# General Discussion

**Dr Langford** opened the discussion of Prof. Butler's paper: In the work presented by Prof. Butler and co-workers on nitric acid photodissociation the dominant $OH + NO_2^*$ product channel that they have as yet not assigned has also been seen by J. R. Huber in Zurich[1] who additionally could not see the coincidentally produced $NO_2$ fragment. Is there any evidence for a three-body fragmentation or crossing to a dissociative parent triplet state? The latter mechanism has been shown to be important in recent work in Bristol on $HCOOH$[2] and $HFCO$[3] photodissociation following analogous $n \rightarrow \pi^* C{=}O$ parent electronic excitations.

1 P. Felder, X. Yang, J. R. Huber, *Chem. Phys. Lett.*, 1993, **215**, 221.
2 S. R. Langford, A. D. Batten, M. Kono and M. N. R. Ashfold, *J. Chem. Soc., Faraday Trans.*, 1997, **93**, 3757.
3 C. L. Reed, M. Kono, S. R. Langford, R. N. Dixon and M. N. R. Ashfold, *J. Chem. Soc., Faraday Trans.*, 1997, **93**, 2721.

**Prof. Butler** responded: First, let me compare the assignments of our work and of Huber's to which you refer. They had very similar data to ours, but misassigned both $OH + NO_2$ channels. The one producing the higher relative kinetic energies, where the $NO_2$ product survives secondary dissociation, was tentatively assigned in their paper to production of ground state $NO_2$, but we show in our paper that this channel corresponds to $OH + NO_2$ $(1\,^2B_2)$, the adiabatic dissociation product on the $2A'$ potential energy surface. The second channel, the more probable one to which you refer, produces $NO_2$ which undergoes secondary dissociation. Huber speculated that this was electronically excited $NO_2$ formed on the $2A'$ potential energy surface calculated by Bai and Segal (the asymptote should be the $1\,^2B_2$ state of $NO_2$ but was mistakenly given in both papers as the $1\,^2B_1$ state), but our paper showed this was the product corresponding to the other kinetic energy distribution (see Fig. 3). Thus, the stable $NO_2$ product is $NO_2$ $(1\,^2B_2)$, not ground state $NO_2$ as Huber thought, and the unstable $NO_2$ product is a higher excited state of $NO_2$ that predissociates, not the $NO_2$ $(1\,^2B_2)$ product that the $2\,^1A'$ surface correlates to adiabatically.

I do have a reasonable guess as to what this $NO_2$ product is that undergoes secondary dissociation, and it does indeed, as you suggest in your question, require intersystem crossing to the triplet manifold of nitric acid. The measured kinetic energy distribution in our experiment clearly showed that this second $OH + NO_2$ dissociation channel did not give $NO_2$ in any of the three low-lying doublet excited states, but rather a higher excited electronic state of $NO_2$. At our photon energy, the only other excited states of $NO_2$ that are energetically allowed are two quartet states of the $NO_2$ product; their high energies are roughly consistent with the very high energies partitioned into internal energy of the $NO_2$ product in this second channel, but we did not get a quantitative match when we did the same Franck–Condon analysis as we did for the channel producing $NO_2$ $(1\,^2B_2)$. Thus, the assignment is not definitive. Of the two possible quartet states, we speculate that the more likely product is the $NO_2$ $^4B_2$ excited state because this product state has the same character electronic configuration as the initially excited $\pi_{nb, O} \rightarrow \pi^*$ nitric acid state excited at 193 nm, thus this channel requires a change in spin, but not of orbital character. It is given in the nitric acid triplet correlation diagrams in our full paper on nitric acid, ref. 12 of our paper in this volume. I did find it surprising that a channel requiring intersystem crossing to a triplet state would compete on the timescales suggested by the anisotropic angular distributions; one can

only presume that there is a crossing between the singlet and triplet surfaces that facilitates this.

**Prof. Gerber** asked: In my view, the approach of Prof. Butler based on semi-quantitative analysis of electronic structure matrix elements is very promising. Two technical issues are: (a) is it sufficient to consider through space energy transfer, or can through band transfer dominate; (b) is it not difficult to use the magnitude of the matrix element for energy transfer as a criterion, given that the magnitude is enormously sensitive to the configuration?

**Prof. Butler** answered: Thank-you for the interest. I think the most important aspect of this work is an attempt to look at the dominant electronic configurations of the reactant and the electronic configuration of potential energetically allowed products to give us back-of-the-envelope predictive ability for what product channels, both adiabatic and nonadiabatic, are electronically accessible to a reactive system. It is clear that one must go beyond considering just the barrier height and steric factors of potential product channels.

With regard to your question on the mechanism in the case of the two-electron configuration change required along the $C-Br$ fission adiabat in bromoacetyl and bromopropionyl chloride, a configuration change corresponding to intramolecular electronic energy transfer, I think that at separations of one or two $CH_2$ units, the through space mechanism is dominant, but our experiments do not directly probe this. It is interesting to note that our crude *ab initio* calculations of the splitting between adiabats along the avoided crossing seam, giving us (in a two-state model) the off-diagonal coupling matrix elements (obtained for the conformers where the $C-Br$ bond is in the same plane as the $C=O$ bond), indicate the matrix element for the intramolecular energy transfer goes down a factor of ten when one goes from one to two intervening $CH_2$ groups. This is in close accord with Closs's and many subsequent studies of the distance dependence of intramolecular energy transfer and electron transfer (if one views energy transfer as a double electron transfer). I agree that calculating such small off-diagonal matrix elements accurately is problematic, but the qualitative trend as to what configuration interaction matrix elements are likely to be small is a clear and informative one. I should comment that our early attempts to use semiempirical electronic structure calculations (ZINDO) gave very poor results for the splitting between adiabats along the $C-Br$ fission reaction coordinate for these systems, despite the fact that those semiempirical packages claim to include some configuration interaction, so I do not recommend such calculations even for qualitative purposes when there are intervening $CH_2$ groups.

**Dr Fuß** asked: (i) Would you comment on the origin of the barriers which you showed? I am used to situations where the dissociation of an organic halide just proceeds along a purely repulsive surface.

(ii) Can your model make quantitative estimations as to what extent the energy flows to the less probable state? We once investigated the photodissociation of a di-iodide with two slightly different end groups:[1] $I-CH_2CH_2CF_2CF_2-I$. The absorption is practically localized in the end groups, and the two absorptions are slightly shifted against each other so that selective excitation is possible in the wings. In fact, we found that the selectivity of dissociation is equal to the selectivity of absorption. We asked ourselves how much shortening of the insulating chain is possible without destroying the selectivity. In 1,2-di-iodides there is already a one-electron interaction, except probably if in such a 1,2-di-iodide the two $C-I$ bonds have perpendicular orientation. Would the two-electron integrals be small enough? Your model might give an answer.

1 L. Zhang, W. Fuß, K. L. Kompa, *Chem. Phys.*, 1990, **144**, 289; W. M. Kwok, W. Fuß, D. L. Phillips, *Chem. Phys. Lett.*, 1996, **261**, 685.

**Prof. Butler** replied: (i) To your first question, in the alkyl halides the repulsive $n\sigma_{C-X}*$ states that you refer to are well characterized; in the bromoacetyl and bromopropionyl chloride that same group of configuration states is present, but they undergo an avoided crossing with the bound $n\pi_{C=O}*$ configuration, forming the barrier you see in these systems. In bromopropionyl chloride, a fraction of the molecules absorbing the photon directly access the upper adiabat where its character is repulsive $n\sigma_{C-X}*$ (we have subtracted those from the data); direct C—Br fission then occurs, but to do this it must traverse the avoided crossing diabatically, just as most of the trajectories do that are excited to the lower adiabat. I should comment that we have swept strong spin–orbit coupling under the rug so as not to obscure the differing orbital character of the configurations involved.

(ii) To your second comment, that is a beautiful experiment that I was not aware of. The only light I can shed on this is the following. We do indeed expect a marked conformation dependence to the configuration interaction matrix elements. We have proved this directly by experiment and calculation on C—Cl fission in allyl chloride.[1] As you would expect, when the one-electron matrix elements can contribute, evidenced by the mixed character of the orbitals in an orthogonal basis in a typical *ab initio* calculation, the configuration interaction matrix elements get much larger. I would think that for the molecule you show, with four intervening carbons that one could view the electronic excitation as being to two uncoupled locally excited repulsive electronic states, consistent with your experimental results. Guessing from our work on 1-bromo-3-iodopropane[2] (where the coupling between the locally excited configurations would evidence itself not in the absorption spectrum but in the avoided crossing outside the Franck–Condon region which influences the C—Br : C—I product branching ratios) excited in the $n_{Br}\sigma_{C-Br}*$ region of the absorption spectrum at 222 nm, the uncoupled nature of your states would degrade even with one fewer intervening group. We observed 80% C—Br fission and 20% C—I fission, so 20% of the molecules did not reach the diabatic asymptotic products. The coupling matrix elements between the $n_{Br}\sigma_{C-Br}*$ and the $n_I\sigma_I*$ configurations must thus be non-negligible, although if the matrix elements were too large these systems are excited to a bound adiabat so would not evidence the subpicosecond dissociation times they do! Interestingly, the photodissociation of $CH_2BrI$ (ref. 3) was highly selective for C—Br fission over C—I fission, again evidencing the dependence of the matrix elements on relative orientation of the orbitals involved as you speculate, but our understanding of this selectivity is not quantitative. However, the bond angle in $CH_2I_2$ is not sufficiently close to 90° to suppress the coupling, as is evident from its absorption spectrum (it does not show an A absorption band consistent with two non-interacting repulsive configurations, it differs markedly from $CH_3I$) so I would not expect the 1,2-di-iodo compound you suggest to show the same selectivity as your 1,4 compound. We of course considered the obvious experiment on halogen substituted cyclohexanes to control the conformation, but those compounds were too expensive for us!

1 T. L. Myers, D. C. Kitchen, B. Hu and L. J. Butler, *J. Chem. Phys.*, 1996, **104**, 5446.
2 J. E. Stevens, D. C. Kitchen, G. C. G. Waschewsky and L. J. Butler, *J. Chem. Phys.*, 1995, **102**, 3179.
3 L. J. Butler, E. J. Hintsa, S. F. Shane and Y. T. Lee, *J. Chem. Phys.*, 1987, **86**, 2051.

**Prof. Guo** asked: Have you seen any exceptions to the rules based on the electronic coupling matrix elements?

**Prof. Butler** answered: This hierarchy in what electronic configuration changes are inaccessible to a molecule is relatively new, so most experiments have not been re-analyzed with testing this model in mind. There is a qualitative aspect to the hierarchy,

as of course even one-electron configuration changes are difficult if they involve electron transfer over long distances, so one must keep this in mind. The most rigorous test is from systems with more than one energetically allowed product channel where the adiabatic barrier heights and steric factors can be accurately calculated from first principles, so we can compare the experimental results with the adiabatic prediction. These are hard to come by.

As for any apparent exceptions to the electronic inaccessibility of particular product channels, the case of the condensed phase photodissociation of *p*-methoxybenzylalcohol is an interesting one.[1] It is crudely analogous to nitric acid analyzed in our paper in this volume, except the product channel with two electrons in the in-plane (the plane being perpendicular to the benzene ring) non-bonding orbital of the OH is observed. This then is a two-electron change in configuration involving two functional groups, but it might be useful to look at an electronic structure calculation to see if there is significant mixing between this OH orbital and the $\pi^*$ orbitals of the benzene. It is hard to conclude that this is an exception to the qualitative hierarchy in matrix elements since this observed channel only has a quantum yield of 1/1000, but it would be an interesting case for theoretical study.

1 M. Fujiwara and K. Toyomi, *J. Chem. Phys.*, 1997, **107**, 2829.

**Prof. Neumark** said: In your first example, the photodissociation of bromoacetyl chloride, both the C—Cl and C—Br bond fission channels occur *via* two-electron configuration interaction matrix elements. How do you explain the propensity for C—Cl dissociation within the intuitive model discussed in your paper?

**Prof. Butler** responded: This is a competition between two channels that are non-adiabatically suppressed, the C—Br fission more so than the C—Cl fission. There is an intramolecular distance dependence to the matrix elements (adding a $CH_2$ group decreases the splitting at the avoided crossing by a factor of 10, as you can see from the comparison of the off-diagonal matrix elements in bromoacetyl, *vs.* bromopropionyl, chloride) so it is easy to see why C—Br fission would be more suppressed than C—Cl fission in bromopropionyl chloride. I should note, however, that on the basis of the differences in splitting alone, the C—Br to C—Cl fission ratio in bromoacetyl chloride is hard to understand. (It is also difficult to get a good back-of-the-envelope guess based on Landau–Zener theory, since the splitting along the avoided crossing seam varies along the seam so markedly for C—Cl fission, and in such a non-obvious way, see Table I in ref. 7 of our paper.) There may be an effect of non-statistical sampling of the transition states that is also playing a role, although it is plain from the *ab initio* calculations that C=O stretching dominates the first motion out of the Franck–Condon region. All that said, the comparison between C—Br fission in bromoacetyl and bromopropionyl chloride is compelling to anyone that one should not assume that the barrier height in the controlling factor for the branching, non-adiabatic suppression of the reaction rates (both are suppressed, but C—Br fission is much more than C—Cl fission in bromopropionyl chloride) is playing the dominant role.

**Dr van der Zande** asked: Adiabatic and diabatic states are already complex entities in diatomics, let alone in polyatomics.

(i) Is your model restricted to direct dissociation or does it survive long-lived complexes?

(ii) What kind of derivative coupling dominates non-diabatic interactions: is it $\delta/\delta R_{ij}$ (where $R_{ij}$ is the interatomic coordinate) or a more complex derivative and why?

**Prof. Butler** responded: (i) This model is more appropriate for systems which have a chance to sample the transition states of all energetically allowed reaction coordinates, so is more applicable to long-lived complexes than to direct dissociation.

(ii) I should first comment that the transformation to an approximately diabatic basis is only an approximate one when there is more than one internuclear degree of freedom; I refer to an approximate diabatic basis in the paper to give people a qualitative feel for what kind of matrix elements (before diagonalizing the electronic Hamiltonian) are needed to help the electronic wavefunction change en route along the adiabatic potential energy surface. It is much better in any calculation to treat the problem in the adiabatic representation with derivative coupling in the equations for nuclear motion. That said, in the systems I have presented in this paper, the dominant term driving the nonadiabaticity is the $\partial/\partial R_{ij}$ term you refer to. (You can think of it as an interatomic distance to first order, but keep in mind that the derivative coupling depends on what the geometry of the rest of the molecule is as the molecule traverses the avoided crossing). In other systems, because the Born–Oppenheimer approximation neglects the $\partial/\partial R$ term where this term involves the vector $R$, other terms like Coriolis coupling can result in electronic non-adiabaticity, and geometric phase and second derivative terms can play a role. There is also a problematic convention with what to do with spin–orbit coupling. Tully (ref. 3 in our paper) reviews all the terms left out in the Born–Oppenheimer approximation, (except he sets a phase to zero so does not have the geometric phase term; geometric phase is reviewed clearly in ref. 4 and papers therein).

**Prof. Hutson** opened the discussion of Prof. Gerber's paper: Your paper shows that the recombination probability for HCl photodissociation in Ar clusters is greater for the two-shell $n = 54$ cluster than for the single-shell $n = 12$ cluster. An obvious interpretation of this is as a simple steric effect, arising because the second-shell atoms sit behind and block gaps in the first shell. However, there are other effects that might be important: for example, the second and subsequent shells compress the first shell, contracting the holes in it and making it more rigid. Burkhard Schmidt's poster presented at this meeting demonstrates that the compression also causes qualitative changes in the anisotropic potential experienced by the HCl molecule. Do you have a feeling for which physical effects actually matter most for the cageing probability?

**Prof. Gerber** responded: We did not carry out a detailed analysis of this interesting question. My impression is that the increased steric hindrance in the two-shell system is the main cause for the higher recombination yield. Also, the non-adiabatic transitions are enhanced in a direction that favours increased recombination. However, the compression effect definitely plays a significant role.

**Dr Schmidt** commented: As an addition to the presentation by Prof. Gerber I would like to mention our recent work on the quantum dynamics of photodissociation of HCl in Ar matrices which in many respects resembles the photodissociation in clusters having complete solvation shells. In our treatment of the dissociation process, the excited state dynamics is modelled by time propagation of representative wavepackets. The time-dependent Schrödinger equation is solved in order to describe the fully three-dimensional dynamics of the H atom while the remaining atoms are considered to be rigid ($T = 0$ K). As an additional approximation we neglect non-adiabatic transitions. Both approximations can be justified for the short timescales ($t \leqslant 50$ fs) considered in our work.

Because small hydrides like HF and HCl are known to be nearly freely rotating in Ar matrices, our emphasis is on the role of the initial orientation of the guest molecule with respect to the crystallographic axes of the rare gas matrix. Indeed, preliminary calculations based on classical trajectories showed a strong dependence of the cage effect on the initial orientation of the HCl molecule.[1] This points to the important role of the initial rotational state of the guest molecule in a quantum mechanical treatment.

Examples of rotational wavefunctions in the electronic ground state and corresponding wavepacket dynamics in the excited state are shown in Fig. 1. As a consequence of the relatively weak coupling in the ground state, the rotational ground state ($J = 0$, $A_{1g}$) of HCl in Ar is almost completely isotropic (c). The corresponding dynamics of the radial wavepacket is also shown. Driven by the short range repulsion of the excited state, after 7.5 fs the wavepacket reaches the region of the nearest neighbour atoms at $r \approx 0.25$ nm where a first bifurcation of the wavepacket occurs. Some probability amplitude is reflected by the matrix atoms while the remainder is transmitted. The latter
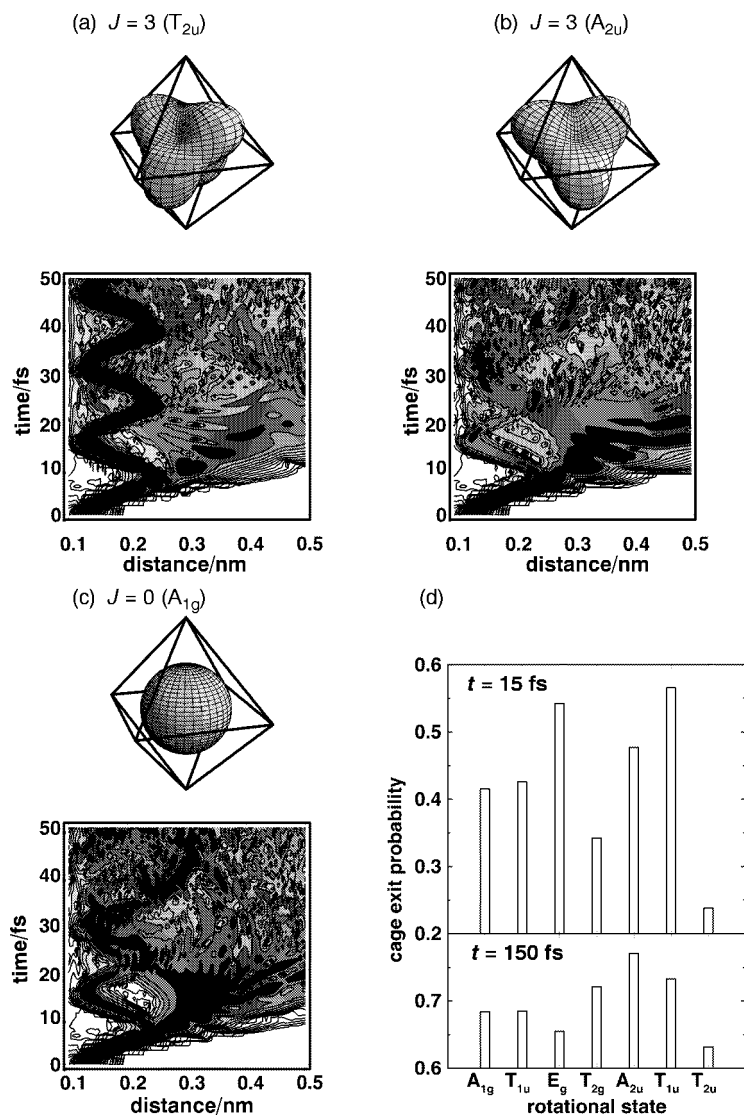


**Fig. 1** Quantum dynamics of photodissociation of HCl in an Ar matrix. (a), (b) and (c) show the initial rotational state of the HCl molecule together with the corresponding dynamics of the radial wavefunction upon dissociation. Here two different substates of the $J = 3$ level and the $J = 0$ level induced by the interaction with the matrix are illustrated. In (d) a summary of our results is given showing the cage exit probability *vs.* initial rotational state.

undergoes another bifurcation at the position of the second-nearest neighbours ($r \approx 0.35$ nm) after 15 fs. Another typical quantum phenomenon can be seen from the interference patterns where two wavepackets come together again.

As an example of rotationally excited states, two different states of the $J = 3$ manifold are compared in Fig. 1(a) and (b). The $T_{2u}$ state, with its preferential orientation along the $\langle 110 \rangle$ direction, is strongly influenced by the twelve nearest neighbour atoms. The wavepacket undergoes almost coherent oscillations inside the cage with very little cage exit. In contrast, the $A_{2u}$ rotational state is peaked along the $\langle 111 \rangle$ channels of the fcc lattice. Consequently, the wavepacket dynamics exhibits almost unhindered separation of the photofragments.

Our results are summarized in Fig. 1(d) where the cage exit probability as a function of the initial rotational state is illustrated. After one vibrational period (15 fs) this probability varies between 25% and 55%.[2] These results imply a new way to control the quantum yield of an elementary photochemical reaction and open the way for a rotationally mediated photochemistry of molecules in an ordered environment such as a rare gas cluster or matrix. (Supported by the Deutsche Forschungsgemeinschaft through SFB 337.)

1 B. Schmidt, P. Jungwirth and R. B. Gerber, in *Femtochemistry*, ed. M. Chergui, World Scientific, Singapore, 1996.
2 J. Manz, P. Saalfrank and B. Schmidt, *J. Chem. Soc., Faraday Trans.*, 1997, **93**, 957.

**Prof. Gerber** responded: Dr Schmidt's calculations show that quantum effects associated with the H atom motion can be quite important for this system. Our paper showed that the role of non-adiabatic transitions in photolysis of HCl in Ar is a major one. It thus seems desirable to pursue calculations which include non-adiabatic transitions, and at the same time treat the H atom quantum mechanically. Such challenging calculations have not yet been carried out.

**Prof. Alexander** commented: The DIM method described by Gerber and co-workers seems to neglect the $H^+Cl^-$ component of the HCl ($X\,^1\Sigma_g^+$) wavefunction. It is this component that is responsible for both the deep well in this state, as well as for the oscillator strength of the $A\,^1\Pi \leftarrow X\,^1\Sigma_g^+$ transition. In the trajectory simulations, neglect of this component, and hence the deep well in the X state, may affect the ease with which caged systems leave the X state.

There has been considerable interest in the determination of the Cl atom spin–orbit branching ratios subsequent to the photodissociation of free HCl.[1–9] The wavelength dependence of these branching ratios is a measure of the dependence on intermolecular distance of the HCl valence state potentials and the relative magnitudes of the couplings and splittings between these. Presumably, the presence of one (or more) Ar ligands will affect these branching ratios and hence shed light on the HCl–Ar potentials in both the ground and electronically excited states. Have you thought of extracting these branching ratios for the HCl fragments which fragment while escaping from the cluster?

1 S. C. Givertz and G. G. Balint-Kurti, *J. Chem. Soc., Faraday Trans.*, 1986, **82**, 1231.
2 M. H. Alexander, B. Pouilly and T. Duhoo, *J. Chem. Phys.*, 1993, **99**, 1752.
3 T. Duhoo and B. Pouilly, *J. Chem. Phys.*, 1995, **103**, 182.
4 I. H. Gersonde, S. Hennig and H. Gabriel, *J. Chem. Phys.*, 1994, **101**, 9558.
5 J. Park, Y. Lee and G. W. Flynn, *Chem. Phys. Lett.*, 1991, **186**, 441; 1992, **192**, 138.
6 Y. Matsumi, P. K. Das, M. Kawasaki, K. Tonokura, T. Ibuki, G. Inoue, S. Satyapal and R. Bersohn, *J. Chem. Phys.*, 1992, **97**, 5261, and references therein.
7 R. Liyanage, Y. Yang, S. Hashimoto, R. J. Gordon and R. W. Field, *J. Chem. Phys.*, 1995, **103**, 6811.
8 J. Zhang, M. Dulligan and C. Wittig, *J. Chem. Phys.*, 1997, **107**, 1403.
9 H. M. Lambert, P. J. Dagdigian and M. H. Alexander, *J. Chem. Phys.*, 1998, **108**, 4460.

**Prof. Gerber** responded: The suggestion of computing the branching ratio is a very useful one. In recent work, we estimated the effect of clustering on the $P_{3/2} : P_{1/2}$ branching ratio for a somewhat different system: HCl absorbed on the surface of an $Ar_{12}$ cluster; Prof. Buck at Gottingen is planning to measure this.

On the ionic contribution to DIM: physically, the ionic forms certainly contribute. Here, the semiempirical DIM potentials were fitted to yield the known potential curves of 'bare' HCl. The deep well in the X state is thus correctly there, and this problem does not arise.

**Prof. Schatz** asked: I have two questions about your TSH algorithm. This algorithm is similar to Tully's, but it differs in some potentially important ways, though in such a way that it is not clear to me which is going to be better for this particular application. You compare instantaneous probabilities with a random number to decide whether to hop. Do you then reinitialize the orbital coefficients before continuing the integration so as to avoid chattering between states? Second, what do you do if a transition is forbidden?

**Prof. Gerber** answered: We actually tested Tully's algorithm against the version used here, for the purposes of this paper. The results are very similar when a sufficient number of trajectories is used. As Prof. Schatz has suggested, we reinitialize the orbital coefficients after each hopping event. Although our variant gives results similar to Tully's, other modifications of 'surface hopping' can actually lead to significantly different results. The choice of nuclear momenta after hopping events can, for instance play a significant role. For 'weak coupling' non-adibatic systems, different algorithms can give very different results.

The extensive symmetry breaking in this system (due to the Ar atoms and to the large amplitude motions away from the initial configurations) is such that forbidden transitions do not play a significant role. In general, such transitions must be treated on an *ad hoc* basis in systems where the issue arises—the problem can be addressed by adding suitable constraints.

**Dr Balint-Kurti** said: I am concerned by the use of a 'two-electron' picture of the electronic structure of HCl [eqn. (2) of your paper]. If taken literally this representation would lead to an incorrect ordering of the $^2P_{1/2}$ and $^2P_{2/3}$ states of the Cl atom. We have shown how a similar description of the bonding of HCl may be given in terms of an 'all valence electron' model.

1 S. C. Givertz and G. Balint-Kurti, *J. Chem. Soc., Faraday Trans. 2*, 1986, **82**, 1231.

**Prof. Gerber** responded: From a formal point of view, an 'all electron' approach seems more satisfactory. However, the DIM potentials in our study were obtained semi-empircally, using empirical Ar–Cl($^2P$) interactions provided in terms of a single p-orbital orientation only, *etc*. We believe that for this determination of the DIM surfaces, the 'all electron' approach would give identical results to our 'two-electron' model. The 'all electron' approach could provide an improvement only if one could use additional input data or calculations, beyond those we employed.

**Prof. Apkarian** commented: To dissect chemistry in condensed media, it is imperative to learn how to treat coupled electronic–nuclear dynamics, or non-adiabatic dynamics controlled by many-body interactions. The challenge to theory in this regard is two-fold, determination of off-diagonal matrix elements that connect adiabatic surfaces, and the treatment of the surface switching process which is inherently quantum in nature. To this end we have sought to provide detailed experimental data in model

systems. There now are several quantitative investigations of solvent induced non-adiabatic dynamics of diatomics isolated in rare gas matrices which can be used as models to test theoretical treatments of the subject. Three main effects can be identified.

(i) Differential solvation of electronic states, whereby the solvent can dramatically shift the couplings. A good example of this was provided in studies of SH(A) isolated in solid Ar and Kr.[1] In the gas phase, SH(A) is known to predissociate *via* nearby lying dissociative surfaces, even in the vibrationally relaxed state which is presumed to undergo tunneling predissociation *via* a($^4\Sigma^-$) state. A detailed analysis of this process is presented in a poster at this meeting by Wheeler *et al.* In rare gas solids, and for that matter upon complexing with a single rare gas atom, the A state which correlates with S($^1$D) is stabilized while the dissociative states that correlate with S($^3$P) are destabilized. As a result, the predissociation channel is completely blocked and SH(A) relaxes strictly radiatively.

(ii) Electrostatic perturbation induced by the solvent is the most natural coupling to consider, and $I_2$(B) in various condensed phase media has served as a model system for the dissection of this mechanism. The B($^3\Pi_{ou}$) state of iodine is crossed by a variety of dissociative surfaces, however, the couplings are weak enough in the molecule such that in the gas phase the B state relaxes by radiation on $\mu$s timescales. In the liquid phase, predissociation is extremely fast, with a probability of 50% per vibrational period, and the dominant channel is ascribed to the a($1_g$) surface.[2,3] In solid rare gases, this probability reduces to *ca.* 5% per period, even though the local density of perturbers is significantly higher.[3] This could be very nicely quantified using off-diagonal matrix elements extracted from a diatomics in molecules analysis of $I_2$–Rg interactions.[4] The main effect can be understood by noting that the solvent induced coupling surface $V_{12}$ between $O_u$ and $1_g$ surfaces of iodine is dominated by the dipolar term of odd parity, which when summed over a symmetric distribution of perturbers (in sites of cubic symmetry) leads to cancellation.[3] This dramatic collective effect should be quite general, since the leading term in electrostatic expansions is the dipolar coupling. Quite clearly higher multipolar interactions can be effective, but their contributions will be much weaker, as is the case for magnetic coupling, or the external heavy atom effect.

(iii) Non-adiabatic transitions induced by the anisotropy of solute–solvent atom–atom interactions is another mechanism which will dominate where the molecular bond stretches far enough to switch the quantization axis. Time resolved studies of $I_2$ isolated in rare gas solids has allowed clear documentation of this effect in a variety of electronic states. In the case of the B state, when prepared near the lower part of the potential where the main crossings are located, $I_2$(B) is observed to predissociate on timescales of several picoseconds, after many vibrational periods (see Fig. 2). However, in solid Xe, when prepared at wavelengths shorter than 546 nm, the molecule is observed to undergo a fast non-adiabatic transition to the manifold that correlates with I($^2$P$_{3/2}$) + I*($^2$P$_{1/2}$), *i.e.* to states that asymptotically mix with the B state (see Fig. 3). These statements can be directly read from the pump–probe data provided in Fig. 2. At pump wavelengths between 580 and 556 nm the molecule is observed to undergo *ca.* eight regular oscillations in the B state prior to predissociation. When prepared between 546 and 510 nm, the outgoing packet on the B state can be observed as the sharp resonance at a delay of *ca.* 170 fs. However, less than 10% of the packet returns on the B state as evidenced by the vanishing intensity in the recoiling packet at *ca.* 400 fs. The coherence is revived on an unmistakably different electronic surface after 600 fs, where it can be observed to oscillate with a period of *ca.* 800 fs on at least two surfaces of similar character. These final states can be identified as the cage-bound I*I potentials, of which there are ten that coalesce on the cage wall. The assignment is based on consideration of the probe resonance (see Fig. 3) and on the fact that the probability of this transition increases as we reach the dissociation limit of the B state.

The most physical description of this effect is obtained when considering the elec-
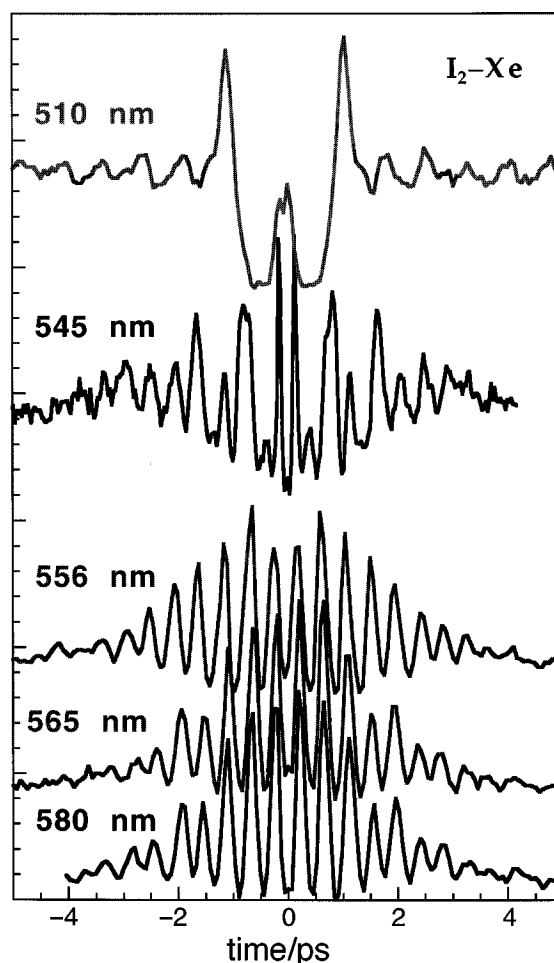
**Fig. 2** Single color pump-probe measurements of $I_2$ isolated in solid Xe (wavelengths indicated in the figure). Near the bottom of the potential, between 580 and 556 nm, the vibrational coherence evolves on the B state, showing regular oscillations with the vibrational period of a significantly softened B potential, and decays due to predissociation *via* the lower crossings (see Fig. 3). At 545 and 510 nm, the first resonance after $t = 0$ is due to the outgoing packet on the B state, the second resonance which is barely visible in the 510 nm data, is due to the returning packet on the B surface. The subsequent oscillations show coherent vibrations after a non-adiabatic transition to a new surface, with a vibrational period of *ca.* 800 fs. The final surface is assigned to the cage-bound I*–I potentials (see Fig. 3).

tronic orbitals (spin-orbitals).[5] Given the anisotropy of the $I(^2P)$ interaction with a rare gas atom ($\Pi$ or $\Sigma$ approach), an electronic torque will be exerted when upon stretching the I atom collides with rare gases at angles other than 0 or $\pi/2$ (relative to the electronic coordinate).[5] To flip orientation, which is equivalent to changing states, the torque must be larger than the I–I interaction. Indeed this non-adiabatic transition is only observed in Xe, where the cage provided by the lattice is large enough to allow the molecule to stretch out to *ca.* 5 Å to collide with the cage atoms.

While the above categorization of solvent effects is useful, it should be recognized that in a given system all three mechanisms—differential solvation, electrostatic coupling, and potential anisotropy induced transitions—occur simultaneously. This is true
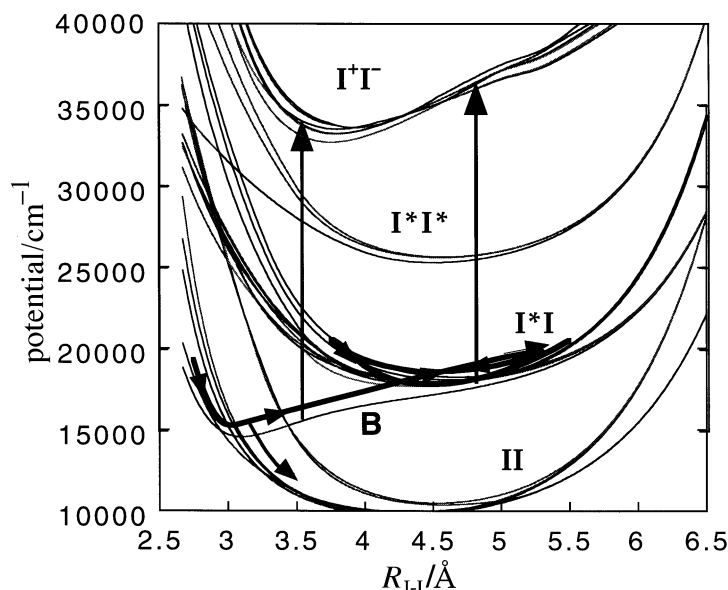
**Fig. 3** Potentials of $I_2$ isolated in solid Xe relevant to the pump–probe measurements in Fig. 2. When the population is created high up on the B surface, a small fraction leaks *via* the lower crossings, while the majority undergo a cage induced non-adiabatic transition to the cage-bound manifold of I*–I potentials. The probe transitions are indicated by the vertical arrows.

for the simulations of HCl–Ar discussed by Gerber *et al.* It is worth noting that quantitative comparisons are possible between theory and experiment, as in the case of the simulations of $I_2$ by Batista and Coker,[4] and our own experiments,[3] the discrepancy is disconcerting.

1  J. Zoval, D. Imre and V. A. Apkarian, *J. Chem. Phys.*, 1993, **98**, 1.
2  N. F. Scherer, D. M. Jonas and G. R. Fleming, *J. Chem. Phys.*, 1993, **99**, 153.
3  R. Zadoyan, M. Sterling, M. Ovchinnikov and V. A. Apkarian, *J. Chem. Phys.*, 1997, **107**, 8446; R. Zadoyan, M. Sterling and V. A. Apkarian, *J. Chem. Soc., Faraday Trans.*, 1996, **92**, 1821.
4  V. Batista and D. Coker, *J. Chem. Phys.*, 1996, **105**, 4033; 1997, **106**, 7102.
5  W. G. Lawrence and V. A. Apkarian, *J. Chem. Phys.*, 1994, **101**, 6648.

**Prof. Gerber** responded: The calculation of non-adiabatic dynamics in condensed phases or in large molecular systems is a major open problem. The semiclassical state of the art 'surface hopping' methods are the best available level at present, but doubts as to their validity remain. It seems essential in this field to extend further applications to experimentive systems, while attempting to test and improve the methods.

**Prof. Ashfold, Dr Langford** and **Dr Orr-Ewing** communicated: Amidst all this discussion of the huge strides now being made in our understanding of photochemistry of molecules embedded in rare gas clusters, Prof. Gerber reminds us of the chastening fact that our detailed level of understanding of the photochemistry of the corresponding isolated gas phase molecule is still far from perfect. Hydrogen halides, HX (X = I, Br, Cl) have long been regarded as 'benchmark' systems, where we might reasonably expect very good accord between experiment and theory when considering such properties as, for example, the branching ratio between dissociation pathways (1) and (2)

$$HX + h\nu \rightarrow H + X(^2P_{3/2}) \tag{1}$$

$$HX + hv \rightarrow H + X^*(^2P_{1/2}) \tag{2}$$

leading to the two possible spin–orbit states of the halogen atom product, the recoil anisotropies exhibited by these two product channels, and the way these observables vary as a function of excitation wavelength. To this end, we have reinvestigated the near UV photochemistry of jet-cooled HI and HBr molecules using the technique of H (Rydberg) atom photofragment translational spectroscopy[1,2] to provide the definitive experimental measurements necessary for any rigorous comparison with theory. By way of illustration, Fig. 4 shows our measured wavelength dependence of the spin–orbit branching ratio (I*/I) amongst the iodine atom products resulting from HI photolysis throughout the wavelength range 200–300 nm, and highlights deficiencies in previous estimates (both experimental[3–7] and theoretical[8]) of this spin–orbit branching at the longer excitation wavelengths ($\lambda > 250$ nm). Our measured anisotropy parameters, (Fig. 5) show that dissociation channels (1) and (2) involve, respectively, essentially pure perpendicular ($\beta = -1$) and parallel ($\beta = +2$) photoexcitation processes at all excitation wavelengths studied; the latter finding is in marked disagreement with the previous experimental measurements of $\beta$ for the H + I* channel at 222 and 248 nm (ref. 5 and also shown in Fig. 5), which have heavily influenced the current theoretical model of this process.[8]

1 M. N. R. Ashfold, D. H. Mordaunt and S. H. S. Wilson, in *Advances in Photochemistry*, ed. D. C. Neckers, D. H. Volman and G. von Bünau, Wiley, New York, 1996, vol. 21, p. 217.
2 S. R. Langford, P. M. Regan, A. J. Orr-Ewing and M. N. R. Ashfold, *Chem. Phys.*, in press.
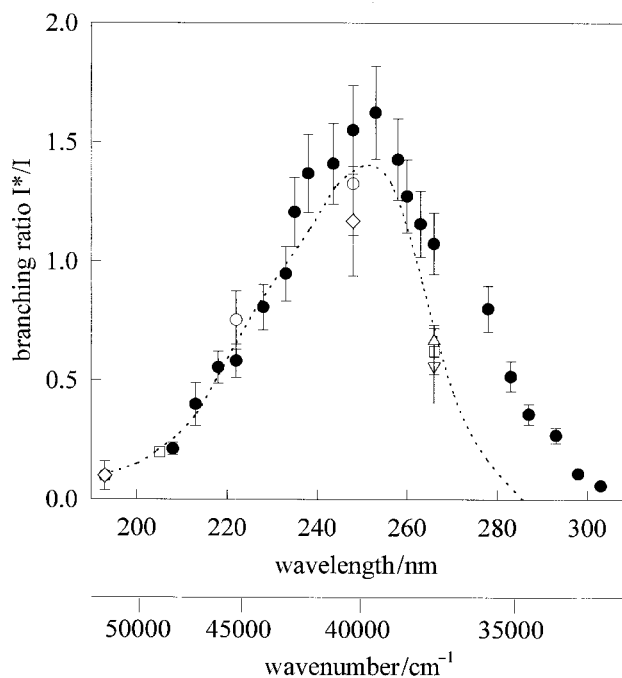3 R. D. Clear, S. J. Riley and K. R. Wilson, *J. Chem. Phys.*, 1975, **63**, 1340.

**Fig. 4** Measured I*/I photofragment branching ratios from the present study (●) plotted as a function of excitation wavelength; also shown in the figure is the calculated[8] wavelength dependence of this branching ratio (– – – –) and the previous experimental values reported by the groups of Wilson and co-workers[3] (▽), Welge and co-workers[4] (△), de Vries and co-workers[5] (○), Wittig and co-workers[6] (◇) and Chandler and co-workers[7] (□)
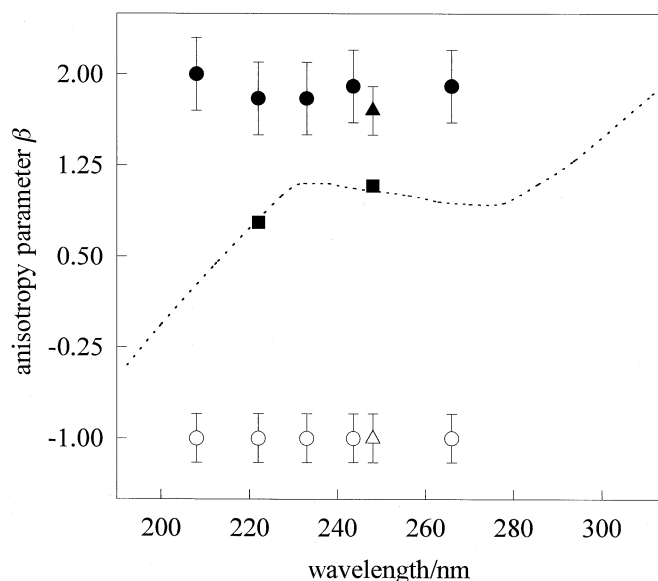
**Fig. 5** Best fit anisotropy parameters, $\beta$, from the measured H + I ($\bigcirc$) and H + I* ($\bullet$) angular distributions, plotted as a function of excitation wavelength; also shown are the previous experimental data of Wittig and co-workers[6] ($\triangle$ and $\blacktriangle$) and van Veen *et al.*[5] ($\blacksquare$) and the wavelength dependence of $\beta$ for the H + I* channel as calculated by Levy and Shapiro[8] (– – –). Schmiedl *et al.*[4] and Kitsopoulos *et al.*[7] have also reported $\beta$ values for both the H + I and H + I* channels arising in the 266 nm photodissociation of HI in good agreement with the present values but, for clarity, these are omitted from the figure.

4  R. Schmiedl, H. Dugan, W. Meier and K. H. Welge, *Z. Phys. A*, 1982, **304**, 137.

5  G. N. A. van Veen, K. A. Mohamed, T. Baller and A. E. de Vries, *Chem. Phys.*, 1983, **80**, 113.

6  Z. Xu, B. Koplitz and C. Wittig, *J. Phys. Chem.*, 1989, **90**, 2692.

7  T. N. Kitsopoulos, M. A. Buntine, D. P. Baldwin, R. N. Zare and D. W. Chandler, *Proc. SPIE-Int. Soc. Opt. Eng.*, 1993, **1858**, 2.

8  I. Levy and M. Shapiro, *J. Chem. Phys.*, 1988, **89**, 2900.

**Prof. Donovan** opened the discussion of Prof. Apkarian's paper: I was surprised to see that you label the ion-pair states of $I_2$ using the nomenclature for the free gas phase molecule, despite the fact that the surrounding matrix must strongly perturb the ion-pair states. It is known that interstate mixing and vibrational relaxation occur very efficiently during collisions with noble gas atoms. What is the evidence for the retention of electronic symmetry in matrices?

**Prof. Apkarian** responded: The concern about the nature of ion-pair states of iodine, upon solvation in a rare gas host, is well placed. The picture is far from complete. Nevertheless, statements can be made about some of the characterized sections. To be clear about the issues let me note that in the first tier of ion-pair states there are six nested potentials that arise from the $I^-(^1S) + I^+(^3P_2)$ configuration, and six members in the second tier that arise from the $I^-(^1S) + I^+(^3P_{1,0})$ configuration. Besides solvation in the dielectric of the host, $Rg + I_2^-$ charge transfer configurations must play an increasingly important role as one proceeds from the lighter to the heavier rare gases. Given this large density of states, one may expect a featureless charge transfer band to emerge. This does not prove to be the case, at least near the potential minima of the characterized states. Indeed, in the case of Xe, the ion-pair states are unstable: they either react to

form the fluorescent product $Xe_2^+I^-$ (a process well characterized in the gas phase by Professor Donovan and co-workers), or predissociate to the $I^*(^2P_{3/2}) + I^*(^2P_{3/2})$ manifold, states which are strictly trapped by the host cage, and which relax through the $I^*I^* \rightarrow I^*I$ emission in the near IR. In Ar and Kr, the ion-pair states can be observed in both excitation and emission. In Ar, the main emission is due to the vibrationally relaxed $D'(1_g) \rightarrow A'(1_u)$ transition, while in Kr vibrationally relaxed emission is observed over both $\beta(2_g) \rightarrow A(2_u)$ and $D'(1_g) \rightarrow A'(1_u)$ transitions. Even though these transitions are red shifted by *ca.* 0.5 eV, the $\beta$ and $D'$ states maintain their gas phase characters (as verified by polarization measurements, $\Omega$ remains a good quantum number, and the known propensity of $\Delta\Omega = 0$ for charge transfer transitions in $I_2$ is retained). These emission spectra can be well reproduced by using gas phase ion-pair potentials, and the self-consistent electrostatic potential described in our paper. There, we have shown a rather acceptable reproduction of the wavepacket motion in the B state, probed either *via* the first tier $f(0_g^+)$ or *via* the second tier $E(0_g^+)$ ion-pair states, again using gas phase $I^+-I^-$ potentials and strictly electrostatic guest–host interactions. Thus, in Kr, the studied $D'$, $\beta$, f, and E ion-pair states, near their potential minima, retain their gas phase character.

**Prof. Dantus** asked: The pump–probe data from iodine in solid Kr, shown in Fig. 5 and 6 of your paper, present two sequences of oscillations. The first belonging to the B state (periods in the 450–350 fs range) and the second, with a constant period of 700 fs, is assigned to lattice dynamics. Experiments on solid Xe also show the 700 fs oscillations. Have you considered the possibility that the 700 fs oscillations correspond to iodine vibrations in the A or A' states? This assignment would be consistent with the spectroscopic constants of these states for wavepackets near $v = 8$, 9 and $v = 24$, 25 in the A and A' states, respectively. Furthermore, it would explain why the 700 fs oscillations are observed for both Kr and Xe matrices that have different phonon frequencies.

**Prof. Apkarian** answered: The oscillations in Kr (Fig. 6 of our paper), which were assigned to the cage motion, have a period of *ca.* 660 fs (50 cm$^{-1}$). The oscillations in Xe once the packet leaves the B state (Fig. 2 above), have a period of *ca.* 850 fs (39 cm$^{-1}$). Neither of these persistent coherences can be assigned to the A/A' state, where the period of motion is *ca.* 410 fs (80 cm$^{-1}$) as illustrated in Fig. 3 of the paper. Note, in contrast with the gas phase, dissipation prevents the packet from being trapped in the anharmonic region of the potential and although chirped, the limiting frequency of 80 cm$^{-1}$ is reached within a period after recombination on A/A'. The frequencies assigned to cage motion correspond to resonant local phonon modes which can be sustained on dissociative potentials of iodine which become bound by the cage (explanation advanced in the case of Xe) or may be seen through the 'eyes' of the chromophore as a modulation of the difference potential of the probe transition (explanation advanced in the case of Kr).

**Prof. Chergui** commented: In relation to Prof. Apkarian's paper and Prof. Dantus's remark about the possibility that the coherent oscillations attributed to cage motions in the case of matrix-isolated $I_2$ could be due to intramolecular oscillations in the A/A' states, I would like to present another example that should lift any doubts as to whether coherent matrix cage oscillations can exist in condensed rare gases. Fig. 6 shows a femtosecond pump–probe scan of the dynamics of cage relaxation following excitation of the A $^2\Sigma^+$ (3s$\sigma$) Rydberg state of NO in Ar matrices. The details of the experiment are given in ref. 1 and 2 below. In this example, no intramolecular excitation is excited and the impurity can be treated as an atom (anyway intramolecular frequencies of NO are high and would not be resolved with our time resolution). Briefly, the A state is impul-

sively excited by a femtosecond pulse. This induces an expansion of the cage surrounding the impurity and we follow its evolution by means of a near-IR fs pulse by inducing absorptions from the A state to the next higher lying Rydberg states $C\,^2\Pi$ and $D\,^2\Sigma^+$. The detected signal is the depletion of the A state fluorescence as a function of pump–probe delay. From Fig. 6, we can clearly see coherent cage oscillations which modulate the absorption by the probe pulse and last for several picoseconds. One can also see that the oscillations are damped due to relaxation processes. Results have also been obtained for other pump and probe wavelengths and in Ne matrices, which confirm the occurrence of coherent recurrences of the cage motion.[3] They are at variance with those obtained in the case of the soft and floppy $H_2$ matrices, in which no recurrences (coherent or incoherent) seem to occur.[2,4] These results represent the first unambiguous visualization of the cage motion to photoexcitation of a chromophore.

The data have been obtained by my co-workers: Catherine Jeannin and Marcia Portella-Oberli.

1 M. T. Portella-Oberli, C. Jeannin and M. Chergui, *Chem. Phys. Lett.*, 1996, **259**, 475.
2 C. Jeannin, M. T. Portella-Oberli, F. Vigliotti and M. Chergui, *Chem. Phys. Lett.*, 1997, **279**, 65.
3 C. Jeannin, M. T. Portella-Oberli and M. Chergui, submitted.
4 C. Jeannin, M. T. Portella-Oberli and M. Chergui, *J. Phys. Chem.*, submitted.

**Prof. Jortner** commented: Prof. Apkarian has presented very interesting evidence for vibrational coherence in $I_2$ dissociation in a solid Kr cage, interpreting his results in terms of wavepacket dynamics of phonons localized at the impurity site. The ubiquity of impact induced vibrational coherence phenomena, ranging from bubble formation around Rydberg excitations in rare gas solids and clusters, to dissociation of diatomics and tritomics in the condensed phase, through to dissociation of biomolecules such as haemoglobin and NO, calls for a unified approach. The simplest source of information is
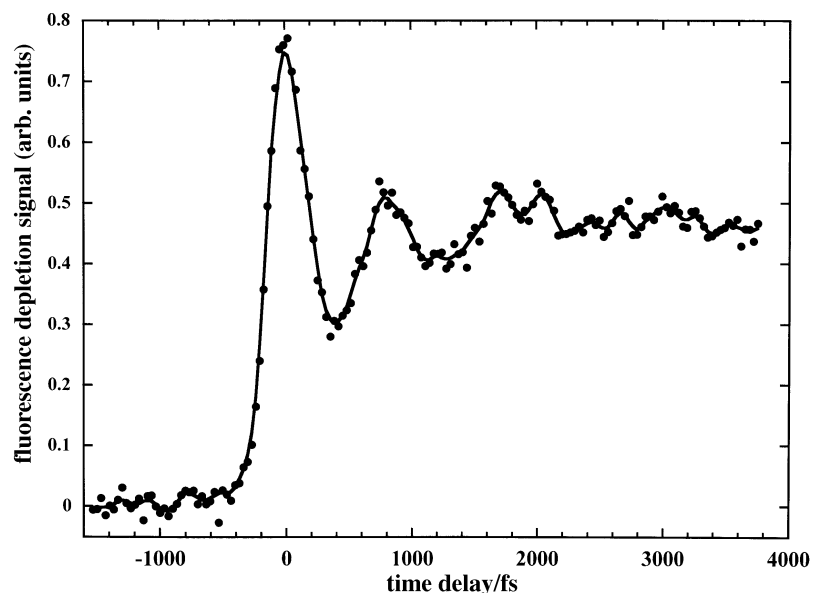


**Fig. 6** Femtosecond pump–probe transient following excitation of the lowest $A(3s\sigma)$ Rydberg state of NO at 196 nm with a 200 fs pulse. The probe wavelength is 1.25 μm and the detected signal is the depletion of A-state fluorescence as a function of pump–probe delay.

the relevant vibrational frequencies. In the context of $I_2$ cage recombination in solid Kr it will be instructive to describe quantitatively localization and resonance effects in the phonon spectrum of the solid induced by the impurity.

**Prof. Apkarian** responded: A variety of languages can be used in the description of many-body dynamics. Be it in liquids, solids or clusters, there is significant economy in describing collective motions in terms of phonons (with real and imaginary frequencies, and with real and imaginary decays) rather than an atom at a time. Where small amplitude motions are involved, descriptions in terms of phonons (normal modes) is the preferred language. We have recently provided such a description in our analysis of the absorption spectrum of $Cl_2$ doped Ar (see ref. 14 of our paper). In the case of a strong impact driven large amplitude non-linear dynamics, there is more economy in discussing motions in terms of classical trajectories. To be concrete, when a photodissociatively generated I atom undergoes a head-on collision with a cage atom at a velocity of 100 km s$^{-1}$, at least initially the impact is localized on the single collision partner, which is set into flight. Such a localized excitation can of course be described in terms of phonons, as a superposition of a few hundred phonons! The physics does not change, rather, the representation basis is changed. After the generation of shock waves and dissipation, we are back to a regime where excitations and decays of collective normal modes becomes more economical, and there is a transition region where it is difficult to promote one language over the other. Perhaps instantaneous normal modes, which can be significantly different from the equilibrium modes, is a useful tool for descriptions in the transition from non-linear to linear dynamics.

**Prof. Fleming** said: I would like to pick up on the point you made concerning the differing descriptions of dynamics in liquids and rare gas matrices. Your beautiful data and analysis effectively remove the ensemble average effect. Free energy surfaces shown for solution systems are ensemble averaged pictures. For Markovian systems the distinction between the ensemble and the individual molecule is irrelevant. However, none of the systems we are talking about is Markovian. Your work and the work of many others using non-linear spectroscopy shows that many of the timescales previously thought to apply to individual molecules arise from the ensemble averaging. As molecules react 'one at a time' the distinction between the ensemble timescales and the individual molecule timescales is important. For liquids, where for times longer than 100 fs, it will be necessary to use collective coordinates, the correct choice with the appropriate level of averaging currently seems a challenging task.

**Prof. Apkarian** asked: Indeed the Markovian assumption, as well as the assumption of ergodicity, are conveniences that can be seriously misguiding. We agree that molecules do not evolve on mean potentials or on free energy surfaces. Nevertheless, as long as the observables do not contain sufficient detail, the assumptions are made with pragmatism even where we know they cannot hold. They do not hold in the case of short time dynamics even in high temperature liquids, as ascertained by non-linear spectroscopies that measure high order correlations (as in your work). The combination of local structural order and cryogenic temperatures limit initial phase space distributions in the case of matrices ensuring that even in the case of linear spectroscopies ensemble averages do not completely mask the underlying molecular dynamics. The proper connection between molecular motions and spectral observables is through quantum time correlation functions, the implementation of which is a daunting task in condensed media. The good news is that methods are becoming available to construct such correlation functions by the explicit treatment of hundreds of degrees of freedom and for timescales of picoseconds. In this regard the mixed-order semiclassical molecular dynamics method is particularly promising (see ref. 13 and 14 of our paper) in injecting a

new level of rigor in the analysis of linear and non-linear spectroscopies in condensed media in general.

**Prof. Gerber** asked: Are the time domain experimental data as presented less demanding on the accuracy of the potentials used for interpretation than those of high resolution frequency domain experiments?

**Prof. Apkarian** answered: One of the main messages of our paper was to illustrate that the time domain data sets of the type presented are extremely detailed and therefore their exact reproduction impose accuracy in the description of potentials and dynamics. We have only given a semi-quantitative interpretation of the data, and would strongly encourage attempts at more exact reproductions. Let us recall that the high resolution spectroscopy of $I_2$–rare gas complexes has a long history. Yet, except for very limited configurations, accurate descriptions of the interaction potential have not been extracted. Whether $I_2$–Ar is T-shaped or linear has not found convincing resolution from experiments. This is a very important consideration to keep in mind. High resolution spectroscopy probes a very limited range of interactions, limited to the Franck–Condon window accessible from the initial state. Time resolved measurements of the type described are significantly more informative, since a very large range of configuration space is probed, and reproduction of the time dependent resonances requires knowledge of the entire potential surface (initial and final states of the probe transition) and an accurate representation of the time dependent many-body Hamiltonian.

**Prof. Apkarian** continued: One of the main highlights of the paper presented on time resolved measurements of photodynamics of $I_2$ isolated in rare gas solids in the detailed information content of the experimental data. We have given a semi-quantitative analysis of the data, but to date, we are far from an exact quantitative reproduction of the observables. Given the dimensionality of the system, this is a non-trivial task. The message to be emphasized is that, at least in this model system, the condensed phase data impose rather unique and detailed interpretations. To reproduce pump–probe data sets with high time resolution, it is necessary to fully characterize the time dependent Hamiltonian: the many-body potentials and the accompanying dynamics over a multitude of electronic surfaces. The approximate treatments to date have only allowed the interpretation of the gross features, and undoubtedly iterations to refine assumed interactions will lead to significant learning. It should also be appreciated that the iteration process is quite tedious, and to be effective will require innovation in methods. Let us consider some of the outstanding fundamental issues that can be expected to be resolved through such an exercise.

(i) Rigorous descriptions of interatomic forces and torques in condensed media is perhaps the most fundamental issue. This can be summarized in the form of potential energy functionals, which more generally take the form of matrices with diagonal and off-diagonal terms. The latter is necessary if we wish to account for coupled electronic–nuclear degrees of freedom. Indeed, the diatomics in molecules (DIM) formalism provides one of the more useful frameworks for such analyses. However, it is important to recognize that this is a semi-empirical tool, implemented at very different levels of scrutiny. Beside the fact that the method has an obvious starting point, namely, accurately known pair interactions, its major attributes are flexibility in encoding multi-body effects, and the incorporation of physics consistent with chemical intuition. Thus, data of the type presented may teach us how to proceed from pair to many-body interactions.

(ii) Given accurate potential matrices, it is not clear how to best treat non-adiabatic processes in condensed media. Indeed, in systems of high dimensionality, there are many approximate methods in use for the implementation of this inherently quantum process. Some of the reservations about these methods have already been discussed (see the
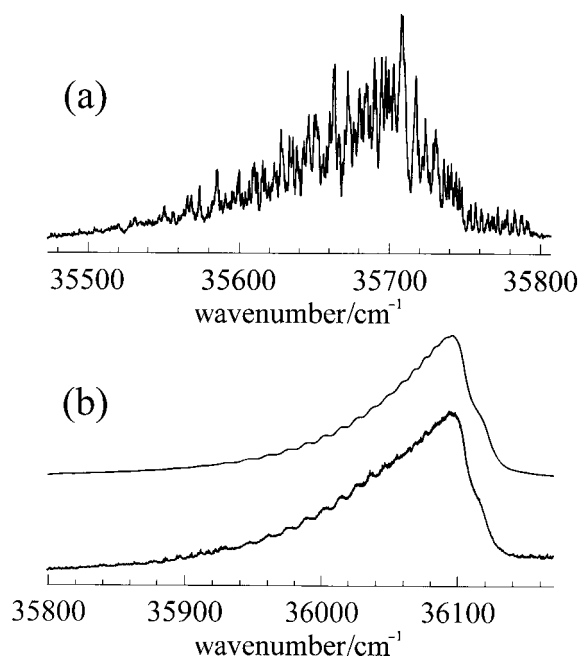
**Fig. 7** CRDS spectra of vibrational bands of the $S_2$ $B\,^3\Sigma_u^- - X\,^3\Sigma_g^-$ transition: (a) the (10, 0) band; (b) the (11, 0) band. Also shown in (b) above the experimental spectrum is a spectral simulation.

paper by Schatz *et al.*). Detailed experimental data in model systems are of obvious value to make progress. Such data are only recently becoming available. Regarding the data on $I_2$, the work of Batista and Coker deserves special mention.[1] They have constructed DIM matrices for the full stack of electronic surfaces that arise from the interaction of $I(^2P) + I(^2P)$ and $I^+(^3P,\ ^1D,\ ^1S) + I^-(^1S)$ and they have carried out simulations of dynamics in condensed phase $I_2$ including non-adiabatic processes. Although the quantitative predictions of the treatment is in significant discord with experiment, it provides an important framework for refinements with iterations *vis à vis* experiment.

(iii) Finally, the establishment of a rigorous connection between atomistic simulations of dynamics in condensed media and time or frequency domain observables remains to be clarified. In the absence of exact methods for treating quantum dynamics in extended systems, the inherent assumptions in statistical treatments will remain subject to doubt. Due to the reduced phase space of initial conditions, cryogenic solids provide systems in which observables relay direct information about specific dynamics over potentials, and as such force rigorous analysis of the supersystem (chromophore and bath). Thus understanding the tool—time or frequency domain spectroscopy—is very much a part of the quest in these model systems.

1 V. Batista and D. Coker, *J. Chem. Phys.*, 1996, **105**, 4033; 1997, **106**, 7102.

**Prof. Hutson** opened the discussion of Dr van der Zande's paper: Your paper shows how Hanle type experiments can be used to determine predissociation lifetimes for $N_2$ $(e^1\Pi_u)$. Would there be any major complications in applying it to magnetic states of non-linear molecules?

**Dr van der Zande** responded: This method is as general as fluorescent Hanle type experiments, having very similar disadvantages and advantages. The method is Doppler-

free but one measures a product of lifetime and the *g* factor, implying that for non-singlet states a lifetime determination may not be as straightforward. Without having gone into the details of a calculation, we found that the anisotropy parameter in a magnetic field decreases the anisotropy parameter by a factor of four. I have no reason to expect that this will be different in the case of a non-linear molecule. If the value for a long-lived state is significantly different from zero, then this decrease can be observed and a lifetime extracted.

**Dr Orr-Ewing** commented and asked: The variation of the rate of predissociation of an electronically excited state with vibrational level ($v'$) is well known to provide detailed information on the predissociation mechanism. As an illustration, we have used the technique of cavity ring-down spectroscopy (CRDS) to unravel the contributions from different repulsive states to the predissociation of SH/SD A $^2\Sigma^+$ and S$_2$ B $^3\Sigma_u^-$.[1–3] Predissociation rates were determined from homogeneous line broadening in the CRD absorption spectra. In these studies, the variation of the rate of predissociation with $v'$ was explored, thereby enabling us to construct models based on *ab initio* and empirical potentials that reproduce quantitatively the measured predissociation rates. CRD spectra of the S$_2$ B $^3\Sigma_u^-$–X $^3\Sigma_g^-$ (10, 0) and (11, 0) bands are shown in Fig. 7, and the much greater predissociation rate for $v' = 11$ is evident from the substantial homogeneous broadening that washes out the rotational structure observed in the (10, 0) band. Fits to band contours for the ($v'$, 0) bands of the S$_2$ B–X transition with $v' = 11$ to 19 give the linewidths plotted in Fig. 8 for the different $v'$ levels. The fitting procedure neglects variation of the linewidth with rotation of the S$_2$. Also shown in Fig. 8 are the results of Fermi golden rule calculations of the predissociation rates, represented as homogeneous linewidths, that were performed using an RKR potential for the B $^3\Sigma_u^-$ state and *ab initio* potentials for the B'' $^3\Pi_u$, $1^1\Pi_u$, $1\,^5\Sigma_u^-$ and $1\,^5\Pi_u$ states, all of which can, in principle, predissociate the B $^3\Sigma_u^-$ state. The results of our calculations demonstrate that the primary mechanism for predissociation up to $v' = 16$ is *via* spin–orbit coupling to the $1\,^1\Pi_u$ state, whereas for $v' \geqslant 17$, coupling to a higher lying repulsive state (either the $1\,^5\Sigma_u^-$ or $1\,^5\Pi_u$ state, but assumed here to be the former) dominates.
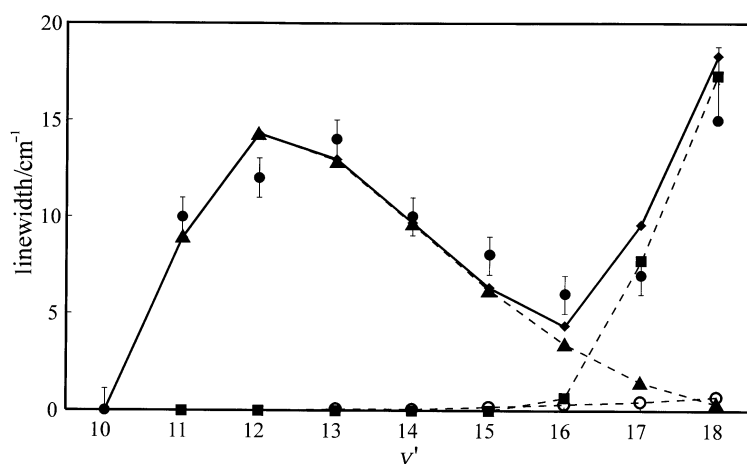


**Fig. 8** Experimentally observed (●) variation of the linewidths of S$_2$ B $^3\Sigma_u^-$–X $^3\Sigma_g^-$ ($v'$, 0) transitions with upper-state vibrational quantum number, $v'$. Also shown are the theoretically calculated linewidths for contributions to the predissociation from: ○ the B'' $^3\Pi_u$ state: ▲ the $^1\Pi_u$ state; ■ the $^5\Sigma_u^-$ state. The diamonds (◆) connected by the solid line show the sum of the calculated linewidths.

The data presentation for the predissociation of $N_2$ e $^1\Pi_u$ are restricted to the $v' = 0$ level, although a rotational level dependence is shown. Using your novel technique, were you able to measure rates of predissociation of other vibrational levels of the e $^1\Pi_u$ state to assist in determining the mechanism for dissociation? Do the limitations that are described in the paper for measuring lifetimes shorter than those presented prevent studies of the predissociation of higher vibrational levels?

1  M. D. Wheeler, A. J. Orr-Ewing, M. N. R. Ashfold and T. Ishiwata, *Chem. Phys. Lett.*, 1997, **268**, 421.
2  M. D. Wheeler, A. J. Orr-Ewing and M. N. R. Ashfold, *J. Chem. Phys.*, 1997, **107**, 7591.
3  M. D. Wheeler, S. M. Newman and A. J. Orr-Ewing, *J. Chem. Phys.*, in press.

**Dr van der Zande** replied: The results presented by Dr Orr-Ewing show that lifetime information can give important information on predissociation mechanisms. I note that in the case of homogeneous linewidths of 5–15 cm$^{-1}$, a direct linewidth analysis is the preferred technique. Our method has given lifetime information ranging from 1–18 ns implying linewidths which could not have been measured without very narrow bandwidth lasers. Dr Orr-Ewing mentions that the fitting procedure assumed lifetimes independent of $J$ which is not obvious in the case of the predissociation mechanisms suggested by the authors.

The general remark that one should not restrict oneself to one vibrational level, if one wants to pin down predissociation mechanisms is completely true and we have plans to extend our studies in molecular nitrogen to other vibrational levels.

**Prof. Neumark** said: The lifetimes you report are in the 1–10 ns range and could presumably be extracted from the linewidths in a high resolution photofragmentation experiment using a single mode laser in a coaxial geometry. Such an experiment would allow you to eliminate the magnetic field. While the experiment might be somewhat more difficult, the analysis would be straightforward and provide a useful check on the lifetimes reported here.

**Dr van der Zande** responded: Prof. Neumark is completely right in pointing out that a coaxial experiment with a single mode laser would have provided the same lifetime from analysis of the homogenous linewidths of the transition. If I would be in the position to perform such an experiment, it would be done immediately.

I want to stress that our paper also carried the educational message connecting the information contents of anisotropy parameters to intramolecular dynamics. I would like to take the opportunity to state that being able to measure anisotropy parameters with an accuracy of 0.01 or better would provide a very powerful diagnostic tool for assessing effective Hund's coupling cases as well as predissociation mechanisms.

**Prof. Gerber** opened the discussion of Prof. Dagdigian's paper: What is the structure of the electronic ground state of B $^1H_2$—is it T-shaped, or is the $H_2$ freely rotating? Does it affect the result?

**Prof. Dagdigian** responded: In conjunction with our experiments on the B$\cdot\cdot$H$_2$ complex (see our paper and references therein), Prof. Alexander and co-workers[1,2] have computed the potential energy surfaces (PESs) correlating with the ground state B(2p $^2$P) + H$_2$ asymptote and have used these to calculate energies and wavefunctions of the lowest bend–stretch vibrational levels of the complex. The equilibrium geometry for the lowest energy PES ($^2B_2$ in $C_{2v}$ symmetry) is T-shaped. However, as the anisotropy of the B–H$_2$ interaction is less than the H$_2$ rotational energy spacings, the H$_2$ rotational levels are not significantly mixed by the anisotropy of the interaction.

There are, in fact, two nuclear spin modifications of the complex, involving the binding of *p*- and *o*-H$_2$. The former involves H$_2$ in its $j = 0$ rotational level, and in this

case the $H_2$ moiety is indeed freely rotating within the complex, as described by a $j = 0$, $m = 0$ free rotational wavefunction. The binding energy $D_0$ is significantly greater for $B \cdots o\text{-}H_2$ than for $B \cdots p\text{-}H_2$ [38.6 *vs.* 27.9 $cm^{-1}$ (ref. 2)] since the $H_2$ molecule within the $B \cdots o\text{-}H_2$ complex can align itself in approximately T-shaped geometry to optimize the $B\text{-}H_2$ attraction. Near the most probable $B\text{-}H_2$ separation, the rotation of $H_2$ within $B \cdots o\text{-}H_2$ is well described by the rotational quantum numbers $j = 1$, $|m| = 1$, having an angular distribution of $\sin^2 \theta$, where $\theta$ is the angle between the $H_2$ internuclear axis and the vector connecting the B atom and the $H_2$ center of mass.

We believe that the $B(^2P) \cdots H_2$ complexes in our beam are predominantly the $B \cdots o\text{-}H_2$ nuclear spin modification, for several reasons. Firstly, the statistical ratio of free $o\text{-}H_2$ to $p\text{-}H_2$ in normal hydrogen is $3:1$. Secondly, $B \cdots o\text{-}H_2$ complexes can be more efficiently produced in the supersonic beam expansion than $B \cdots p\text{-}H_2$ complexes because the former have a significantly larger building energy, as discussed above. Finally, we find that our observed $3s \leftarrow 2p$ laser fluorescence excitation spectrum nearly quantitatively agrees with a simulation of the spectrum of the $B \cdots o\text{-}H_2$ complex and is significantly narrower than that predicted for $B \cdots p\text{-}H_2$.[3] These simulations[3] were carried out using calculated $B(^2P) \cdots H_2$ bend–stretch wavefunctions, mentioned above, and a computed $B(^2S)\text{-}H_2$ PES.[2]

A T-shaped geometry within the electronically excited $B(^2D) \cdots H_2$ complex allows the chemical reaction to occur efficiently since the overlap of the in-plane B atomic 2p orbital ($2p_x$ in Fig. 11 of our paper) and the antibonding $H_2$ $\sigma_u^*$ orbital is optimized.

1. M. H. Alexander, *J. Chem. Phys.*, 1993, **99**, 6014.
2. M. H. Alexander and M. Yang, *J. Chem. Phys.*, 1995, **103**, 7956.
3. X. Yang, E. Hwang, M. H. Alexander and P. J. Dagdigian, *J. Chem. Phys.*, 1995, **103**, 7966.

**Prof. Hutson** said: Prof. Gerber asked about the nature of the vibrational motion in the ground state of the $B\text{-}H_2$ complex. I would like the same information for the $B(^2D)$ state. Would I be right in interpreting your Fig. 2 as showing that, in the Franck–Condon region, the anisotropy of the potential is no more than a few hundred $cm^{-1}$? If so, since the splitting between the $j = 1$ and $j = 3$ states of $H_2$ is 500 $cm^{-1}$ or more, the $H_2$ presumably rotates fairly freely in the complex until the distances change enough for reaction to start.

**Prof. Dagdigian** replied: An upper limit to the anisotropies of the $B(^2D)\text{-}H_2$ potential energy surfaces within the Franck–Condon region is given by the width of the fluorescence depletion spectrum displayed in our Fig. 2(a). As we showed by a comparison of experimental and simulated $3s \leftarrow 2p$ spectra for the $B \cdots H_2$ complex,[1] the width of the spectrum depends upon the variation of the excited state energy over the range sampled by the $B(^2P) \cdots o\text{-}H_2$ ground bend–stretch vibrational levels of both the $B\text{-}H_2$ separation and the angle between the $H_2$ internuclear axis and the vector connecting the B atom and the $H_2$ center of mass. Your supposition about the rotational motion of the $H_2$ molecule within the electronically excited $B(^2D) \cdots H_2$ complex before reaction occurs appears to be correct.

1 X. Yang, E. Hwang, M. H. Alexander and P. J. Dagdigian, *J. Chem. Phys.*, 1995, **103**, 7966.

**Prof. Alexander** commented: Exact[1] and quantum Monte Carlo[2] simulations of the ground vibrational state of the binary $B(^2P) \cdots H_2$ complex indicate that the dissociation energy of the $o\text{-}H_2$ cluster is 39 $cm^{-1}$ as compared to 28 $cm^{-1}$ for the $p\text{-}H_2$ cluster. These studies show further that the rotational motion of the $H_2$ moiety is essentially unhindered by the presence of the B atom. Since the complex with $o\text{-}H_2$ is more strongly bound and because of the greater $(3:1)$ statistical weight of $o\text{-}H_2$, in a supersonic expansion the vast majority of the $B \cdots H_2$ clusters in the experiments described by Dagdigian

and co-workers[3] will all involve $o$-$H_2$. The first-order rate constant for *ortho* $\rightarrow$ *para* conversion in pure $H_2$ is very small (*ca.* $10^{-2}$ $h^{-1}$ ref. 4). The presence of an open shell atom is expected to increase the conversion rate constant dramatically ($k = 10^2$–$10^3$ $h^{-1}$).[5] Notwithstanding, this conversion will be extremely slow on the timescale of a typical molecular beam experiment.

Our study[3] on the $B(^2P)\cdots H_2$ complex indicates that the vibrational wavefunction of the lowest bend–stretch level of the electronic ground state of the complex extends from *ca.* 5.5 to 11 $a_0$ multiplied by $\sin^2 \theta$ in the Jacobi angle. As Prof. Hutson suggests, the width of the features in Fig. 2 of the paper by Dagdigian and Yang is a measure of the variation in the excited state $B(2s2p^2\,^2D)H_2$ potential energy surfaces in the region sampled by the vibrational wavefunction in the ground state.

Unfortunately, we were unsuccessful in attempts to use multi-reference, configuration interaction techniques to determine high quality potential energy surfaces for the five states which correlate with $B(2s2p^2\,^2D) + H_2$. The active space includes, in addition to the five valence orbitals [2s and 2p on B and $1\sigma$ and $1\sigma^*$ on $H_2$], the 3s orbital on the B as well as three 3p and five 3d orbitals on the B which describe the nearby $B(2s\,^23p)$ and $B(2s\,^23d)$ states. The presence of the $H_2$ will cause the latter states to mix strongly with the $B(2s2p^2\,^2D)$ state. In addition, the calculation wants to bring in five additional 3d orbitals to correlate the 2s and 2p orbitals. These virtual orbitals are very different from the B Rydberg 3d orbitals which are normally occupied in the $B(2s\,^23d)$ state. We found it impossible to maintain, at all geometries, the same set of orbitals in the active space. Even if a uniform set of orbitals could be maintained in the CASSCF calculations, such a large active space would render subsequent CI calculations prohibitive.

1 M. H. Alexander and M. Yang, *J. Chem. Phys.*, 1995, **103**, 7956.
2 A. Vegiri, M. H. Alexander, S. Gregurick, A. McCoy and R. B. Gerber, *J. Chem. Phys.*, 1994, **100**, 2577.
3 X. Yang, E. Hwang, M. H. Alexander and P. J. Dagdigian, *J. Chem. Phys.*, 1995, **103**, 7966.
4 A. Farkas, *Orthohydrogen, Parahydrogen and Heavy Hydrogen*, Cambridge University Press, Cambridge, UK, 1935.
5 P. Chapovsky, personal communication.

**Prof. Scoles** commented: In the context of the remark by Prof. Alexander on the difficulty of calculating excited state potential energy surfaces I would like to note that at Princeton we are presently exploring, in collaboration with M. Gutowski, the possibility of extending to the excited states the HFD method utilized by us and many others for several years for the interactions between ground state atoms.[1] Recently, we have obtained encouraging results for both alkali–alkali and alkali–noble-gas interactions when (one of) the alkali atom(s) is excited (asymptotically) to the p state. While the excited states are highly polarizable and, as a consequence, the contributions of the correlation energy should be quite important, we find that (*e.g.* for $^3\Sigma_g^+$ $Na_2$) the uncorrelated energy contributions are quite dominating. This is probably due to the large value of the quadrupole moment of the excited atoms.

1 C. Douketis, G. Scoles, S. Marchetti, M. Zen and A. J. Thakkar, *J. Chem. Phys.*, 1982, **76**, 3057.

**Prof. Alexander** added: Accurate *ab initio* calculations for the excited states of the alkali metals, where there is only one electron outside of closed shells, are far simpler than for excited states of other atoms (or molecules) with two or more valence electrons. The difficulty is the size of the active space, which grows far more rapidly.

**Prof. Neumark** asked: Your action spectra of B–$H_2$ seem to be somewhat structured, particularly when chemiluminescence of the BH triplet band is monitored [Fig. 2(c) of your paper]. This is reminiscent of work by Soep and Polanyi[1,2] in which such structure has been interpreted as the transition state spectrum of the excited complex. Do you think that the features in your spectrum have a similar origin?

1 B. Soep, S. Abbès, A. Keller and J. P. Visticot, *J. Chem. Phys.*, 1992, **96**, 440.
2 X. Y. Chang, R. Ehlich, A. J. Hudson, J. C. Polanyi and J-X. Wang, *J. Chem. Phys.*, 1997, **106**, 3988.

**Prof. Dagdigian** answered: I agree that there appears to be structure in the action spectra in our Fig. 2, similar to that reported by other workers for reaction within electronically excited weakly bound complexes. It is quite possible that these are due to resonances in the excited state, although the sharp features in our spectra are seen only very weakly above a broad background. We have not attempted to interpret the structure in our spectra since more than one potential energy surface is required to describe the excited state dynamics. There are five potential energy surfaces correlating with the $B(^2D) + H_2$ asymptote, two of which are strongly attractive and lead to the observed $BH(A\,^1\Sigma^-,\, b\,^3\Sigma^-) + H$ channels. I believe that calculation of these potential energy surfaces represents a severe challenge of present quantum chemistry calculational capabilities.

**Dr Orr-Ewing** asked: Have you been able to observe any preferred polarization of the BH chemiluminescence? This should be a valuable indicator of the form of the reaction dynamics.

**Prof. Dagdigian** replied: We have not investigated the polarization of the BH chemiluminescence in our experiments. All spectra were recorded with the laser polarization in the plane containing the laser beam and the optical detection system, and the polarization of the emission was not determined. Recording of the chemiluminescence spectra with good signal-to-noise ratio required pulse energies of the 209 nm laser well into the saturation regime, and hence the optically excited $B\cdots H_2$ complexes are not expected to have appreciable alignment. I agree that measurements of the product alignment could provide interesting insights into the $B(^2D)\cdots H_2 \rightarrow BH^* + H$ reaction dynamics.

**Prof. Casavecchia** commented: We‡ would like to make a comment in relation to the interesting work of Dagdigian and Yang on the reaction of electronically excited boron atoms $B(^2D) + H_2$. In these kinds of studies a call is always made for theoretical calculations of both potential energy surfaces and reaction dynamics. We have studied the reaction with $H_2$ of another atomic species in the $^2D$ electronically excited state, that of atomic nitrogen $N(^2D) + H_2$. What we would like to show in this comment is that today for systems of this complexity (more than one PES involved) it is possible to carry out detailed and combined experimental and theoretical studies of the reaction dynamics. Specifically we have carried out crossed molecular beam scattering experiments and measured reactive double differential cross-sections, developed high quality potential energy surfaces based on accurate *ab initio* electronic structure calculations and the reproducing kernel Hilbert space interpolation method, and computed the dynamics on these surfaces by quasiclassical trajectory (QCT) methods.

We have measured angular and velocity distributions of the ND product from the $N(^2D) + D_2$ reaction at two different collision energies by exploiting the capability of generating intense supersonic beams of nitrogen atoms which contain, as determined from a Stern–Gerlach magnetic analysis,[1] about 72% $N(^4S)$, 21% $N(^2D)$ and 7% $N(^2P)$. The reaction of $N(^4S)$ with $H_2$ is strongly endoergic and that of $N(^2P)$ about two orders of magnitude slower[2] than that of $N(^2D)$, so the measured ND product comes entirely from the $N(^2D)$ reaction. Product angular and translational energy distributions in the center-of-mass (cm) were derived. About 30% of the total available energy is found to be

channeled in translation, which points to a high internal ro-vibrational excitation, consistent with the results of recent spectroscopic investigation of this reaction by Umemoto and co-workers.[3] The cm angular distributions at $E_c = 3.8$ (see Fig. 9) and 5.1 kcal mol$^{-1}$ are backward–forward symmetric and reflect an insertion dynamics presumably *via* the ground state PES correlating with the ground state $1\,^2B_1$ of $NH_2$. The absence of a preferential backward scattering with respect to the similar reaction $O(^1D) + D_2$ at $E_c = 5.3$ kcal mol$^{-1}$ (ref. 4) suggests that a direct abstraction mechanism does not occur, at least in this energy range.

Fig. 10 shows the schematic energy level and correlation diagram for the reaction $N(^2D) + H_2 \rightarrow NH + H$ according to accurate *ab initio* calculations of the PESs. The insertion pathway on the ground state surface leading to the $1\,^2B_1$ state of $NH_2$ is found to have a barrier of about 1.7 kcal mol$^{-1}$ in $C_{2v}$ geometry and of about 4.7 kcal mol$^{-1}$ for collinear approach ($C_{\infty v}$ geometry). These values can be contrasted with corresponding values of 0 and 0.7 kcal mol$^{-1}$, respectively, for the ground state PES of $O(^1D) + H_2$.[5] The first two excited PESs, $^2A_1$ and $^2B_2$, do not correlate with ground state $NH(X\,^3\Sigma^-)$, but with $NH(a\,^1\Delta)$ and $NH(b\,^1\Sigma^+)$, respectively, so neither can contribute adiabatically to the formation of ground state $NH + H$. For collinear approach the first excited PES $^2\Delta$ has a large barrier ( $> 20$ kcal mol$^{-1}$) and does not correlate with ground state NH, which is quite different to what happens in the related $O(^1D) + H_2$ reaction, where the first excited PES $^1\Pi$ (in collinear geometry) has a barrier of 2.4 kcal mol$^{-1}$ and correlates with ground state OH. These theoretical calculations suggest that only insertion plays a role in $N(^2D) + H_2$ at thermal energies, in contrast to $O(^1D) + H_2$. Our study of the various surfaces involved, currently in progress,[6] shows a rather complex coupling scheme between the ground state PES and the first two excited PESs, which could lead to a significant contribution to reaction *via* the excited state surfaces even at fairly low collision energies. In fact, insertion can come not only from the ground state PES, but also from the $^2A_1$ PES which is adiabatically connected to the $^2B_2$ state
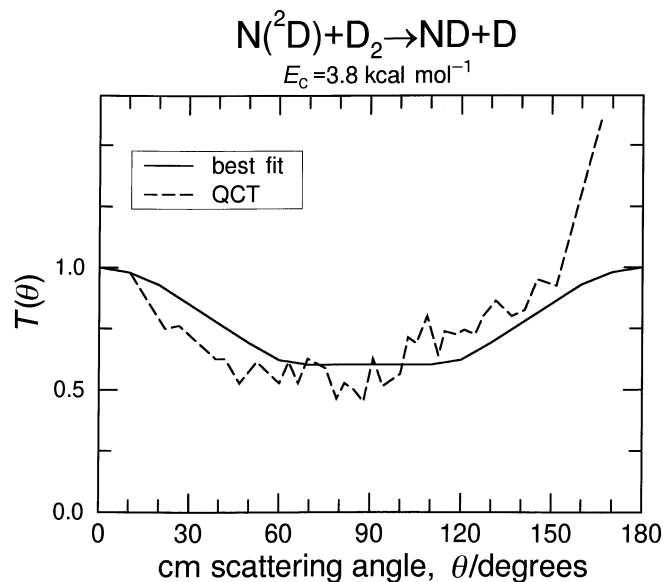


**Fig. 9** Comparison between the experimentally determined center-of-mass (cm) ND product angular distribution (———) for the $N(^2D) + D_2$ reaction at $E_c = 3.8$ kcal mol$^{-1}$ and that calculated by the quasiclassical trajectory method (– – – –) on a new potential energy surface based on accurate *ab initio* computations and the reproducing kernel Hilbert space interpolation method
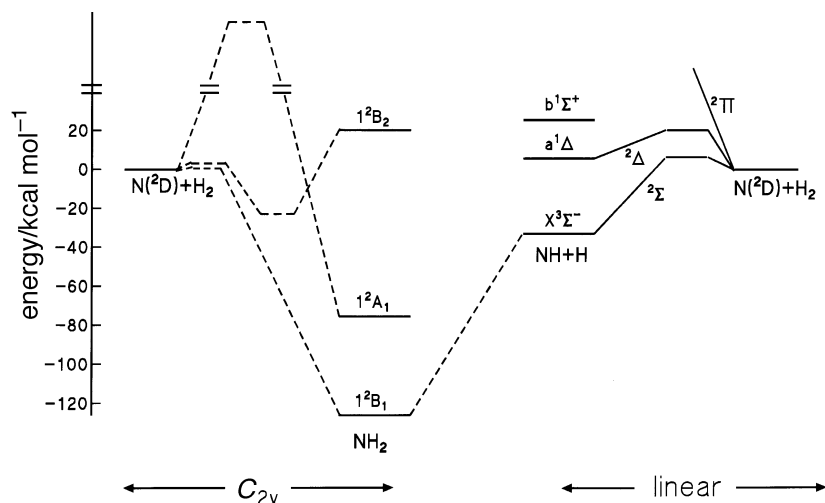
**Fig. 10** Schematic energy level and correlation diagram for the reaction $N(^2D) + H_2$ based on *ab initio* electronic structure calculations of the ground and first excited potential energy surfaces. The surfaces for both $C_{2v}$ and linear geometry are shown.

*via* non-$C_{2v}$ geometry (a conical intersection exists between $^2A_1$ and $^2B_2$ surfaces) and the $^2B_2$ surface has a modest barrier of only 2.7 kcal mol$^{-1}$ (for $C_{2v}$ geometry) followed by a fairly deep well (see Fig. 10). QCT calculations were performed at the collision energies of the experiments on the ground state PES and calculated product angular and translational energy distribution were compared with the experimentally derived quantities. Quite good agreement is found for the angular distributions as can be seen in Fig. 9 for $N(^2D) + D_2$ at $E_c = 3.8$ kcal mol$^{-1}$ and very good accord exists for the translational energy distributions. Under our experimental conditions ND can only be formed in the ground state, but raising the collision energy sufficiently also allows for formation of $ND(a\ ^1\Delta)$: this will be explored in future experiments together with calculations of the excited $^2A_1$ PES correlating with $ND(a\ ^1\Delta)$ which are currently in progress.

Recently, the dynamics of the $N(^2D) + H_2$ reaction has also been studied by QCT methods on a previous *ab initio* PES,[7] and the results are quite different (backward scattered) since the abstraction barrier on this surface is lower than the insertion barrier. Very recently,[8] this surface has been modified to make the insertion barrier lower, and the new results are very similar to what we have obtained. Dynamical calculations on this system have been carried out by quantum scattering methods (QM) for total angular momentum $J = 0$ using several of the available potential energy surfaces, including the new one discussed here. The results are generally quite similar to the QCT results, indicating that the QCT results should be accurate.

1  M. Alagia, N. Balucani, P. Casavecchia, D. Stranges and G. G. Volpi, *J. Chem. Soc., Faraday Trans.*, 1995, **91**, 575; M. Alagia, V. Aquilanti, D. Ascenzi, N. Balucani, D. Cappelletti, L. Cartechini, P. Casavecchia, F. Pirani, G. Sanchini and G. G. Volpi, *Isr. J. Chem.* 1997, **37**.

2  T. Suzuki, Y. Shihira, T. Sato, H. Umemoto and S. Tsunashima, *J. Chem. Soc., Faraday Trans.*, 1993, **89**, 995.

3  H. Umemoto and K. Matsumoto, *J. Chem. Phys.*, 1996, **104**, 9640; H. Umemoto, T. Asai and Y. Kimura, *J. Chem. Phys.*, 1997, **106**, 4985.

4  M. Alagia, N. Balucani, L. Cartechini, P. Casavecchia, E. H. van Kleef, G. G. Volpi, P. J. Kuntz and J. J. Sloan, *J. Chem. Phys.*, in press.

5  T-S. Ho, T. Hollebeek, H. Rabitz, L. B. Harding and G. C. Schatz, *J. Chem. Phys.*, 1996, **105**, 10472; G. C. Schatz, A. Papaioannou, L. B. Harding, T-S. Ho, T. Hollebeek and H. Rabitz, *J. Chem. Phys.*, 1997, **107**, 2340.

6  L. Harding and G. C. Schatz, work in progress.
7  T. Takayanagi, H. Koboyashi and S. Tsunashima, *J. Chem. Soc., Faraday Trans.*, 1996, **92**, 1311; H. Koboyashi, T. Takayanagi, K. Yokoyama, T. Sato and S. Tsunashima, *J. Chem. Soc., Faraday Trans.*, 1996, **91**, 3771.
8  H. Koboyashi, T. Takayanagi and S. Tsunashima, *Chem. Phys. Lett.*, 1997, **277**, 20.

**Prof. Casavecchia** commented: In relation to the interesting work of Dagdigian and Yang on the reaction of electronically excited boron atoms $B(^2D) + H_2$, we§ would like to report on the reactions of another species in the electronically excited $^2D$ state, $N(^2D)$, with molecules more complex than diatomics. We have recently carried out product angular and velocity distribution measurements in crossed beam experiments with mass spectrometric detection on the reactions of $N(^2D)$ with acetylene and ethylene.[1] Supersonic beams of N atoms are generated by RF discharge[2] in high pressure $N_2$–rare gas mixtures; a magnetic analysis[3] by a Stern–Gerlach magnet has given the following beam composition: $N(^4S)$ 72%, $N(^2D)$ 21%, $N(^2P)$ 7%. The reaction of $N(^4S)$ with $C_2H_2$ and $C_2H_4$ are nearly thermoneutral and have high activation energies.[4] The possible reactions of $N(^2P)$ are expected to be slow on the basis of simple adiabatic electronic energy correlation diagrams (see Fig. 11). From product angular (see Fig. 12) and velocity distribution measurements at different collision energies we conclude that HCCN (cyanomethylene) formation, the major pathway, arises from the reaction of $C_2H_2$ with $N(^2D)$ and proceeds through a long-lived cyanomethyl ($H_2CCN$) complex. Very recently, Takayanagi and co-workers[5] have carried out high quality electronic structure calculations on the geometry and energy of the possible reaction intermediates and products of this reaction. Their work shows that $N(^2D)$ attacks the two C atoms of acetylene forming a cyclic intermediate which can lead to the very stable $CH_2CN$ intermediate complex by (1, 2) H-shift and ring opening, or to a somewhat less stable linear HNCCH intermediate by simple ring opening. The internally hot complex will then
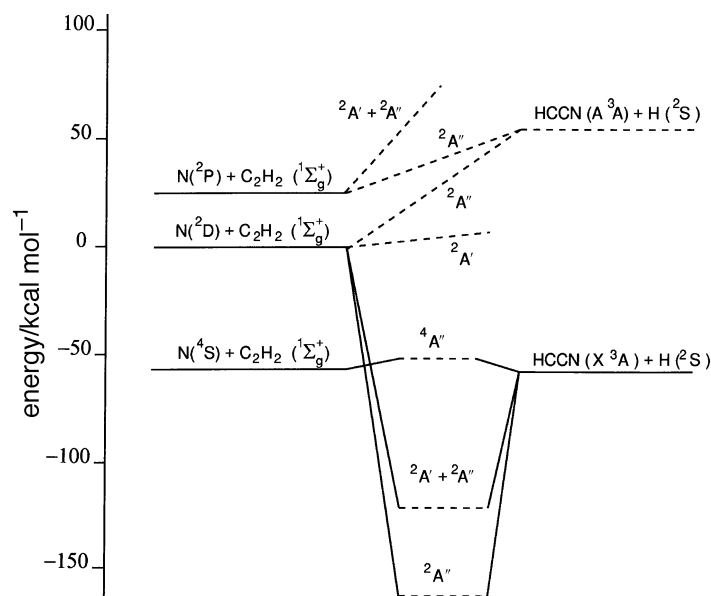


**Fig. 11** Schematic energy level and correlation diagram for the $N(^4S, \,^2D, \,^2P) + C_2H_2$ system
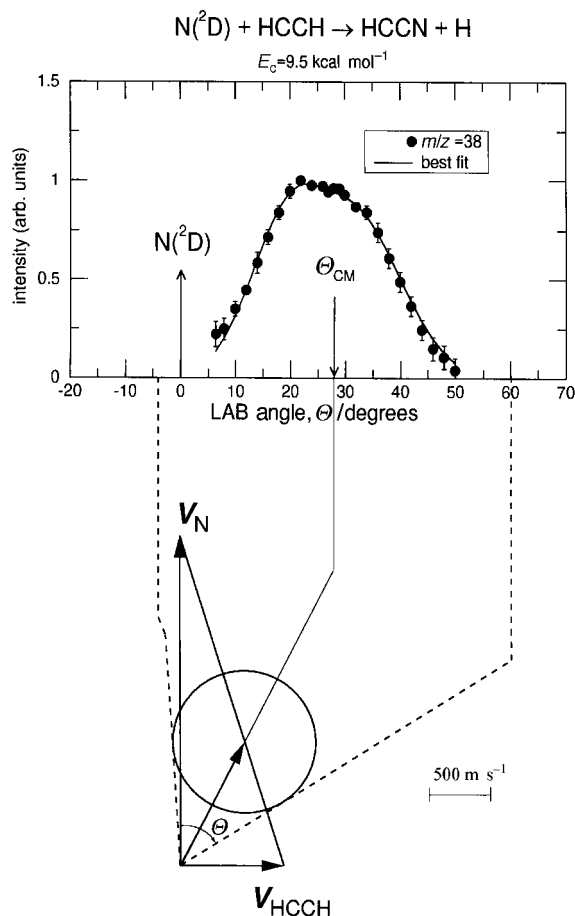
$N(^2D) + HCCH \rightarrow HCCN + H$

$E_c = 9.5$ kcal mol$^{-1}$

**Fig. 12** Laboratory angular distribution of the HCCN product (detected at $m/z = 38$) from the $N(^2D) + C_2H_2$ reaction at $E_c = 9.5$ kcal mol$^{-1}$. The circle in the canonical Newton diagram delimits the maximum speed that the HCCN product can attain if all the available energy is channeled into translation.

dissociate under single collision conditions to HCCN + H by C—H or C—N bond cleavage. The H-displacement pathway has also been observed in the study of the $N(^2D) + C_2H_4$ reaction.

1 M. Alagia, N. Balucani, L. Cartechini, P. Casavecchia and G. G. Volpi, in preparation.
2 M. Alagia, N. Balucani, P. Casavecchia, D. Stranges and G. G. Volpi, *J. Chem. Soc., Faraday Trans.*, 1995, **91**, 575.
3 M. Alagia, V. Aquilanti, D. Ascenzi, N. Balucani, D. Cappelletti, L. Cartechini, P. Casavecchia, F. Pirani, G. Sanchini and G. G. Volpi, *Isr. J. Chem.*, 1997, **37**.
4 J. V. Michael, *Chem. Phys. Lett.*, 1980, **76**, 129.
5 T. Takayanagi, personal communication.

**Prof. Polanyi** opened the discussion of Prof. Guo's paper: Guo and Chen have used a time dependent quantum computation to contrast the two major contending models of photodesorption dynamics; the MGR (Menzel–Gomer–Redhead) model, and the Antoniewicz model. Such studies are needed and promising.

In the work reported by Guo and Chen evidence is presented that the calculated positive correlation between translational excitation and rotational excitation in the

photodesorbed species provides a valuable diagnostic for establishing the dynamics (MGR or Antoniewicz).

At first sight this is surprising. Whichever model is operative the final step in desorption must involve repulsion between the desorbing species and the surface. The magnitude of this is likely to be an important factor in giving rise to the product translation and (to the extent that the repulsion exerts a torque on the desorbate) the product rotation. If this were indeed the whole story, a positive correlation between product translation and rotation would be expected—whether the mechanism was the MGR or the Antoniewicz one.

Would you care to comment?

**Prof. Guo** responded: First, I want to emphasize that the results presented in this work do not provide a conclusive identification of the desorption mechanism. Many uncertainties in the potential energy surfaces and in the theoretical model prevented such an identification. However, our calculations do indicate that the positive rotational–translational correlation of the desorbed product is related to a repulsive excited state, *i.e.*, an MGR-type potential energy surface.

For the desorption to occur, repulsive forces must be present. However, in the MGR model the repulsion occurs on the excited state, while on the ground state in the Antoniewicz model. There is an added twist to the dynamics in multidimensional space: the coupling between the internal and the desorption modes dictates the rotational–translational correlation in the final product. In the MGR case, the correlation created by the repulsive excited state is largely preserved after quenching. The Antoniewicz desorption, on the other hand, involves strong intramolecular energy transfer upon scattering with the substrate, thus it is dominated by the indirect desorption pathway which is characterized by a negative rotational–translational correlation.

Very recently, we have investigated the influence of the ground state topology on the desorption dynamics.[1] The results with different ground state potentials are consistent with the conclusions reached in this work.

1 F. Chen and H. Guo, *Chem. Phys. Lett.*, in press.

**Prof. Gerber** asked: Can the 'charge transfer' and the 'neutral' mechanisms not be tested *via* the angular distribution of the desorbed species? The effect of the charge/image charge on the angular distribution can be large!

**Prof. Guo** replied: The desorbed product is actually neutral, which has a weak electrostatic interaction with the substrate. Thus, its angular distribution is unlikely to reflect the charged nature of the excited adsorbate. The adsorbate–substrate interaction in the Antoniewicz case does include a charge–image charge interaction term.

**Dr McKinnon** said: You have carried out an examination of the influence of the excited state potential upon the desorption of NO and $NH_3$ from a non-insulating surface following irradiation with light. In the case of NO you find that an attractive excited state potential diminishes the direct desorption pathway, and conclude that the negative ion excited state in the photodissociation of NO may require reevaluation. I would like to bring to your attention the work of Siller *et al.*[1] in which they study the photodissociation of submonolayer CO and $O_2$ physisorbed at the surface of graphite. They observe sharp resonances in the photodesorption at energies corresponding to the absorption of light in the gas phase and a suppression of the yield of $C^+$ ions in the case of the dissociation of the physisorbed CO and a suppression of the yield of $O^+$ ions in case of the dissociation of the physisorbed $O_2$. From their observations Siller *et al.* conclude that the physisorbed molecule is photoexcited directly and that the excited

molecule then attracts an electron from the substrate, leading to the observed asymmetry in the dissociation products. Sîller *et al.*'s results seem to me to support your own suggestion that the excited NO is uncharged. Could you comment on these results from the perspective of your understanding of substrate mediated desorption dynamics?

1 L. Sîller, S. L. Bennett, M. A. MacDonald, R. A. Bennett, R. E. Palmer and J. S. Foord, *Phys. Rev. Lett.*, 1996, **76**, 1960.

**Prof. Guo** answered: It is true that many excitation mechanisms exist for different systems, including the direct excitation of the adsorbate. However, the experimental evidence for the photon-stimulated desorption (PSD) of both $NH_3$ and NO from metal and semiconductor surfaces indicated a substrate-mediated mechanism, in which the substrate carriers were first excited by incident photons. For example, the desorption cross-section was found to be weakly dependent on the photon wavelength. Thus, the excitation mechanism is quite different from the case that you mentioned. It should also be noted that photons used in the work of Sîller *et al.* are much more energetic.

**Prof. Schatz** asked: Your model omits vibrational relaxation of the excited molecule near the surface. Is it possible that one consequence is that the indirect component in the MGR mechanism is more important than should really be the case?

**Prof. Guo** replied: This is a very important point. The substrate-induced vibrational relaxation is treated in this work in a rudimentary way: the propagation of the quenched wavepacket is truncated at approximately 1 ps, under the assumption that the further dynamics will be overwhelmed by relaxation. Because of the simple model, the results presented here only provide an upper limit for the indirect desorption channel.

**Prof. Hutson** said: One of the themes of this Discussion is to identify similarities and differences between processes in the gas and condensed phases and at surfaces. One common thread is becoming clear to me. In the gas phase, our main problem is that we do not know much about excited state potentials. In condensed phases, the problem is that we do not know much about excited state potentials. And on surfaces, we do not know anything at all about excited state potentials.

**Prof. Alexander** responded: Yes, but one should not be completely pessimistic. Fifteen years ago you might have made the same statement about ground state potentials.

**Prof. Gerber** added: There is, in my view, grounding for optimism as to the emergence of excited state potentials for many more systems: (a) many useful potentials came from fitting experimental data, and more suitable data are becoming available, (b) important progress is being made in a variety of *ab initio* methods, *e.g.* in the groups of Head–Gordon and Bonacic–Koutecky.

**Prof. Schatz** added: Excited state potentials have traditionally been obtained from DIM methods, and this is still the only option for many problems. CASSCF-CI and similar methods are now available, and they should produce much higher quality surfaces, but they are really hard to implement and are not feasible to use for a large fraction of the problems of interest. DFT based methods for calculating excited state potentials are just starting to appear, and they have the advantage of being much simpler than CASSCF-CI, so it is likely that they will become very popular in the next few years. However, it is not at all clear whether they will be useful for small molecule dynamics problems.

**Prof. Jortner** commented: Let me address the central issue of the bridging between the dynamics of large and small systems. For small systems geminal experimental and theoretical studies provided extensive information on the nuclear dynamics. We would like to proceed to large systems, where collective nuclear effects have to be explored. Prof. Fleming pointed out that a basic difference between a large molecule and a liquid is the number of nuclear degrees of freedom coupled to an electronic excitation. Of course, the 'transition' between the large and the macroscopic systems is gradual, as 4–5 mode systems already exhibit dissipative dynamics.[1] The key concept for large system dynamics is the weighted density of states for nuclear motion. Central information on this quantity was inferred from femtosecond studies of the fluorescence of a probe molecule in a liquid, impurity Rydberg excitation in a molecular cluster or solid, electron localization in a large bubble (radius 17 Å) in liquid He or cage effects for I + I recombination in a solid. This amounts to interrogating medium nuclear dynamics in the cages of a microscopic probe as stated by Prof. Apkarian. The challenge will be to provide the microscopic description for the weighted density of states. This will be done on different levels of course graining, gradually bridging between small and huge system dynamics.

1  M. Bixon and J. Jortner, *J. Chem. Phys.*, 1997; W. Domke, *Adv. Chem. Phys.*, 1996.

**Prof. Butler** commented: There is an underlying prejudice that electronically non-adiabatic effects are important for excited state chemical reactions but not for ground state chemical reactions. This is not the case. From Prof. Schatz's work (in this volume) it can be seen that even one of the benchmark systems for reaction scattering on the ground state $O + H_2$ reaction potential energy surface can, at higher collision energies, access conical intersection when electronically non-adiabatic effects become important. For other systems, as soon as you have enough energy to surmount the barrier to the reaction on the ground state PES you can reach parts of the PES on the exit channel where electronically non-adiabatic effects become important.