

GENERAL DISCUSSION

Prof. Stolte opened the discussion of Dr. Delon's paper: Both the concatenated ICLAS and LIF stick spectrum of Fig. 2 of your paper as well as the low resolution absorption cross-section (divided by photon energy) exhibit spectral oscillations (of a period close to 720 cm^{-1}) suggested to be due to the bending motion in the \tilde{A}^2B_2 electronic state. In the thermal measurements of Fig. 4 of the paper, one has to deal with a rather broad distribution of initial states of the NO_2 target molecule. In the supersonic experiments of Fig. 2, the excitable NO_2 molecules are typically residing in the lowest rotational states. Is it numerically feasible to broaden and to adapt the stick spectrum of Fig. 2 to synthesize (or predict) the observed spectrum of Fig. 4? Does one expect the NO_2 initial state distribution at room temperature (as in Fig. 4) to reflect itself in the chaotic (broad band) excitation spectrum?

Dr. Delon responded: A precise simulation of the room-temperature absorption cross-section of NO_2 from the knowledge of its supersonic jet, absorption or excitation spectrum is very difficult for several reasons. (1) The intensities measured in our supersonic jet experiment (excitation or absorption) are, at the maximum, precise to within a factor of two. Concerning the excitation spectrum, one must remember that the measured intensities depend on the lifetimes, the optical filters and the PMT. Concerning the ICLAS experiments, many parameters can influence the measured intensities, and have not been systematically controlled.

(2) The room-temperature absorption spectrum corresponds mainly to transitions occurring from the vibrationless level of the ground state (the cold vibrational bands dominate the spectrum above 13000 cm^{-1}), and from various initial rotational levels $K = 0, 1, 2, \text{etc.}$ Since the A rotational constant is very different in the electronic ground state and in the excited one, and because the effective rotational constants of the excited levels depend on the vibronic couplings, the rotational envelopes are shifted randomly and broadened.

As a conclusion, I would say that, if on one hand the bending progression appears on both vibrograms corresponding to Fig. 2 and 4, on the other hand any vibrational feature corresponding to a small energy range (of the order of, or smaller than, 200 cm^{-1}) should be erased in the FT of the room-temperature spectrum.

Dr. Schinke said: I would like to point out that some of your observations, concerning the visible spectrum of NO_2 , are very similar to what we have recently found, on the basis of time-independent and time-dependent quantum calculations, for HO_2 .¹ Like NO_2 , the dynamics of HO_2 shows a gradual transition from regular to chaotic behaviour as the energy increases. Nevertheless, some portion of regularity persists to even very high energies where the main part of the phase space is already irregular. This persisting regularity is mainly associated with large-amplitude O_2 stretching motion as demonstrated by unstable periodic orbits. If a wavepacket, with mean energy high in the irregular regime, is started near such an orbit, some portion of it stays close to the orbit for at least a few vibrations and so leads to pronounced recurrences in the autocorrelation function and consequently to diffuse structures in the low-resolution absorption spectrum. The existence of recurrences depends obviously on the starting conditions of the wavepacket and therefore on the initial state from which the optical transition takes place.

1 A. J. Dobbyn, M. Stumpf, H.-M. Keller and R. Schinke, *J. Chem. Phys.*, 1995, 103, 9947.

Dr. Delon replied: A surprising fact for NO₂ is that the bending period also appears when performing a statistical FT (see Fig. 1 of our paper). Such an FT does not correspond to any particular initial state because all the intensities are equal to one. Therefore it is a property of the ²B₂ excited levels only, and more precisely of the corresponding density of states. It would be interesting to follow the intensity of the bending peak in the FT up to the dissociation energy; unfortunately no high resolution complete vibronic spectrum of NO₂ exists in the blue or UV range over a wide energy range (*i.e.* larger than the bending frequency ω_2).

Dr. Abel asked: The squared Fourier transform ($|FT|^2$) of your windowed NO₂ spectra seems to be a nice tool for the investigation of intramolecular dynamics in the frequency domain. My two questions concern Fig. 5 and 6 of your paper.

(1) Is it possible to 'assign' the features at times larger than 0.1 ps? Since they are stable and independent of the data processing procedure, I would like to know whether there is a physical picture (do they correspond to 'stable' states within 'a sea of chaos'?) behind or not? In addition, I would like to know if there is an easy explanation or a physical picture available for the branching of one 'line' in the vibrogram into two lines at increasing energy or the condensation of two into one.

(2) From your paper one may conclude that intramolecular energy redistribution close to the dissociation threshold proceeds on two different timescales. The vibronic chaos seems to be established within a few hundred femtoseconds. How long does it take until rovibronic chaos is established? How long does it take for a wavepacket to explore the whole rotational and vibrational phase space? Is it possible that this process may compete effectively with the bond fission process above the dissociation threshold?

Dr. Delon answered: Until now we have not been able to assign the features displayed in our vibrogram for times larger than 0.1 ps. In fact, even for the simple case of one single potential-energy surface (PES), it is not necessarily easy to interpret the various peaks appearing in a vibrogram, if one has no complementary information about the PES. The interplay of harmonic frequencies and harmonics can modify the intensities of the peaks in such a way that the stronger ones do not correspond to the fundamental frequencies. However, I have no easy explanation for the branching of one line into two or the condensation of two into one. Realistic quantum and semiclassical calculations are necessary if one wants to understand better the vibrograms.

While the vibronic chaos is established within typically 100 fs, the rovibronic couplings need *ca.* 4 ps to be established. Therefore, the whole vibronic and rotational phase space is explored within a few ps. This time is significantly smaller than the time for unimolecular dissociation (just above the dissociation threshold) which is *ca.* 50 ps. However, the 4 ps time for rovibronic mixings is an average over $\Delta K = 1$ and $\Delta K = 2$ (*K* mixing). It could be interesting to study, just below the limit of dissociation, the individual time constants of these two processes, using both simulations¹ and experimental methods.

¹ D. S. Perry, C. A. Bethardy, M. J. Davis and J. Go, *Faraday Discuss.*, 1995, **102**, 215.

Prof. Perry said: You have used a windowed Fourier transform approach to identify the timescales labelled as A, B, C and D. How do these compare with the timescales obtained using the hierarchical tree analysis of Michael Davis?¹ It struck me that the timescales that are important for understanding the intramolecular dynamics might show up in both methods of analysis.

¹ M. J. Davis, *J. Chem. Phys.*, 1993, **98**, 2614; *Int. Rev. Phys. Chem.*, 1995, **14**, 15.

Dr. Delon replied: In our paper concerning the vibronic couplings,¹ we had discussed the correspondence between the hierarchical tree analysis and the statistical FT

and we noted that two plateaux of Fig. 13 of that paper corresponded to two peaks in the FT. Surprisingly, when looking at Fig. 5 of our paper,² I remarked that the four peaks A, B, C, D correspond relatively well to the four plateaux of the insert of Fig. 13 of ref. 1 of respective ordinates 4, 11, 14, 21. Unfortunately the windowed Fourier transform corresponds to an average energy of $22\,500\text{ cm}^{-1}$ while the hierarchical tree analysis is performed around $18\,000\text{ cm}^{-1}$. When looking at the positions of the peaks at $18\,000\text{ cm}^{-1}$ on the vibrogram (Fig. 6 of ref. 2), it is not so clear that there are any dominating peaks B' and C' in the vibrogram which would correspond to the plateaux at 11 and 14. Only the peak at *ca.* 700 cm^{-1} is clearly visible with both analyses. The same conclusion stands for the vibrogram performed on the excitation spectrum.

Strictly speaking, there is exactly the same information in the two types of analysis. Practically, I would say that the vibrogram is very efficient when there are very stable frequencies hidden in the spectrum. On the other hand, when there are different energy scales in a spectrum which do not correspond to any precise frequency, the hierarchical tree analysis is powerful. As an example, for Fig. 11 of our paper dealing with rovibronic interactions,³ one clearly sees the two timescales corresponding to the vibronic and rovibronic processes. I tried very recently to Fourier transform the whole rovibronic spectrum (*i.e.* all the $J = 1/2$ and separately all the $J = 3/2$ lines). As a result the two energy scales did not appear as two different timescales in the survival probability.

1 R. Georges, A. Delon and R. Jost, *J. Chem. Phys.*, 1995, **103**, 1732.

2 A. Delon, R. Georges, B. Kirmse and R. Jost, *Faraday Discuss.*, 1995, **102**, 117.

3 A. Delon, R. Georges and R. Jost, *J. Chem. Phys.*, 1995, **103**, 7740.

Prof. Reisler asked: Why don't you see the bending progression at excitation energies above, but near to, the dissociation threshold where the dissociation time is $> 1\text{ ps}$?

Dr. Delon said in reply: First, I would like to highlight the fact that, on the low resolution absorption cross-section (Fig. 4 of our paper), we see the bending progression above the dissociation threshold, up to *ca.* $26\,000\text{ cm}^{-1}$. The reason why the amplitude of the bending modulation is decreasing is related to the strength of the vibronic couplings. If the vibronic chaos is strong enough, even the bending motion is completely mixed with the two other vibrational degrees of freedom. The decrease of this bending feature cannot be attributed to the dissociation process, but to the vibronic couplings within the excited levels.

Prof. Troe opened the discussion of Prof. Reisler's paper: Often phase-space theory is applied using a van der Waals-type interaction potential. I recommend that this is not done, because, for the considered reactions, a r^{-6} potential has no realistic meaning. How would your distributions from phase-space theory change when the interaction potential changes?

Prof. Reisler responded: The point raised by Prof. Troe is very important, and refers to one of the recurrent themes of this Discussion, namely that knowledge of the potential-energy surface is necessary for an accurate state-to-state description of the dissociation. In our work on NO_2 , we attempted first to approximate the long-range attraction by a Lennard-Jones potential $V_{\text{attr}}(r) = -C_6 r^{-6}$ (where r is the distance between the O atom and the NO centre-of-mass). From the known atomic polarizability of $\text{O}(^3\text{P})$ and the dipole moment of NO, we estimated C_6 as 10^{-78} J m^6 .¹ However, we found that using this value for C_6 in our phase-space calculations caused truncation of the NO rotational distributions below the maximum allowed by energy conservation. For example, at excess energy 1949 cm^{-1} , no rotational levels with $j \geq 30.5$ should have been observed, while the highest observed level was $j = 34.5$, the highest allowed by

energy conservation. Since our experimental distributions did not show any evidence of truncation at the higher j_{NO} levels, we arbitrarily increased the C_6 value to 10^{-76} J m^6 , in order to reproduce better this behaviour. A similar behaviour was observed in the singlet-channel decomposition of ketene.² It appears, therefore, that the long-range attractive forces are underestimated, and that a better description of exit-channel interactions beyond the transition state is required to reproduce faithfully the experimental observations. We have not carried out such a systematic study.

1 M. Hunter, S. A. Reid, D. C. Robie and H. Reisler, *J. Chem. Phys.*, 1993, **99**, 1093.

2 I.-C. Chen, W. H. Green Jr. and C. B. Moore, *J. Chem. Phys.*, 1988, **89**, 314.

Dr. Hancock said: You show in your paper the small variation in the rotational alignment parameter $A_0^{(2)}$ with excess energy, and the correlation between it and the fluctuations in the PHOFRY spectrum. You also hint at corresponding variations in the translational anisotropy factor, β . Do measurements of this β factor give a better measure of the fluctuation in the dissociation dynamics?

Prof. Reisler answered: Both the alignment parameter $A_0^{(2)}$ and the recoil anisotropy parameter β_{rec} are related to bipolar moments describing the vector alignments in the photodissociation: $A_0^{(2)} = \frac{4}{3}\beta_0^2(02)$ and $\beta_{\text{rec}} = 2\beta_0^2(20)$.¹ In physical terms, the alignment parameter $A_0^{(2)}$ describes the correlation between the parent transition dipole moment μ and the product rotational vector J ($\mu \cdot J$ correlation), while the anisotropy parameter β_{rec} reflects the correlation between μ and the product recoil velocity vector v ($\mu \cdot v$ correlation). Since in the photodissociation of a planar molecule, v lies in the molecular plane, and product rotation is also in this plane, both bipolar moments are related to each other and their deviations from the limiting values may be due to parent rotation. In this sense, both $A_0^{(2)}$ and β_{rec} are useful tools for exploring fluctuations in dissociation lifetime (relative to the parent rotational period). Both, however, give rise to relatively small changes in the measured bipolar moments when the rates change. Experimentally, the methods are somewhat complementary. Measurements of the rotational alignment are easy to perform, but owing to hyperfine depolarization, the limiting values can be obtained only for high J values of the fragments. The recoil anisotropy parameters, which are not affected by hyperfine depolarization, have to be deconvolved from Doppler profiles that usually include other broadening mechanisms and are therefore obtained most accurately for low J products (however, see ref. 2 for a different method). Variations in β_{rec} in NO_2 photodissociation have been observed, but not studied systematically. The measurements show a reduction of β_{rec} with increasing $E_{\text{NO}}(J)$, both near threshold² and at higher E^E .³ Thus, it appears that both $A_0^{(2)}$ and β_{rec} can deviate from their limiting values when the relative separation velocities of the fragments are small. We emphasize that because of the many factors that can affect the values of the bipolar moments, we feel comfortable in making relative comparisons (*e.g.* fluctuations as a function of E^E), but not in inferring absolute values of the dissociation rates.

1 R. N. Dixon, *J. Chem. Phys.*, 1986, **85**, 1866.

2 T. J. Butenhoff and E. A. Rohlfing, *J. Chem. Phys.*, 1993, **99**, 5460; 5469.

3 H. Meyer, personal communication, 1995.

Dr. Delon asked: The simulated PHOFRY spectra of NO_2 , presented on p. 35, have been calculated with a density of parent states $\rho = 1 \text{ level cm}$. The corresponding excess energy E^E is between 100 and 300 cm^{-1} .

It is reasonable to assume that the vibronic density that must be used, in the range 100–300 cm^{-1} above the dissociation threshold, is not lower than the vibronic density just below the dissociation threshold. In fact, recent high resolution LIF experiments (performed in Grenoble) have shown that, just below the dissociation threshold (at

25 128.58 cm^{-1}), the rovibronic density of the states $J = 1/2$ and $J = 3/2$ is *ca.* 15 levels cm^{-1} . By assuming that J is a good quantum number and that the rovibronic chaos is strongly developed,¹ one can deduce the vibronic density: $\rho_{\text{vibro}} = 15/6 \approx 2.5$ vibronic level (A_1 or B_2) cm^{-1} . Since you do not specify, in your paper, what the rotational assignment of the intermediate level (1, 0, 1) selected with your IR tunable laser is, I do not know what the J values of the excited levels are and, in turn, how many rovibronic levels J are coupled together. However, we have shown that around 24 600 cm^{-1} , if we consider the particular case of $J = 1/2$ ($J = 3/2$), 2 (4) levels, J are strongly coupled, within a time of *ca.* 4 ps. This time being lower than the inverse of the dissociation rate k ,² the rovibronic density that should be used is 5 levels per cm^{-1} for $J = 1/2$ and 10 levels per cm^{-1} for $J = 3/2$.

Therefore, I do not understand the density of states that you have used in the simulation corresponding to Fig. 5 of your paper.

I do not understand, for the same reasons, the density of states that you have used in the simulation corresponding to Fig. 4 of your paper (excess energy between 2000 and 2500 cm^{-1}). Have you precise reasons to use a density of states ($\rho = 0.5$ level per cm^{-1}) smaller than the one used at lower energy?

In fact, the dissociation rate measured just above the threshold² is larger than that deduced from the observed density of states. This may imply that the density of coupled levels is lower than the total density of levels, and that a detailed study of the internal rovibrational redistribution is necessary. The random matrix model that we have developed (in order to study the rovibronic interactions) can be used to study carefully the time constant for the K mixing, and could also be extended to high values of J .

1 A. Delon, R. Georges and R. Jost, *J. Chem. Phys.*, 1995, **103**, 7740.

2 B. Abel, H. H. Hamann and N. Lange, *Faraday Discuss.*, 1995, **102**, 147.

Prof. Reisler answered: First, let me restate that the purpose of the calculations shown in Fig. 4 and 5 of our paper is to simulate qualitatively the changes in the final state-selected spectra as the degree of resonance overlap increases. They neither purport to simulate rate measurements, nor to provide accurate values of densities of states, ρ . In fact, as stated in our paper, the simulations are less sensitive to the number of independent decay channels, n , and ρ and more sensitive to $\langle \Gamma \rangle$. Our choice of ρ was based on our assessment of whether vibronic or rovibronic densities of states should be used and our success in best reproducing the experimental state-selected spectra in these two excess energy regimes. The chosen values represent (within a factor of two or so) the reactive density of states, as distinct from the total density of states.¹ In fact, our decision whether to use values reflecting the rovibronic or vibronic density of states was based on the spin-rotation matrix elements published by Delon *et al.*² At $E^{\text{E}} = 100\text{--}300$ cm^{-1} , the measured rate is *ca.* 0.5 ps^{-1} (*i.e.* lifetime *ca.* 2 ps).³ If K mixing takes *ca.* 4 ps, then dissociation already competes with K mixing, and Coriolis and spin-rotation interactions may not have sufficient time to act before coupling to the continuum occurs. Thus, the reactive density of states is closer to the vibronic density of states, and the value used, $\rho = 1$ per cm^{-1} , is close to the value recommended by Ionov *et al.*¹ At higher excess energies, where the dissociation lifetimes are only a few hundred femtoseconds, the assumption that IVR is complete may increasingly fail, and the value we chose, $\rho = 0.5$ per cm^{-1} , simply gave the best fit to the experimental spectra. A more detailed discussion of this issue can be found in ref. 1 and 4. We emphasize that although the qualitative conclusions derived from the simulations would not change for a two-fold change in the value of ρ , the simulations can distinguish between values reflecting vibronic *vs.* rovibronic densities of states. Note that the results presented by Abel and co-workers⁵ were all obtained very close to threshold, where the correct reactive density of states is the rovibronic one.

The issue of what is the exact reactive density of states at different excess energies is still open. Behaviour that can be reproduced on average by statistical theories does not necessarily imply that the whole phase space is sampled and that IVR is complete. More accurate measurements of IVR near dissociation threshold, as you suggest, are very desirable. Unfortunately, we presently lack the experimental tools to extend them to higher excess energies where the reaction rate is faster. Our simulations show that the best qualitative fit to the spectra measured at $E^E = 2000\text{--}2500\text{ cm}^{-1}$ is obtained when using $\rho = 0.25\text{--}0.50$ per cm^{-1} , values which suggest restricted IVR.

- 1 S. I. Ionov, H. F. Davis, K. Mikhaylichenko, L. Valachovic, R. A. Beaudet and C. Wittig, *J. Chem. Phys.*, 1994, **101**, 4809.
- 2 A. Delon, P. Dupre and R. Jost, *J. Chem. Phys.*, 1993, **99**, 9482.
- 3 S. I. Ionov, G. A. Brucker, C. Jaques, Y. Chen and C. Wittig, *J. Chem. Phys.*, 1993, **99**, 3420.
- 4 S. A. Reid and H. Reisler, *J. Chem. Phys.*, 1994, **101**, 5683.
- 5 B. Abel, H. H. Hamann and N. Lange, *Faraday Discuss.*, 1995, **102**, 147.

Dr. Abel said: In your paper you very clearly show that product state distributions with double resonance excitation are characterized by strong fluctuations just above the dissociation threshold and far above E_0 . Since in the case of NO_2 a tightening of the transition state is predicted, one may expect a colder rotational distribution on average with a maximum in the J distribution shifted to lower J compared with the distribution predicted from phase-space theory. In the case of large fluctuations, one may employ a pattern recognition technique that can identify residual structures in the fluctuating product state distributions. Averaging of (many) PSDs of neighbouring lines in the PHOFEX spectra may be suitable for such an approach. Since it looks as if we have some evidence for colder rotational distributions in our averaged product state distributions, my question is whether you have any indications for such a behaviour in your spectra or not?

Prof. Reisler answered: We have obtained many rotational distributions for NO $v = 0$ and 1 in the range $E^E = 100\text{--}3000\text{ cm}^{-1}$, using both one- and two-photon excitation. Some of these were for excess energies differing by only *ca.* 50 cm^{-1} . We have not seen a systematic trend indicating that the PSDs become progressively colder than PST expectations as E^E increases, although we have not undertaken the painstaking task of averaging many distributions obtained for adjacent excitation energies at different regions of E^E . Perhaps a different way to observe the effect of averaging is by determining rotational distributions at higher temperatures, where distributions associated with many different initial parent rotational states are superimposed at a specific value of E^E . This was done by Changlong *et al.*, who reported that at 300 K and $E^E = 3030\text{ cm}^{-1}$, the $\text{NO } v = 1$ rotational distribution was smooth and well described by PST.¹

As we have pointed out previously, when the TS of a barrierless reaction tightens, the NO PSDs may reflect the geometry of the TS.^{2,3} We have shown that the prominent oscillations in the rotational distributions can be modelled qualitatively by mapping bending-like wavefunctions associated with a tight TS into free rotor states of the NO fragment. It is intriguing that the oscillations consistently cluster about the statistical predictions of PST, which assumes a very loose (*i.e.* fragment-like) TS. This apparent contradiction can be reconciled by recognizing that the range of rotational excitations allowed in this mapping is a sensitive function of the TS bending angle and frequency. The TS parameters used were based on values derived from *ab initio* calculations,⁴ and happen to correspond to rotational excitations that cover the full range allowed by energy conservation up to the highest E^E studied ($E^E \approx 3000\text{ cm}^{-1}$). The qualitative agreement observed with PST at these energies thus reflects in part the specific geometry of the tight TS, and does not constitute a valid test for the location of the TS. This underscores the importance of the PES, and illustrates the important point that distribu-

tions which can be fit by a statistical model do not prove that such a model correctly describes the dissociation mechanism. Note that the observation of PST-like distributions may also arise from exit-channel interactions beyond the TS, which can lead to population of all levels allowed by energy and angular momentum conservation.

1 N. Changlong, L. Hua and J. Pfab, *J. Phys. Chem.*, 1993, **97**, 7458.

2 S. A. Reid and H. Reisler, *J. Chem. Phys.*, 1994, **101**, 5683.

3 S. A. Reid and H. Reisler, *J. Phys. Chem.*, 1996, **100**, 474.

4 H. Katagiri and S. Kato, *J. Chem. Phys.*, 1993, **99**, 8805; S. J. Klippenstein and T. Radivoyevitch, *J. Chem. Phys.*, 1993, **99**, 3644; A. Harding, personal communication.

Prof. Smith opened the discussion of Dr. Abel's paper: The paper presented by Dr. Abel reports rate constants for state-to-state energy transfer in collisions between NO₂ molecules (one highly excited, one from the thermal bath). Such collisions are, of course, characterised by the strong attractive chemical forces which lead to formation of N₂O₄ and one might expect to see the facile transfer of large amounts of energy. I should like to ask if he has looked for and observed the results of collisions in which large transfers of energy occur.

Dr. Abel replied: I certainly agree when you point out the relevance of the chemical forces or the chemical interaction for the collisional energy transfer in NO₂ self collisions. I think that this feature of the PES (a quite pronounced well depth) certainly influences the magnitude of the observed cross-sections. Chemical forces and interaction (reaction) may also be responsible for the experimentally observed 'strong' collisions which transfer large amounts of energy. However, in the experiments we showed here we are specifically looking for energy transfer events in the vicinity of the initial state (on a small energy scale). In these collisions the energy transferred in a collision (rotational and vibrational energy) is small, such that we cannot see the strong collisions you are referring to. This does not mean that these collisions do not exist, but they are just not sampled by our present setup. In this sense our technique is complementary to that of H. L. Dai *et al.*¹ and Barker *et al.*,² who have some experimental evidence for strong collisions with large $\langle \Delta E \rangle$ values which actually may proceed *via* a long lived NO₂-NO₂ complex.

1 G. V. Hartland, D. Qir and H. L. Dai, *J. Chem. Phys.*, 1994, **101**, 1.

2 B. M. Toselli, T. L. Walunas and J. R. Barker, *J. Chem. Phys.*, 1990, **92**, 4793.

Prof. Moore asked: What is the density of states appropriate for calculating the rate constant as energy increases above threshold? If this density were to decrease as energy increases, could this be understood as a decrease in available phase space as the transition state tightens?

Dr. Abel replied: Your question is very interesting and obviously of great importance for the statistical calculation of specific rate constants. Since the specific rate constants $k(E, J \dots)$ in the framework of statistical theories such as SACM are given by $k(E, J) = W(E, J)/[h^* \rho(E, J)]$, the energy dependence of the specific rate constant is strongly influenced by the energy dependence of $\rho(E, J)$ and $W(E, J)$. While $W(E, J)$ can be calculated in a straightforward manner within the framework of SACM, the determination of $\rho(E, J)$ above E_0 turned out to be non-trivial for the NO₂ molecule. Wittig and co-workers¹ discussed that IVR may be complete at the dissociation threshold and possibly incomplete at larger excess energies. His conjecture was that, owing to hierarchical IVR, the effective density of states may be reduced as energy increases. If this picture were true there would be no way of predicting the appropriate density of states and its energy dependence above the threshold, because it would strongly depend on the IVR

dynamics and the preparation of the excited molecule. We have some problems with this picture because IVR still seems to be fast compared with the reaction (see also Delon *et al.*¹). If IVR is fast, then the relevant density of states will be the total density of states of the molecule above E_0 . This quantity may be reduced and affected by the position of the reaction bottleneck ('transition state'). In this picture, states beyond the bottleneck would not count for the calculation of specific rate constants and related dynamic quantities. While, in the case of NO_2 , the density of states below and just at the threshold has been determined, it was not possible to derive any information about the energy dependence of $\rho(E, J)$ experimentally. We have used the anharmonic stretch-bend coupling model of Troe (which has been proposed recently) for the calculation of $\rho(E, J)$ and its energy dependence. Above E_0 the density of states is assumed to be a continuation of $\rho(E, J)$ from below the dissociation threshold. But since these states are unstable, one needs to define parent molecule states and product states along the reaction coordinate. The only model available up to now, which defines the relevant limited phase-space volume of the parent molecule above E_0 through adiabatic channel threshold maxima and reaction bottlenecks, is Troe's stretch-bend coupling model.² Only the case of a loose transition state without a barrier (for $J = 0$) is still not yet very well defined. This anharmonic count model predicts densities of states for NO_2 which agree with published experimental data within a factor of 1.5. However, recent unpublished experimental densities of states from Jost and Delon⁴ show a density of states (just below E_0) which is a factor of *ca.* 2.7–3 larger than that determined by the state count. Whether the high density of states is relevant for reaction dynamics depends on the position of the transition state (bottleneck) for the reaction. From k_0 values from high pressure experiments [which are sensitive to $\rho(E, J)$] and the absolute values of $\langle k(E, J) \rangle$ we propose that maybe only a part of the density of states is relevant for the reaction dynamics, although the other states are unambiguously there. They may belong to a fraction of states above the threshold which may be located beyond the reaction bottleneck (but which are detected in high resolution spectra just above the dissociation threshold). This fraction may change (decrease) as energy increases and channel maxima move. However, we find that the relevant density of states as a function of E in this case does not decrease and can be calculated as a function of E [using additional experimental information from the energy dependence of $k(E, J)$ and k_0 rate constants from high pressure recombination experiments] in a straightforward fashion, as has been done in our paper.

1 S. I. Ionov, G. A. Brucker, C. Jaques, Y. Chen and C. Wittig, *J. Chem. Phys.*, 1993, **99**, 3420.

2 A. Delon, R. Georges, B. Kirmse and R. Jost, *Faraday Discuss.*, 1995, **102**, 117.

3 J. Troe, *Chem. Phys.*, 1995, **190**, 381.

4 A. Delon and R. Jost, personal communication.

Prof. Stolte asked: Fig. 6 of your very interesting paper shows that the exponential gap law (EGL) approximation provides an excellent vehicle to model the measured state-to-state energy transfer rates ($R-T$, R) from the highly excited state $N = 9$, $K_a = 0$, $J = 9.5$ of NO_2 at $17\,750.07\text{ cm}^{-1}$. Is it possible to retrieve additional information about the rate of energy transfer by applying different laser polarizations?

Dr. Abel replied: With your question you raise an interesting point. Since all of the reported data in the experiments have been obtained for parallel polarizations of the lasers, one may ask the question whether the results depend on the relative polarization of the two lasers and whether alignment effects play a role here or not. Just recently we have performed polarization experiments in which we measured the state-to-state rates with the polarizations of the lasers parallel and perpendicular to each other. From these experiments we determined the rates for the m_j changing collisions (the elastic events in collisions between two NO_2 molecules) and we studied the influence of alignment on the state resolved rates of population transfer. These experimental results do not have a

significant impact on the results shown here (cross-sections for population changes in collisions) but they provide nice additional information about the collision dynamics. The results will be reported soon.

Prof. Troe said: Do you assume that NO_2 - NO_2 collisions proceed *via* an N_2O_4 -collision complex? In this case the cross-sections should be comparable to those of the high pressure limit of the $\text{NO}_2 + \text{NO}_2 \rightarrow \text{N}_2\text{O}_4$ recombination¹ which are known for this reaction.

If one finds agreement between measured specific rate constants and a calculation, *e.g.* a flexible TST-RRKM estimate, this does not mean that the calculation is correct. $k(E, J)$ depends on the ratio $W(E, J)/\rho(E, J)$ where errors in the number of 'activated complex states' $W(E, J)$ may cancel errors in the density of states $\rho(E, J)$.

1 M. Quack and J. Troe, *Ber. Phys. Chem.*, 1975, **79**, 180.

Dr. Abel responded: The question whether the collisions sampled in our experiment proceed mainly *via* a (long-lived) N_2O_4 -collision complex deserves some attention, because if they do, the cross-sections can be compared with data for the high pressure recombination reaction of this molecule (energy transfer cross-sections and limiting rate constants k_∞ for the reaction $2 \text{NO}_2 \rightarrow \text{N}_2\text{O}_4$). This would provide direct information about the energy transfer mechanism in NO_2 self collisions. We think that in our experiments, where we only sample a small fraction of all collision events and channels (small energies transferred in a collision; large cross-sections), this mechanism can be neglected for two reasons. (1) In a long-lived collision complex the energy is randomized and partitioned statistically between the two fragments after the collision. The energy transferred in such a collision will be (much) larger than the energies transferred in our case. In addition, the propensities for vibrational energy transfer and the magnitude of the cross-sections we report in our paper do not support or suggest such a mechanism. This may not be true for collisions with larger ΔE . In our present experiment we seem to be sensitive to the fraction of collisions which (most likely) do not proceed *via* an NO_2 - NO_2 complex. This does not mean that these collisions do not exist, but they are just not sampled by our present set-up. On the other hand, we expect that the strong chemical interaction (leading to a deep well depth in the interaction potential), which is a particular feature of the PES, will very likely have an impact on the magnitude of the measured cross-sections. (2) In the case of pure rotational energy transfer, we have seen a residual alignment after one collision, from which we conclude that in particular these collisions do not proceed *via* a collision complex which would destroy the alignment owing to its long lifetime. In addition, the propensities for J transfer in a collision favour the long range dipole forces to be more important than short range multipole or chemical forces. In summary, we conclude that in our present experiments the complex mechanism for collisional energy transfer does not play a significant role. In order to measure additional energy transfer channels (*e.g.* collisions which proceed *via* a collision complex) we very recently modified our technique in such a way that we will be able to probe states which are much lower in energy compared with the initial state. Owing to the very small signal left for one quantum state at low energies, we try to sample as many states as possible with a probe laser of larger bandwidth. In this case the technique is no longer state but energy selective. Such experiments are in progress.

Dr. Delon said: This comment concerns the problem of the RRKM relation between the density of states $\rho(E, J)$ and the dissociation rate $k(E, J)$, just above the dissociation threshold of NO_2 , where there is one open reaction channel: $k(E, J) = 1/h\rho(E, J)$.

Recent high resolution (FWHM = 120 MHz) LIF experiments performed in Grenoble have shown that just below the dissociation threshold, $\rho(E, 1/2) + \rho(E, 3/2) = 15$

levels per cm^{-1} . By assuming a complete rovibronic redistribution, which implies that $\rho(E, 3/2)/\rho(E, 1/2) = 4/2$, it follows that: $\rho(E, 1/2) = 5$ levels per cm^{-1} and $\rho(E, 3/2) = 10$ levels per cm^{-1} . From this, one deduces that $k(E, 1/2) = 6 \times 10^9 \text{ s}^{-1}$ and $k(E, 3/2) = 3 \times 10^9 \text{ s}^{-1}$. These new experimental (and theoretical) results raise some contradictions.

(1) The calculated vibronic density of states at the threshold lies between 0.4 and 0.5 level cm^{-1} (see ref. 1). The corresponding rovibronic densities are therefore: $\rho(E, 1/2) = 1$ level per cm^{-1} and $\rho(E, 3/2) = 2$ levels per cm^{-1} , which are lower than the observed ones.

(2) The experimentally measured average dissociation rate (see Dr. Abel's paper), just above the threshold, is $2 \times 10^{10} \text{ s}^{-1}$ (average of $J = 1/2$ and $J = 3/2$), which corresponds to a lower density of states than the observed one.

I conclude that, if the measured average dissociation rate is correct, the whole phase space is not spanned before dissociation, because the redistribution among the internal degrees of freedom does not occur within a time shorter than $1/k$. Then, it is important to study the redistribution *vs.* the various internal degrees of freedom (vibronic and rovibronic).

In addition to this, the question of the understanding of the experimental (and unexpected) density of states can bring information about the long range behaviour of the potential-energy surface of NO_2 .

1 A. Delon, R. Georges and R. Jost, *J. Chem. Phys.*, 1995, **103**, 7740.

Prof. Reisler commented: The issues raised during the discussion on NO_2 decomposition indicate that exact comparisons between experimental and calculated reaction rates for this molecule will be difficult. The calculations of the reactive density of states are complicated not only by the lack of information about the long ranges of the PES near and above D_0 , as pointed out by Prof. Troe, but also by the increasing competition at higher E^E between intramolecular rovibrational couplings and the couplings to the dissociative continuum. As the dissociation rate increases, the weak Coriolis and spin-rotation couplings are expected to diminish in importance, since they would evolve on a timescale longer than dissociation. The decay rate is already less than 1 ps^{-1} at relatively low E^E , and thus IVR may become progressively restricted. This will reduce even further the reactive density of states and will increase the likelihood of direct dissociation events. The uncertainties due to considerations of density of states are augmented by difficulties in extracting meaningful state-specific rates from linewidths in the regime of overlapping resonances, and in obtaining the correct average width for ensembles as small as those in NO_2 decomposition. Thus, for NO_2 an agreement within a factor of two between experiment and theory is probably all that can be expected at this point; better agreement may be fortuitous, arising from a serendipitous cancellation of errors in the parameters that appear in the rate equation.

Another open issue concerns the conservation of K in NO_2 dissociation. Abel *et al.* report in their paper that a preliminary analysis of their results obtained for $J = 0.5$ and 1.5 indicates that K is not conserved. I would like to point out that Wittig and co-workers recently reported measurements of unimolecular reaction rates for rotationally selected NO_2 , $1 \leq N \leq 15$.¹ This was achieved using a double resonance excitation scheme in which molecules were first excited to selected N states in the (1, 0, 1) vibrational level (using an IR laser with 500 MHz linewidth), and then brought to energies above D_0 with irradiation from a picosecond laser (30 cm^{-1} FWHM). In these experiments the photolysis laser photon energy was constant and the photon energy of the IR laser was varied to access the selected rotational levels. Consequently, the total energy ranged from 15 to *ca.* 120 cm^{-1} above D_0 for N levels 1 to 15, respectively. The measured dissociation rate, $1.6 \times 10^{11} \text{ s}^{-1}$, was independent of N within the uncertainty of

the measurements, although the total photolysis energy increased by *ca.* 100 cm^{-1} . Preliminary calculations indicate that agreement between the experimental results and PST can be obtained only if it is assumed that K is conserved. Thus, the calculations suggest that K mixing is limited at best, at least for the $K = 0$ levels prepared in the experiment.

1 P. I. Ionov, I. Bezel and C. Wittig, *Femtochemistry: The Lausanne Conference*, ed. M. Chergui, World Scientific Publishers, Singapore, 1995.

Dr. Abel commented: In the general discussion of the papers by Delon *et al.*, Reid *et al.* and Abel *et al.* the question was raised whether K is a good quantum number and conserved in highly excited NO_2 (at the dissociation threshold) or not. Beyond the general statement that K cannot be conserved during the whole process of dissociation because the molecule finally dissociates and K becomes undefined, we have strong evidence against a conservation of K close to E_0 from (i) double resonance spectra at the threshold (see the sequential double resonance technique in our paper), (ii) the numbers of lines in our double resonance spectra below and above the dissociation threshold as a function of J , and (iii) the J -dependent average rate constants at the threshold (ref. 47 in our paper). We therefore conclude that K is not a good quantum number at high internal energies ($E > E_0$) and thus not conserved during the dissociation process.

Prof. Moore asked: Do you see a number of lines in the spectrum which increases as $2J + 1$? Can you give a range for the experimental value of the coefficient of J ?

Dr. Abel replied: The question you raise is very fundamental in the context of K conservation in this molecule. By just looking at the number of lines I think we are not in a good position to conclude whether K is conserved or not. Owing to an increasing overlap of lines in the spectra with $J' = 0.5/1.5, 2.5/3.5$ and $4.5/5.5$ (J' dependence of the near threshold spectra not presented here) it is very difficult to estimate precisely whether the density of lines increases as $2J + 1$ or not. The coefficient of J you are referring to I estimate to be between 1.5 and 2. This evidence against the conservation of K at energies close to the dissociation threshold agrees with other experimental results from double resonance spectra, densities of states (below E_0) and average lifetimes (above E_0).

Dr. Delon asked: My questions concerns Fig. 9 of your paper. (1) Theoretically, it seems to me that the number of resonances is given by the density of eigenstates. Therefore, what is the density of Lorentz profiles used in the fit, compared with either the calculated density of states or the observed density of states just below the dissociation threshold? (2) Knowing the experimental laser bandwidth (0.04 cm^{-1}), can you estimate (by assuming a χ^2 distribution), the number of missed (*i.e.* unresolved) resonances? This number may be not negligible because the laser bandwidth is not very small compared with the mean value of the linewidth ($\Gamma_{\text{av}} = 0.11 \text{ cm}^{-1}$ for $J = 1/2$ and $3/2$, respectively; 0.09 cm^{-1} for $J = 5/2$ and $7/2$, respectively). In addition to this, is this number of missing resonances in agreement with the difference between the density of states and the density of Lorentz profiles used in the fit? (3) By assuming that you observe a truncated χ^2 distribution (due the laser bandwidth), can you estimate what would be the real (*i.e.* corrected) mean value of the linewidth compared with the observed Γ_{av} ?

Dr. Abel replied: (1) The number of lines fitted in the double resonance spectra was about 10–11 lines cm^{-1} ($J = 0.5/1.5$). This belongs to a density of states of *ca.* 1.8 cm^{-1} . This value is in good agreement with densities of lines/states below the dissociation threshold published in the literature. The experimental density/number of states just above E_0 matches the calculated density of states within a factor of 1.5.

Table 1 Overview of measured lines by absorption spectroscopy, laser-induced fluorescence and bolometric detection

int.	band origin	ICLAS ^a ($\pm 0.01 \text{ cm}^{-1}$)	FS/cm ⁻¹	LIF ^b ($\pm 0.02 \text{ cm}^{-1}$)	bolometer ^b ($\pm 0.02 \text{ cm}^{-1}$)	FS/cm ⁻¹
0.8	13 510.96	R(0) 13 511.75/13 511.88 R(2) 13 513.37/13 513.71	(0.13) (0.34)	13 511.77/13 511.90 13 513.39/13 513.74	13 511.77/13 511.90	(0.13)
0.8	13 477.11	R(0) 13 477.9	(0)	'no fluorescence'	13 477.95	(-0.01)
2.5	13 395.65	R(2) 13 477.57/13 479.61 R(0) 13 396.58/13 396.64	(0.04) (0.06)	'no fluorescence' 13 396.60/13 396.66	not measured	(0.06)

^a Ref. 1. ^b This work.

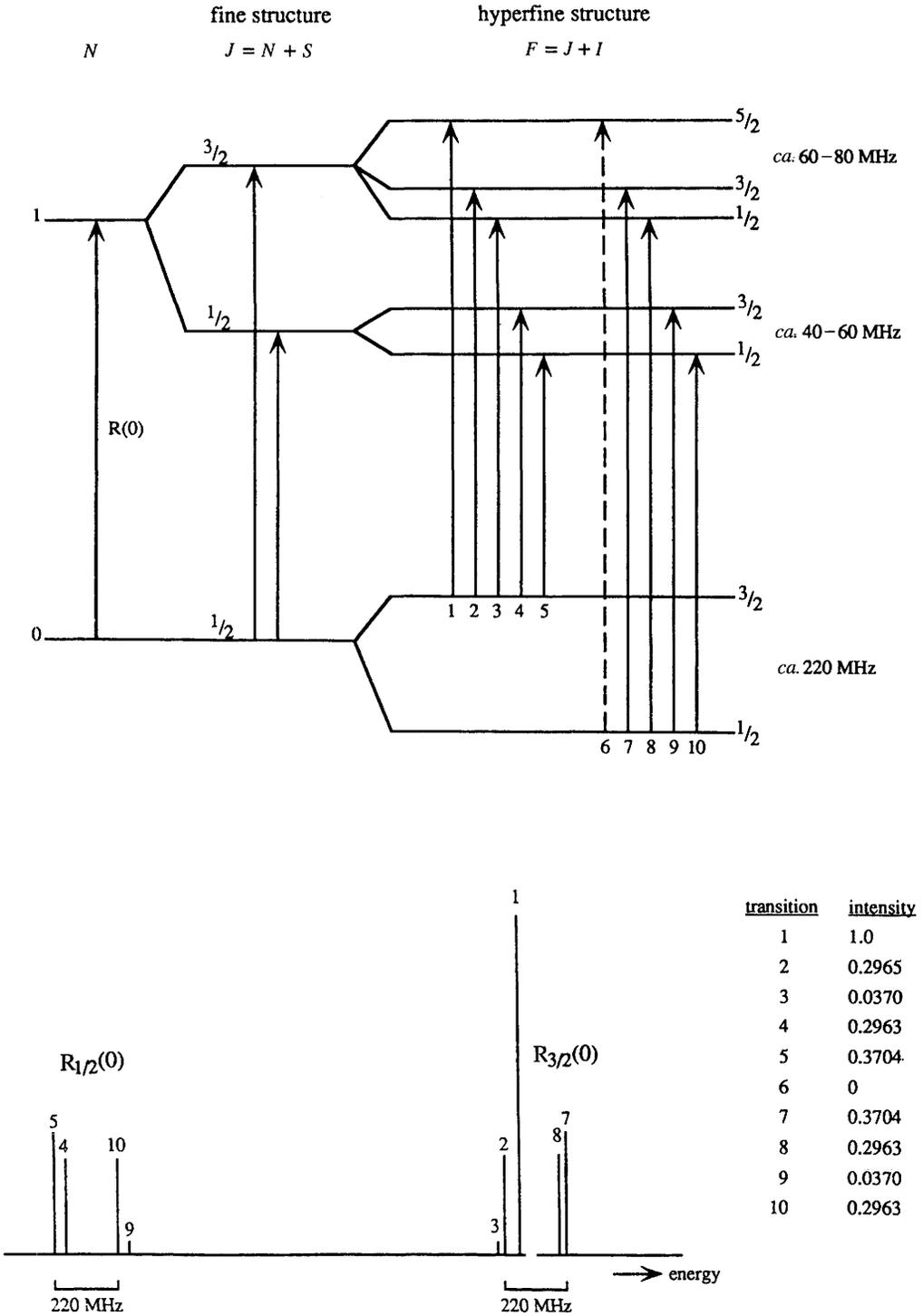


Fig. 1 Stick spectrum of an R(0) line following the J-coupling scheme with positive coupling constants

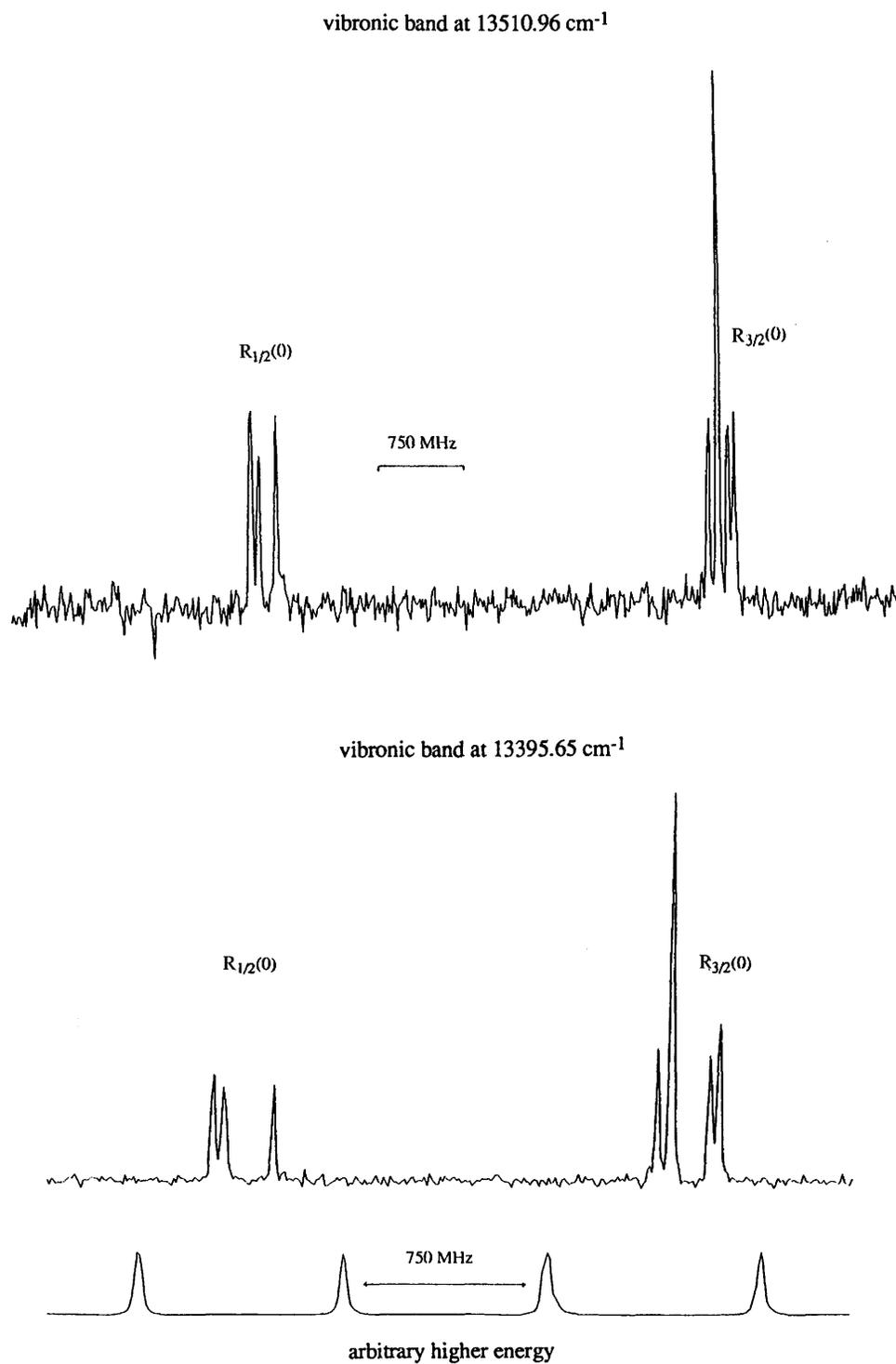


Fig. 2 Laser-induced fluorescence spectra of two $R(0)$ transitions of different vibronic band origins

(2) From your experimental densities of states just below E_0 (unpublished results), we conclude that we (probably) may miss up to *ca.* one third of the lines/states above E_0 due to the limited resolution and/or the background problem.

(3) It is difficult to estimate a corrected average value $\langle \Gamma \rangle$ for the linewidths. Taking into account the missing lines (which may have very narrow or large linewidths with different statistical weights) and the truncated linewidths distribution (on both ends), we think that the true average will be in agreement with our value of $\langle \Gamma \rangle$ within *ca.* 30%.

Dr. Biesheuvel, Mr. ter Steege, Dr. Janssen, Dr. Bulthuis and Prof. Stolte communicated: To inform you about complementary experimental methods to study the high resolution ${}^2A_1-{}^2B_2$ excitation spectrum of NO_2 we would like to report on our first and very recent results obtained by optothermal detection and laser induced fluorescence.

The experiments are typically done with a supersonic molecular beam of a few percent NO_2 seeded in He resulting in a rotational temperature of 10–15 K. This beam is perpendicularly crossed by a light beam of a continuous wave Ti : sapphire ringlaser with a bandwidth of *ca.* 100 kHz but a limited scan range of 40 GHz and the excited molecules are detected either by LIF or by a bolometer. By this we can resolve the fine structure doublets and the hyperfine structure of *ca.* 50–100 MHz. The Fermi-contact term in the first pure electronically excited state 2B_2 is zero. Since the hyperfine coupling constant is dominated by this term, the magnitude of the hyperfine splitting is an indication of vibronic coupling with the electronic groundstate. If on the other hand, the fine structure splitting shows irregularities this is indicative of the presence of rovibronic coupling.

The photomultiplier, provided with a cut-off filter, is placed perpendicular to both the molecular beam and the laser beam, resulting in LIF spectra with 10 MHz Doppler widths. This mode of detection is limited to fluorescent states. Another limitation of the use of a photomultiplier is its low sensitivity for IR light.

A bolometer is essentially an energy-content measurement device. In our case the element is a silicon semiconductor at a working temperature of 2 K. The bolometer is much more sensitive in the IR than a photomultiplier. Long-lived states are easier to detect than fluorescent states, so bolometric detection is also supplementary to LIF detection.

Table 1 shows an overview of some measured absorption lines (with equal intensities) by Jost and Delon.¹ We can resolve several vibronic lines by LIF within our accuracy. When an R(0) line follows the regular J -coupling scheme with positive coupling constants one expects to see the stick spectrum of Fig. 1. Fig. 2 shows two R(0) spectra of different vibronic band origins measured by LIF. The splittings observed in the excited state are similar to those observed by Persch² and are in good agreement with the stick spectrum. The 'missing' absorption line around 13477 cm^{-1} (with a small fine structure constant) is, however, detected by the bolometer (Fig. 3). Note that just the long-lived state shows a small fine structure splitting, but whether this observation may be generalized will be a subject of further investigation.

1 R. Georges, A. Delon, F. Bylicki, R. Jost, A. Campargue, A. Charvat, M. Chenevier and F. Stoeckel, *Chem. Phys.*, 1995, **190**, 207.

2 G. Persch, H. J. Vedder and W. Demtröder, *J. Mol. Spectrosc.*, 1987, **123**, 356.

Prof. Wardlaw communicated: This is a general comment motivated by the general discussion. It pertains to fluctuations in rates and product properties in collision (bimolecular) and half-collision (unimolecular) processes in the overlapping resonance (*i.e.* chaotic) regime of quantum dynamics. To facilitate discussion, let us consider decay rate as a function of energy. It is true that this function is unique for each system since it is determined by the Hamiltonian and the initial conditions. However, there are two

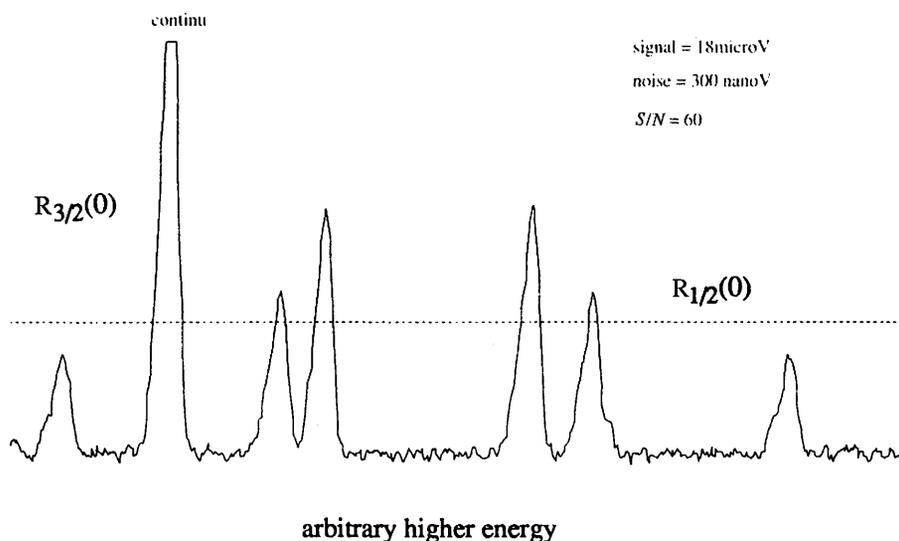
vibronic band at 13477.11 cm^{-1} 

Fig. 3 $R(0)$ line of the vibronic band around 13477 cm^{-1} by bolometric detection (spikes caused by the bolometer element are suppressed)

complementary reasons for it not being worthwhile trying to calculate such a property to this level of detail. First, the (quantum) chaos generally renders numerical calculations of the exact dynamics intractable. Secondly, the very nature of chaotic dynamics is sensitivity to initial conditions and external perturbations so that the measured function with which one is comparing a calculated function may fluctuate wildly under slightly different but uncontrollable experimental conditions. In addition, a slight difference between the actual Hamiltonian and the model Hamiltonian used in the dynamics calculation may lead to similar disparities. The appropriate approach under these conditions is to forego the desire to know all the details of the energy dependence of the decay rate and go over to a statistical characterization of the fluctuations (the energy-averaged auto-correlation function of the decay rate is one such example). The interesting feature which emerges is that fluctuation properties of observables such as the decay rate are universal (*i.e.* not system dependent). That is, the functions characterizing the fluctuations have a universal functional form and differ from system to system only through averaged quantities as the density of states and the energy-averaged (RRKM) decay width. Analysis of fluctuations reveals whether a particular system is in the chaotic regime. If so, one can extract the averaged quantities mentioned above. This is all one can usefully know about observable properties in the overlapping resonance regime. For an excellent discussion of this philosophy with applications to nuclear physics the reader is referred to an article by H. A. Weidenmuller.¹

1 H. A. Weidenmuller, *Comments Nucl. Part. Phys.*, 1986, **16**, 199.

Dr. Delon contributed: In order to probe the rotational redistribution among the excited levels of NO_2 located just below the dissociation energy, I propose the following dispersed fluorescence experiment.

Let us consider the 2B_2 levels excited *via* the R_0 lines ($K = 0$ parallel transitions) from X^2A_1 . These levels are either $J = 1/2$ or $J = 3/2$. By dispersing the fluorescence towards various rovibrational levels of the electronic ground state X^2A_1 , one can obtain information about the K mixing. (i) If there were no K mixing, we would observe fluorescence only towards the $N = 0$ and 2 , $K = 0$ levels of a_1 vibrational symmetry. (ii) In case of $\Delta K = 1$ couplings, we would observe fluorescence towards $N = 1, 2$ and 3 , $K = 1$ levels of b_2 vibrational symmetry. (iii) $\Delta K = 2$ couplings would induce fluorescence towards $N = 2$ and 3 , $K = 2$ levels of a_1 vibrational symmetry. We already know, from previous LIDFS experiments, that these three possibilities exist when exciting levels around $23\,000\text{ cm}^{-1}$. However, the intensity ratios of these various rotational transitions have never been studied statistically in order to put into evidence the rovibronic couplings of the excited states.

I think that such an experiment would allow one to obtain statistical information about the rotational basis states which compose the rovibronic eigenstates $J = 1/2$ and $3/2$, located just below the dissociation threshold. It must be compared with the similar two photon experiment of Dr. Abel (performed on levels around $17\,700\text{ cm}^{-1}$, see his paper) for which the third level is the 2^2B_2 electronic state. Surprisingly, Abel's experiment seems to indicate an exclusive $\Delta K = 0$ selection rule. This (apparent) contradiction can be solved by dispersing the fluorescence from the levels studied by Dr. Abel.

Prof. Reisler commented: NO_2 occupies a special place in the study of unimolecular reactions, since it allows good selection of initial and final states, as required for the exploration of state-specific effects characteristic of resonant scattering, while also exhibiting vibronic (and even rovibronic) chaos near D_0 , justifying comparisons with statistical theories. Its decomposition is characterized by fast rates, *i.e.* greater than 1 ps^{-1} at modest excess energies, a sparse density of states, and a modest number of final product states. The question we wanted to answer was whether deviations from statistical behaviour would first manifest themselves as clear dynamical signatures related to progressively restricted IVR as E^E increases, or would they be related to the small size of the ensembles, revealing fluctuations that cluster about the statistical average. Our studies show that the latter dominates; the first deviation from a smooth statistical behaviour appears in the form of fluctuations about the average from the onset of dissociation. Fluctuations were observed in the final state-selected spectra, product state distributions, and the state-specific decay rates. A careful examination of these fluctuations revealed the effects of overlapping resonances, and provided experimental probes of the transition state and exit channel interactions. Thus, state-to-state studies of the kind described here help unravel the causes and manifestation of statistical behaviour. On the other hand, the prominent fluctuations and oscillations, which are the hallmarks of NO_2 decomposition, may obscure dynamical signatures that become significant at high excess energies owing to the competition between decomposition and IVR and the tightening of the transition state. To detect such dynamical biases, larger molecules where fluctuations are averaged out are more desirable.

Prof. Herman opened the discussion of Prof. Rizzo's paper: The fluctuation observed by Rizzo and co-workers of the resonating peaks only is a phenomenon observed in many other cases, *e.g.* N_2O , probably H_2O , and certainly acetylene. It is most likely that the resonances responsible for that observation are already acting at much lower energies and that they could be revealed by high resolution systematic investigations. Such resonances only scale with the energy difference between the interacting levels. The same set of resonances is acting all the way to the highly excited range.

Prof. Rizzo responded: The beautiful work performed in the laboratories of Michel Herman and others in which they track vibrational resonances from low energy all the

way up to high energies has certainly given us a complete picture of the intramolecular dynamics of a number of small molecules. There are two problems in applying this approach to methanol, however. The first is that the strong coupling that we observe between the $5\nu_{\text{OH}}$ level and the $4\nu_{\text{OH}} + 1\nu_{\text{CH}}$ level will not appear at energies below about the $4\nu_{\text{OH}}$ energy because the pertinent levels will be too far out of resonance in this region. Moreover, one expects quartic coupling terms to become increasingly more important at higher energies owing to their stronger dependence on the vibrational quantum numbers.

As far as tracking some of the finer couplings that we observe in the $5\nu_{\text{OH}}$ region of methanol, because the splittings are relatively small and the density of states relatively high (ca. 800 per cm^{-1} at the $5\nu_{\text{OH}}$ energy), we feel that this would be a somewhat daunting task.

Prof. Mills commented: I would like to comment on the origin of the strong resonance between the $|5,0\rangle$ and $|4,1\rangle$ states of CH_3OH to which Prof. Rizzo draws our attention in the paper by Lubich *et al.* One might naively assume that this arises from a bilinear coupling term in the Hamiltonian of the form

$$H/hc = (\text{in part}) C_{12}(a_1^+ a_2^- + a_1^- a_2^+) \quad (1)$$

Here $a_r^+ = (q_r - ip_r)/\sqrt{2}$ and $a_r^- = (q_r + ip_r)/\sqrt{2}$ denote shift-up and shift-down operators, respectively, in the normal-mode eigenstates corresponding to the coordinates q_1 (the OH stretch) and q_2 (the A' component of the antisymmetric CH_3 stretch). However, the point of normal coordinates is that they are chosen to eliminate all such bilinear coupling terms, whether their origin is from the potential energy or the kinetic energy, so that this cannot be the origin of the coupling.

It is not possible to produce the desired coupling with a cubic anharmonic term in the normal coordinates, such as those which give rise to Fermi resonance. It is, however, possible that a quartic anharmonic resonance might give rise to the $|5,0\rangle$ with $|4,1\rangle$ resonance coupling, as discussed by Lehmann.^{1,2} Quartic resonances involve a total of four shift operators. For example, a term in the Hamiltonian of the type $(a_1^+)^2 a_1^- a_2^-$ will have a matrix element satisfying the desired selection rule $\Delta v_1 = \pm 1$, $\Delta v_2 = \mp 1$. The required matrix element is given by the expression

$$\langle v_1 + 1, v_2 - 1 | H/hc | v_1, v_2 \rangle = (1/4)K_{11,12}(v_1 + 1)^{3/2}v_2^{1/2} \quad (2)$$

The matrix element (2) has a higher power dependence on v_1 , *i.e.* $(v_1 + 1)^{3/2}$, than would the corresponding matrix element resulting from the operator (1), which would involve $(v_1 + 1)^{1/2}$. Thus the strength of the coupling grows rapidly with v_1 . For example, eqn. (2) gives

$$\langle 6,0 | H/hc | 5,1 \rangle = (1/4)6^{3/2}K_{11,12} = 3.67K_{11,12}$$

$$\langle 5,0 | H/hc | 4,1 \rangle = (1/4)5^{3/2}K_{11,12} = 2.80K_{11,12}$$

$$\langle 4,0 | H/hc | 3,1 \rangle = (1/4)4^{3/2}K_{11,12} = 2.00K_{11,12}$$

... ..

$$\langle 1,0 | H/hc | 0,1 \rangle = (1/4)1^{3/2}K_{11,12} = 0.25K_{11,12}$$

Thus the $\langle 5,0 | 4,1 \rangle$ coupling is more than ten times larger than the $\langle 1,0 | 0,1 \rangle$ coupling. Lubich *et al.* find the coupling matrix element $\langle 5,0 | H/hc | 4,1 \rangle$ to be approximately equal to 25 cm^{-1} , giving a value for the quartic coupling coefficient $K_{11,12}$ defined as in eqn. (2) of ca. 8.94 cm^{-1} . The quantum number dependence of the coupling is given here on the customary assumption of the harmonically coupled anharmonic-

oscillator approximation (HCAO), in which the unperturbed energy levels (the diagonal elements of the resonance matrix) are calculated from a formula including the anharmonic constants x_{11} and x_{22} , but the coupling matrix elements are calculated assuming harmonic oscillator formulae.

Because quartic anharmonic resonances grow more rapidly with the energy than cubic resonances, they are likely to play an important role in overtone spectra, and hence in the process of IVR. Cubic resonances, involving three shift operators, are usually called Fermi resonances, and some authors use this term to describe any anharmonic resonance. However, quartic resonances differ in a number of ways from cubic resonances, and it would seem sensible to restrict the use of the term Fermi resonance to its classical meaning of a cubic resonance, satisfying the selection rule $\Delta v_r = \pm 1$, $\Delta v_s = \mp 2$ (or $\Delta v_r = \pm 1$, $\Delta v_s = \mp 1$, $\Delta v_{s'} = \mp 1$). The most familiar form of a quartic resonance is that between hydrogen stretching overtones satisfying the selection rule $\Delta v_r = \pm 2$, $\Delta v_s = \mp 2$, usually called a Darling–Dennison resonance.^{3,4} However, there are other examples of quartic resonance for which the name Darling–Dennison resonance is not really appropriate, such as the well known resonance between ν_3 and $\nu_2 + \nu_4 + \nu_5$ in acetylene.⁵ More generally the name quartic resonance is appropriate for any resonance involving a total of four shift operators.

The coefficient $K_{11,12}$ is written with a comma separating the subscripts corresponding to quanta created from those annihilated (or *vice versa*) in the resonance coupling. Thus in this case two quanta of ν_1 are created and both one quantum of ν_1 and one quantum of ν_2 are annihilated. This notation follows the suggestion of Lehmann in his erratum,² and is also the notation adopted by Borro *et al.*,⁵ it makes the origin of the resonance (in terms of shift operators) clear from the symbol for the coefficient.

Although cubic (Fermi) resonance coefficients are a single cubic anharmonic force constant, quartic resonance coefficients are more complicated. They can be calculated from the anharmonic force field by perturbation theory, as described by Lehmann,¹ Mills and Robiette⁴ and by Borro *et al.*⁵ The resulting expressions always involve a quartic anharmonic force constant in first order and a number of cubic anharmonic force constants in second order. The expressions for the coefficients are closely similar to the perturbation theory expressions for the anharmonic constants x_{rs} , and the quartic coefficients are expected to be of the same order of magnitude as the anharmonic x_{rs} constants. The formula for the $K_{11,12}$ resonance coefficient that appears in eqn. (2) is given by Lehmann¹ in eqn. (9) of his paper, subject to the correction in his erratum,² and see also Law.⁶

Note that other quartic constants may also contribute to this interaction, namely $K_{1n,2n}$ where the index n relates to any other normal mode, other than ν_1 . However, the $K_{11,12}$ resonance is likely to be the most important because of its high dependence on ν_1 , which is why I have chosen to emphasise this term in the discussion here. The $K_{11,12}$ resonance may be thought of as expressing the ν_1 dependence of the bilinear term in eqn. (1); it gives rise to a change in the degree of mixing between the two normal coordinates as the mode ν_1 is excited. Although the bilinear term [eqn. (1)] itself cannot be present in the Hamiltonian, its ν_1 dependence can be present.

1 K. K. Lehmann, *Mol. Phys.*, 1989, **66**, 1129.

2 K. K. Lehmann, *Mol. Phys.*, 1992, **75**, 739.

3 B. T. Darling and D. M. Dennison, *Phys. Rev.*, 1940, **57**, 128.

4 I. M. Mills and A. G. Robiette, *Mol. Phys.*, 1985, **56**, 743.

5 A. F. Borro, I. M. Mills and E. Venuti, *J. Chem. Phys.*, 1995, **102**, 3938.

6 M. M. Law, PhD Thesis, University of Aberdeen, 1992.

Prof. Quack communicated: Rizzo and co-workers¹ have presented in their paper most beautiful spectroscopic results on intramolecular redistribution (IVR²) in methanol, which certainly deserve the most careful attention as to their theoretical analysis.

Their wonderful technique of double resonance IRLAPS will certainly prove useful for further problems also.

I believe that at present we do not know enough about the potentially fairly complex situation of the resonances observed in methanol in order to ascertain the precise mechanism of the couplings. Therefore, I will start my comment with some general aspects from established results and then turn to some more speculative considerations on the methanol system and related problems.

Lubich *et al.*¹ have justly drawn attention to the importance of couplings arising through low order anharmonic resonances and Ian Mills has amplified this point by a discussion of quartic resonances as a possible source for the doublet observed in the $5\nu_{\text{OH}}$ overtone in methanol. We applied the concept of sequential coupling through low order anharmonic resonances to the understanding of IVR in the early 1980s.³⁻⁵ More recently quite a few groups have followed up along similar lines, such as the Russian group around Letokhov, the group of Lehmann and Scoles, cited extensively by Lubich *et al.*, and Mills, M. Kellmann, Marcus and co-workers, the group of Field, of Nesbitt, of M. Herman, of Moore and co-workers and also others. We started originally from ideas widely available in spectroscopy on the size ordering of terms in the Taylor expansion of the potential, which we write here, retaining only some terms as an example for just two modes 's' and 'b', in rectilinear, dimensionless normal coordinates q (for reasons to be discussed below^{6,7}):

$$\begin{aligned} \left(\frac{V}{hc}\right) &= \frac{1}{2}\omega_s q_s^2 + \frac{1}{2}\omega_b q_b^2 \\ &+ C_{sbb} q_s q_b^2 + C_{ssbb} q_s^2 q_b^2 + C_{b^4} q_b^4 \\ &+ C_{sb^4} q_s q_b^4 + C_{s^3b^2} q_s^3 q_b^2 + \dots \end{aligned} \quad (1)$$

The first line contains quadratic and cubic terms (there are no mixed quadratic terms in these coordinates by construction, as Mills pointed out), the next line contains quartic terms, the third line quintic *etc.* The size ordering that has been folklore in vibrational spectroscopy is approximately a decrease by an order of magnitude for the coefficients C for an increase in order of the power (sum of exponents for the coordinates) by one. I remember early discussions with Jim Watson and Georges Graner on this question many years ago, but there are surely places where this role has been more formalized (see also ref. 8). In any case, it has been customary to add terms in this order as required by the fit to experiment. If such a quick convergence in the Taylor expansion holds true and if we use harmonic oscillator basis functions, then, as also pointed out by Ian Mills, the analysis of anharmonic resonances becomes very easy indeed, because of harmonic oscillator selection rules for the matrix elements involving powers of the q_i and the quick convergence of the series, since all coupling in the chosen coordinates is due to the potential (the kinetic energy operator is diagonal in rectilinear normal coordinates as it is in Cartesian atomic coordinates). For the cubic resonance with $\omega_s \approx 2\omega_b$ (the classic 'Fermi resonance'⁹) this implies, for instance, that the effective coupling constant exchanging two quanta 'b' against one quantum 's' k'_{sbb} , in a tridiagonal effective Hamiltonian matrix (also called algebraic Hamiltonian) would be equal to the anharmonic potential constant:

$$k'_{sbb} \approx C_{sbb} \quad (2)$$

(see ref. 4-7 for the structure of such matrices). For other (quartic, quintic *etc.*) resonance couplings, simple algebraic expressions can be derived, as mentioned by Mills for the case of a quartic resonance.

When we investigated the validity of eqn. (2) (and the underlying theory) for the case of CH stretch-bend Fermi resonances in CHX_3 molecules, we found that it fails badly

(typically by factors between 2 and 5). I believe that this class of Fermi resonances is by now one of the best analysed and systematically understood (with about 10 examples of the type CHX_3 , C_{3v} and many more of lower symmetry CHXY_2 , CHXYZ , where also Darling–Dennison resonances are important, see references cited in the reviews^{2,10,11}). The interesting point here is that the algebraic effective Hamiltonian theory works fine qualitatively, *i.e.* experimental and ‘theoretical’ spectra can be well fitted by effective Hamiltonian matrices of precisely the structure predicted by the simple theory. This can be understood by transforming the ‘true’ (variational) Hamiltonian in the basis chosen to the effective Hamiltonian H_{eff} of the derived algebraic structure⁶ (in matrix notation)

$$(VZ^T)^T H_{\text{var}} VZ^T = H_{\text{eff}} \quad (3)$$

The basis functions χ_i of the effective Hamiltonian are related to the basis functions φ of the variational Hamiltonian

$$\chi_i = \sum_{k(N_j)} Z_{ik} \sum_j V_{ij} \varphi_j \quad (4)$$

The existence of such a transformation thus hides the deficiency of the simple algebraic (perturbation) theory. Such a situation is more frequently observed in science than people tend to believe, when they take the empirical ‘success’ of the theory as a sign for its validity.

What are the implications of these results for the interpretation of IVR through ‘low order’ anharmonic resonances? We quote here for the one example of CHD_3 , for which we have also *ab initio* calculations of excellent quality, some of the numerical results (other examples are similar). The potential constant C_{sbb} for the CH stretch–bend resonance is between *ca.* 100 and 150 cm^{-1} for typical potential models, k'_{sbb} is, however, $30 \pm 15 \text{ cm}^{-1}$ and the established discrepancy from eqn. (2) must thus fall in the range between more than a factor of 2 and 10. For one *ab initio* potential, one has $C_{\text{sbb}} \approx 150 \text{ cm}^{-1}$ and $k_{\text{sbb}} \approx 30 \text{ cm}^{-1}$, *i.e.* a well defined theoretical discrepancy of a factor of five. One can go beyond perturbation theory and derive an analytical ‘exact’ expression⁷ for k'_{sbb} in terms of a pure cubic constant C_{sbb}

$$k'_{\text{sbb}} = \frac{8\omega_b^2 C_{\text{sbb}}}{\omega_s(2\omega_b + \omega_s)} \quad (5)$$

This coincides with eqn. (2), if $\omega_s = 2\omega_b$.

For our example, one finds then $k'_{\text{sbb}} \approx 75 \text{ cm}^{-1}$, still a discrepancy of a factor of 2.5, which is what one can get with a pure cubic coupling. If we add a quartic term, an analytical theory gives:⁷

$$k'_{\text{sbb}} = (1 - \frac{3}{4}a^2\bar{N})\{AC_{\text{sbb}} + a\bar{N}C_{\text{ssbb}}\} - 2.6 \frac{C_{\text{sbb}}^2}{\omega_s} a\bar{N} \quad (6)$$

$$A = \frac{8\omega_b^2}{\omega_s(2\omega_b + \omega_s)} + \frac{4\omega_b + \omega_s}{2\omega_b + \omega_s} a^2\bar{N} \quad (7)$$

In these expressions \bar{N} is an average polyad quantum number and a is the Morse parameter for the stretching mode, which has been represented by

$$y = [1 - \exp(-aq_s)]/a \quad (8)$$

coinciding with q_s as $q_s \rightarrow 0$ (see ref. 7 for a detailed discussion). With cubic and quartic terms one finds from eqn. (6) $k'_{\text{sbb}} \approx 54 \text{ cm}^{-1}$. These results can, of course, also be obtained numerically by retaining just the cubic and quartic terms. Finally, the fully numerical result is obtained, when *ca.* 30 terms (*sic!*) are retained for convergence in the expansion of eqn. (1): $k'_{\text{sbb}} = 30 \text{ cm}^{-1}$. When one considers these numbers, one may

write

$$k'_{\text{sbb}} \text{ (cubic)} \approx 75 \text{ cm}^{-1}$$

$$k'_{\text{sbb}} \text{ (cubic + quartic)} \approx 54 \text{ cm}^{-1}$$

$$k'_{\text{sbb}} \text{ (cubic + quartic + many higher)} \approx 30 \text{ cm}^{-1}$$

Therefore, the apparent low order resonance expressed by the single Fermi resonance constant k'_{sbb} is corrected by *ca.* 70% of its true value when going from the 'cubic' theory to the 'quartic' theory and by again about as much when going from the 'quartic' to the 'high order' theory. These results are independent of any uncertainty in the empirical analysis of the spectra of CHD_3 , as they can be obtained by pure theory on a model potential, which is, however, realistic for CHD_3 . Thus one might say that in terms of potential coupling, the Fermi resonance in CHD_3 (and the whole class of CHXYZ compounds) is as much a 'high order resonance coupling' as it is 'cubic' or 'quartic'.

Two further remarks may be necessary. One might say that the 'order' of the resonance is not defined by the order of the potential coupling terms in eqn. (1), but by the number of quanta exchanged in the effective Hamiltonian basis. While this is, indeed, a somewhat better concept, one must note that in terms of harmonic oscillator functions ξ in normal coordinates the effective Hamiltonian functions are (schematically only)

$$\chi_i(v_i) = c_1 \xi(v=0) + c_1 \xi(v=1) + c_2 \xi(v=2) + \dots \quad (9)$$

Therefore, when the χ_i are coupled only in adjacent blocks of the effective Hamiltonian corresponding to an apparent three quantum exchange in χ_i , in the harmonic oscillator functions this corresponds, in a part of the expansion, to exchanges of many more quanta. Since one might also construct another effective Hamiltonian basis, say γ , where blocks are coupled with apparent four, five, six or more quantum exchanges, this type of definition for the order of the resonance becomes arbitrary, once one has left the perturbation theory range.

The second remark concerns the use of internal coordinates (or other coordinates, such as polar, hyperspherical *etc.*) to obtain a potential expansion with fewer terms than eqn. (1), only of low order. This is indeed possible, and this is done in practice, when representing the potential.^{6,7,12} However, when one formulates the Hamiltonian in such coordinates, it is not diagonal in the kinetic energy and the high order couplings arise from the kinetic energy expansion, very similar to the potential-energy expansion in eqn. (1).^{7,12,13} For the particular examples of Fermi resonances discussed here, it turns out that the representation in rectilinear normal coordinates or polar normal coordinates⁶ is better than a representation in internal coordinates¹³ when retaining only the subset of CH stretching and bending modes, but of course, when the problem is fully treated including *all* degrees of freedom and all couplings, the choice of coordinates is irrelevant, the exact result being coordinate independent (the analytical calculations mentioned were carried out using special coordinates which we called 'Fermi modes').

We therefore conclude that in quantitative terms the concept of a low order resonance is somewhat volatile, as far as real molecules are concerned, once we go beyond perturbation theory and harmonic oscillator models. I might add that some of the successes of theoretical treatments for the substituted acetylenes mentioned by Lubich *et al.*¹ and investigated by us,^{11,14} as well as others,¹⁵ seem to me more apparent than real, if one has a closer look at the predictive power (for instance *ab initio* or with isotope effects) of these models.¹⁶ As far as qualitative concepts are concerned, I think other factors are at least as important or more so than the order of the resonance. I might mention here the concepts of locality and transferability of anharmonic couplings in chemical functional groups,^{10,11} the concept of adiabatic separation of modes important

in the acetylenic CH stretch,^{10,14,17} in HF stretching vibrations of hydrogen bonded complexes (HF)_n¹⁸ and related systems, direct *vs.* sequential (chain) couplings, off-resonance intermediate couplings, the influence of local symmetry (for instance C_{3v} *vs.* C_s and C₁ symmetry in alkyl CH,¹⁹ the influence of molecular (non-)rigidity and special electronic factors such as delocalization in π bond systems, hyperconjugation *etc.* and finally, trivial but important, the influence of the amplitude A of the resonance which depends both on the coupling strength V and on the resonance defect D

$$A = \frac{2V^2}{4V^2 + D^2} \quad (10)$$

The amplitude of a resonance is only large (and thus the resonance visible) if the resonance defect D is not much larger than the coupling strength V (for large D the amplitude decreases quadratically with D : $A \approx 2V^2/D^2$). It would be incorrect to restrict attention only to the strength of the coupling, which may or may not be related to the order of the coupling.

We can use now some of these ideas for a look at the methanol molecule. This will be conjecture, subject to testing. We first note that there are low order coupling paths for the resonance observed in $5\nu_{\text{OH}}$ by Lubich *et al.*, which involve sequences of two cubic resonances as shown in Fig. 4. Some of the excited CH bending levels are interconnected by Darling–Dennison type resonances. Of course, we do not know which of the couplings will be sizeable (if any), but we can anticipate that some of the CH stretch–bend couplings will be large.¹⁰ Thus a relatively modest cubic initial coupling of OH stretch with CH bend may be sufficient. Another possibility is an initial cubic coupling with OH stretch and OH bend (ν_6), which is expected to be strong but further off resonance, and subsequent Darling–Dennison coupling between OH bend and CH bend followed by the strong cubic CH stretch bend coupling, or else cubic OH bend–CH

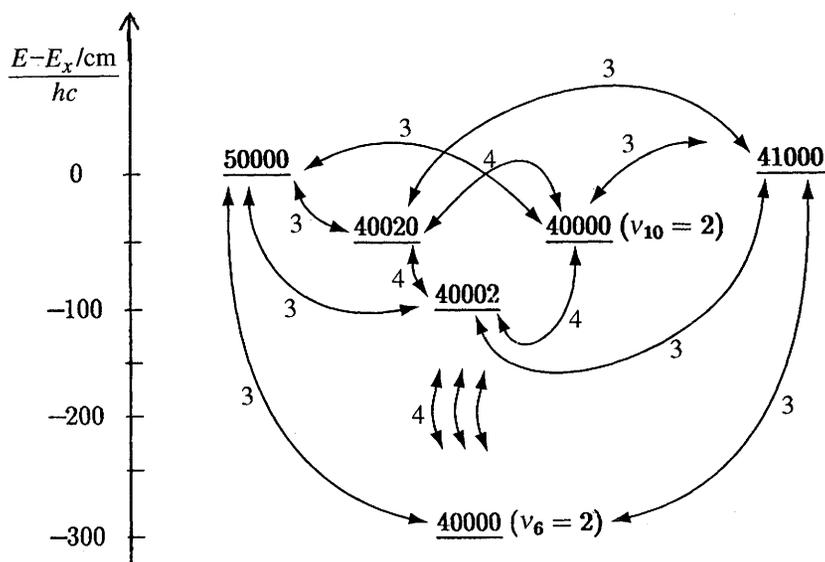


Fig. 4 Sequential resonance coupling scheme for methanol CH₃OH ($5\nu_{\text{OH}}$ polyad). The order of the resonance coupling is indicated over the arrows. The five-figure numbers indicate the quantum numbers $\nu_1 \nu_2 \nu_3 \nu_4 \nu_5$ in conventional order. Except where otherwise indicated, the remaining quantum numbers are assumed to be zero. The energy scale is only approximate, with $E_x \approx hc \times 16\,700 \text{ cm}^{-1}$. $\nu_1 = \text{OH stretch}$, $\nu_2, \nu_3 = \text{CH stretch}$, $\nu_4, \nu_5 = \text{CH bend}$.

stretch coupling. Although Prof. Rizzo has mentioned to me in private discussions that experimental evidence is rather opposed to such a scheme, because of the absence of visible intermediate levels, I am not yet convinced that they are really excluded. A back of the envelope estimate would attribute realistic intensity of about a few percent of the total to the intermediate levels and the complex interference patterns as well as further couplings may render this intensity scattered and thus weak and noise-like. Looking carefully at Fig. 3 of Lubich *et al.*,¹ I see some weak bands in the right range near $10\,150\text{ cm}^{-1}$ for the $3\nu_{\text{OH}}$ polyad. For the $5\nu_{\text{OH}}$ polyad this is not visible, but the noise level is higher. Of course, I do not have any evidence that this is the true coupling scheme. I rather would like to demonstrate therewith that there are numerous possibilities, including even sequences of simple (cubic) Fermi resonances, which could give rise to the observed effects. Prof. Mills proposed that a direct quartic $K_{11,12}$ resonance is likely to be the most important contributor to the coupling, not involving other degrees of freedom, although he mentioned also the contributions to the quartic coupling which arise from the involvement of other modes such as $K_{1n,2n}$ in his notation. This is quite plausible. We have, however, found in the past in work on other molecules that the terms involving such indirect cubic couplings to other modes can be very large. If something like the coupling scheme in Fig. 4 is correct (or other schemes involving the CH stretch–bend Fermi resonance), then there would be fast (100 fs range) exchange of energy, not only between the OH stretching and CH stretching system discussed by Lubich *et al.*, but also with the CH bending vibration (perhaps also OH bending *etc.*), although the exchange might still be of low amplitude in the $5\nu_{\text{OH}}$ energy range. This view would modify the opinion expressed by Lubich *et al.* at the end of section 3.1. in their paper that ‘it is only on a much longer (*i.e.* longer than 100 fs) timescale that the mixed OH–CH stretch states redistribute their energy to the other vibrational modes of the molecule’.

One may also ask where the couplings come from in qualitative physical terms. For the large CH stretch–bend coupling we refer to ref. 6, 7 and 10 which contain a detailed analysis of the effects. For the OH stretch–CH bend coupling, we can think of either the steric interaction between the bending CH group and the OH group (including the bulky free electron pair) or of hyperconjugation type effects similar to our observations for the CH stretch–CH bend and CCC bend coupling in $\text{R}_3\text{C}-\text{C}\equiv\text{C}-\text{H}$.^{14,18} Of course, a good approach to estimate anharmonic couplings nowadays are *ab initio* calculations.

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- 2 M. Quack and W. Kutzelnigg, *Ber. Bunsen-Ges. Phys. Chem.*, 1995, **99**, 231; see also whole special issue in that journal including papers in a session on IVR.
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- 19 D. Luckhaus and M. Quack, *Chem. Phys. Lett.*, 1993, **205**, 277.

Prof. Rizzo communicated in reply: I would like first to respond to the comments of Prof. Quack and then address those of Prof. Mills. Prof. Quack has made a number of very important points, none of which we disagree with in principle. However, careful examination of the data we have presented here on methanol as well as extensive isotopic substitution data yet to be published suggests that many of his concerns may be unjustified in this particular case.

Prof. Quack rightly points to the non-equivalence between apparent coupling terms in an effective spectroscopic Hamiltonian and the anharmonic potential constants of a true (variational) Hamiltonian. The work of his group on the substituted methanes, particularly in the case of CHD_3 , clearly illustrates a case where a feature that appears in the vibrational spectra to be a simple third-order (cubic) resonance is actually a collection of cubic, quartic and higher-order terms. In this case, ignoring these higher-order terms results in large errors in the evaluation of the true potential coupling terms. This leads them to conclude that the concept of low-order resonances is somewhat 'volatile'.

One must be careful not to extrapolate conclusions based upon one type of molecule or chromophore to other chemically different moieties, however. The fact that a wide variety of coupling paths of various orders could account for the splitting of the $5\nu_{\text{OH}}$ vibrational overtone band of methanol does not indicate that all these paths will be important. As explained below, the spectroscopic evidence on methanol clearly points to the importance of a simple quartic anharmonic resonance between the $5\nu_{\text{OH}}$ and $4\nu_{\text{OH}} + 1\nu_{\text{CH}}$ levels as the dominant mechanism for IVR in this energy region. Let me begin with a summary of the spectroscopic evidence.

(1) We can unambiguously assign the zeroth-order character of the two states involved in the strong interaction in the region of the $5\nu_{\text{OH}}$ level. We do this in two ways. First we have tracked this resonance as a function of vibrational energy from the $4\nu_{\text{OH}}$ to the $6\nu_{\text{OH}}$ regions and observe that the participating states move in a manner consistent with their zeroth-order assignment. In addition, we have measured overtone spectra of a number of isotopic invariants of methanol (*i.e.* CDH_2OH , CD_2HOH , CD_3OH and $^{13}\text{CH}_3\text{OH}$) and find that the resonance at the $5\nu_{\text{OH}}$ levels behaves as we would expect from our zeroth-order assignment of the participating states.

(2) We can determine the positions of the zeroth-order states with reasonable accuracy. We obtain the position of the zeroth-order bright state, $5\nu_{\text{OH}}$ from a Birge-Sponer plot of all the pure OH stretch energy levels from $\nu_{\text{OH}} = 1-6$. The OH stretch potential is accurately known, allowing us to predict the position of the zeroth-order bright state to be $16702.4 \pm 3 \text{ cm}^{-1}$. To find the position of zeroth-order dark states such as $4\nu_{\text{OH}} + 1\nu_{\text{CH}}$, we add the energy of the ν_{CH} fundamental to the $4\nu_{\text{OH}}$ energy determined from the Birge-Sponer plot. The resulting value of 16708 cm^{-1} for the energy of $4\nu_{\text{OH}} + 1\nu_{\text{CH}}$ therefore lacks just a single off-diagonal anharmonicity term, $4x_{\text{OH,CH}}$ which should not be more than a few cm^{-1} . *Ab initio* calculations estimate $x_{\text{OH,CH}}$ to be 0.7 cm^{-1} , and use of this value would place the $4\nu_{\text{OH}} + 1\nu_{\text{CH}}$ level at 16705 cm^{-1} . A deconvolution of the spectrum in the $5\nu_{\text{OH}}$ region (which assumes direct coupling of the zeroth-order states) results in an estimate of 16695.5 cm^{-1} for this level, which would mean that $x_{\text{OH,CH}} = 3.1 \text{ cm}^{-1}$. The vibrational overtone spectrum in the $4\nu_{\text{OH}}$ region reveals a small peak almost exactly at the position of the $3\nu_{\text{OH}} + 1\nu_{\text{CH}}$ that we would predict using $x_{\text{OH,CH}} = 3.1 \text{ cm}^{-1}$. Moreover, the spectrum in the $6\nu_{\text{OH}}$ region is consistent with this anharmonicity constant. We therefore have confidence that the $4\nu_{\text{OH}} + 1\nu_{\text{CH}}$ level is close to 16696 cm^{-1} .

(3) The splitting that we observe between the $5\nu_{\text{OH}}$ level and the $4\nu_{\text{OH}} + 1\nu_{\text{CH}}$ level (50 cm^{-1}) is much greater than uncertainty in the zeroth-order positions of these levels. The two peaks in the spectrum of the $5\nu_{\text{OH}}$ region lie at 16726 cm^{-1} and 16676 cm^{-1} . This means that the lower of these two peaks is pushed down in energy by an amount of the order of 20 cm^{-1} .

In light of this evidence, we now reply to Prof. Quack's comment. Indeed, as expressed in his initial statement, he believes 'that at present we do not know enough

about the potentially fairly complex situation of the resonances observed in methanol in order to ascertain the precise mechanism of the couplings'. Therefore, in addition to the direct quartic resonance proposed to be likely by Prof. Mills, he suggests possible alternative sequential couplings involving cubic, quartic and higher terms, in particular the anticipated CH stretch-bend Fermi resonance.

We disagree with this point and believe the coupling between the $5\nu_{\text{OH}}$ level and the $4\nu_{\text{OH}} + 1\nu_{\text{CH}}$ level in methanol does indeed result from a direct quartic resonance without significant involvement or mediation by other states. A look at Fig. 4 of Prof. Quack's comment reveals that all the potential candidates for intermediate states that can be coupled to both $5\nu_{\text{OH}}$ and $4\nu_{\text{OH}} + 1\nu_{\text{CH}}$ by third-order terms lie below these states in energy. Consider for example the 40 020 level (in Prof. Quack's notation, shown in his Fig. 4) which lies *ca.* 42 cm^{-1} below the zeroth-order $5\nu_{\text{OH}}$ level. If there is no direct interaction between $5\nu_{\text{OH}}$ and $4\nu_{\text{OH}} + 1\nu_{\text{CH}}$ levels, their interaction with 40 020 (or any intermediate state lying lower in energy) will push these levels higher in energy. In a sequential coupling scheme in which the 40 020 is the intermediate, a 50 cm^{-1} splitting between the $5\nu_{\text{OH}}$ and $4\nu_{\text{OH}} + 1\nu_{\text{CH}}$ levels would have to result from a differential push of these two states to higher energy. This key point will be true in general and can be proved analytically: in a sequential scheme in which states 1 and 3 are coupled to some lower energy state 2 but not directly coupled to each other, both 1 and 3 will be pushed to higher energy by the interaction. This is not what we observe experimentally, however. The eigenstates that we observe in the spectrum are shifted symmetrically from their zeroth-order positions by 20 cm^{-1} . The fact that the lower of these two states is pushed down from its zeroth-order position rules out the possibility of a sequential coupling mechanism *via* intermediate levels that lie below the $5\nu_{\text{OH}}$ and $4\nu_{\text{OH}} + 1\nu_{\text{CH}}$ states in energy.

Perhaps the strongest evidence in favour of our assertion of direct coupling comes from spectra in the region of the $6\nu_{\text{OH}}$ vibrational overtone band. In this region, we observe a peak near the expected position of the $5\nu_{\text{OH}} + 1\nu_{\text{CH}}$ band which appears to be coupled to the $6\nu_{\text{OH}}$ bright state. All the intermediate levels that could be coupled by simple cubic terms in the potential (*i.e.* the corresponding levels to the intermediates proposed by Prof. Quack in the $5\nu_{\text{OH}}$ region) now lie between the $6\nu_{\text{OH}}$ vibrational overtone band and the $5\nu_{\text{OH}} + 1\nu_{\text{CH}}$ band. If sequential coupling between $6\nu_{\text{OH}}$ and $5\nu_{\text{OH}} + 1\nu_{\text{CH}}$ was at all significant, these intermediate levels would now have greater intensity than the peak resulting from the $5\nu_{\text{OH}} + 1\nu_{\text{CH}}$ level since this scheme has them directly coupled to $6\nu_{\text{OH}}$ and they lie closer in energy. We observe no such additional peaks in the $6\nu_{\text{OH}}$ region, indicating that sequential coupling must be many times weaker than direct coupling between the levels $n\nu_{\text{OH}}$ and $(n - 1)\nu_{\text{OH}} + 1\nu_{\text{CH}}$.

In summary, given the apparent downward push of the zeroth-order $4\nu_{\text{OH}} + 1\nu_{\text{CH}}$ level and the lack of any observed intermediate states in the $6\nu_{\text{OH}}$ spectrum, we are left with the simple conclusion that the coupling between these states is direct in nature and not the result of a sequential coupling mechanism.

In light of this conclusion, we agree entirely with the comment of Prof. Mills regarding the importance of quartic coupling terms in high overtone spectra. It is clear that in a normal mode basis there are no quadratic coupling terms to coupling the $5\nu_{\text{OH}}$ and $4\nu_{\text{OH}} + 1\nu_{\text{CH}}$ levels, and hence a direct coupling must involve quartic terms of the type that Prof. Mills mentions. Because these terms involve higher powers of the vibrational quantum numbers, they should become increasingly more important in high vibrational overtone spectra.

Prof. Perry communicated: I would like to support Prof. Quack's comment about the importance of localised interactions in the context of IVR. In our study of the acceleration of IVR in flexible molecules,¹ we found that the acceleration was greatest for excited hydride stretches adjacent to the centre of flexibility, but was also evident for

those two bonds away. For hydride stretches three bonds away from the flexible centre, no acceleration of IVR attributable to molecular flexibility was evident. (A centre of flexibility is a single bond about which the barrier to internal rotation is low.) For the cases studied, the length scale for the locality of the interactions responsible for IVR appears to be 2–3 bond lengths.

1 G. A. Bethardy, X. Wang and D. S. Perry, *Can. J. Chem.*, 1994, **72**, 652.

Prof. Herman asked: I agree with Prof. Quack that some resonances might not clearly appear at lower energy, because of energy mismatch. However methanol is a molecule light enough that a deep high resolution spectroscopic-type investigation should allow one to understand and predict its rovibrational energy pattern. After all, this is what we have been doing for acetylene and we are now able to predict almost any rovibrational energy level up to highly excited ranges. This is not the real problem. The real issue is: is it worth spending 10 years of your life understanding the spectroscopy of a molecule, to interpret the resonances, in particular for larger molecules? Or is there any clever way to predict the dynamics?

Prof. Quack communicated in response: It remains to be established by experiment, perhaps aided by high-level *ab initio* calculations, what the actual coupling mechanisms are in methanol. Prof. Herman has suggested that one should work one's way through by identifying all levels and couplings from the low energy spectrum up to the $5\nu_{\text{OH}}$ range, where the resonance is observed. Such a procedure would be tedious routine for a triatomic molecule (NO_2 is a somewhat special case of this kind discussed at this meeting) and perhaps possible in a major project for four-atom molecules. However, starting with five-atom molecules, the task becomes rather gigantic and while we have embarked on such studies for molecules such as CF_3H , CD_3H and CF_3I , there is a tendency to get stopped at the level of the fundamental or first overtone of the highest frequency vibration. Prospects of doing the full job for $5\nu_{\text{OH}}$ in methanol do not seem good to me. I think that it is more reasonable to try to identify the most important coupling paths from intuition, experimental evidence and *ab initio* calculations and test the model systematically on its predictions. A very powerful tool for such a test are 'heavy' (non-hydrogen) isotope substitutions, which selectively shift certain vibrational states away from resonance (including intermediates as discussed above). We have been able recently, for instance, using our newly developed ISOS (isotope selective overtone spectroscopy) on a natural abundance isotope mixture of CHCl_3 , to assign a resonance in the $N = 4$ polyad of the CH chromophore almost with certainty to a coupling with the CCl_3 umbrella vibration, by means of the effect from the small ^{37}Cl isotope shift on the resonance patterns, which essentially excluded the numerous other, energetically allowed couplings.¹ In the case of methanol, one might think of using ^{13}C , ^{17}O and ^{18}O , presumably in enriched samples.

In addition, the deuterium isotope effect offers nice opportunities, as already discussed by Lubich *et al.*² In particular CHD_2OH would be a good candidate for isolating the effects of the CH stretch–bend Fermi resonance mentioned above, which would be rather similar in this isotopomer to the isoelectronic case CHD_2F investigated by us.³ I would like to mention here a special opportunity, which has been investigated by us on other alcohols, but could also be looked for in methanol CHD_2OH . The OH stretching vibration at low energies (below $5\nu_{\text{OH}}$) seems to be rather well separated adiabatically from the frame vibrations in many alcohols. The reason for this is the high stretching frequency and the moderately high bending frequency. The situation is not as extreme as in the adiabatic decoupling of the acetylenic CH stretch, but certainly the OH chromophore is generally much more decoupled from the frame than the alkyl CH stretching mode. The discovery of a resonance between $5\nu_{\text{OH}}$ and the $4\nu_{\text{OH}} + \nu_{\text{CH}}$ levels is thus very

important as it opens a coupling route to the frame. For instance, one might think that the isomerisation process corresponding to the conformers in CHD_2OH is adiabatically decoupled from the OH stretching vibration until $4\nu_{\text{OH}}$ (i.e. the effective potential for internal rotation changes, but there is no mixing), whereas mixing may set in at energies corresponding to $5\nu_{\text{OH}}$ and beyond, owing to coupling with CH stretch, CH bend and finally torsion, at some level.

- 1 M. Hippler and M. Quack, *J. Chem. Phys.*, 1996, **104**, 7426.
- 2 L. Lubich, O. V. Boyarkin, R. D. F. Settle, D. S. Perry and T. R. Rizzo, *Faraday Discuss.*, 1995, **102**, 167; see also O. V. Boyarkin, R. D. F. Settle and T. R. Rizzo, *Ber. Bunsen-Ges. Phys. Chem.*, 1995, **99**, 504.
- 3 D. Luckhaus and M. Quack, *Chem. Phys. Lett.*, 1992, **190**, 581; T. K. Ha, D. Luckhaus and M. Quack, *Chem. Phys. Lett.*, 1992, **190**, 590.

Dr. Abel asked: In your paper the power of your double resonance IRLAPS technique is clearly demonstrated. You show nicely that double resonance overtone spectra can provide detailed insight into the mechanisms and timescales of IVR in small and medium sized molecules. In order to draw general conclusions about IVR timescales in molecular reaction dynamics, it would be nice to investigate other modes than OH and CH stretch overtones. Since these are somewhat special (decoupled local modes) compared with other combination bands, they may show different behaviour than the 'rest of the molecule'. Did you (or are you able to) investigate combination bands with your technique as well?

Prof. Rizzo responded: Thus far we have used the double resonance IRLAPS detection technique to measure highly resolved overtone spectra of light atom stretch vibrations. While in general spectroscopy of high overtone levels is restricted to pure light-atom stretch vibrations, one can also use the double resonance scheme to access combination levels involving several quanta of light-atom stretch vibration along with one quantum of lower frequency vibrational excitation. This has been illustrated in some of our earlier work on the hydrogen peroxide molecule¹ where we first excite combination bands such as $\nu_{\text{OH}} + \nu_{\text{OO}}$ or $\nu_{\text{OH}} + \nu_{\text{OOH, bend}}$ to select a particular rotational state and then excite an OH stretch overtone vibration originating from these intermediates. This procedure permits spectroscopic access to states such as $5\nu_{\text{OH}} + \nu_{\text{OO}}$ and $5\nu_{\text{OH}} + \nu_{\text{OOH, bend}}$.

As far as accessing states of very different vibrational character, in principle there is no reason why we could not use stimulated emission pumping (SEP) to prepare a highly vibrationally excited molecule and then detect the transition with the IRLAPS method since IRLAPS detection is quite general for any type of vibrational excitation. The crucial factor in our being able to do such an experiment would be our ability to dissociate vibrationally excited molecules in the electronic ground state and not those promoted to the intermediate electronic state. This might be achieved if we excite close to the electronic band origin and if the non-radiative relaxation from the electronic state were slower than the timescale of our experiment (50–100 ns).

Whether or not using IRLAPS to detect SEP is more sensitive than other means of detection (i.e. fluorescence dip or grating techniques) is not clear.

- 1 X. Luo and T. R. Rizzo, *J. Chem. Phys.*, 1991, **94**, 889.

Dr. Softley said: With reference to Fig. 6 of your paper, the two states observed could be considered as $|a\rangle + |b\rangle$ and $|a\rangle - |b\rangle$. Could the sign of the admixture be sufficient to cause constructive interference with the coupling to the background states in one case and destructive interference in the other case? This would certainly be true for approximately equal coupling of $|a\rangle$ and $|b\rangle$ to a single background state $|c\rangle$.

Prof. Rizzo replied: Dr Softley's comment on the nature of the splitting in the $5\nu_{\text{OH}}$ overtone band of methanol is quite interesting. As shown in Fig. 6 of our paper, this band is first split by a strong anharmonic resonance into two bands of roughly equal intensity, separated by 49 cm^{-1} . As we have discussed, this splitting results from coupling between the zeroth-order $5\nu_{\text{OH}}$ and $4\nu_{\text{OH}} + 1\nu_{\text{CH}}$ levels. The fact that they are of nearly equal intensity means that the eigenstates differ by only a sign. If we call the $5\nu_{\text{OH}}$ level $|a\rangle$ and the $4\nu_{\text{OH}} + 1\nu_{\text{CH}}$ level $|b\rangle$ then the higher energy state would be approximately $|a\rangle + |b\rangle$ and the lower energy state $|a\rangle - |b\rangle$.

If one looks at the structure of each of these individual bands caused by further coupling on the background states, one observes that the high energy band is further split into four or five sub-features while the lower energy band is essentially unsplit. Dr. Softley suggests that the difference in coupling to the background may result simply from the difference in sign.

If the splitting of the high energy band were only into two components rather than four or five, it might be easy to see how there could be one background level that has equal coupling to both the zeroth-order states $|a\rangle$ and $|b\rangle$. In this case, the difference in sign between the two eigenstates would be sufficient to cause constructive interference in one case ($|a\rangle + |b\rangle$) and destructive interference in the other case ($|a\rangle - |b\rangle$), thus accounting for a difference in splitting. In other words, if $|c\rangle$ is the dark state with equal coupling to $|a\rangle$ and $|b\rangle$, and V is the term in the Hamiltonian responsible for the coupling, then

$$\langle c|V|(|a\rangle + |b\rangle) = \langle c|V|a\rangle + \langle c|V|b\rangle = 2\langle c|V|a\rangle$$

while

$$\langle c|V|(|a\rangle - |b\rangle) = \langle c|V|a\rangle - \langle c|V|b\rangle = 0$$

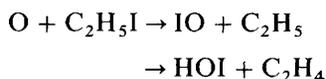
While it is clear that interferences of this type will occur, it is difficult to imagine how there might be three or four different background levels that are relatively close in energy that would have equal coupling to both the zeroth-order $5\nu_{\text{OH}}$ and $4\nu_{\text{OH}} + 1\nu_{\text{CH}}$ levels. Because these levels have different number of quanta in the two modes, the matrix elements between these states and other zeroth-order states will in general be different.

If the background states were essentially statistical mixtures of all available states in this energy region, then one can see how the two zeroth-order levels might on average couple these states with roughly equal strengths. But if this were the case, it would be difficult to see why four particular background states would be selected out of the *ca.* 800 states per cm^{-1} available for coupling.

We suspect that the difference in coupling to the background levels between the two major bands in the $5\nu_{\text{OH}}$ energy region simply reflects the fact that although there is a relatively high density of states, the density of states that could couple to the $5\nu_{\text{OH}}$ and $4\nu_{\text{OH}} + 1\nu_{\text{CH}}$ levels by low-order resonances is relatively small. The difference we observe in the spectrum may simply reflect the fluctuations in the density of low-order resonances over the 49 cm^{-1} splitting of the band.

Prof. Grice opened the discussion on Dr. Brouard's paper: Recent measurements on the reactive scattering of ground state $\text{O}(^3\text{P})$ atoms with $\text{C}_2\text{H}_5\text{I}$ molecules^{1,2} indicate that both mechanisms outlined by Brouard *et al.*³ for the appearance of backward scattering in long-lived collision complex dynamics may operate in this case. At low initial translational energy $E \approx 16\text{ kJ mol}^{-1}$, the reaction is observed to proceed *via* a long-lived collision complex mechanism giving scattering which is symmetrical in the forward and backward directions for both the IO and HOI reaction products. This arises by intersystem crossing from the initial triplet potential-energy surface to a bound singlet OIC_2H_5 intermediate, which dissociates with roughly equal probability according to the

reaction pathways



as shown in Fig. 5. At higher initial translational energy $E \approx 51 \text{ kJ mol}^{-1}$, the HOI product shows a mild tendency toward increased backward scattering which is attributed to singlet OIC_2H_5 complexes formed in small impact parameter collisions, *i.e.* Model 2 of Brouard *et al.*³ However, the relative intensity of IO scattering increases more strongly and shows a much stronger tendency toward rebound scattering as shown in Fig. 6. This is attributed mainly to direct reaction over the triplet potential-energy surface without undergoing intersystem crossing at the seam of intersection of the triplet $^3\text{A}''$ and singlet $^1\text{A}'$ potential-energy surfaces as shown in Fig. 5. Hence this provides an example of Model 1 of Brouard *et al.*³ and suggests that, at least in the case of the $\text{O}(^3\text{P}) + \text{C}_2\text{H}_5\text{I}$ reaction, the mechanisms of Models 1 and 2 arise from dynamics on different potential-energy surfaces.

Perhaps a role for Model 1 should not be entirely rejected for $\text{O}(^1\text{D}) + \text{CH}_4$, where the excess backward scattering of Fig. 1, 2 and 3 of the paper contributes only *ca.* 10% to the total reaction cross-section for $\text{OH}(v=0)$. If just this small proportion of reactive trajectories arose from a direct abstraction mechanism on the singlet potential-energy surface, the consequent increased product translational energy might pass unresolved.

1 R. W. P. White, D. J. Smith and R. Grice, *Chem. Phys. Lett.*, 1992, **193**, 269.

2 J. J. Wang, D. J. Smith and R. Grice, *J. Phys. Chem.*, 1996, **100**, 6620.

3 M. Brouard, H. M. Lambert, C. L. Russell, J. Short and J. P. Simons, *Faraday Discuss.*, 1995, **102**, 179.

Dr. Brouard replied: Prof. Grice points out that the backward scattered peak for OH ($v'=0$, $N=5, 8$) contributes *ca.* 10–20% to the cross-section for these specific channels. As a consequence, a high f_T component might be difficult to resolve in the OH translational-energy release distributions, $P(f_T)$. Although the absence of such a high f_T component on its own is inconclusive, it should be borne in mind that in the real time $\text{O}_3 \cdot \text{CH}_4$ experiments of van Zee and Stephenson (ref. 11 of our paper), no prompt $\text{OH}(v=0)$ signal was seen. The weight of evidence to date favours a mechanism involv-

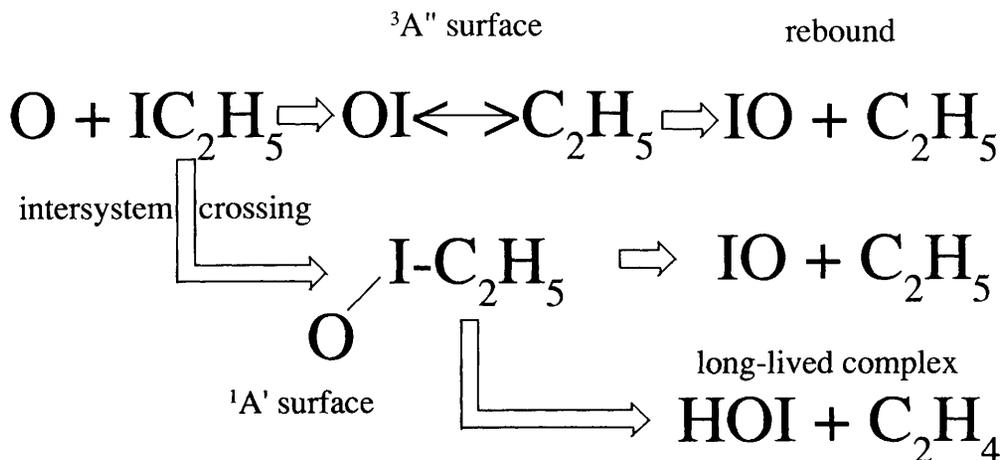


Fig. 5 Competing reaction pathways in the $\text{O}(^3\text{P}) + \text{C}_2\text{H}_5\text{I}$ reaction, including intersystem crossing from the initial triplet $^3\text{A}''$ potential-energy surface to the underlying $^1\text{A}'$ potential-energy surface

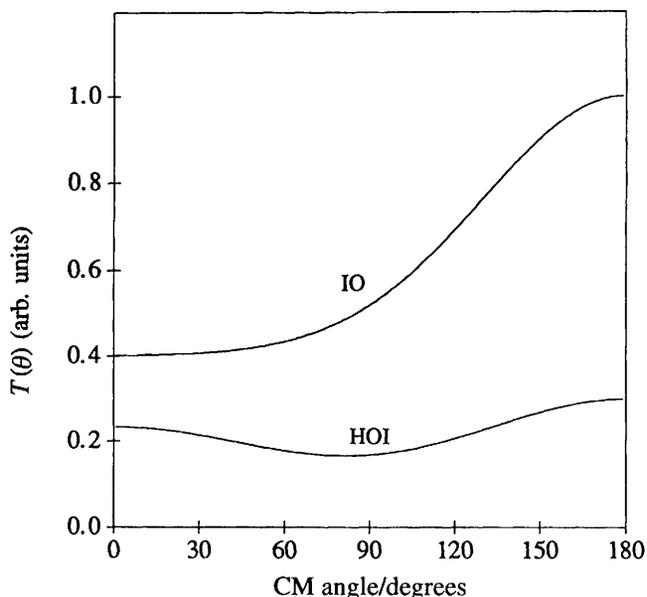


Fig. 6 Centre-of-mass angular distribution of IO (upper curve) and HOI (lower curve) scattering from $O(^3P) + C_2H_5I$ at an initial translational energy $E \approx 51 \text{ kJ mol}^{-1}$

ing the production of a complex with lifetimes of the order of a picosecond, even for the backward scattered $OH(v=0)$ fragments.

Unlike the system described by Prof. Grice, potential-energy surface calculations by Arai *et al.*¹ suggest that, of the five that correlate with the reagents, $O(^1D) + CH_4$, only one surface is attractive and likely to be involved in reaction at our collision energies. The form of this ground state surface (which has a minimum energy path leading to methanol) would appear to allow for more direct trajectories which do not sample the well, but how important they are is unknown at present, to our knowledge. The two models presented in our paper represent extremes: Model 1 ascribes backward scattering purely to direct, short lifetime processes (abstraction in the kinetics language) and the broad isotropic component to a complex mechanism, whilst Model 2 ascribes the form of the differential cross-section to the distribution of impact parameters and hence rotational clock rates. The truth almost certainly lies somewhere between the two extremes as there will always be a distribution of reactive impact parameters and collision lifetimes: the evidence to date, however, is that the latter of the two extreme pictures (Model 2) is the more appropriate in the methane system.

In conjunction with A. J. Alexander and Professor F. J. Aoiz,² we have recently been performing quasi-classical trajectory calculations on the lighter, but related $O(^1D) + HD$ reaction, using the Schinke–Lester surface.³ For this system, we have found that the differential cross-sections associated with the $OH(v=4)$ fragments, in both high and low rotational states, are characterized by near symmetric forward–backward scattering, with a preference for scattering into the forward hemisphere. Differential cross-sections for $OH(v=0)$ fragments, in contrast, are highly sensitive to the OH rotational state, ranging from strongly forward scattering at low j to backward scattering at high j . In spite of the fact that D is not CH_3 , this behaviour is reminiscent of that observed experimentally for the methane system. What is clear from the calculations is that the $OH(v=4)$ fragments have opacity functions very strongly peaked to high b (or L) values and hence have trajectories characterized by fast rotational clock

rates, whilst those for the $v = 0$, high j products (the predominantly backward scattered fragments) are skewed to lower b values, and thus possess slow rotational clock rates. We have also looked at the delay times associated with the OH $v = 0$ and $v = 4$ fragments: these are shown in Fig. 7 plotted as a function of reagent orbital angular momentum, L . The smooth line in the figure is an estimate of the rotational period of a water complex assuming that it has an equilibrium geometry. The figure demonstrates that both the OH $v = 0$ and 4 channels are characterized by trajectories with widely varying delay times, with the mean delay times for $v = 0$ being only slightly shorter than those for $v = 4$. Thus the change in differential cross-sections with product state would appear to be associated with different state-specific opacity functions, and hence rotational clock rates, rather than differences in delay times. It is certainly not clear to us, at this stage, that it is possible to associate the different state resolved differential cross-sections with abstraction *vs.* insertion type pathways in the HD system.

- 1 H. Arai, S. Kato and S. Koda, *J. Phys. Chem.*, 1994, **102**, 6946.
- 2 A. J. Alexander, F. J. Aoiz, M. Brouard and J. P. Simons, in preparation.
- 3 R. Schinke and W. A. Lester, *J. Chem. Phys.*, 1980, **72**, 3754.

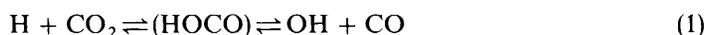
Dr. Schinke commented: I would like to bring to your attention a recent time-dependent wavepacket study concerning the reaction $O(^1D) + H_2$, which was initiated by the question whether or not the deep potential well will lead to pronounced resonances in the reaction cross-sections.¹ To our surprise, the reaction probability, even for $J = 0$, is a smooth function of the collision energy showing only very diffuse undulations. The total energy of the system is apparently so high above the deep potential well and the coupling between the modes is so strong that all resonance features are almost completely washed out.

- 1 T. Peng, D. H. Zhang, J. Z. H. Zhang and R. Schinke, *Chem. Phys. Lett.*, submitted.

Dr. Brouard responded: It would be of interest to compare the exact quantum reaction probabilities, state resolved differential cross-sections and delay times with those calculated by classical trajectories, especially in this case where the reaction proceeds over such a deep well. The mean delay times we observe in the QCT calculations of the $O(^1D) + HD$ system are of the order of 100 fs, which would certainly appear time enough for several vibrational periods, but may not perhaps be inconsistent with the smooth quantum reaction probabilities, given the high total energy above the well.

Prof. Simons commented: The dependence of unimolecular reaction dynamics on the method of state preparation has been alluded to by a number of participants. Most of the discussion has centred on methods, consequences and interpretation of optical excitation of levels high up in the ground electronic state rovibrational manifold, usually from the 'bottom-up'. The alternative, kineticists' route is from the 'outside-in', the collisional path where excitation follows a scattering event rather than photon absorption. Provided the collision is of short enough duration, it too can lead to coherent excitation of more than one quantum state and their subsequent evolution *via* IVR. The choice of an appropriate density of states under these conditions is clearly a problematic one.

A chemical system which has been widely studied *via* the collisional path is the reaction



Direct, femtosecond studies of the rate of appearance of $OH(v = 0, N)$ indicate unimolecular decay times for the (HOCO) intermediate, in the range 0.25–1.5 ps at energies 4000–8000 cm^{-1} above threshold.¹

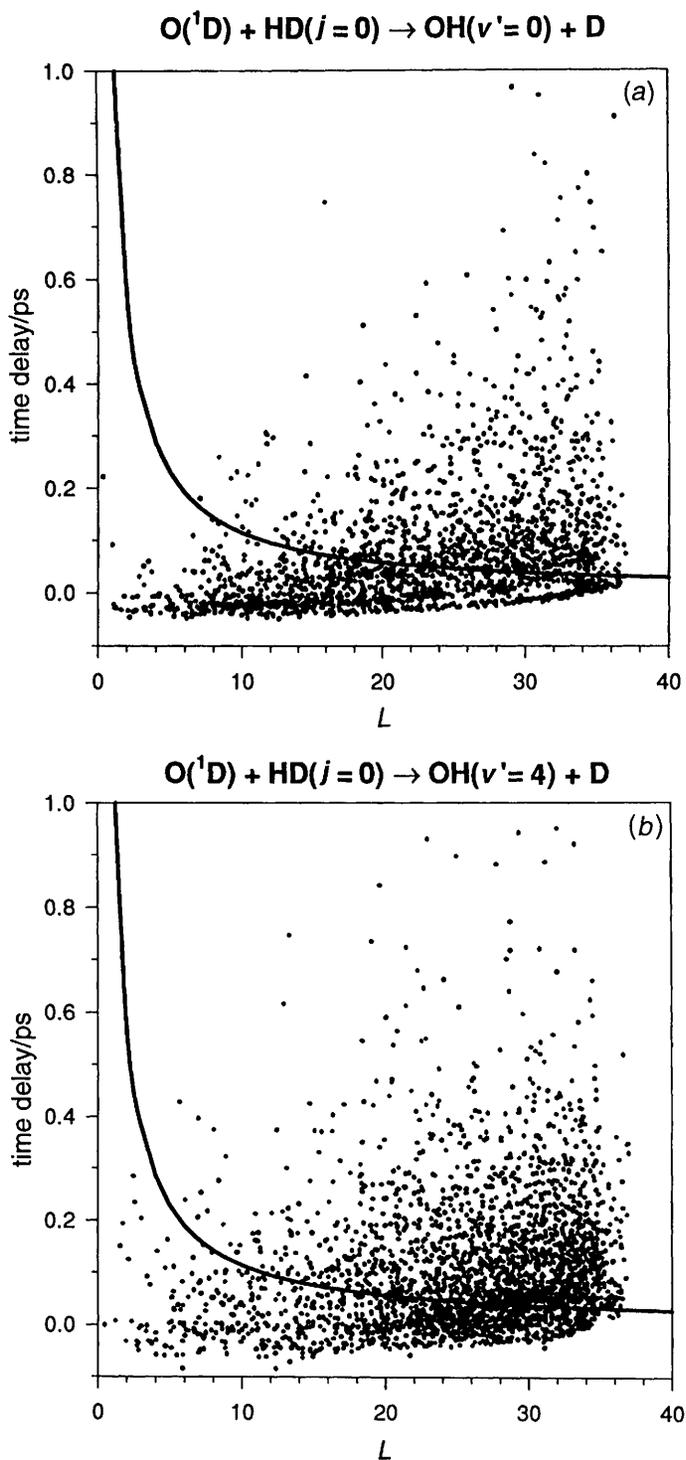


Fig. 7 QCT calculations of trajectory time delays plotted as a function of L for the $\text{OH}(v=0)$ (a) and $\text{OH}(v=4)$ (b) channels of the $\text{O}(^1\text{D}) + \text{HD}$ reaction.² The smooth curve in the figures is an estimate of the rotational period of a water complex in its equilibrium geometry.

New product state-resolved measurements of the differential cross-section [for $\text{OH}(v=0, N=5)$]² show both forward and backward scattering, with backward slightly more favoured; the energy of the (HOCO) was $12\,000\text{ cm}^{-1}$ above threshold however, and its lifetime cannot be greater than *ca.* 0.2 ps, which is shorter than the period of the fastest conceivable rotational clock.† At these high energies, the reaction would appear to follow a direct path, perhaps with two alternative microscopic pathways.²

1 S. Ionov, G. A. Brucker, C. Jacques, L. Valachovic and C. Wittig, *J. Chem. Phys.*, 1992, **97**, 9486.

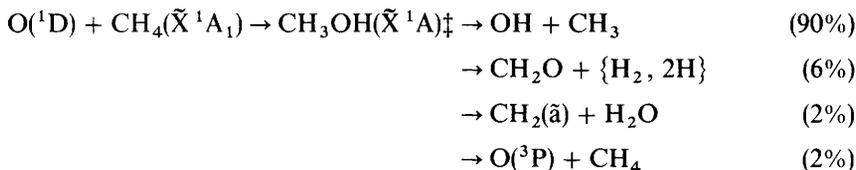
2 M. Brouard, S. P. Rayner and J. P. Simons, *Mol. Phys.*, in press.

Prof. Walsh stated: One should consider whether the reaction channel



plays any role in your system.

Prof. Hack commented: The products of electronic chemically activated methanol produced *via*:



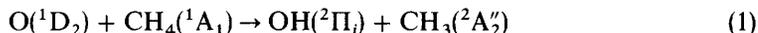
were studied at room temperature and pressures in the range $0.5 \leq p/\text{mbar} \leq 105$. The absolute concentrations of the products were determined by LIF.¹

It was concluded that if the reaction proceeds completely *via* insertion of the O^1D into the C—H bond [as can be concluded from the observed products of the reaction $\text{O}^1\text{D} + \text{CH}_4 \rightarrow \text{CH}_4\text{OH}$ in liquid argon²] the initially formed complex $\text{CH}_3\text{OH}\ddagger$ decomposes with a product distribution which is non-statistical, *i.e.* prior to energy randomisation.

1 W. Hack and H. Thiesemann, *J. Phys. Chem.*, 1995, **99**, 17364.

2 W. Hack and K. Menz, to be published.

Prof. Quack said: The experiments reported in the paper by Brouard *et al.*¹ on the reaction



are most admirable and I would certainly hesitate to question their interpretations on restricted vibrational redistribution. Nevertheless, I should like to make a historical comment related somewhat to their historical introduction. As Brouard *et al.* correctly point out, the question of restricted vibrational exchange in reactions passing through quasibound intermediate complexes has been repeatedly the subject of papers and discussions during previous Faraday Discussions.² In particular, the extensive work on reactions of halogen atoms with unsaturated organic molecules reported here and elsewhere has become a classic in unimolecular reactions (see reviews on some experimental and theoretical aspects^{3–6}). One conclusion drawn originally on some of the reactions was that the product translational energy distributions were inconsistent with PST and RRKMAM models but could be represented by models in which only a restricted number of vibrational modes participated in energy exchange in the intermediate complex.^{2,3} Thus it was originally concluded that there was restricted vibrational redis-

† In sharp contrast to the reaction of O^1D with CH_4 .

tribution in these cases. However, when these experimental results were reanalysed using the statistical adiabatic channel model,^{7,8} it was found that the measured product translational energy distributions were consistent with SACM calculations assuming complete statistical vibrational redistribution between all vibrational modes in the intermediate complex. The cautious conclusion from the theoretical study⁸ was that the question of statistical or non-statistical vibrational redistribution in these reactions remained open, and it has remained open until today.

In that context I disagree with the statement in the introduction by Brouard *et al.* that phase-space theory with a completely 'loose transition state' would be the proper statistical theory to be applied to methanol decomposition investigated by them. From all experience that we have gained over the last two decades, the adiabatic channel model^{6,9} would be a better theory for such a case, other assumptions about statistical redistribution being the same. I suggest that the authors compare their experimental results to SACM calculations: the computer program should still be available in Oxford from the work of Beresford *et al.* on CF₃CN decomposition.¹⁰ This is not to say that I believe that SACM will remove the discrepancies between experiment and theory for CH₃OH, it is just the technically more appropriate statistical model for such a case. There are, by the way, many ways in which memory is introduced in this statistical model.¹¹

The questions that I have concern two points. (i) In the entrance channel O(¹D₂) + CH₄(¹A₁) correlates to five electronic states of the intermediate methanol, some of which will coincide by degeneracy, but the ground state is non-degenerate. Must one not take the several states into account (also in the product channel) and is there a quantum chemical calculation doing so for the entrance channel? (ii) A very attractive feature of this reaction is the possibility of investigating the consequences of the validity (and possibly violations) of the principle of nuclear spin symmetry conservation in chemical reactions¹² by looking at the symmetry of the product levels in CH₃ produced as a function of the symmetry of the CH₄ reactant. Do you see a possibility of carrying out such a study?

As a very general remark I would say that looking for product state distributions from collision complexes remains a very indirect method to look for redistribution processes within the collision complex (useful, but indirect¹³). More direct answers on the behaviour of highly excited molecules could be obtained by looking at the quantum dynamics of highly excited molecules.¹⁴

- 1 M. Brouard, H. M. Lambert, C. L. Russell, J. Short and J. P. Simons, *Faraday Discuss.*, 1995, **102**, 179.
- 2 *Faraday Discuss.*, 1967, **44**; *Faraday Discuss.*, 1973, **55**; *Faraday Discuss.*, 1979, **67**.
- 3 J. M. Farrar and Y. T. Lee, *Annu. Rev. Phys. Chem.*, 1974, **25**, 357.
- 4 S. A. Rice, in *Excited States*, ed. E. C. Lim, Academic Press, New York, 1975.
- 5 M. Quack and J. Troe, in *Gas Kinetics and Energy Transfer*, ed. P. G. Ashmore and R. J. Donovan, The Chemical Society, London 1977, vol. 2.
- 6 M. Quack and J. Troe, in *Theor. Chem. Ad. and Persp.*, 1981, **6B**, 199.
- 7 M. Quack, *J. Phys. Chem.*, 1979, **83**, 150.
- 8 M. Quack, *Chem. Phys.*, 1980, **51**, 353.
- 9 M. Quack and J. Troe, *Ber. Bunsen-Ges. Phys. Chem.*, 1975, **79**, 469.
- 10 J. Ross Beresford, G. Hancock, A. J. MacRobert, J. Catanzarite, G. Radakrishnan, H. Reisler and C. Wittig, *Faraday Discuss. Chem. Soc.*, 1983, **75**, 211.
- 11 M. Quack and J. Troe, *Ber. Bunsen-Ges. Phys. Chem.*, 1976, **80**, 1140.
- 12 M. Quack, *Mol. Phys.*, 1977, **34**, 477.
- 13 M. Quack, *Chimia*, 1986, **40**, 386; see also M. Quack and W. Kutzelnigg, *Ber. Bunsen-Ges. Phys. Chem.*, 1995, **99**, 231.
- 14 M. Quack, in *Femtosecond Chemistry*, ed. J. Manz and L. Woeste, Proc. Berlin Conf. Femtosecond Chemistry, Berlin 1993, Verlag Chemie, Weinheim 1994, p. 781.

Prof. Simons replied: Our new experiments do indeed bear upon the pioneering studies of the unimolecular decomposition of 'activated' fluoroethyl radicals generated

by the addition of fluorine atoms to vinyl halides under crossed-beam collision conditions.¹ The forward-backward symmetry of the scattered product differential cross-sections was interpreted in terms of persistent collision complexes, decomposing on timescales long in terms of their mean rotational periods. The message conveyed by the new measurements of product state resolved differential cross-sections, however, is that caution should be exercised in making tacit assumptions about the period of the rotational 'clock'. It may not 'tick' at the same rate for every product channel and can change dramatically as different product quantum states are sampled, as evidenced in our studies of the unimolecular decomposition of 'chemically activated' (OCH₄). QCT calculations of the reaction



also show a wide scatter of product state resolved differential cross-sections, although for OH($v = 0, N$), the angular distribution summed over all N is completely symmetric.²

1 R. J. Buss, M. Coggiola and Y. T. Lee, *Faraday Discuss. Chem. Soc.*, 1967, **44**, 108.

2 A. J. Alexander, F. J. Aoiz, M. Brouard and J. P. Simons, *Faraday Discuss.*, 1995, **102**, 56; *Chem. Phys. Lett.*, in press.

Prof. Simons communicated additionally: The statistical calculations in our paper were used to model the conditional translational energy distribution $P(E'_i; v'_{\text{OH}}, j'_{\text{OH}})$, rather than the overall distribution, $P(E'_i)$. The phase-space theory calculations were highly successful in reproducing the former, but are totally inconsistent with the latter. Of course it may well be true that SACM is a more 'appropriate statistical model' but, as Prof. Quack points out, SACM is unlikely to recover the inverted internal states distribution $P(v'_{\text{OH}}, j'_{\text{OH}})$, correctly. The biggest uncertainty in the PST calculations lies in the choice of the opacity function $P(b) (\equiv P(L))$, a particularly acute problem for the near thermoneutral channels correlating with OH($v = 4, N = 8$). Angular momentum constraints are, of course, much less restrictive for the channels leading to OH($v = 0, N = 5/8$) because the energy available for disposal in internal motion of the CH₃ is now large. Given these uncertainties, we chose to use the simplest 'least biased' model, in the first instance. So far as the symmetry of the electronic state of the relative potential energy surface is concerned, our assumption is that only the lowest, ¹A' surface is involved. We note a slight preference for populating the $\pi(\text{A}')$ Λ -doublet component of the OH. Finally, IR diode laser spectroscopy has been employed to monitor the CH₃ fragment. So, too, has REMPI spectroscopy. Measurements of the rotationally resolved intensity distribution could provide the information you seek.

Prof. Wardlaw commented: The paper by Brouard *et al.* inspires the following general comment. Scattering events generally proceed by one of two mechanisms: direct (regular) or chaotic (irregular). The vast majority of inelastic and reactive collision processes consist of a mixture of both types of mechanism. Situations in which one mechanism operates exclusively are rare, particularly in the chaotic limit. The clearest theoretical understanding of the dynamics arises if these two contributions can be identified and separated. Unfortunately such identification is not easy. That is, it is generally not intuitively obvious, being dependent on the potential energy and initial conditions. Experience reveals that the separation does not usually correspond to a simple partitioning of impact parameter or internal states and often depends in an unpredictable way on vibrational phases.

Various criteria exist for making the separation in classical mechanics but applying them is far from routine and is generally not done. One method, based on an exponential rate of separation of trajectories initially adjacent in phase space, was developed and implemented for several systems in the late 1970s by Duff and Brumer.¹ Trajectories

separating by more than a pre-set amount before the collision is over are deemed chaotic and are not further propagated. The remaining trajectories are deemed direct and integrated to completion. The product properties of the direct component of the dynamics are thus not modelled but are determined directly from Hamilton's equations of motion. The product properties of the chaotic component are obtained from a statistical model appropriate to the strong coupling region defined by the particular criterion employed to identify the chaotic trajectories. It is important to recognize that the resulting statistical product property distributions for the chaotic trajectory subset are generally not the same as those that would be obtained from standard statistical models such as phase-space theory, SACM, or RRKM theory extended to provide product properties. The complete product property distributions are obtained by combining those for the direct and chaotic trajectory subsets with weighting factors determined by the relative sizes of the two subsets.

1 J. W. Duff and P. Brumer, *J. Chem. Phys.*, 1977, **67**, 4898; 1979, **71**, 2693; 1979, **71**, 3895.

Prof. Rizzo said: I have a general comment directed toward both Prof. Schinke and Prof. Perry which is related to an earlier comment of Prof. Miller. In comparison of calculated results with experiment, one must consider exactly how the experiment prepares the excited molecule undergoing unimolecular dissociation. In most of the cases we have heard about at this meeting, some sort of photoexcitation technique is used to prepare the excited reactant molecule. In this case, one must consider which eigenstates fall within the coherence bandwidth of the laser and then consider what the time evolution would be for this particular coherent superposition of states. This is a question that many early studies of IVR had initially ignored, and it is an equally important question for state-to-state studies of unimolecular reactions. Fine details related to the mode structure of the excitation laser can have a big influence on exactly what is observed experimentally. Even in the case of more highly averaged experiments, as in the case of collisional excitation or chemical activation, one must make assumptions about the nature of the state that is initially prepared.

In comparing experiment and theory, one must therefore be careful to know exactly what is measured experimentally and how that is influenced by what eigenstates are initially prepared.

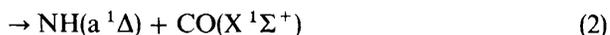
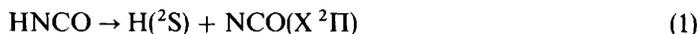
Dr. Schinke replied: I completely agree with Prof. Rizzo; in principle it is necessary to take into account how the experiment is performed and which superposition of stationary states is prepared by the laser excitation. Of course, this would make the direct comparison of theoretical and experimental data quite difficult. However, if a resonance is isolated, like in the case of HCO, the particular preparation scheme is unimportant. In such cases the resonance position, the width and the final state distribution is independent of how the resonance state was prepared.

Prof. Perry responded: The importance of carefully identifying the initially prepared state cannot be over-emphasised. In discussing frequency-resolved experiments on hydride stretches and their overtones, we talk about hypothetical coherent excitations of these motions. We are fortunate that the selectivity of IR and overtone excitation gives us a pretty good idea of what the initial state would be. However, there are likely still contributions of a few percent from other nuclear motions and these could be crucial in determining the rate of particular relaxation processes.

Mr. M. Zyrianov, Dr. Th. Droz-Georget, Mr. A. Sanov and Prof. Reisler communicated: The calculations presented by Schinke and co-workers are extremely important since they bridge the gap between the quantum scattering approach encompassing reso-

nances, fluctuations and dependence on the shape of the potential-energy surface with smooth, averaged quantities which are well described by statistical theories. It is therefore regrettable that so far comparisons with experimental results are available only for HCO (DCO), a decidedly non-statistical case. State-resolved studies of HNO and HO₂ present great experimental challenges and have not been reported yet. It is hoped that theoretical comparisons with NO₂, for which fully state-resolved data are available, will become possible.

We would like to propose another system that may serve as a benchmark for exploring statistical behaviour and its manifestations, namely the photodissociation of HNCO. We have recently undertaken a study of its jet-cooled photodissociation near the thresholds for formation of the two main spin-allowed channels:



Although uncertainty still exists regarding the respective thresholds for dissociation,¹⁻³ our jet-cooled photofragment-yield spectra indicate that NCO appears at $h\nu = 38\,370\text{ cm}^{-1}$ while the NH(*a*¹Δ) fragment population increases significantly at $h\nu > 42\,900\text{ cm}^{-1}$. Barriers to dissociation appear to be insignificant. The photofragment yield spectra shown in Fig. 8(a) and 9(a) exhibit distinct spectral structures which persist up to the highest photolysis energy used thus far [$45\,500\text{ cm}^{-1}$ (220 nm)] suggesting strongly that HNCO predissociates, possibly *via* the ground electronic state, ¹A'. This interpretation is supported by the 300 K absorption spectrum which exhibits rotational structure at long wavelengths, but becomes progressively diffuse as the wavelength shortens.⁴

Thus, HNCO provides opportunities for studying unimolecular decomposition in a system where two allowed channels separated by $< 5000\text{ cm}^{-1}$ are available. In this regard, it is similar to the dissociation of HO₂. Previous photolysis results obtained at shorter wavelengths (*e.g.* 193 nm)^{1,3} were interpreted using a direct, impulsive dissociation mechanism, with product distributions controlled by dynamics, and will have to be reconciled with the predissociative mechanism which apparently dominates near *D*₀. It is also intriguing that Crim and co-workers could alter the branching ratio between reactions (1) and (2) by selectively implanting excitation in ground state HNCO prior to photolysis.^{5,6} These findings raise interesting questions regarding selectivity in unimolecular reactions where the density of states near *D*₀ is $> 200\text{ per cm}^{-1}$. A detailed understanding of HNCO photodissociation and its dependence on excitation energy is a prerequisite to understanding such selectivity. It is also likely to provide important insights into issues ranging from interference and overlapping resonances; product state distributions and their dependence on the potential-energy surface; the relation between initial vibrational excitation and the evolution of the dissociative wavefunction towards specific outgoing channels; competition between the strength of coupling to the continuum (or dissociation rate) and couplings responsible for IVR and radiationless transition; the geometry of the transition state (TS) *etc.* Many of these issues have been discussed at this meeting.

The preliminary results presented here were obtained using a typical pump-probe arrangement described previously,⁷ and preparation and purification of HNCO followed published procedures.^{8,9} HNCO was seeded in He or in 30 : 70 He-Ne mixtures at a typical pressure of 760 Torr by passing the carrier gas through HNCO kept at -41°C (*ca.* 15 Torr vapour pressure). The rotational temperature of HNCO is estimated at 5-10 K. NH(¹Δ) and NCO(²Π) were probed by LIF, as shown in Fig. 8 and 9.

Our preliminary results can be summarized as follows. (1) In the range from *D*₀ to at least 5000 cm^{-1} above threshold, the photodissociation of HNCO appears to evolve by predissociation. The structure in the 'clumpy' NH yield spectrum (Fig. 2a) is real and

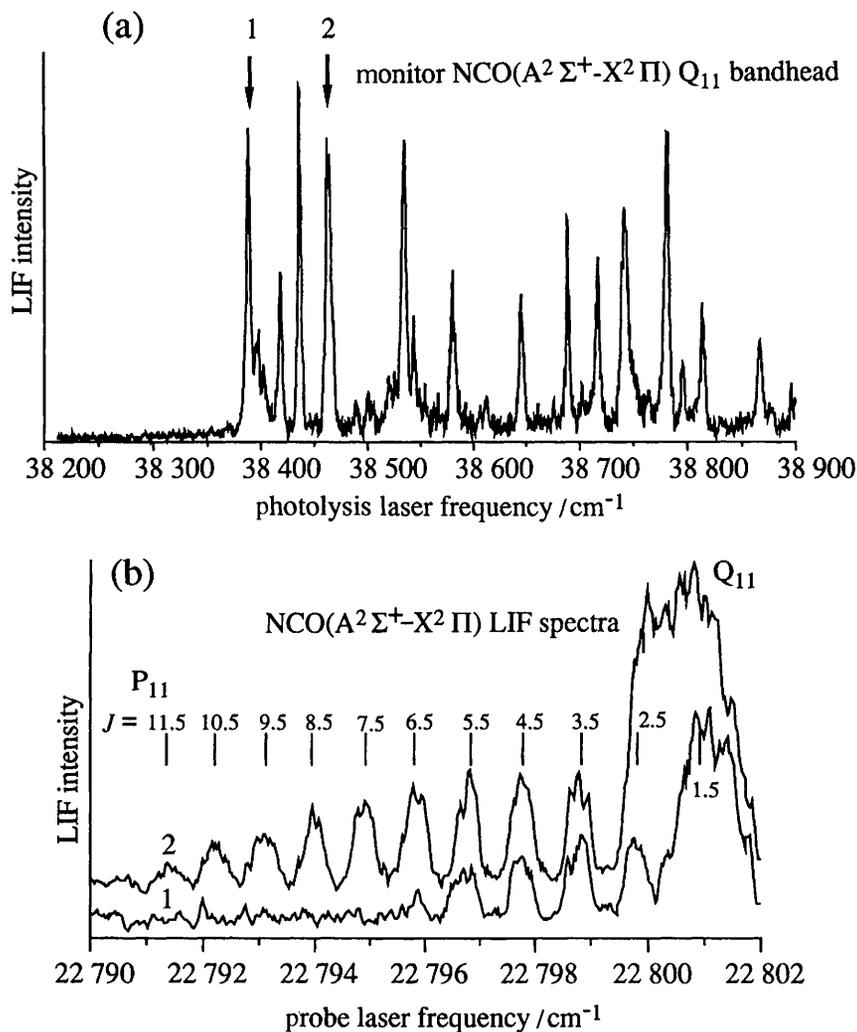


Fig. 8 (a) Photofragment-yield spectrum of the $\text{NCO}(X^2\Pi)$ fragment obtained following photolysis of jet cooled HNCO seeded in He. Detection is *via* LIF using the blue side of the Q_{11} bandhead of the ($A^2\Sigma^+ \leftarrow X^2\Pi$) transition which corresponds to low rotational states of NCO . (b) Two LIF spectra of the $\text{NCO } A^2\Sigma^+ \leftarrow X^2\Pi$ transition taken with the photolysis laser set at the frequencies shown by the arrows in part (a). The numbers correspond to rotational levels in the P_{11} branch. The unstructured peak at the blue end includes the Q_{11} bandhead and low lying rotational lines of the P_{11} branch.

includes some fairly narrow features even at the highest photolysis energies. (2) Near their respective thresholds, NH and NCO are cold [see Fig. 8(b) and 9(b)], and the fragments' internal excitations increase monotonically with increasing excess energy. The distributions appear to exhibit some dynamical biases (*e.g.* there is less rotational excitation in the NCO fragment than predicted by statistics). Note that the photofragment yield spectra displayed in Fig. 8(a) and 9(a) were obtained by monitoring low rotational levels of the fragments whose fractional populations decrease with excess energy. The spectra were not normalized for this decrease. (3) The NH yield increases sharply as the dissociation energy increases. The apparent levelling off at higher energies displayed in

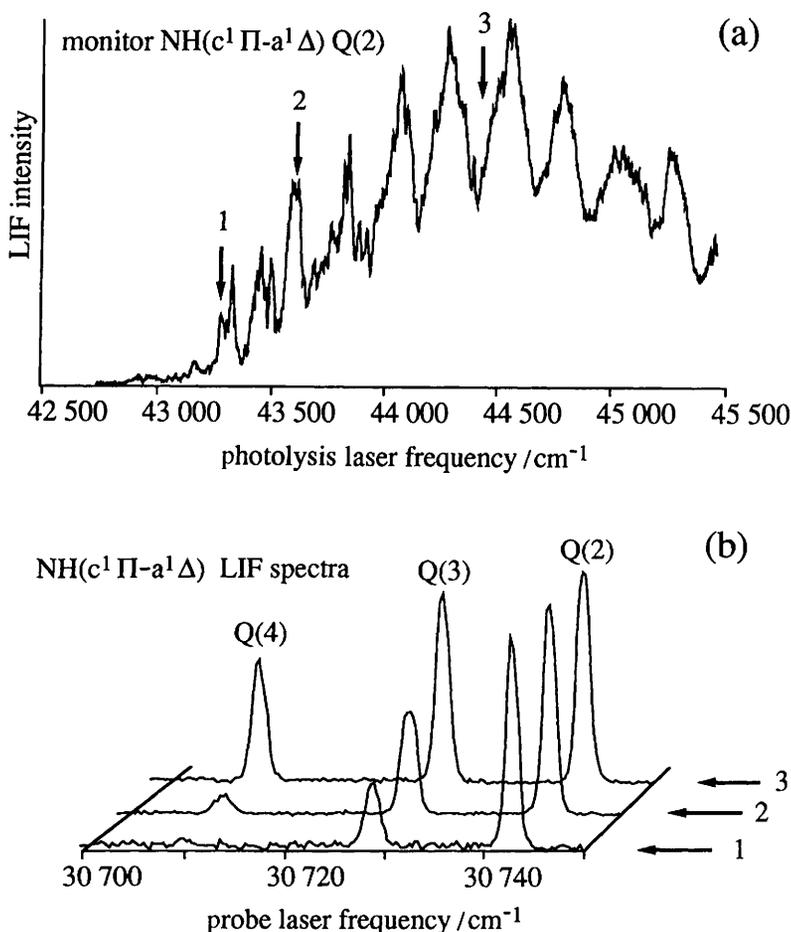


Fig. 9 (a) Photofragment-yield spectrum of the $\text{NH}(a^1\Delta)$ fragment obtained following photolysis of jet cooled samples of HNCO seeded in He . Detection was *via* LIF monitoring the $\text{Q}(2)$ line of the $c^1\Pi \leftarrow a^1\Delta$ transition. (b) Three LIF spectra of the $\text{NH } c^1\Pi \leftarrow a^1\Delta$ transition taken with the photolysis laser set at the frequencies shown by the arrows in part (a). The numbered notations correspond to rotational levels in the Q branch.

Fig. 9(a) is a consequence of the reduced fractional population of the lowest rotational level of $\text{NH}(a^1\Delta)$ ($J = 2$) which is monitored [see Fig. 9(b)]. Preliminary RRKM calculations indicate that the observed increase can be reconciled by statistical rate calculations assuming that near its threshold the TS for NH formation is loose, while the TS for reaction (1), a simple bond fission reaction, has already tightened at this energy and can be described with low frequency vibrations. Recall also that the number of 'disappearing oscillators' for the two channels is different: HNCO has six vibrational degrees of freedom, and the linear NCO fragment has four, while NH and CO together have two non-degenerate vibrations. Therefore, the rate of channel (2) can rise more steeply with excess energy than the rate for channel (1), accounting for the fast increase in the relative yield of NH . This fast increase may be moderated at higher excess energies by the tightening of the TS of channel (2). In summary, HNCO provides many opportunities for studying unimolecular reactions in a system with two open channels,¹⁰ we hope that theoretical work will follow.

- 1 T. A. Spiglanin and D. W. Chandler, *J. Chem. Phys.*, 1987, **87**, 1577; T. A. Spiglanin, R. A. Perry and D. W. Chandler, *J. Chem. Phys.*, 1987, **87**, 1568.
- 2 B. Rusic and J. Berkowitz, *J. Chem. Phys.*, 1994, **100**, 4498.
- 3 J. Zhang, M. Dulligan and C. Wittig, *J. Chem. Phys.*, 1995, **99**, 7446.
- 4 R. N. Dixon and G. H. Kirby, *Trans. Faraday Soc.*, 1968, **64**, 202.
- 5 S. S. Brown, H. L. Berghout and F. F. Crim, *J. Chem. Phys.*, 1995, **102**, 8440.
- 6 F. F. Crim, personal communication.
- 7 A. Ogai, C. X. W. Qian and H. Reisler, *J. Chem. Phys.*, 1990, **93**, 1107.
- 8 W. S. Drozdowski, A. P. Baronavski and J. R. McDonald, *Chem. Phys. Lett.*, 1979, **64**, 421.
- 9 G. T. Fujimoto, M. E. Umstead and M. C. Lin, *Chem. Phys.*, 1982, **65**, 197.
- 10 H. Zyrianov, Th. Droz-Georget, A. Sanov and H. Riesler, *J. Chem. Phys.*, submitted.

Dr. Abel said: In your paper, which was very interesting to me, you show the different dissociation dynamics of small molecules above their dissociation thresholds. Although their dynamics is quite different, they all show pronounced fluctuations in the lifetimes as a function of excess energy. Since these results are obtained only for non-rotating molecules, my question would be whether these calculations are feasible (with regard to computer power) for rotating molecules. Is it possible that rotation of the parent molecule (rotational coupling) changes the dynamical behaviour (distributions of lifetimes) above threshold qualitatively? With regard to thermally averaged rates it would be interesting (as you pointed out) to compare averaged rate constants with thermal rate constants, because it is not clear yet whether the fluctuations have an impact on high pressure thermal rate constants k_{∞} and/or bimolecular recombination reaction dynamics or not. In this context another question also arises: do we have to worry about the predictability of average thermal rate constants of small molecules (in combustion systems or atmospheric chemistry) with statistical theories? It is, of course, possible that all fluctuations will be averaged out in thermal systems. In this case only the average lifetimes count (which may be in good agreement with RRKM or SACM theory). In addition, one may also think about different scenarios (see also the discussion in ref. 1). In a recombination reaction of a small molecule (e.g. $\text{H} + \text{O}_2 \rightarrow \text{HO}_2$) with strong fluctuations in the lifetimes one may conclude that the long lived states (resonances) mainly contribute to the reaction flux (of the recombination reaction) because molecules in these states are easily stabilized (by collisions). In such a case these states (fraction of the lifetime distribution) play a more important role than states with intermediate or very short lifetimes. As you point out, more theoretical and experimental efforts are necessary to clear this point. From our point of view detailed high pressure recombination experiments (e.g. $\text{H} + \text{CO}$, $\text{H} + \text{NO}$ and $\text{H} + \text{O}_2$) would be nice test cases for the above mentioned conjectures. It would be very interesting to investigate the impact (if there is any!) of the strong lifetime fluctuations of HCO (found experimentally and theoretically), HNO and HO_2 molecules on their high pressure thermal rate constant k_{∞} and the fall-off range.

- 1 S. Dertinger, A. Geers, J. Kappert, J. Wiebrecht and F. Temps, *Faraday Discuss.*, 1995, **102**, 31.

Dr. Schinke replied: The calculations become significantly more complicated and time consuming if the molecule is initially rotating ($J \neq 0$). At the present time we are investigating the influence of initial rotation on the dissociation rates in HCO. Preliminary calculations for very few resonance states and J up to 5 indicate, however, that the influence is quite small, by a factor of two or smaller. In principle, we do not expect dramatic changes of the dynamics when $J \neq 0$. The question as to whether or not the fluctuations of the decay rates will affect the thermally averaged rates is very interesting and should be investigated in the future. This would require, however, the approximation of the influence of overall rotation on the rates, because the calculation of rates for all resonances and many rotational states by exact quantum mechanical methods will be extremely difficult.

Prof. Troe commented: I would like to emphasize that the potential for HO₂ used in your work must still be unrealistic. The measurements on the H + O₂ → HO₂ association in the high pressure limit clearly indicate that the potential must be totally 'loose', similar to the HNO potential that you use.

Prof. Troe then asked: Are the discrepancies between the statistical and classical trajectory calculations, which you observe, really significant in the sense that you really do the same in both cases? Do you use the same densities of states? What do you do with the densities of states in the dissociation continuum? Can you say whether adiabatic channel potentials with avoided crossings or without avoided crossings are better?

Dr. Schinke answered: It is not surprising that the potential, which we use in our study of the dissociation of HO₂, does not describe correctly all details of the 'true' potential. However, that is not pertinent for the main goal of our investigations, namely the study of quantum mechanical resonances and their decay when the classical dynamics is mainly chaotic. For this purpose, the employed potential surface is very useful.

As discussed in the paper, the density of states in the continuum is extrapolated from the density of states in the bound region of the molecular spectrum. That is the only way for defining the density of states in the continuum that I can think of. The fact that this enormously important quantity cannot be defined in a most unique manner also underlines the fact that the statistical models are approximations that one should not overinterpret! It is difficult to decide whether adiabatic potential curves with or without avoided crossings give better results compared with more exact calculations of dissociation rates, *e.g.* classical trajectories. One should distinguish avoided crossings between curves belonging to different vibrational manifolds and between curves belonging to the same vibrational quantum number *n*. The coupling between different vibrational states is usually very weak at large distances and therefore these avoided crossings should be ignored (as done in SACM).

Concerning the question about the discrepancy between the classical rates and the statistical estimates, let us consider HNO as an example. As seen in Fig. 9 of the paper, the distribution of lifetimes embraces (at least) two exponentials, one at short times with a fast rate and another one at intermediate times having a slower rate. Shown in Fig. 6 of the paper is only the slow rate; it is definitely smaller than the statistical rate but agrees quite well with the average of the quantum mechanical rates extracted from the resonances. The rate extracted from the exponential at short times is larger than the statistical rate. The weighted average of the two classical rates, however, is in reasonable agreement with the statistical value. In other words, one has to take into account both classical rates when one wants to make comparison with statistical models. In the quantum calculations, only the narrower resonances are considered for extracting dissociation rates, while the broader structures, partly hidden in the 'background', are not taken into account. Therefore, it is not surprising that the average quantum mechanical rate agrees quite well with the classical rate extracted from the slower component while it is significantly smaller than the statistical rate. We are currently investigating how one can determine a quantum mechanical average rate which would also include the faster processes; it will be interesting to compare this average with the statistical result. In the case of HO₂, where there are no significant bottlenecks for internal energy redistribution, the classical lifetime distribution is a single exponential and, not unexpectedly, the quantum mechanical average, the classical rate, as well as the statistical rate, all agree very well.

Dr. Delon said: Here I would like to make some comments concerning Section 3 of your paper. You have used the nearest-neighbour spacing distribution $P(S)$ and the

Metha statistic $\Delta_3(L)$, in order to test to what extent a system is irregular. I think that such statistical tests, and especially the $\Delta_3(L)$ statistic, must be handled carefully, because they give a very partial information (hereafter I will ignore the nearest-neighbour distribution). The reasons are the following.

(1) The $\Delta_3(L)$ statistic gives very smooth information about the long range correlations. Indeed, $\Delta_3(L)$, being in fact a weighted average of $\Sigma^2(L)$ between 0 and L , is roughly equivalent to $\Sigma^2(L/4)$. In addition to this, for a very irregular system such as HO_2 , the small remaining deviation from the GOE limit that one can observe cannot be interpreted physically (which is disappointing) by means of a statistical test.

(2) Because a real excited system is never fully irregular, the knowledge of both the different regular and irregular subparts of the phase space, and of the original state from which the photodissociation transition occurs, are essential.

(3) The correlation properties evolve with energy: generally the system is regular at low energy and becomes irregular at higher energy. Your global analysis of all the energy levels gives only average properties. A study of the evolution of the correlation properties with energy is desirable.

As a conclusion, statistical tests are poor in nature, and must be completed by further analysis (such as an inspection of the wavefunctions, Fourier transform, trajectory calculations, *etc.*) in order to gain evidence of, and to understand, the remaining regularities.

Dr. Schinke said in reply: I agree with all the comments. The behaviour of a molecule changes more or less gradually from regularity at low energies to irregularity at higher energies close to the threshold for dissociation. Therefore, it would be better to make the statistical analyses separately for different energy intervals. However, our primary goal was to demonstrate that *e.g.* HO_2 is mainly irregular close to the threshold and Fig. 4 of our paper clearly shows this. A separate analysis for low and for high energies definitely would be more suitable for HNO . It would probably show that the energy regime close to the threshold is mainly irregular. In order to fully understand a system, visual inspection of the bound as well as resonance wavefunctions is essential and therefore we always show many examples of wavefunctions in our recent publications on unimolecular dissociation.

Prof. Hynes asked: Could you clarify just what is meant by the RRKM rate constant in your calculations? In particular, is the classical density of states being exactly calculated (given the potential surface), or are further approximations (*e.g.* adiabatic assumptions) being introduced? In this connection, could you comment on Prof. Troe's earlier remark about the general inability to calculate anharmonic densities of states for triatomics?

Dr. Schinke responded: The way we calculate the statistical rates is fully described in the text of the paper. We first calculate the adiabatic potential curves as a function of the dissociation coordinate R by diagonalizing the two-dimensional Hamiltonian in the angular coordinate γ and the vibrational coordinate r of the asymptotic diatom. Then, we define the transition state for a particular energy as the maximum of each of these adiabatic curves (including the cusps due to avoided crossings). The density of states at a particular energy in the continuum is determined by extrapolation of the density of states in the bound region of the molecule. For a triatomic molecule it should, in principle, be possible to calculate exactly, for a given potential, the density of states all the way to the dissociation threshold.

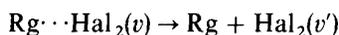
If that is not feasible, because of the large number of states, a semiclassical prescription based on the equivalence between the number of states up to a certain energy and the volume of phase space for the same energy is expected to provide an accurate esti-

mate of the density of states. This has been tested by us for the two examples HO₂ and HNO and found to work beautifully. Other cases are also reported in the literature.

Dr. A. A. Buchachenko, Mr. A. A. Granovsky, Mr. A. V. Medvedev and Prof. N. F. Stepanov communicated: The paper under discussion illustrates that the IVR-assisted unimolecular decay may follow different mechanisms, from the state specific to the almost statistical, even in triatomic systems. Taking into consideration the triatomic van der Waals (vdW) complexes, one can recover the opposite limit of direct or impulsive, unimolecular decay.

Although the quantum picture of a different decay mechanism is understood well qualitatively, there are still unresolved problems with their classical interpretation and quantum classical correspondence. Indeed, classical decay proceeds in general *via* chaotic phase-space trajectories. This means that the distinct decay mechanisms may differ classically by quite delicate features, *e.g.* the amount of phase-space available for chaotic dynamics or by the statistical properties of chaos.

In order to demonstrate some unexpected features of the classical decay dynamics, let us consider vibrational predissociation of the rare gas-halogen complexes Rg ··· Hal₂ :



the rupture of the weak bond due to the transfer of $|\Delta v| = |v' - v|$ vibrational quanta of diatomic fragment. From the viewpoint of quantum mechanics, the mechanism of this process depends strongly on the metastable state density. Hence, the $\Delta v = -1$ process is the direct discrete-continuum transition (direct mechanism), whereas $\Delta v < -1$ decay proceeds through intermediate resonance(s) (IVR-assisted mechanism). In the former case, one should expect a monotonical decrease of the lifetime with v , whereas in the latter, the lifetime varies irregularly, being crucially dependent on the position of intermediate states.¹

Classical mechanics predicts the distinct behaviour. Fig. 10 shows the results of two-dimensional quasiclassical trajectory calculations for the He ··· Br₂ complex which is known to decay *via* $\Delta v = -1$ transitions.² In contrast to the quantum case, classical lifetime dependence is irregular. Each maximum on this dependence is connected to the certain phase-space bifurcation which results in the appearance of a new stable non-linear resonance. The influence of these stable phase-space structures on the decay dynamics is very strong since, owing to the small volume of the phase space of the bound complex, a large portion of chaotic trajectories experiences a resonant trapping.

In the family of Rg ··· I₂ (Rg = He, Ne and Ar) van der Waals (vdW) complexes the first two are similar to He ··· Br₂, while the latter decays *via* the $\Delta v = -3$ channel. According to the quantum calculations, its lifetime varies strongly with v .³ On the other hand, classical mechanics does not show any qualitative difference in the lifetime patterns of these systems. As is shown in Fig. 11, they are sufficiently close to each other. Again, the strong effects of phase-space bifurcations are evident, and there is almost complete correspondence in the bifurcation sequences observed for all complexes.

These qualitative examples indicate that the simple quasiclassical relation between the quantum metastable state density and classical phase-space volume does not provide an understanding of the correspondence between classical and quantum decay dynamics even in qualitative terms. More detailed analysis of non-linear dynamics is needed for this purpose.

- 1 N. Halberstadt, J. A. Beswick, O. Roncero and K. C. Janda, *J. Chem. Phys.*, 1992, **96**, 2404; N. Halberstadt, S. Serna, O. Roncero and K. C. Janda, *J. Chem. Phys.*, 1992, **97**, 341.
- 2 D. G. Jahn, S. G. Clement and K. C. Janda, *J. Chem. Phys.*, 1994, **101**, 283; A. A. Buchachenko, A. Yu. Baigolov and N. F. Stepanov, *11th Symposium and School on High-Resolution Molecular Spectroscopy*, 1994, **2205**, 178.
- 3 S. K. Gray, *Chem. Phys. Lett.*, 1992, **197**, 86; O. Roncero and S. K. Gray, *J. Phys. Chem.*, 1995, **99**, 2512.

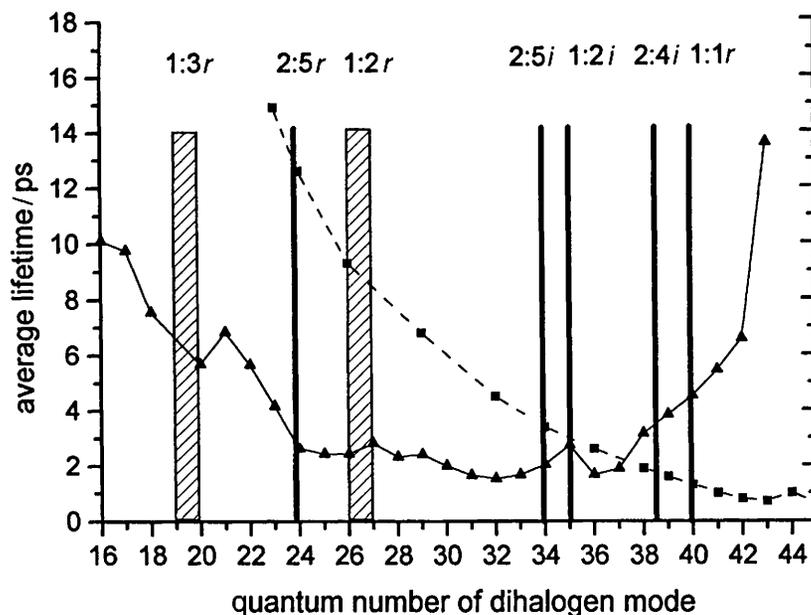


Fig. 10 Lifetimes of the $\text{He} \cdot \text{Br}_2$ complex computed by the quasiclassical trajectory (solid line) and by the quantum Fermi Golden rule (dashed line) methods within the two-dimensional model. Also shown are the phase-space bifurcations with the appearance of regular and irregular $n:m$ non-linear resonances.

Dr. Schinke replied: If classical trajectory calculations yield lifetimes that deviate significantly from the (exact) quantum mechanical calculations (see Fig. 1 of our paper), it is, at least in my opinion, not worthwhile analysing all the little details in the classical results to try to understand them in terms of non-linear dynamics effects. If the discrepancies between classical and quantum results are as severe as in Fig. 11 one should analyse the quantum lifetimes rather than the apparently wrong classical data.

Prof. Quack opened the discussion on Prof. Perry's paper: Prof. Perry addresses in his paper the central question of rovibrational redistribution, IVRR,¹ in polyatomic molecules. As a historical note I should say that the nature of this phenomenon was not originally quite adequately introduced in RRKM theory. Although rotation and angular momentum were discussed in RRKM theory, this was done by introducing one, two or three adiabatic (or 'active' or non-adiabatic) rotational degrees of freedom in the theory.

The first proper discussion of rovibrational mixing in unimolecular rate theory subject to angular momentum J (and nuclear spin) conservation, with a correct calculation of densities of states $\rho(E, J)$ and adiabatic reaction channels $W(E, J)$, was given in the adiabatic channel model (ACM).² The most frequent assumption in applications of RRKM theory was conservation of all rotational quantum numbers, it seems to me, with calculation of just the vibrational density of states ρ_{vib} and W_{vib}^\ddagger in the statistical rate formula, in contrast to what is stated in the introduction to the paper by Perry *et al.*³ One reason for this deficiency of RRKM theory was that there was actually no scheme to assign properly total angular momentum quantum numbers J to reaction channels with correct angular momentum couplings in unimolecular dissociation, for example. Again, such a scheme was developed in the ACM, where it was also speculated whether additional conserved quantum numbers such as the rotational quantum number K might be introduced. The reasoning at the time was that there is no good

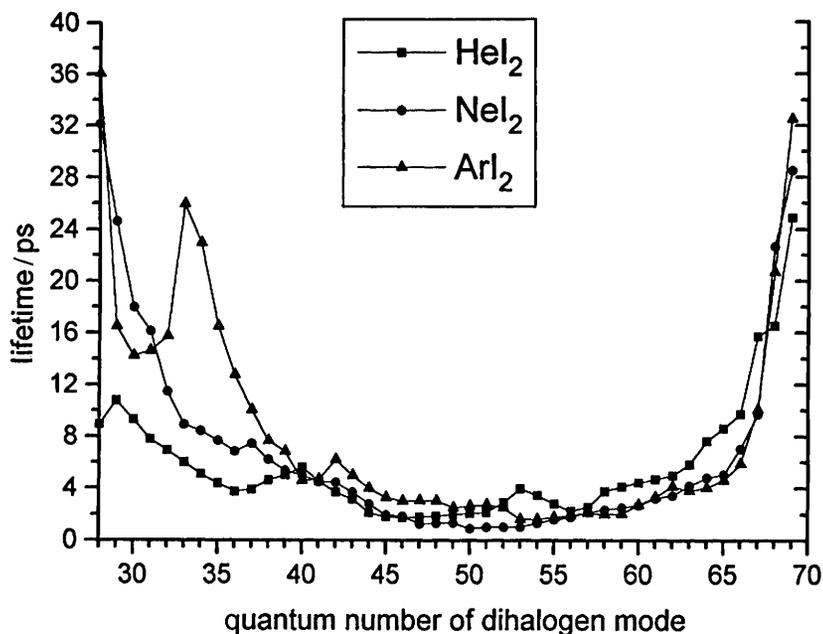


Fig. 11 Lifetimes of $Rg \cdots I_2$ ($Rg = He, Ne, Ar$) computed by quasiclassical trajectory method within the two-dimensional model

reason to treat K differently from vibrational quantum numbers, but that the quantitative degree of mixing must presumably be derived from either dynamical calculations (classical or quantum) or from experimental evidence (see the discussion in Section IV of ref. 2). It is gratifying to see now some experimental evidence on this problem being presented in the beautiful papers by Moore⁴ and by Perry *et al.*³ at this meeting.

It seems to me that nicer examples for the study of K mixing would be the symmetric top molecules such as CD_3H , CF_3H or $CF_3-C\equiv C-H$, $(CF_3)_3C-C\equiv CH$, as they have been studied in our work,⁵⁻⁸ because K would be a good quantum number in the absence of rovibrational coupling. While we have not yet analysed K mixing (or conservation) in these systems, we have looked at the conservation of the vibrational angular momentum quantum number l . Although l is not a rigorously good quantum number, it is rather well conserved on a ps timescale in the C_{3v} molecules after $l = 0$ CH stretching excitation.⁹ Of course, quite a few vibrational quantum numbers are conserved as well on such a timescale, *i.e.* there is increasing evidence that on timescales of a few ps randomization is often restricted to a subset of degrees of freedom, symmetry and adiabatic decoupling being important factors preventing complete redistribution.¹⁰

- 1 M. Quack and W. Kutzelnigg, *Ber. Bunsen-Ges. Phys. Chem.*, 1995, **99**, 231; see also whole issue.
- 2 M. Quack and J. Troe, *Ber. Bunsen-Ges. Phys. Chem.*, 1974, **78**, 240.
- 3 D. S. Perry, G. A. Bethardy, M. J. Davis and J. Go, *Faraday Discuss.*, 1995, **102**, 215.
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- 5 K. von Puttkamer, H. R. Dübal and M. Quack, *Faraday Discuss. Chem. Soc.*, 1983, **75**, 197.
- 6 H. R. Dübal and M. Quack, *Chem. Phys. Lett.*, 1982, **90**, 370.
- 7 H. R. Dübal and M. Quack, *J. Chem. Phys.*, 1984, **81**, 3779.
- 8 M. Lewerenz and M. Quack, *J. Chem. Phys.*, 1988, **88**, 5408.
- 9 D. Luckhaus and M. Quack, *Chem. Phys. Lett.*, 1993, **205**, 277.
- 10 M. Quack, *J. Mol. Struct.*, 1993, **292**, 171; 1995, **347**, 245; *Annu. Rev. Phys. Chem.*, 1990, **41**, 839.

Prof. Perry responded: Thank you Prof. Quack for your historical perspective on RRKM theory and for your suggestions of interesting systems for the study of K relax-

ation. The asymmetry mixing in ethanol and but-1-yne is very small for the rotational levels represented in the experiments.¹ Of course, true symmetric tops offer the possibility of studying l mixing as well as K mixing.

¹ J. Go and D. S. Perry, *J. Chem. Phys.*, 1995, **103**, 5194.

Prof. Troe asked: Have you investigated the energy dependence of the rate of K relaxation?

Prof. Perry replied: We have not directly investigated the rate of K relaxation on energy because the random matrix calculations are a fit to experiment and the experiment accessed total energies near 3000 cm^{-1} . However, since most unimolecular reactions occur at energies much greater than this, it is worth considering how the rate might change as the energy is increased.

In the context of rotational energy, the rotational quantum number dependence of the K relaxation rate is considered explicitly in our paper. The initial decay of the bright state becomes faster as J and K are increased, but the population of the most distant K state takes somewhat longer at high J because more steps of $\Delta K = \pm 1$ are required. The rate of relaxation of the average K does not appear to depend critically on the rotational quantum numbers.

The dependence of the K relaxation rate on vibrational energy is more to the point because it is usually vibration that is essential for the promotion of unimolecular reaction. The classical rotational period provides a natural limiting timescale for the decay of an initial rotational state as a result of Coriolis coupling. On this scale, K relaxation in ethanol is already relatively fast at 3000 cm^{-1} . The classical period at $J = 4$, $K = 0$ is *ca.* 12 ps as compared to the calculated bright state decay time of 30 ps. Thus at higher vibrational energies, the rate may increase somewhat but it would be hard to imagine a rate 10–100 times faster. The slow population of some K states is the result of multiple stages of sequential coupling, and we expect this qualitative result will carry through to higher energies. For the but-1-yne data considered, the rate of K relaxation is unobservably slow, so at higher energies, it could increase dramatically until a similar upper limit is reached.

In contrast, the corresponding limiting timescale for anharmonically induced vibrational relaxation is the classical vibrational period (10–100 fs for typical normal modes). Therefore as the energy in ethanol is increased, one could find a dramatic increase in the vibrational relaxation rate if some strong anharmonic resonances come into play.

Dr. Delon said: I do not understand why, on Fig. 5, 6 and 7 of your paper which correspond to a strong IVR, you did not observe any so called 'correlation hole'. This correlation hole should be observed for a time longer than the survival probability and shorter than the density of states in the clumps. It corresponds to the correlations among levels of the bath–bright system. For a time longer than the density of levels, the system recovers a fraction of its initial state (given by the dilution factor ϕ), which is a purely quantum effect. At the limit of a redistribution towards the continuum, the process becomes fully irreversible.

I do not see any reasons for which, when increasing sufficiently the statistic, such a correlation hole should not appear. As an example, it has been observed for rovibronic clumps of NO_2 , both on experimental data and on the corresponding simulations: see ref. 1.

¹ A. Delon, R. Georges and R. Jost, *J. Chem. Phys.*, 1995, **103**, 7740.

Prof. Perry answered: Whether or not a correlation hole should be expected in the bright state survival probabilities that we have calculated is an interesting question.

However, to be honest, we had not thought of it up to now and therefore made no attempt to look for one. A correlation hole reflects the repulsion between levels that results from the coupling between them. Such a hole is most marked when all intensities are set equal before Fourier transforming the spectrum, but, as you point out, it can still be discernible when actual spectral intensities are used if the strength of the coupling and the extent of averaging are sufficient.

Our calculations averaged only decays computed from pure sequence spectra and the anharmonic interactions among the bath states were strong enough to approach the GOE limit.¹ However, we also included tiers of rotational states which were coupled by Coriolis coupling in steps of $\Delta K = \pm 1$. The Coriolis coupling was not strong enough for the final distribution over K states to reach the statistical limit (Fig. 3 of our paper). This implies that the intensity distribution did not reach the GOE limit. Since it converges to GOE more slowly than the intensity distribution, the level-spacing distribution cannot be close to GOE. The correlation hole could then be washed out by a larger number of weakly coupled, closely spaced levels. It is therefore reasonable that no correlation hole is seen in Fig. 5, 6 and 7 of our paper.

One still might expect to see a correlation hole in Fig. 4 of our paper where only $J = 0$, $K = 0$ is involved. For this case, the relevant density of states, which is only the purely vibrational density of states (10 cm/symmetry), is much less than for the other figures. Therefore, the correlation hole would extend well beyond the limited time interval plotted in Fig. 4. Also, for our calculation the anharmonic coupling of the bright state to the bath is much weaker than the anharmonic coupling among the bath states. For these reasons, it is not too surprising that a correlation hole is not easily visible in Fig. 4.

1 D. S. Perry, *J. Chem. Phys.*, 1993, **98**, 6665.