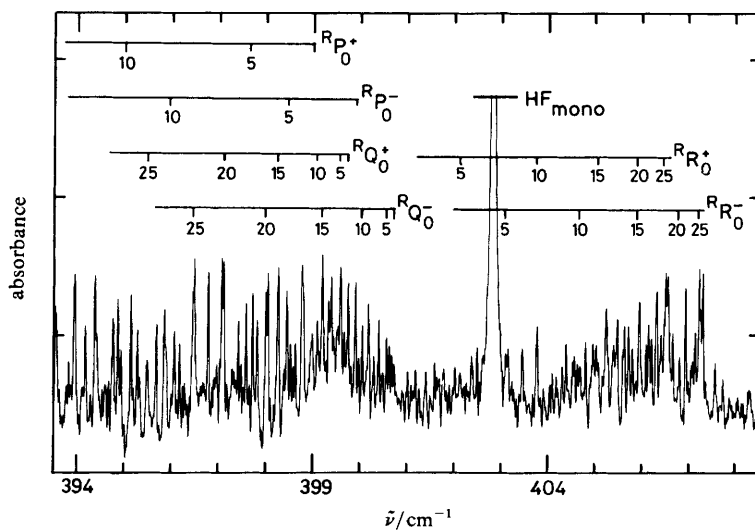

Fig. 5. Overview spectrum of the $K = 1 \leftarrow 0$ sub-band transition of a low-frequency mode in the 400 cm^{-1} region ($p = 2$ kPa, $l = 10$ m, $T = 250$ K, resolution $= 0.02$ cm^{-1}).

particularly relevant. It may be noted also that another theoretical approach has been quite successful both in reproducing the narrow linewidths for the HF stretching fundamental[8] and in predicting long-lived overtone states.[9]

Prof. N. Sheppard (*University of East Anglia*) commented on a remark made by Ms. von Puttkamer: Because of the information known about the geometry of the HF···HF dimer from microwave studies, it does seem to me to provide a very favourable starting point for the evaluation of the photofragmentation of this complex. May I ask whether the high-frequency absorption band that you studied was associated with the stretching of the 'free' or the 'hydrogen-bonded' HF bond within the dimer? Also does the *ca.* 400 cm^{-1} absorption band correspond to the stretching of the intermolecular hydrogen bond?

Ms K. von Puttkamer and **Prof. M. Quack** replied: We may note that a preliminary assignment for the HF stretching overtones to $2\nu_1$ and $2\nu_2$ ($3\nu_1, 3\nu_2$) has been obtained, whereas $\nu_1 + \nu_2$ seems to be absent, as is evident particularly from the spectra of HF–DF, where there is little ambiguity in the potential assignment of $\nu_1 + \nu_2$. The 400 cm^{-1} band probably does not correspond to the dimer stretching mode because of its polarization, but rather to either the bending or torsional vibration.

1 A. C. Peet, D. C. Clary and J. M. Hutson, *Faraday Discuss. Chem. Soc.*, 1986, **82**, 327.
2 S. K. Gray and S. A. Rice, *Faraday Discuss. Chem. Soc.*, 1986, **82**, 307.
3 G. G. Balint-Kurti and I. F. Kidd, *Faraday Discuss. Chem. Soc.*, 1986, **82**, 241.
4 D. S. King, M. P. Casassa and J. C. Stephenson, *Faraday Discuss. Chem. Soc.*, 1986, **82**, 251.
5 K. von Puttkamer and M. Quack, *Chimia*, 1985, **39**, 358.
6 A. S. Pine, W. J. Lafferty and B. J. Howard, *J. Chem. Phys.*, 1984, **81**, 2939.
7 M. Quack and J. Troe, *Theor. Chem. Adv. Persp.*, 1981, **6B**, 199.
8 N. Halberstadt, Ph. Bréchignac, J. A. Beswick and M. Shapiro, *J. Chem. Phys.*, 1986, **84**, 170.
9 N. Halberstadt, personal communication, more detailed calculations are in preparation in a collaboration of the Paris, Rehovot and Zürich groups.

Prof. R. N. Zare (*Stanford University, USA*) said: I believe Prof. Polanyi is pioneering the opening of a new and most exciting uncharted territory in photochemistry. I wonder if he can provide us with an estimate of the fraction of molecules photodissociated and those photodesorbed. Are there molecules which are 'promptly' photodesorbed? If so, they might undergo photodissociation in the gas phase near the surface during the laser pulse, thus giving rise to photofragments, which may be responsible, in part, for the observed photoreaction?

Prof. J. C. Polanyi (*University of Toronto*) said: Prof. Zare has asked about the yield, and hence the possible role, of desorbing gas in our observations of the photolysis of adsorbates. Other participants in the Discussion have raised closely related questions. Owing to space limitations we could not present all of our results in our Discussion paper. I shall present some more results which bear upon the possible role of desorbing gas, in what follows. These findings will be set out in a forthcoming paper.[1] Most of the points are made in our Discussion paper, but in less detail.

A single laser pulse of *ca.* 5 mJ photolyses *ca.* 10^{-4} of the adsorbate, as calculated from the integrated yield of neutral photofragments coming from the surface. By contrast, the same laser pulse typically desorbs *ca.* 50% of the adsorbate.

The fact that desorption can be orders-of-magnitude more efficient than photolysis, raises two questions. (i) Could the photolysis be taking place just above the surface in the dense cloud of gas that exists directly following desorption? (ii) Could this cloud of gas be involved in collisions with photofragments and hence be responsible for the reaction H + H$_2$S yielding the observed fast-moving H$_2$ product?
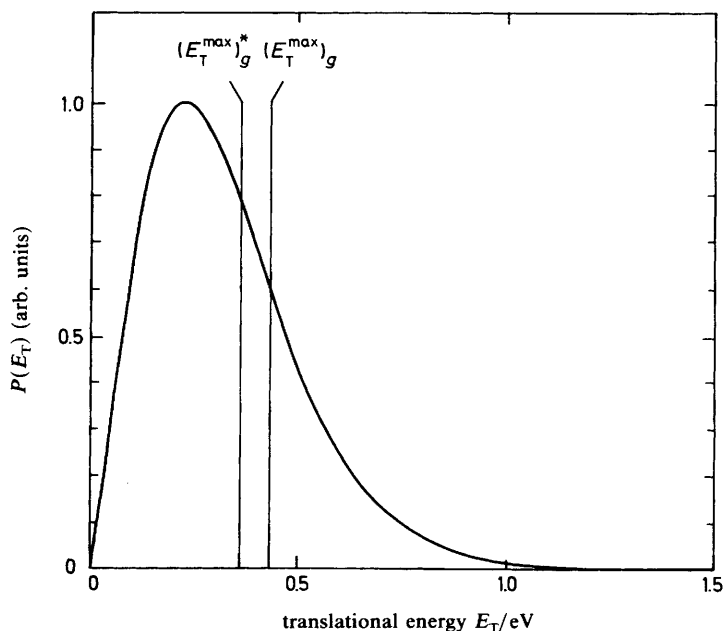
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Fig. 6. Translational energy distribution of the Br photofragment from the 222 nm photodissociation of CH_3Br adsorbed on annealed LiF(001) at low coverage (0.003 Torr s per laser pulse). The maximum translational energies for Br* and Br from the analogous gas phase photodissociation are labelled as $(E_T^{max})_g^*$ and $(E_T^{max})_g$.

In regard to (i) it is noteworthy that all the photofragments that we observed (CH_3 and Br from CH_3Br and H from H_2S) have translational energy distributions, $P(E_T)$, that differ significantly from those measured in the gas phase. They are shifted to lower E_T for CH_3 and H, and to higher E_T for Br; fig. 6 shows the shift to higher E_T in the case of Br. These fragments cannot, therefore, be the products of gas-phase photolysis [question (i)].

The second important point to bear in mind is that the $P(E_T)$ for the photofragments do not shift toward lower energy, nor do they broaden, as the coverages and hence the density of the desorbed gas-cloud are increased by approximately an order of magnitude. This point is made on p. 50 of our Discussion paper in relation to the H photofragments from H_2S [fig. 5(*b*)]. Fig. 7 of the present remarks shows two $P(E_T)$ for CH_3 photofragments at very different coverages and corresponding different gas-cloud densities. They do not differ significantly. It follows that the CH_3 and H photofragments escape from the surface without encountering the desorbing gas. They cannot, therefore, react with the desorbing gas [question (ii) above].

We can demonstrate the absence of photofragment-plus-gas collisions in other ways. As noted in our paper, a marginal increase in CH_3Br coverage in the neighbourhood of 1 monolayer causes the molecular photodesorption to decrease by two orders of magnitude. The effect on the translational energy distribution, $P(E_T)$, of the CH_3 photofragments [see fig. 5(*b*) of our Discussion paper] is in the direction of a small *decrease* in E_T, which we attribute to the altered phase of the adsorbate ('ice' formation). If CH_3 photofragments were being cooled in gas collisions with the desorbed CH_3Br as the coverage approached one monolayer (a stringent test, since the desorbed gas cloud will be at its maximum), then the elimination of 99% of this gas cloud would evidence itself as a marked *increase* in E_T of CH_3. This is not observed.
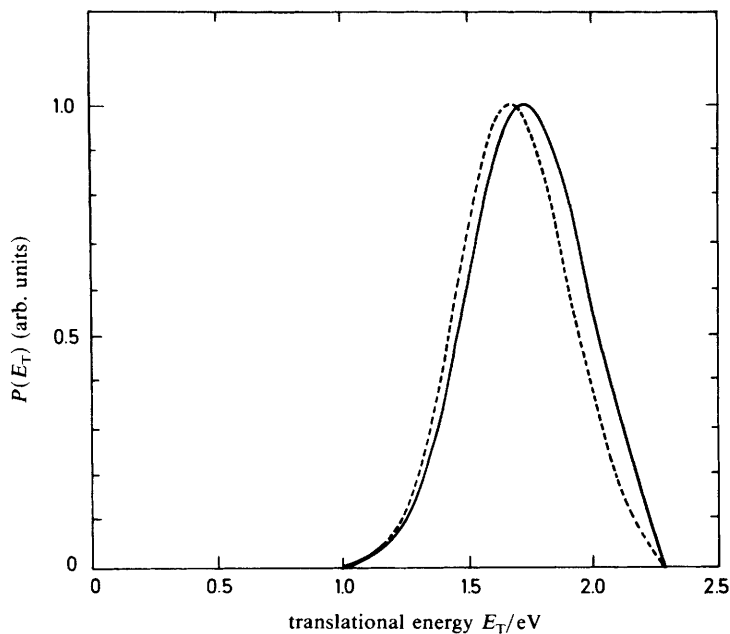
Fig. 7. Translational energy distributions of the methyl photofragment from the 222 nm photodissociation of CH_3Br adsorbed on annealed LiF. The dashed curve is for a dosing of 0.05 Torr s per laser pulse and the solid curve for 0.4 Torr s per laser pulse. (The data were taken on different days; the differences lie within the uncertainty, for the apparatus as then configured.)
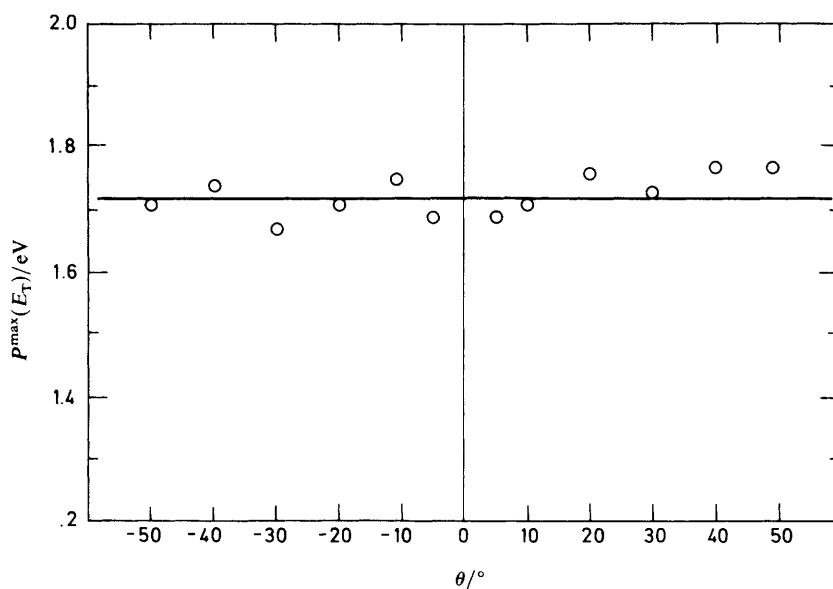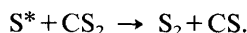

Fig. 8. Most-probable translational energy of the methyl photofragments from the 222 nm photodissociation of adsorbed CH_3Br as a function of angle from the surface normal. The data were taken at CH_3Br dosing of 0.05 Torr s per laser pulse on annealed LiF.

Alternatively, one can test for the presence of photofragment-plus-gas collisions at a single coverage, by altering the angle of observation of the photofragments. Reproduced here (fig. 8) is the most probable translational energy of the CH_3 photofragments as a function of angle to the surface normal. If CH_3 were encountering desorbing CH_3Br, collisional degradation would be least for those radicals that left perpendicular to the surface ($\theta = 0°$), and greatest for those that take a longer path through the desorbing gas ($\theta > 0°$, and $\theta < 0°$). In fact, the mean translational energy is observed to be invariant with θ. Once again we see that photofragment-plus-desorbate collisions are unimportant [question (ii)].

How does it come about that the answers to questions (i) and (ii) are in the negative? A simple explanation suggests itself. The photodesorption, we know, is mediated by the crystal. An acoustic shock will take 10^{-6}–10^{-7} s to propagate through the crystal, moving at sonic speeds. The desorption that results once this shock is transmitted to the surface could well be delayed to a time after the u.v. laser light has been switched off ($>10^{-8}$ s), thus ensuring that desorption takes place 'in the dark', and desorbate photolysis is not observed [(i)]. In addition, the slow-moving adsorbate, starting its journey away from the surface well after the photofragments start theirs, will never catch up with these fragments. This eliminates effects stemming from photofragment plus desorbate collisions [question (ii)].

1 I. Harrison, J. C. Polanyi and P. A. Young, in preparation.

Prof. N. Nishi (*Okazaki, Japan*) said: Prof. Polanyi has presented a very nice paper with well characterized analysis of the time-of-flight signals of photofragments, photoproducts and photodesorbed molecules. Some time ago, we also observed similar phenomena for the surface CS_2 molecules on a CO_2 crystal. The sample was actually the mixed CO_2 crystal containing CS_2 as impurity. The four time-of-flight signals were obtained for atomic sulphur ($m/e = 32$), CS and CO_2 ($m/e = 44$), S_2 ($m/e = 64$) and CS_2 ($m/e = 76$). They are all dissimilar. Particularly interesting is the translational energy of the S_2 molecules. Since our system is allowed to have photochemistry inside of the crystal (cage reaction), the S_2 formation in the crystal was also considered. In most cases investigated so far the cage-reaction products were photodesorbed with average kinetic energies of 1–2 kcal mol^{-1} when they appeared on the surface due to the desorption of molecules in higher layers. However, the S_2 molecules desorbed from the CO_2 surface showed an average kinetic energy of 7.9 kcal mol^{-1}. In the time-of-flight spectrum of S_2, a low-energy component with an average energy of 1.1 kcal mol^{-1} was also observed very weakly and attributed to the desorption of the cage-reaction products. The energy of 7.9 kcal mol^{-1} is considered to originate from the hot-atom reaction of a photofragment S atom with another CS_2 molecule:

$$S^* + CS_2 \rightarrow S_2 + CS.$$

The average translational energy of the recoiling S fragment was 15.5 kcal mol^{-1}, which can provide sufficient activation energy for the above reaction. On the surface, most of the excess energy for the reaction will be carried by S_2 as kinetic and internal energies.

Similar to the observation of CH_3Br photodissociation, we also observed the photodissociation signals of Cl and CH_3 fragments from surface CH_3Cl on a CO_2 crystal. The time-of-flight spectrum of Cl (fig. 9) contains two components. The peak position of the high-energy component is nearly the same as that seen in the molecular beam experiment with the same flight distance. Characteristic features of the surface signals are the rise at the high-energy region (40 kcal mol^{-1}) and the appearance of the low-energy component, as seen in other systems like NH_3 on H_2O[1] and CS_2 on CO_2. The former feature cannot be explained by the dissociation of isolated molecules detached from the surface, but it was elucidated by taking the momentum conservation for the surface photodissociation into account.
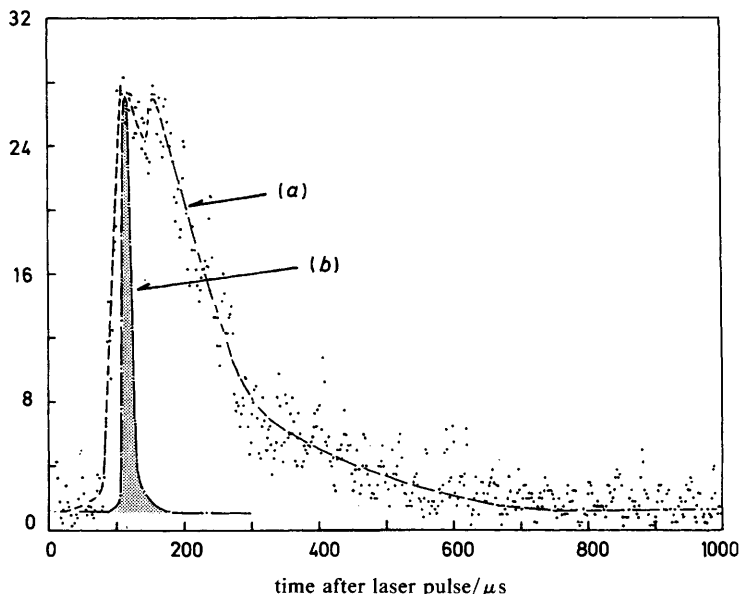
Fig. 9. The time-of-flight spectrum of Cl from $CHCl_3$; (*a*) CO_2 surface, (*b*) molecular beam.

I now question Prof. Polanyi. You have proposed an optoacoustic-shock model for photodesorption. Did the translational energy distribution of the photodesorbed molecules change on the increase of photon density? If your model is right, it should change. We observed the photon-density-dependence of the energy distribution in some cases.

1 N. Nishi, H. Shinohara and T. Okuyama, *J. Chem. Phys.*, 1984, **80**, 3898.

Prof. Polanyi replied: Yes, it was dependent on photon density.

Dr D. S. King (*NBS, Gaithersburg, USA*) said: Prof. Polanyi described the varied processes that can compete within a framework designed to probe photochemistry at surfaces. We have used a somewhat different approach to study thermally driven processes at surfaces using the technique known as laser-induced thermal desorption (LITD).[1] These experiments were performed under conditions designed to produce a slight transient temperature jump at the surface of a Pt foil, resulting in the thermal desorption of adsorbed NO, and to have been free of photochemical or electronically driven processes.

A 0.25 mm thick Pt foil was initially flash-cleaned, cooled to 200 K and saturated with NO in an ultra-high-vacuum chamber (base pressure of *ca.* 2×10^{-10} Torr). The foil was maintained at a steady-state temperature of 200 K by LN2 cooling. Pulsed heating was accomplished using 2 ns duration pulses at 532 nm from a Q-switched YAG laser. Pulse energies of 0.5 mJ in a collimated beam of 1.5 mm diameter (peak intensities of 15 MW cm^{-2}), at near-normal incidence were used and are estimated to have given transient temperature rises of 120 K from the optical and thermal properties of Pt,[2] resulting in a peak surface temperature of 320 K. The surface temperature rise is expected to follow closely the temporal profile of the heating laser pulse, achieving a maximum at the peak of the laser pulse and being rapidly quenched on a nanosecond timescale by heat conduction from the surface into the bulk. For adsorbates, with adsorption

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energies, E_{ads}, desorbing with a temperature dependent rate given as

$$\text{rate}(T_s) \approx A \exp\left(-E_{ads}/kT_s\right)$$

most of the species desorbed by LITD should leave the surface during the *ca.* 1 ns period when the surface temperature is at its maximum, *i.e.*, $T_s = 300 \pm 20$ K.

In conventional temperature-programmed thermal desorption experiments (t.p.d.) for NO from Pt(111) we have shown that the desorbing NO is described by internal and kinetic energy distributions reflecting nearly full equilibration, or accommodation, with the surface.[3] This behaviour is followed even in the presence of strongly interacting adsorbates such as NH_3. Therefore, our naïve expectation in the NO/Pt(foil) 2 ns-LITD experiments was to observe desorbing NO, reflecting accommodation with the surface.

This was not the observed result. The desorbed NO were detected by single-photon laser-excited fluorescence, using a frequency-doubled excimer pumped dye laser. The probed volume was a *ca.* 1 mm cube, *ca.* 4 mm away from the surface and determined in part by field stops on the fluorescence collection optics and detector. Internal energy distributions were obtained by recording fluorescence excitation spectra, *i.e.* scanning the probe laser wavelength across the NO A-X absorption band with a fixed time delay, set between the firing of the heating and probing lasers. Kinetic energy distributions for species in individual quantum states were obtained by an optically detected time of flight (TOF) technique, incrementing the time delay between lasers with the probe laser tuned to a particular NO transition.

The TOF and rotational-state distributions suggested that there were at least two distributions of NO desorbing from this surface: a fast component with moderate internal excitation and a slower component with a 'cold' internal energy distribution. For all $v = 0$ quantum states measured (ranging in internal energies up to 2162 cm^{-1}) the slow component was fit by a velocity distribution with a mean kinetic energy $\langle E_t \rangle = 52 \pm 5$ meV; for the fast component $\langle E_t \rangle$ continually increased from 240 ± 35 to 460 ± 50 meV. The measured kinetic energy distributions were not Maxwellian in character, having larger energy spreads than would Maxwell–Boltzmann distributions at the same average energies; if these distributions were to be described by effective translation temperatures, *e.g.* $\langle E_t \rangle / 2k$, the corresponding values would be 300 K for the cold distribution and ranging from 1400 to 2650 K for the energetic distribution. The rotational and spin–orbit state distributions were Boltzmann in character, described by rotational temperatures of 170 ± 20 and 410 ± 50 K, respectively, for the slow and fast distributions. A substantial population was observed in $v = 1$ levels, *ca.* 5% of the fast $v = 0$ population.

In summary, two components were identified in the laser-induced thermal desorption of NO from Pt foil at 200 K. Despite the mild temperature-jump conditions employed, incomplete rotational energy accommodation (for the 'cold' distribution) and dramatic departures from thermal behaviour (for the energetic distribution) were observed. These results imply that new, non-equilibrium desorption channels may become manifest under conditions of rapid (*e.g.* 5×10^{10} K s^{-1}) heating, even in the absence of photochemical desorption mechanisms.

1 D. Burgess Jr, D. A. Mantell, R. R. Cavanagh and D. S. King, *J. Chem. Phys.*, 1986, **85**, 3123.
2 D. Burgess Jr, P. C. Stair and E. Weitz, *J. Vac. Sci. Technol.*, 1986, **A4**, 1362.
3 D. A. Mantell, R. R. Cavanagh and D. S. King, *J. Chem. Phys.*, 1986, **84**, 5131; D. Burgess Jr, D. S. King and R. R. Cavanagh, in preparation.

Prof. M. Quack (*ETH Zürich*) addressed Prof. Nishi. Do you observe twofold ionization with subsequent fragmentation?

Prof. N. Nishi (*Okazaki, Japan*) said: If 'twofold' means two-photon, the answer is yes. We observed the two-photon ionization of $NH_3 + H_2O$ binary clusters and that of NH_3 clusters at 193 nm (*Chem. Phys. Lett.*, 1982, **87**, 561 and 1983, **95**, 102). Resonant

two-photon or three-photon ionization of hydrogen-bonded clusters is also adequate to generate cluster ions and also to minimize fragmentation in some cases. Particularly, if the first photon excites a molecule to its lowest Rydberg state, the ionization efficiency may be highly enhanced. Compared with one-photon ionization, proper two-photon ionization may lead to the excitation to the cluster ion state near the potential minimum. Thus, in principle, one could minimize the excitation of inter- and intra-molecular vibration of cluster ions. The excess energy may be carried away by a photoelectron as its kinetic energy.

If twofold ionization means double ionization which produces doubly charged ion clusters, the answer is no. However, such a doubly charged cluster will be generated highly efficiently by the interaction with high-density u.v. photons, although its lifetime must be very short due to 'Coulomb explosion'.

Prof. Welge asked informally 'why the excitation to a Rydberg state is particularly adequate for cluster ionization'. The Franck–Condon factor is important in the final ionization process. As stated before, it is required to generate an ion state close to the potential minimum. In the framework of a molecule, Rydberg excitation such as from a non-bonding orbital to the $3s$ orbital in an ammonia will be followed by the succeeding ionization of an electron from the $3s$ orbital. After the one-photon excitation to the Rydberg vibrationally excited state, the intramolecular excitation energy will be quickly dissipated into intermolecular vibrational motions of the cluster. The Franck–Condon overlap integral between the intermediate state and the lowest ion state must be very large. If the system is followed by the electronic relaxation from the Rydberg excited state to a valence state, this situation changes.

Here, one must notice that the equilibrium structure of a generated ion cluster is expected to be essentially different from that of the parent neutral cluster. The strongest bonding in an ion cluster has enhanced Coulombic nature, which may tend to locate the ion–molecule in the centre of the cluster. The other point is the change of the nature of the Rydberg state in clusters. Similar to the case in molecular cystals, the nature of the Rydberg-state molecule surrounded with neighbours changes owing to large exchange interactions and its state energy is shifted higher as the number of surrounding molecules becomes larger. In this sense, the surface molecule in the neutral cluster may have the lowest state energy for the Rydberg excitation. Thus the structural change on ionization is an unavoidable problem. It is still not a serious problem so long as one can obtain the information on the intermediate excited states of neutral clusters through resonance multiphoton ionization.

Prof. A. W. Castleman Jr (*Penn State University, USA*) said: I am very impressed by the interesting studies made by Prof. Nishi and his research collaborators. We have also been investigating the dynamics of various reactions and changing properties of clusters as a function of the degree of aggregation following multiphoton ionization. For example, as an extension to our work on ammonia clusters, we have investigated various processes in methanol clusters[1] following multiphoton ionization. As with some other hydrogen-bonded neutral clusters, proton-transfer reactions ensue following the ionization event which lead to the production (and detection) of species of the form $H^+(CH_3OH)_n$. Both collision induced and unimolecular dissociation are observed.

In contrast to the ammonia system, a non-evaporative loss process was also observed; namely the elimination of H_2O from the protonated dimer. See fig. 10. This process, however, was not detected for the larger cluster ions. To the best of our knowledge, these data are the first to show definitive differences in reaction channel with cluster size. This observation is in direct correspondence with observations[2] of gas-phase ion–molecule reactions
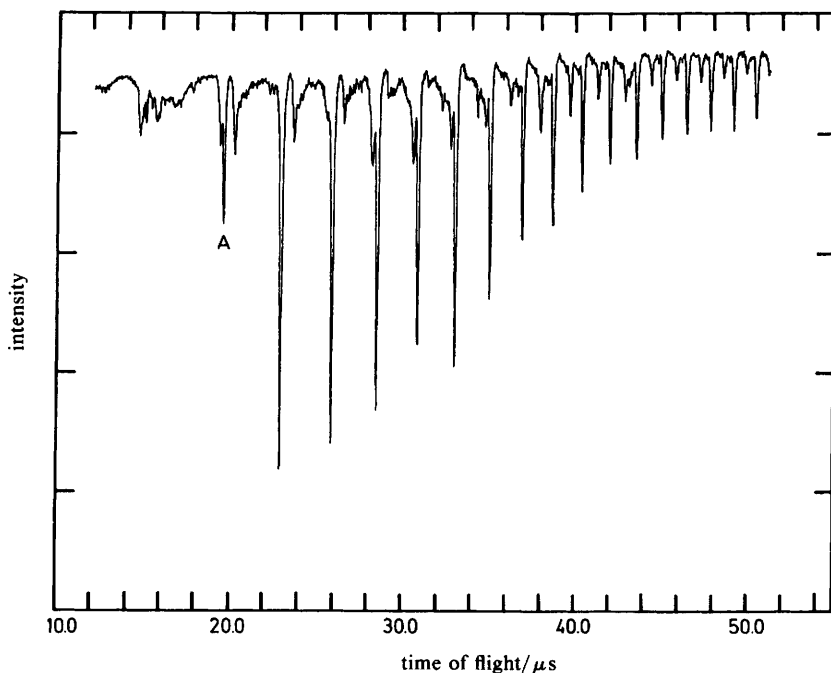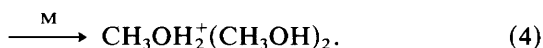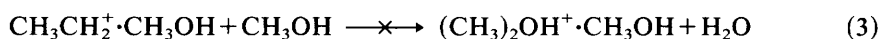
$$CH_3OH_2^+ + CH_3OH \longrightarrow (CH_3)_2OH^+ + H_2O \qquad (1)$$

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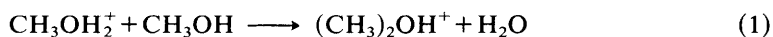
Fig. 10. Time-of-flight mass spectrum at $\lambda = 266$ nm. Daughter ions of $(CH_3OH)_N \cdot H^+$ ($N = 2$–18) are shown. The peaks at 19.4 and 19.6 μs (A) are the daughter ions formed by loss of CH_3OH and H_2O, respectively, from $(CH_3OH)_2 \cdot H^+$.

$$\overset{M}{\longrightarrow} CH_3OH_2^+ \cdot CH_3OH \tag{2}$$

and

$$CH_3CH_2^+ \cdot CH_3OH + CH_3OH \overset{}{\longrightarrow\!\!\!\times\!\!\!\longrightarrow} (CH_3)_2OH^+ \cdot CH_3OH + H_2O \tag{3}$$

$$\overset{M}{\longrightarrow} CH_3OH_2^+ (CH_3OH)_2. \tag{4}$$

The rate for the H_2O loss from $CH_3OH_2^+ \cdot CH_3OH$ has been measured to be 5.5×10^5 s^{-1}, in good agreement with the range of 10^5 to 10^6 s^{-1} estimated for the gas-phase ion-molecule process.

Based on a combination of measurements and estimates for the thermodynamics of various dissociation channels in $H^+(CH_3OH)_3$, one would expect the loss of H_2O from this and larger methanol clusters to be at least as energetically favourable as that for CH_3OH loss. Kleingeld and Nibbering[3] have suggested that intermediate A is important in the rearrangement process which leads to the loss of H_2O. Bowers and his colleagues[2] have suggested that the major product ion in the ion–molecule reaction is the formation of the symmetrical, proton-bound dimer as shown for structure B.
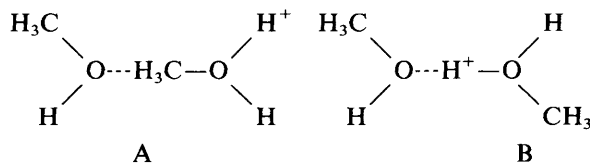
It may be that rearrangement from structure B to structure A is necessary for the water-loss process and that this process occurs readily in the protonated dimer, but is
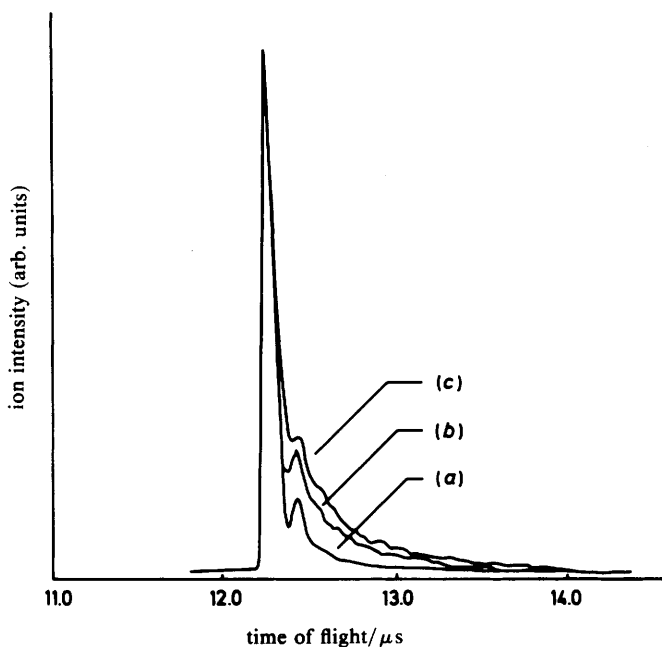
Fig. 11. TOF peak shapes from a two-field acceleration of trimethylamine$^+$ and protonated trimethylamine following two-colour resonant $(1+1)$ ionization of p-xylene $\cdot$ trimethylamine with the ionizing photon at (a) 3.88 eV, (b) 3.688 eV and (c) 3.607 eV. The smooth tails indicate a slow ionization process.

impeded in higher order clusters. Hence, we think these data reflect the importance of structural rearrangements necessary for certain unimolecular processes to be operative and therefore give further insight into differences which may be seen in the condensed phase compared to the gas for ion–molecule reactions.

In another series of investigations we have demonstrated the power of cluster research in investigating internal charge-transfer/electron-transfer processes that have a direct analogy to well studied Penning ionization between isolated gas-phase species.[4]

It occurred to us that a rather interesting possibility existed for charge transfer to an optically transparent partner *via* an internal Penning ionization process if the ionization threshold of p-xylene is higher than that of the partner. The ionization potential of p-xylene is 8.445 eV, with the S_1 state lying 4.45 eV above the ground state. Trimethylamine (TMA) has an ionization potential of 7.82 eV and was chosen as the partner. Ammonia, which has a higher ionization potential than p-xylene, was also studied for comparison. The channels corresponding to NH_4^+ and NH_3^+ become observable, respectively, at 0.1 and 1.8 eV above the ionization threshold of p-xylene. In our studies of ammonia bound to p-xylene, we found that the cluster ion is detected at threshold ionization. When the second ionizing photon is tuned to the appropriate energies the NH_3^+ and NH_4^+ channels are obtainable and observed in the mass spectra. This is also the case at high fluences where three-photon absorption is significant.

For the case of trimethylamine, the onset of ionization produces mainly TMA$^+$ and some protonated TMA (from an internal proton-transfer reaction). None of the cluster ion $(p$-xylene$\cdot$TMA$)^+$ is seen. We believe ionization proceeds through Rydberg states with a transfer of an electron from trimethylamine to the excited p-xylene and subsequent loss of the excited electron. That this process is taking place through the cluster rather than by collisions in the gas phase has been established by tuning the wavelength of

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the first photon and observing that a spectral shift of the S_1 state expected for the bound complex is necessary for the observation of this process. Fig. 11 shows the peak shape of TMA^+ and $TMAH^+$ under dual-field acceleration where a smooth tail can only result from a slow ionization process. Interestingly, the time-constant is longer when the photon absorption is lower in the Rydberg manifold. The fact that the tail corresponds largely to the channel for the production of trimethylamine ions rather than the protonated channel was established through isotopic substitution experiments which yielded $TMAD^+$, with no corresponding shift in the position of the tail.

The data reveal an amazingly slow electron transfer after excitation. In analogy to the ammonia system, it is believed that the excited states of trimethylamine would also be planar and that a large geometry change is required for electron transfer and ensuing ionization. These results compare with observations[5] of slow ionization processes in the condensed phase.

1 S. Morgan and A. W. Castleman Jr, *J. Am. Chem. Soc.*, submitted; S. Morgan, R. G. Keesee and A. W. Castleman Jr, *Proc. 1986 CRDEC Scientific Conference on Obscuration and Aerosol Research*, Aberdeen Proving Ground, MD, June 1986, in press.
2 L. M. Bass, R. D. Cates, M. F. Jarrold, N. J. Kirchner and M. T. Bowers, *J. Am. Chem. Soc.*, 1983, **105**, 7024.
3 J. C. Kleingeld and N. M. M. Nibbering, *Org. Mass Spectrom.*, 1982, **17**, 136.
4 P. D. Dao and A. W. Castleman Jr, *J. Chem. Phys.*, 1986, **84**, 1435.
5 Y. Hatano, personal communication; see also T. Wada, K. Shinsaka, H. Namba and Y. Hatano, *Can. J. Chem.*, 1977, **55**, 2144.