Prof. J. C. Polanyi (*Toronto*) said: Prof. Zare has described some new experiments in which the difficult problem of comparing the efficiency of reagent translation and vibration in promoting significantly endothermic reactions has been successfully overcome.[1-3] The reaction is $HF(v = 0, 1) + Sr \rightarrow H + SrF$, with an endothermicity of ≈ 6.5 kcal mol^{-1} (27 ± 8 kJ mol^{-1}). For a total reagent energy, $T' + V'$, ≈ 5 kcal above threshold, reagent vibration was found to be $\approx 15 \times$ more efficient than reagent translation.

As Prof. Zare remarked, this is in qualitative accord with expectation, but falls short of the increases in reaction rate recorded in endothermic triangle plots.[4] These plots give detailed rate constants, k_{endo} (V', R', T'), that increase by 10^2-10^3 as the reagent energy is shifted in its entirety from reagent translation, T', to reagent vibration, V', (with reagent rotation, R', held constant at an optimal low energy).[5] These earlier data, obtained from detailed balancing, therefore give evidence of a more stringent requirement for reagent vibration than do the recent experiments.

The apparent discrepancy could be accounted for by a purely kinematic effect. The mass-combination $\underline{LH} + H \rightarrow L + \underline{HH}$ is especially favourable for reaction. The dynamics can be represented by the motion of a sliding mass across a scaled potential-energy surface characterised by a long narrow entry valley leading to a short broad exit valley. It is very easy for a sliding mass to negotiate such a surface; even momentum along the entry valley (T') can be deflected into the broad exit valley.[6-8] Expressed differently, the extension of the entry valley (referred to above) displaces the late barrier-crest on the endothermic surface to an earlier location.[6-8]

It is instructive to look at some specimen reactive cross-sections computed on an endothermic energy surface.[7] The surface had a late barrier of 35.7 kcal mol^{-1}. The total reagent energy was $T' + V' \approx 70$ kcal mol^{-1}. For equal reagent masses ($\underline{LL} + \underline{L}$) with $T' = 64$, $V' = 6$ kcal mol^{-1}, $S_r = 0.14 \pm 0.06$ Å^2; and with $T' = 3$, $\underline{V'} = 68.5$ kcal mol^{-1}, $S_r = 11.8 \pm 0.9$ Å^2. It follows that vibrational energy was $\approx 10^2 \times$ as effective as translational energy. However, for the same potential-energy surface but with the mass combination more appropriate to the present discussion, $\underline{LH} + H \rightarrow L + \underline{HH}$ ($L = 1$ a.m.u., $H = 80$ a.m.u.), with $T' = 52$, $V' = 18$ kcal mol^{-1}, $S_r = 3.9 \pm 0.7$ Å^2; and with $\underline{T'} = 3$, $V' = 67$ kcal mol^{-1}, $S_r = 11.5$

[1] R. N. Zare, *Faraday Disc. Chem. Soc.*, 1979, **67**, 7.

[2] D. S. Perry, A. Gupta and R. N. Zare, to be published.

[3] T. J. Odiorne, P. R. Brooks and J. V. V. Kasper, *J. Chem. Phys.*, 1971, **55**, 1980; J. G. Pruett, F. R. Gabriner and P. R. Brooks, *J. Chem. Phys.*, 1975, **63**, 1173. These authors showed $S_r(V)$ to rise $10 \times$ more steeply than $S_r(T)$ for $HCl(v = 0, 1) - K \rightarrow H - KCl$; endothermicity 1.5 kcal mol^{-1}.

[4] K. G. Anlauf, D. H. Maylotte, J. C. Polanyi and R. B. Bernstein, *J. Chem. Phys.*, 1969, **51**, 5716; D. C. Tardy and J. C. Polanyi, *J. Chem. Phys.*, 1969, **51**, 5717; D. S. Perry and J. C. Polanyi, *Chem. Phys.*, 1976, **12**, 419.

[5] The plots derive from related experimental data regarding the corresponding exothermic reactions; the method used in obtaining these plots has been put to an extreme test by D. S. Perry, J. C. Polanyi and C. Woodrow Wilson Jr, *Chem. Phys. Letters*, 1974, **24**, 484.

[6] B. A. Hodgson and J. C. Polanyi, *J. Chem. Phys.*, 1971, **55**, 4745.

[7] D. S. Perry, J. C. Polanyi and C. Woodrow Wilson Jr, *Chem. Phys.*, 1974, **3**, 317.

[8] J. C. Polanyi and N. Sathyamurthy, *Chem. Phys.*, 1978, **33**, 287.

$\pm$ 1.2 Å^2.   The vibrationally-excited reagent was $<10\times$ more effective than the trans-lationally-excited reagent.   This change is (as can be seen) due to the enhanced efficiency of T' in giving reaction for this more forgiving mass combination.   The " forgiving " nature of this mass combination stems from the fact that it is easy for a fast moving light atom L̲ to escape during the extended time that H̲H̲ spend close to one another.

The mass effect will be less extreme for HF + Sr, but it will surely be significant, and helps to account for the recent findings of Perry et al.[1]

There are two distinguishable categories of endothermic potential-energy surface (within the LEPS family of surfaces); both have a late barrier crest and hence are designated type II, but one has a sudden rise to the barrier crest, type IIS, and one a gradual rise, IIG.[2]   Surface IIS viewed in the reverse (exothermic) direction has more attractive energy release than has IIG.   The IIS type of surface is sudden, not only with respect to the upward slope to the endothermic barrier, but also with respect to the curvature of the minimum-energy path in the region linking the entrance valley of the surface to the exit valley (the reason for this correlation is easily seen).[2]   Duff and Truhlar have stressed the importance of this curvature and have explored the effect of making marked changes in curvature.[3]

For the present discussion it is enough to note that on the IIS type of surface the sudden change of direction of the minimum-energy path gives rise to a bend that is difficult to negotiate at high speed; consequently the reactive cross-section diminishes at enhanced collision energy.[2]   This diminution of $S_r(T')$ at enhanced T' is not observed on the corresponding gradual surface, IIG.   In the light of the observed peak in $S_r(T')$ (at $<2\times$ the endothermic barrier height) it appears that the HF + Sr potential-energy surface is of type IIS.

A potential-well on an endothermic surface (mentioned as a possibility by Prof. Zare, for HF + Sr) will have its minimum along the coordinate of approach, before the onset of the endothermic barrier.   The well would probably have its effect by making the barrier even more sudden.   Enhanced reagent translation would, however, carry the system right through a well located in the entrance valley, without the well itself having altered the dynamics profoundly.[4]

This is only the beginning of the menu of dynamical observations on HF + Sr that Prof. Zare has offered us.   There are in addition rotational effects (for which we have some precedent to guide us) and orientational effects (never before observed in con-junction with so much other detail).

The effect of enhanced reagent rotation on the cross-section for endothermic reaction was studied by the trajectory method for the mass combination LH + H → L + HH,[2] since experimental data existed for endothermic reactions HX̄(J', $\bar{v'}$) + Na → H̄ + XNa(X = F, Cl).[5]   The experiments had given evidence of an initial decline in $S_r(J')$ (J' refers to reagent rotation for endothermic reaction), followed by an increase.   The trajectory work suggested that this increase in $S_r(J')$ might be due to extension of the HX bond through vibration–rotation interaction leading, as with vibrational excitation, to longer-range attraction between the HX$^+$ and the Na.

Rotational excitation of the reagent molecule in the exothermic reaction F + $H_2(J)$ → HF(v', J') + H to $J > 1$ is known experimentally to result in enhanced vibrational

[1] D. S. Perry, A. Gupta and R. N. Zare, to be published.
[2] J. C. Polanyi and N. Sathyamurthy, Chem. Phys., 1978, 33, 287.
[3] J. W. Duff and D. G. Truhlar, J. Chem. Phys., 1975, 62, 2477.
[4] Y. Nomura, M.Sc. Thesis (University of Toronto, 1971).
[5] B. A. Blackwell, J. C. Polanyi and J. J. Sloan, Faraday Disc. Chem. Soc., 1977, 62, 147; Chem. Phys., 1978, 30, 299.

excitation in the molecular product,[1,2] as Zare's group have found (for a wider range of J') in HF(J') + Sr.[3] These observations accord nicely with the notion of vibration–rotation interaction: it is well known that an increase in reagent vibrational excitation gives rise to enhanced product vibration. What we are proposing, tentatively, is that in A + BC(v, J) enhanced reagent J or v results in stretching of the bond under attack and this in turn causes the reaction to proceed through a more-stretched intermediate, A—B—C; the stretched intermediate then snaps together to form AB† + C (the dagger indicates enhanced vibration).

As we have heard[4] it is now possible to measure the product vibrational excitation, not only as function of reagent rotation, but also as a function of the relative orientation of the reagents. For lateral approach of HF($v' = 1$) to Sr, Perry *et al.*[5] observe a greater degree of vibration in the SrF product than for the linear approach. There now exists a sufficient variety of evidence for a correlation between a more-stretched activated state and enhanced vibration in the products, to make their argument concerning the preferred line of approach a persuasive one. Trajectory studies indicate that, even for endothermic reactions such as this one, enhanced reagent vibration causes the representative trajectory to " cut the corner " of the endothermic potential-energy surface and fall into the exit valley from the side, with resultant oscillation in the new bond. Cutting the corner in this instance means reacting with Sr—F—H stretched. It would seem that for lateral approach of the reactants the endothermic energy barrier can be crossed with the new bond Sr—F more stretched. This does indeed suggest, as proposed[4] that reaction occurs with larger cross-section if the intermediate is bent.

Dr. A. J. McCaffery and Dr. J. McCormack (*Sussex*) said: In the Polanyi Memorial Lecture, Prof. Zare referred to experiments on Sr + HF which demonstrate the orientation dependence of reaction rate in a simple atom–diatomic molecule reaction. We report the observation of a similar orientation dependence of reaction rate, in this case in an alkali-atom–alkali-dimer reaction. The process, however, is unusual in that it takes place in a heated cell and not in a beam as reported by Prof. Zare; thus the reactive " bath " of atoms is unpolarised with no apparent preferential reaction trajectory.

The system consists of NaK, laser-excited to a single rovibronic state of $C^1\Pi_u$, in a heated cell containing sodium and potassium in roughly equal proportions. An indication of unusual behaviour in this system is seen in the intensity of rotationally resolved fluorescence. Here the intensity of only the populated level is monitored and its variation as a function of foreign gas pressure is shown in fig. 1. The intensity first rises to a maximum at $\approx$4-5 Torr of helium and then slowly falls off towards higher pressures. The fall-off from $\approx$5 Torr is straightforward to explain as the population loss due to inelastic and dissociative processes. The rise at low pressure is very unusual. It is not the result of a change in the dynamical equilibrium within the cell[7] and is most likely due to reactive or quenching K–NaK* collisions. These processes are both known to occur with high efficiency[8,9] and the rise in signal

[1] R. D. Coombe and G. C. Pimentel, *J. Chem. Phys.*, 1973, **59**, 1535.
[2] D. J. Douglas and J. C. Polanyi, *Chem. Phys.*, 1976, **16**, 1.
[3] Z. Karny, R. C. Estler and R. N. Zare, *J. Chem. Phys.*, 1979, **69**, 5199.
[4] R. N. Zare, *Faraday Disc. Chem. Soc.*, 1979, **67**, 7.
[5] D. S. Perry, A. Gupta and R. N. Zare, to be published.
[6] D. S. Perry, J. C. Polanyi and C. Woodrow Wilson Jr, *Chem. Phys. Letters*, 1974, **24**, 484.
[7] J. McCormack and A. J. McCaffery, *Chem. Phys.*, submitted for publication.
[8] J. C. Whitehead and R. Grice, *Faraday Disc. Chem. Soc.*, 1973, **55**, 320.
[9] P. H. Wine and L. A. Melton, *Chem. Phys. Letters*, 1977, **45**, 509.

intensity corresponds to this reaction becoming diffusion controlled before the onset of population-depleting collisions. Thus two pressure regimes appear to exist in the cell used in this study, the first at low helium pressure being dominated by K–NaK* collisions and the second, at higher helium pressure, where He–NaK* collisions predominate.

We now turn to the polarisation measurements: fig. 1 shows the circular polarisation ratio for two typical excited states. It is these plots which are remarkable since,
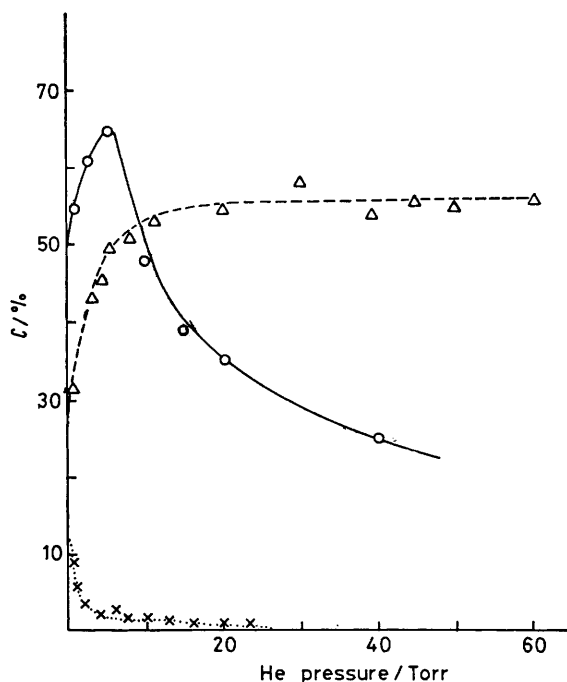

FIG. 1.—Representative plots showing variation of rotationally resolved intensity and polarisation ratio for excited NaK as a function of helium pressure. Several different rovibronic states within the $C^1\Pi$ and $D^1\Pi$ manifolds were excited with similar results in all cases. The full curve shows intensity in arbitrary units for the P excitation to $j' = 24$ (P $\downarrow$ and R $\downarrow$ are summed for intensity determinations). The broken curve shows circular polarisation ratio $C/\%$ for the P $\uparrow$ P $\downarrow$ branch of $j' = 30$ whilst the dotted curve is $Q \uparrow Q \downarrow$ circular polarisation for $j' = 93$. Ref. (1) tabulates theoretical C values for these and other transitions in diatomic molecules.

in the case of a P or R excitation, the polarisation ratio is exceptionally low at low pressure, rises to a maximum at 5 Torr and then remains relatively unchanged to very high helium pressures. When the excitation is a Q transition, on the other hand, the polarisation ratio starts off exceptionally high, a factor of almost 10^3 larger than theoretical,[1] which then drops rapidly before levelling out at ≈ 5 Torr.

This behaviour is very unusual and has not been observed in similar studies on Li_2 alkali dimers.[1,2] The fact that unexpected results are found for polarisation and intensity in the same pressure region suggests very strongly a common origin for the phenomenon and this implies that the reactive or quenching K–NaK$^+$ collisions are M_j selective. Not only are these reaction rates dependent upon the orientation but this dependence varies with the nature of the excitation. Thus for P or R excitation

[1] S. R. Jeyes, A. J. McCaffery and M. D. Rowe, Mol. Phys., 1978, 36, 1865.
[2] M. D. Rowe and A. J. McCaffery, Chem. Phys., 1978, 34, 81.

it is the high M_j values which react fastest, whilst for Q excitation it is the low M_j values. The nature of the transition, P, Q or R, determines the relative populations of M_j states in diatomics excited with circularly polarised light and thus the state multiples created on excitation differ considerably for P, R and Q transitions. Different reaction rates for these multipoles are unlikely to explain the variation in behaviour of P, R, and Q excited levels, since relationships exist between the multipoles of orientation and alignment. More pertinent is the fact that NaK^+ is in an excited Π state and P, R transitions populate the c-Λ doublet component whilst Q transitions excite the d-component. It is known that unexpected propensity rules hold for transfer between the Λ doublet components[1] of Π state alkali dimers. The characteristic of these levels is that they have different orientations of the electronic function in the molecule-fixed frame and it is likely that a potassium atom in its approach to the excited molecule experiences very different chemical forces depending upon both the Λ-doublet component and upon the orientation, or M_j-state of the rotating diatomic molecule.

Mr. A. J. Hynes and Dr. J. H. Brophy (*Leeds*) said: Recent work of Grice and co-workers[2] on a molecular beam study of the reaction $O + CS_2 \rightarrow CS + SO$, when combined with flash photolysis studies,[3] suggests that the product molecules should be formed with considerable rotational excitation. We have recorded laser excitation spectra of the CS product of this reaction at thermal energies and at pressures down to 5×10^{-3} Torr. The intensities of the A-X (0-0) and (1-1) bands indicate that an appreciable amount of the reaction energy is channelled into vibrational excitation of the CS fragment, in agreement with flash photolysis studies. However, at the lowest pressures we are unable to detect rotational excitation and preliminary analysis of the spectra indicates a relatively cold distribution. We are currently extending these measurements to remove the possibility of rotational relaxation of the nascent reaction products.

Dr. P. N. Clough and Mrs. J. Johnston (*Belfast*) said: We have recently made measurements of the relative populations of CS formed in the $v = 0, 1$ vibrational levels in the $O + CS_2$ reaction in an attempt to resolve the question of the large degree of product internal excitation indicated by crossed molecular beam measurements.[4,5] A frequency-doubled c.w. dye laser (linewidth 0.002 nm) was used to excite fluorescence in the (0, 0) and (0, 1) transitions of the CS $A^1\Pi - X^1\Sigma^+$ system with complete resolution of the Q, P branch rotational structure. Reaction conditions at total pressure $\approx 5 \times 10^{-3}$ Torr were chosen to give insignificant collisional relaxation of CS prior observation.[6] Preliminary analysis of the fluorescence intensities of unperturbed lines[7] in these bands yields an estimate of the $v = 1/v = 0$ population ratio of 0.3 ($\pm 25\%$). This is close in value to the ratio deduced by Smith[8] using flash photolysis. Fluorescence from the CS (1, 2) and (1, 1) bands has also been detected, and indicates a similar population of $v = 2$ to that deduced in the flash photolysis measurements. These results are not well-described by trajectory calculations,[8] even for a

[1] C. Ottinger, R. Velasco and R. N. Zare, *J. Chem. Phys.*, 1970, **52**, 1636.
[2] P. A. Gorry, C. V. Nowikow and R. Grice, *Mol. Phys.*, 1979, **37**, 329.
[3] I. W. M. Smith, *Trans. Faraday Soc.*, 1968, **64**, 194.
[4] J. Geddes, P. N. Clough and P. L. Moore, *J. Chem. Phys.*, 1974, **61**, 2145.
[5] P. A. Gorry, C. V. Novikow and R. Grice, *Chem. Phys. Letters*, 1978, **55**, 19.
[6] I. W. M. Smith, *Trans. Faraday Soc.*, 1968, **64**, 3184.
[7] A. Lagerquist, H. Westerlund, C. V. Wright and R. F. Barrow, *Arkiv Fysik*, 1958, **14**, 387.
[8] I. W. M. Smith, *Disc. Faraday Soc.*, 1967, **44**, 194.

model with extremely abrupt product repulsion and a collinear intermediate which most favours CS excitation. Scattering studies indicate that the intermediate is probably bent, favouring SO vibration and product rotation at the expense of CS vibration.[1] A rotational temperature of 500 K fits our (0, 0) band fluorescence reasonably well, and may indicate much higher initial excitation, since substantial rotational relaxation is expected at our working pressure.

Dr. P. A. Gorry, Dr. C. V. Nowikow and Prof. R. Grice (*Manchester*) said: The observations of Hynes and Brophy and of Clough and Johnston on the $O + CS_2$ reaction, which indicate appreciable vibrational excitation of the CS product, are of interest in connection with the molecular beam scattering measurements.[1,2] The angular distribution of reactive scattering peaks strongly in the forward direction and is independent of initial translational energy.[2] This indicates a direct stripping mechanism which would be expected to yield vibrational excitation of the newly formed OS bond rather than the CS bond. Tetra-atomic molecular orbital theory[2] for BAAB molecules, similar to that proposed by Walsh[3] for HAAH molecules, suggests that the OSCS transition state should have a bent planar (*cis*) configuration and result in rotational excitation of the reaction products. However, molecular orbital theory can give only a qualitative prediction. A more quantitative understanding of the $O + CS_2$ reaction dynamics must await direct observation of the unrelaxed OS and CS rotational state distributions.

Dr. D. M. Hirst and Mr. M. F. Jarrold (*Warwick*) **and Dr. K. Birkinshaw** (*Aberystwyth*) said: In ion–molecule reactions one can readily vary the initial relative translational energy over a wide range and the reaction dynamics often show a very strong dependence on translational energy. We are investigating the reaction of CO^+ with O_2 by the crossed molecular beam method at centre-of-mass energies >1.5 eV. Under thermal conditions CO^+ and O_2 are reported to undergo only charge exchange[4] with a rate constant of 1.2×10^{-10} cm³ molecule⁻¹ s⁻¹ (measured at 300 K in a selected ion flow tube[5]). Energy dependent studies by the injected ion-drift tube method show that the cross-section for charge exchange falls from ≈20 to 1 Å² over the energy range 0.04-3 eV.[6] No other reaction was observed.

In our molecular beam experiments we find that the reaction

$$CO^+ + O_2 \rightarrow CO^{2+} + O$$
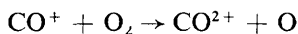
occurs effectively in the energy range in which we are working. The reaction is exothermic by 0.58 eV. The reaction cross-section appears to decrease as the energy is lowered and at energies below 2 eV the intensity of product ions is too low for meaningful experiments to be made.

The velocity contour diagrams show forward peaking indicative of reaction by a direct mechanism. As the energy is increased the product distribution becomes more strongly peaked. The intensity maxima occur at energies below the spectator stripping limit indicating internal excitation of the product CO^{2+} in excess of that predicted

[1] J. Geddes, P. N. Clough and P. L. Moore, *J. Chem. Phys.*, 1974, **61**, 2145.
[2] P. A. Gorry, C. V. Nowikow and R. Grice, *Mol. Phys.*, 1979, **37**, 329.
[3] A. D. Walsh, *J. Chem. Soc.*, 1953, 2288.
[4] F. C. Fehsenfeld, A. L. Schmeltekopf and E. E. Ferguson, *J. Chem. Phys.*, 1966, **45**, 23.
[5] N. G. Adams, D. Smith and D. Grief, *Int. J. Mass. Spec. Ion Phys.*, 1978, **26**, 405.
[6] N. Kobayashi and Y. Kaneko, *J. Phys. Soc. Japan*, 1974, **37**, 1082.

by this simple model.   Fig. 2 shows a preliminary cartesian velocity contour diagram[1] for a relative energy of 5.03 eV.   In addition to the strong forward peak there is also a significant amount of backward scattering.

On the basis of the radiative lifetimes of the $A\,^2\Pi$ and $B\,^2\Sigma^+$ states of CO^+, we believe that negligible amounts of these species reach the crossing region and conclude that the reactive species is CO^+ in the ground $X\,^2\Sigma^+$ state.
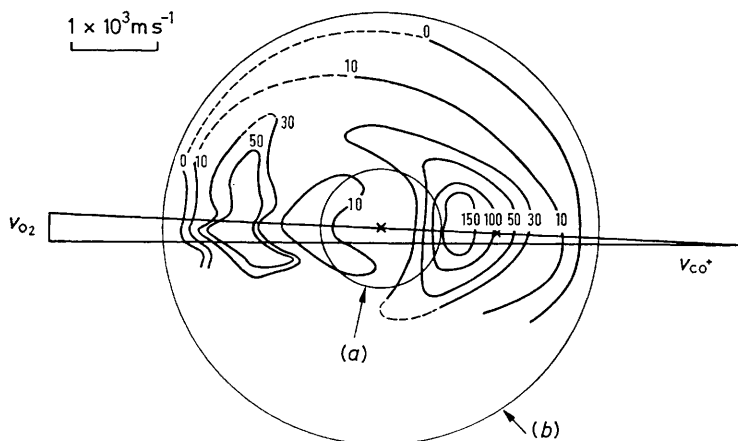

FIG. 2.—Contour map of intensity of CO_2^+ in centre-of-mass coordinate system for relative energy of 5.03 eV.   Crosses mark centre-of-mass and spectator stripping velocity.   Q is the change in relative kinetic energy, with (a) Q = −4.6, (b) Q = +0.58 eV.

The observation of reactive scattering at higher energies is significant in that it implies that there is a translational energy threshold which is unusual for exothermic ion–molecule reactions.

Dr. M. A. D. Fluendy, Dr. K. P. Lawley and Mr. D. Sutton (*Edinburgh*) said: In the paper presented at this meeting Fluendy *et al.*[2] discussed energy losses in the 0.5-5 eV region observed in K/CH_3I collisions.   The same data showed a number of inelastic processes with energy losses in the 5-12 eV region (fig. 3).

The points to be noted about these results are as follows.   (1) There is a relative sparsity of states compared with optical spectra taken in this region.   (2) The energy losses are discrete and with the exception of process (7)[2] constant with increasing scattering angle.   (3) The processes are observed to onset at very narrow scattering angles.

The combination of small scattering angles and large energy losses is evidence for the involvement of strong attractive potentials and suggests that these processes proceed *via* transient excited ionic states.

Fig. 4 shows a possible set of potential energy curves allowing access to highly excited molecular states and leading to only small angles of deflection.

If the intermediate negative molecular ion potential is different from the ground state potential, changes in the CH_3I geometry would be expected to occur during the collision.   Thus process (7) may be associated with harpooning into the $\sigma^*(C\!-\!H)$

[1] R. Wolfgang and R. Cross, *J. Phys. Chem.*, 1969, **73**, 743.

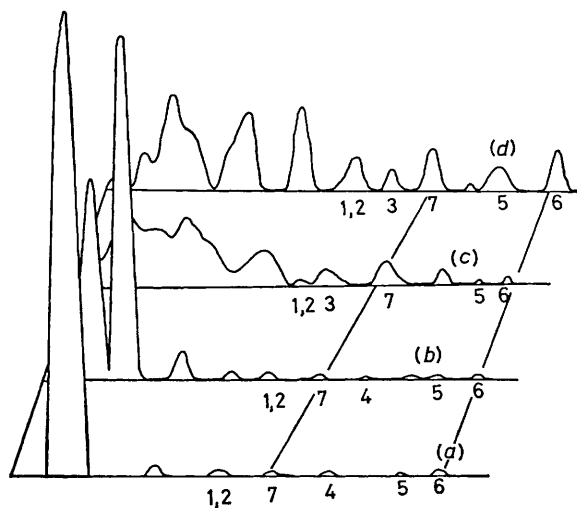[2] M. A. D. Fluendy, K. P. Lawley, J. McCall, C. Sholeen and D. Sutton, *Faraday Disc. Chem. Soc.*, 1979, **67**, 41.

FIG. 3.—Observed energy loss profiles K/CH₃I at c.m. collision energy 164 eV, $E\chi$ in eV°: (a) 97, (b) 287, (c) 656 and (d) 861.

orbital (fig. 5) followed by recapture from the iodine lone pairs. This transient ionic potential would be repulsive in the C—H coordinate. The time spent in this repulsive state varies with the impact parameter and scattering angle so that, in view of the light mass of the H atom, quite rapid variation in geometry and energy deposition can be expected, in accord with these observations.

In general electronic excitation will take place if donation into a high lying, normally vacant orbital is followed by recapture from a lower, normally filled orbital.
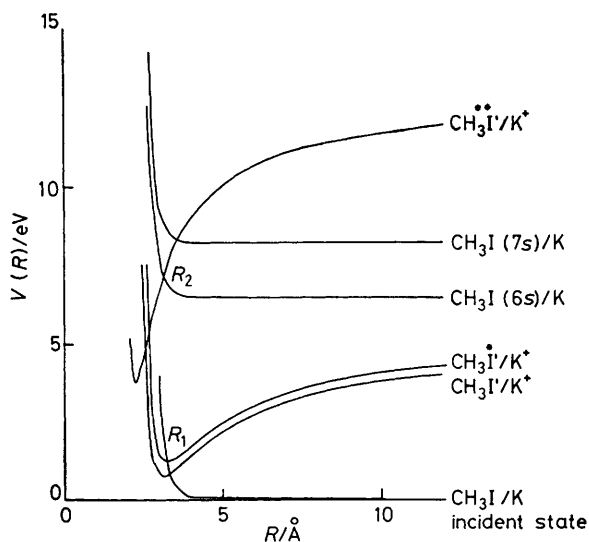

FIG. 4.—Diabatic potentials illustrating incident channel and the electron capture and recapture processes at R_1 and R_2 leading to excited states.
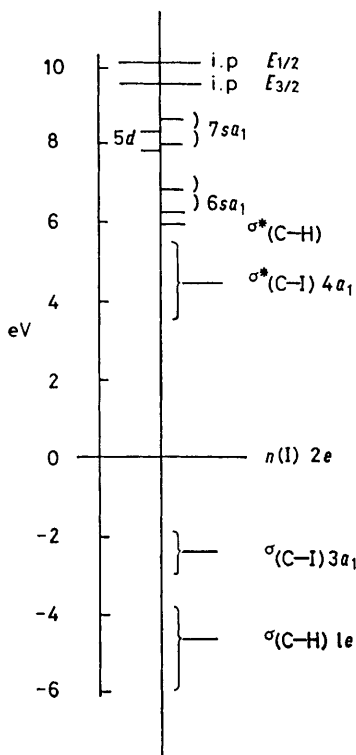
FIG. 5.—Schematic orbital energy diagram for CH_3I.

Possible energy losses arising from such a mechanism have been calculated, allowing us to make tentative assignments to the processes observed.

Dr. M. A. D. Fluendy, Dr. K. P. Lawley and Mr. G. W. Black (*Edinburgh*) said: We have carried out Monte Carlo trajectory surface hopping calculations on the potassium–methyl-iodide system incorporating surfaces corresponding asymptotically to excited potassium atom and methyl iodide molecular states. The potential surfaces used were based upon those developed by Blais and Bunker[1] which correctly describe the individual pair interactions and incorporate a switching function important in the close encounter region. The ionic CH_3I^- potential used was that described by Wentworth *et al.*[2]

Though satisfactory in describing most features of reactive scattering at thermal energies, this potential system was unsatisfactory at high velocities. Only limited access to the ionic surface crossing could be achieved and of those trajectories which crossed to the ionic surface on entrance the majority lead to dissociation rather than to electronic excitation, in contrast to the experimental results.[3]

The difficulty in accessing the ionic surface on entrance arises from the potassium–methyl repulsion, which becomes a dominant feature in the sudden collision, since there is little opportunity for movement within the methyl iodide before harpooning.

[1] D. L. Bunker and N. C. Blais, *J. Chem. Phys.*, 1964, **41**, 2377.

[2] W. E. Wentworth, R. George and H. Teeth, *J. Chem. Phys.*, 1969, **51**, 1791.

[3] M. A. D. Fluendy, K. P. Lawley, J. McCall, C. Sholeen and D. Sutton, *Faraday Disc. Chem. Soc.*, 1979, **67**, 41.

With these surfaces reaction occurs *via* a concerted pre-stretching in the methyl iodide bond as the potassium atom approaches. At high velocities this process is not available and the size of the access window to the ionic surface is correspondingly limited.

After harpooning, these surfaces predict rapid stretching in the CI coordinate and the exit crossing seams to the excited potassium and excited methyl iodide states move to wide internuclear distances. The crossing probability is then small and little electronic excitation can be produced. Comparison of these trajectory results with experiment thus suggests that the isolated pair-wise interactions must be substantially modified in the interaction region.

Dr. M. S. Child (*Oxford*) said: Since submitting our paper Dr. E. Pollak of the Weizmann Institute and I have made further studies of the properties of the trapped trajectories. This work will be published shortly, partly in conjunction with Prof. P. Pechukas. One important result directly relevant to our present contribution is that knowledge of the trapped trajectories A and B in fig. 4 of the paper by Child and Whaley, together with the shorter of the two dashed trapped trajectories in the central region, labelled say trajectory X, is sufficient to establish a rigorous lower bound for the microcanonical reaction probability. The necessary equation, first given as an estimate but not a lower bound to the reaction probability by Pollak and Pechukas,[1] is

$$P_L(E) = (F_A + F_B - F_X)/F_R \qquad (1)$$

where the fluxes $F_v (v = A, B, X)$ are taken as line integrals along the trapped trajectories

$$F_v = \int_v \boldsymbol{p} \cdot \mathrm{d}\boldsymbol{q} \qquad (2)$$

and F_R is the total flux through the energetically accessible reactant phase space.

Fig. 6 compares $P_L(E)$ and the variational upper bounds

$$P_v(E) = F_v/F_R, (v = A, B) \qquad (3)$$

with results from classical trajectory calculations for the $H + Cl_2$ reaction. The significant features are (i) that the new lower bound is also the most accurate estimate of the reaction probability and (ii) that the best single variational transition state lies close to the saddle point (trajectory A) only at energies below 0.5 eV. At higher energies the smallest bottleneck to the reaction is determined by trajectory B which lies across the products valley.

Prof. Zare asked about the effect of rotation on the detection of Condon reflection structure. Two types of rotation are relevant, the initial rotation of the reactant and the overall rotation during the collision. The first will depend on the range at which the potential anisotropy becomes large compared with the reactant rotational energy separation. If this range is large, collinear geometry will apply during the effective part of the collision and rotational quenching of the Condon reflection pattern will be small. The overall rotation may be crudely taken into account by subtracting a rotational energy contribution appropriate to the impact parameter from the total, to leave a collinear contribution

$$E_{1D} = E - E_{rot} = E(1 - b^2/r_0^2) \qquad (4)$$

where r_0 could be approximated by the radius of gyration at the saddle point. In this

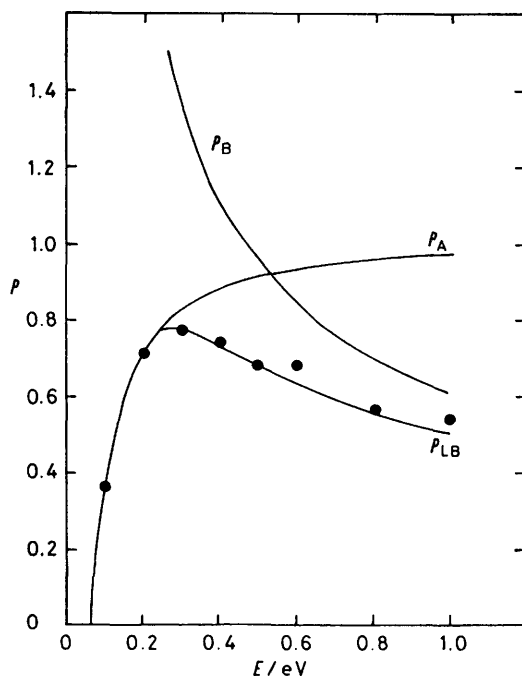[1] E. Pollak and P. Pechukas, *J. Chem. Phys.*, 1978, **69**, 1218.

FIG. 6.—Exact and approximate microcanonical transition probabilities for the collinear $H - Cl_2$ reaction. Dots indicate results from 200 trajectories. P_A and P_B are variational transition probabilities determined by the trapped trajectories A and B in fig. 4 of the paper by Child and Whaley. P_{LB} is the lower bound estimate.

approximation the collinear state-to-state probabilities could be transformed to three dimensions by the equation

$$P_{3D}(E) = \int_0^{r_0} b P_{1D}(E_{1D}) \, db \bigg/ \int_0^{r_0} b \, db \qquad (5)$$

or, after replacing b by E_{1D} as the integration variable,

$$P_{3D}(E) = \frac{1}{E} \int_0^E P_{1D}(E_{1D}) \, dE_{1D}. \qquad (6)$$

This integration over the results presented in fig. 2 of our paper would quench the bimodal pattern in the lower diagram if the relative values of P_{1v} were markedly energy dependent, but this is not the case for this system.

In less favourable situations quenching of this type, due to the overall rotation, could possibly be resolved by measuring a state-to-state differential cross-section, if this were possible. Such an experiment might also clarify whether the bimodal structure arising from a reactant with $v = 1$ is quantum-mechanical or classical in origin.

Dr. J. N. L. Connor (*Manchester*), **Dr. W. Jakubetz** (*Vienna*), **Dr. A. Laganà** (*Perugia*), **Dr. J. Manz** (*Munich*) **and Dr. J. C. Whitehead** (*Manchester*) said: Child and Whaley[1] have presented semiclassical calculations for the collinear $H + Cl_2$ reaction

[1] M. S. Child and K. B. Whaley, Faraday Disc. Chem. Soc., 1979, **67**, 57.

using an unoptimized LEPS surface.[1] Their calculations agree with the more extensive semi-classical calculations of Truhlar *et al.*[2] for the same system. In addition, Truhlar *et al.*[2] also compare the exact quantum results with forward and reverse quasiclassical results and transition state theory.

An interesting feature of these calculations[1-3] is that bimodal product state distributions for the HCl product from the collinear $H + Cl_2(v = 1)$ reaction have been predicted. We have also determined the product state distributions, both one- and three-dimensional, for the reaction of hydrogen and deuterium atoms with vibrationally excited ($v = 1$) chlorine molecules.[4] We have calculated collinear quantum reaction probabilities which are then transformed into 3D vibrotational reaction probabilities by an information-theoretic 1D → 3D transformation.

The potential surface used is an extended LEPS form which was determined by a new inversion procedure applied to detailed and total rate coefficient data for the thermal H and D reactions. In order to obtain the collinear $P_C(v'|1)$, accurate quantum calculations have been performed at a translational energy of 0.1 eV by the State Path Sum Method,[5] using a rotated Morse cubic spline fit[6] to the surface. These calculated collinear probabilities are bimodal in agreement with ref. (1)-(3) for $H + Cl_2(v = 1)$.
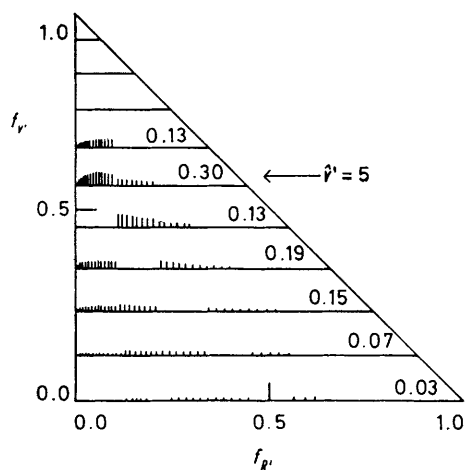

FIG. 7.—Triangle plot of the predicted $P(J',v')$ for $D + Cl_2(v = 1)$. The numbers along the diagonal give the normalised vibrational distribution $P(v')$.

The collinear probabilities are next transformed into vibrotational distributions using an information-theoretic 1D → 3D procedure of Bernstein and Levine[7] together with a constraint to account for angular momentum transfer in light + heavy-heavy atom reactions.[8] The resulting distribution, $P(J', v')$ for $D + Cl_2(v = 1)$ is shown in fig. 7. Clearly, the distribution is double peaked, with peak positions

[1] M. Baer, *J. Chem. Phys.*, 1974, **60**, 1057.
[2] D. G. Truhlar, J. A. Merrick and J. W. Duff, *J. Amer. Chem. Soc.*, 1976, **98**, 6771.
[3] M. S. Child and K. B. Whaley, *Faraday Disc. Chem. Soc.*, 1979, **67**, 57.
[4] J. N. L. Connor, A. Laganà, J. C. Whitehead, W. Jakubetz and J. Manz, *Chem. Phys. Letters*, 1979, **62**, 479.
[5] J. Manz, *Mol. Phys.*, 1974, **28**, 399; 1975, **30**, 899.
[6] J. N. L. Connor, W. Jakubetz and J. Manz, *Mol. Phys.*, 1975, **25**, 347.
[7] R. B. Bernstein and R. D. Levine, *Chem. Phys. Letters*, 1974, **29**, 314.
[8] J. N. L. Connor, W. Jakubetz and J. Manz, *Ber. Bunsenges. phys. Chem.*, 1977, **81**, 165.

at $\approx(0.11, 0.25)$ and $(0.11, 0.55)$ in $(f_{R'}, f_{V'})$ space. As a result, the rotational distribution within each vibrational level, $P(J'|v')$, is bimodal for $v' \leqslant 3$, with the bimodal character decreasing rapidly towards a practically unimodal distribution for $v' = 0$. The three-dimensional product vibrational distribution, $P(v')$, is bimodal.

A similar, but less pronounced, pattern is also observed for the $H + Cl_2(v = 1)$ reaction. Again the $P(J', v')$ distribution is bimodal, but no definite bimodality can be seen in the individual $P(J'|v')$. The HCl vibrational distribution is unimodal in 3D.

Although no direct experimental measurements have been made for H, $D + Cl_2$ $(v = 1)$, there is some experimental evidence available. Ding et al.[1] have found a bimodal $P(J', v')$ but unimodal $P(v')$ for the reaction $H + Cl_2(v \geqslant 1)$. Clearly, experiments performed with only state-selected $Cl_2(v = 1)$ would be welcomed.

Prof. J. C. Polanyi (*Toronto*) said: Connor et al.[2] have described a rotational bimodality in the products of the reaction $H + Cl_2(v = 1) \rightarrow HCl(v', J') + Cl$, as obtained from a collinear quantum calculation transformed into a 3D result by an information-theoretic 1D $\rightarrow$ 3D transformation. It is interesting to consider how such a bimodality might arise.

As Child and Whaley point out in a related study of the same reactive system,[3] there is evidence for vibrational bimodality in the products of $H + Cl_2(v > 0) \rightarrow HCl(v', J') + Cl$.[1] Experimental determination of product vibrational excitation from the reaction $H + Cl_2(v \geqslant 0) \rightarrow HCl(v', J') + Cl$ yielded a product vibrational distribution so markedly broadened in its distribution over v'-states that, following correction for the well-known product distribution from $H + Cl_2(v = 0) \rightarrow HCl(v', J') + Cl$, it implied a grouping of the product vibrators into a batch at low v' and a second, more prominent batch at high v'.

An effect of this type can be explained most simply by a Frank–Condon model, in which chemical reaction is treated as a sudden transposition of BC from a bound to a repulsive state (Child and Whaley[3] give a selection of references to calculations of this type). The $\underline{L + HH}$ (light plus heavy–heavy) mass-combination lends itself to such a treatment.

Classical trajectory calculations on various plausible potential energy surfaces which did not constrain the system to behave in a Frank–Condon-like fashion, showed that the distribution of $\underline{HH}$ separations in the bound condition did indeed evidence itself as a bimodality in the product vibrational excitation.[4,5] Inspection of the reactive trajectories was revealing. A smaller group of molecules XX† (vibrationally-excited halogens) reacted with r_{XX} compressed, to form HX† (v_l) (low vibrational excitation). A larger group reacted with r_{XX} extended, to form HX† (v_h) (high vibrational excitation).

In the language of the theoretical study of $H + XY$ presented in this Discussion,[6] this would be described as induced microscopic branching. The (vibrational) excitation in the reagents has opened up two distinguishable and characteristic paths lead-

[1] A. M. G. Ding, L. J. Kirsch, D. S. Perry, J. C. Polyani and J. L. Schreiber, *Faraday Disc. Chem. Soc.*, 1973, **55**, 252.

[2] J. N. L. Connor, W. Jakubetz, A. Laganà, J. Manz and J. C. Whitehead, *Faraday Disc. Chem. Soc.*, 1979, **67**, 120.

[3] M. S. Child and K. B. Whaley, *Faraday Disc. Chem. Soc.*, 1979, **67**, 57.

[4] C. A. Parr, J. C. Polanyi, W. H. Wong and D. C. Tardy, *Faraday Disc. Chem. Soc.*, 1973, **55**, 308.

[5] J. C. Polanyi, J. L. Schreiber and J. J. Sloan, *Faraday Disc. Chem. Soc.*, 1973, **55**, 124; *Chem. Phys.*, 1975, **9**, 403.

[6] J. C. Polanyi, J. L. Schreiber and W. J. Skrlac, *Faraday Disc. Chem. Soc.*, 1979, **67**, 66.

ing from reactants to products, one *via* a compressed intermediate $(\to v_l)$ and one *via* an extended intermediate $(\to v_l)$ the latter having a larger cross-section.[1,2]

Speculation may be premature, but it is tempting to ask how this same bifurcation of paths through reactive hyperspace could lead to differing rotational outcomes. Fig. 13 and 15 of ref. (3) suggest a rationale. The extension of the bond under attack facilitates migration, and migration in H + XY tends to be accompanied by enhanced internal excitation. That part of the reaction that takes place by way of a stretched intermediate could therefore result not only in enhanced v' but also in enhanced J'. The experiments[4] and trajectory calculations[1] completed to date suggest, however, that if such an effect is contributing to the outcome, it plays a minor role for H + Cl_2 $(v = 1)$.

Could it be that the rather dramatic increase in product rotational excitation for D + $Cl_2(v = 1)$ as compared with D + $Cl_2(v = 0)$ to be found in Whitehead *et al.*'s results has its origins in the method of correcting from the rotationless 1D situation to the 3D outcome that they picture?

Dr. J. N. L. Connor (*Manchester*), **Dr. W. Jakubetz** (*Vienna*), **Dr. A. Laganà** (*Perugia*), **Dr. J. Manz** (*Munich*) **and Dr. J. C. Whitehead** (*Manchester*) (*communicated*): We use an information-theoretic method[5] to transform collinear (1D) quantum vibrational reaction probabilities $P_C(v')$ into three dimensional (3D) vibrotational reaction probabilities $P(J', v')$. The procedure is to synthesize the $P(J', v')$ by minimizing the entropy deficiency of the $P(J', v')$ subject to two constraints. The first constraint assumes the 1D and 3D surprisals for the fraction of internal energy are the same. Physically this is equivalent to assuming that the dynamical effects which determine the $P_C(v')$ are also dominant for the 3D product internal energy distributions. The second constraint accounts for angular momentum transfer in light + heavy–heavy atom reactions by requiring the average fraction of product rotational energy be equal to a predetermined value $\langle f_{R'} \rangle_{pre}$. The theory has been outlined in ref. (6) and in more detail in ref. (7). Applications have been made to the reactions X + F_2 → XF + F[6–8] with X = Mu, H, D, T, F + H_2 → HF + F[8] and H(D) + Cl_2 → HCl (DCl) + Cl.[9]

In order to obtain $\langle f_{R'} \rangle_{pre}$ for the H + $Cl_2(v = 0, 1)$ and D + $Cl_2(v = 0, 1)$ reactions, we have used the thermal experimental values of 0.08 for H[4] and 0.11 for D[10] since the experimental results in ref. (4) indicate that $\langle f_{R'} \rangle$ for the H reaction depends only weakly on the initial vibrational state of Cl_2. Thus in our calculation[9,11] the value of $\langle f_{R'} \rangle$ is the same for D + $Cl_2(v = 0)$ and D + $Cl_2(v = 1)$ although the predicted $P(J', v'|v)$ are quite different. We have also carried out calculations in which the input data $P_C(v')$ and $\langle f_{R'} \rangle_{pre}$ are varied slightly from the values just given. We have also investigated the effect of using three different " prior probabilities "

[1] C. A. Parr, J. C. Polanyi, W. H. Wong and D. C. Tardy, *Faraday Disc. Chem. Soc.*, 1973, **55**, 308.

[2] J. C. Polanyi, J. L. Schreiber and J. J. Sloan, *Faraday Disc. Chem. Soc.*, 1973, **55**, 124; *Chem. Phys.*, 1975, **9**, 403.

[3] J. C. Polanyi, J. L. Schreiber and W. J. Skrlac, *Faraday Disc. Chem. Soc.*, 1979, **67**, 66.

[4] A. M. G. Ding, L. J. Kirsch, D. S. Perry, J. C. Polanyi and J. L. Schreiber, *Faraday Disc. Chem. Soc.*, 1973, **55**, 252.

[5] R. B. Bernstein and R. D. Levine, *Chem. Phys. Letters*, 1974, **29**, 314.

[6] J. N. L. Connor, W. Jakubetz and J. Manz, *Ber. Bunsenges. phys. Chem.*, 1977, **81**, 165.

[7] J. N. L. Connor, W. Jakubetz, J. Manz and J. C. Whitehead, *Chem. Phys.*, 1979, **39**, 395.

[8] J. N. L. Connor, W. Jakubetz and J. Manz, *Chem. Phys.*, 1978, **28**, 219.

[9] J. N. L. Connor, A. Laganà, J. C. Whitehead, W. Jakubetz and J. Manz, *Chem. Phys. Letters*, 1979, **62**, 479.

[10] K. G. Anlauf, D. S. Horne, R. G. MacDonald, J. C. Polanyi and K. B. Woodall, *J. Chem. Phys.*, 1972, **57**, 1561.

[11] Preceding comment.

in the theory.   We found that these changes have only a small effect on the predic-
tions reported above[1] and in ref. (2).

Prof. Polanyi has asked whether our surface for $H + Cl_2(v = 1)$ has a lower
barrier for the Cl_2 bond extended rather than compressed.   This is indeed the case.
Thus, a possible classical explanation of the calculated bimodality in the producte state
distribution for the reaction $H + Cl_2(v = 1)$ may be obtained in terms of " micro-
scopic branching ",[3] as well as the quantum mechanical Condon reflection principle.[4]
It is possible, however, that the classical and quantum mechanical predictions may not
be identical for the reaction $H + Cl_2(v \geqslant 2)$, where " microscopic branching " would
continue to predict bimodality, but a Condon reflection might have more modes.

Dr. J. Allison, Mr. M. A. Johnson and Prof. R. N. Zare (*Stanford*) said: We have
reinvestigated the reaction

$$Ba + CF_3I \rightarrow BaI + CF_3$$
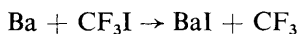
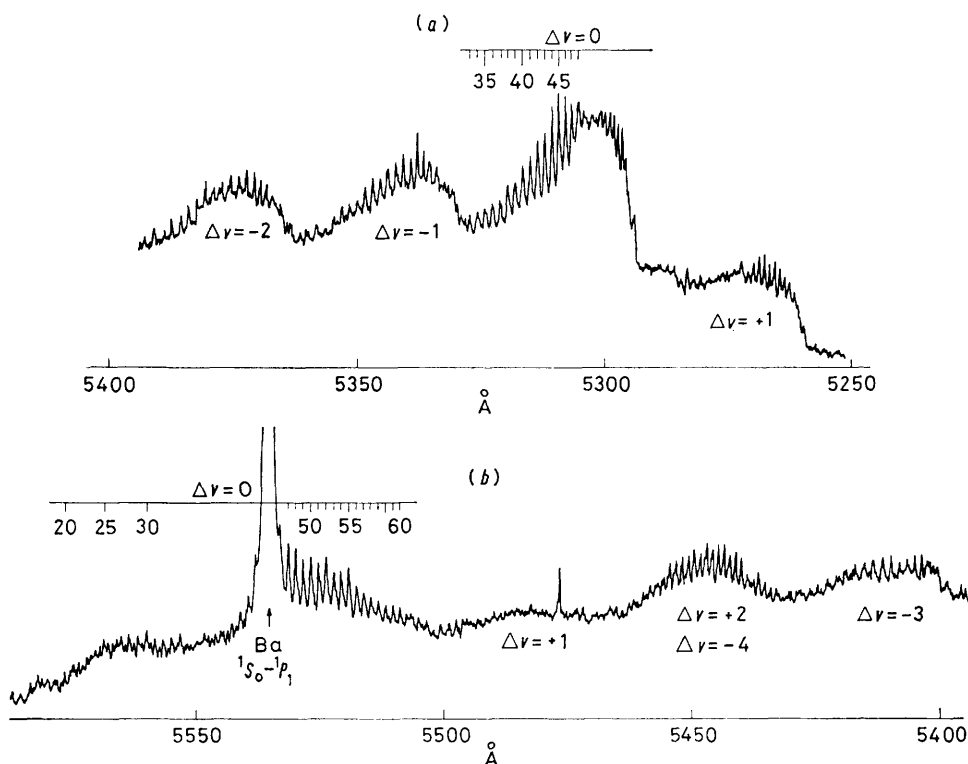which was reported by Smith, Whitehead and Zare to give a bimodal vibrational distri-

FIG. 8.—Unrelaxed BaI excitation spectrum (*a*) $C^2\Pi_{\frac{3}{2}} + X^2\Sigma^+$, (*b*) $C^2\Pi_{\frac{1}{2}} + X^2\Sigma^+$, from the
reaction $Ba + CF_3I$.   The $\Delta v = 0$ sequences are numbered based on the excitation spectra for $Ba + CH_3I$.   The vibrational numbering of the $\Delta v \pm 0$ sequences is under study.

bution of the BaI reaction product.   New spectroscopic evidence indicates that the
$BaI(X^2\Sigma^+)$ products *do not* have a bimodal vibrational distribution, as was previously
believed.

[1] Preceding comment.
[2] J. N. L. Connor, W. Jakubetz and J. Manz, *Ber. Bunsenges. phys. Chem.*, 1977, **81**, 165.
[3] J. C. Polanyi, J. L. Schreiber and W. J. Skrlac, *Faraday Disc. Chem. Soc.*, 1979, **67**, 66.
[4] M. S. Child and K. B. Whaley, *Faraday Disc. Chem. Soc.*, 1979, **67**, 57.

The laser-induced fluorescence (LIF) technique was used to detect the BaI products. We used a Molectron UV-24 nitrogen laser (1 MW) whose output pumped a Molectron DL 14-P dye laser (oscillator–amplifier configuration; bandwidth = 0.3 Å). With this power (≈ 150 kW) we readily saturated the $\Delta v = 0$ sequences of the BaI $C^2\Pi_{\frac{3}{2},\frac{1}{2}} - X^2\Sigma^+$ band systems.

Fig. 8 shows an excitation spectrum obtained with full laser power. The sequences in the $C^2\Pi_{\frac{3}{2}} - X^2\Sigma^+$ system labelled as $\Delta v = -1$ was previously identified as a low
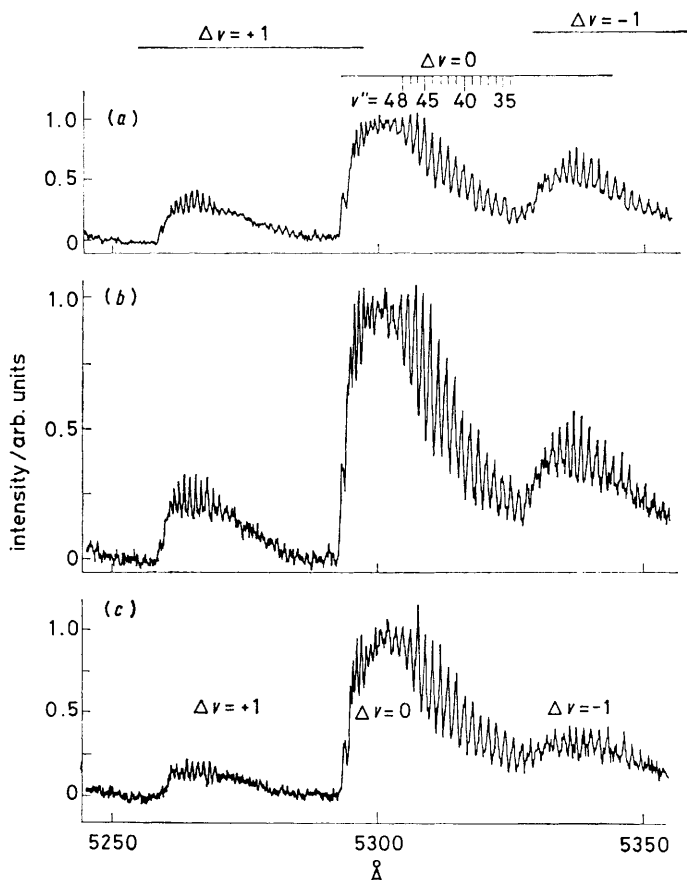

FIG. 9.—Unrelaxed BaI excitation spectra ($C^2\Pi_{\frac{3}{2}} - X^2S^+$) from the reaction Ba + CF$_3$I obtained using (a) full laser power, (b) one-tenth laser power and (c) one-hundredth laser power.

v progression within the $\Delta v = 0$ sequence. The $\Delta v = 0$ and $\Delta v = -1$ sequences severely overlap one another, the differences in bandhead locations being <1 Å in most cases. However, a saturation study (see fig. 9) demonstrates that the $\Delta v = 0$ and $\Delta v = -1$ sequences are as labelled and not both members of $\Delta v = 0$. In fig. 9(a), (b) and (c) the power level of the dye laser is successively reduced by a factor of ten. The ratio of any line intensity in the $\Delta v = 0$ sequence to any line in $\Delta v = +1$ or -1 increases by approximately a factor of two in going from full laser power to 100-fold attenuation. The degree of saturation depends on the absorption coefficient and hence the Franck–Condon factor. Thus the bands labelled $\Delta v = -1$ and $\Delta v = +1$ have significantly different Franck–Condon factors from those of $\Delta v = 0$. We

therefore conclude that the present sequence assignments are correct.   In the previous analysis it was assumed that the Franck–Condon factors for the $\Delta v = 0$ sequence were all near unity.   It appears that, as v increases, the $\Delta v = 0$ Franck–Condon factors decrease, causing $\Delta v \neq 0$ sequences to appear at high v.

In the $C\,^2\Pi_{\frac{3}{2}}\!-X\,^2\Sigma^+$ spectrum, each sequence overlaps the other to such an extent that it is difficult to determine whether or not a low v progression is present.   Fortunately, there is much less overlap in the $C\,^2\Pi_{\frac{1}{2}}\!-X\,^2\Sigma^+$ spectrum.   Analysis of the BaI excitation spectrum obtained from the reaction of Ba with CH_3I gives vibrational populations peaking at $v \approx 20$.   Hence the $\Delta v = 0$ sequence in both the $C\,^2\Pi_{\frac{3}{2}}\!-X\,^2\Sigma^+$ and the $C\,^2\Pi_{\frac{1}{2}}\!-X\,^2\Sigma^+$ spectra is approximately the same intensity.   Therefore, if there is a population in low v levels, we should be able to detect its presence in the $C\,^2\Pi_{\frac{1}{2}}\!-X\,^2\Sigma^+$ spectrum.   Fig. 8 shows that no appreciable intensity occurs in the low v region of the $\Delta v = 0$ sequence, from which we conclude that there is no evidence to support the contention that the vibrational distribution is bimodal.   Instead, the vibrational distribution likely has the bell-shaped form characteristic of Ba $+$ CH_3I, but peaking at higher vibrational levels.

Prof. D. W. Setser (*Kansas State*) said: Polanyi, Schreiber and Skrlac have made an important contribution towards further understanding of the H $+$ XY reaction dynamics by examining the migratory aspects of these systems.   They demonstrated that it was possible to reproduce the broad trends in the experimental data by trajectory calculations on assumed potential surfaces but that matching the detailed experimental features was difficult.   We have recently obtained data which further restrict the choice of potential surfaces for these reactions.[1,2]   Using an arrested vibrational relaxation flowing-afterglow technique, initial vibrational distributions, macroscopic branching ratios and relative rate constants have been obtained for the reactions of H with F_2, Cl_2, Br_2, ClF and ClI.   The vibrational distributions agree with those obtained from the cold-wall arrested vibrational and rotational relaxation technique.   The relative rate constants and macroscopic branching ratios are shown in table 1.   The important new points are (i) the rate constant for H $+$ Br_2 is only

TABLE 1.—H $+$ XY RATE CONSTANTS[a] AND MACROSCOPIC BRANCHING RATIOS[a]

X\Y	F	Cl	Br	I
F	0.053	1.99		
Cl	5.2	1.0		2.4[b]
Br		2.5[c]	≈ 1.6	
I		<0.5	≈ 0.3[d]	≈ 3.0[e]

[a] Data taken from ref. (1) and (2) unless indicated otherwise.   Rate constants are entered on and above the diagonal; branching ratios, with the least exoergic channel in the numerator, are entered below the diagonal.   [b] For the HCl channel only.   [c] J. C. Polanyi and W. J. Skrlac, *Chem. Phys.*, 1977, **23**, 167.   [d] J. Grosser and H. Haberland, *Chem. Phys.*, 1973, **2**, 352.   [e] K. Lorenz, H. G. Wagner and R. Zellner, *Ber. Bunsenges phys. Chem.*, 1979, **83**, 556.

moderately larger than for H $+$ Cl_2 but the $\langle f_v \rangle$ values are 0.48 and 0.35, respectively; (ii) the rate constants for ClF and ClI are only a factor of 2 larger than for Cl_2.   The increased rate constants do not correspond to sufficiently larger impact parameters that the migratory components of the H $+$ ICl or ClF reactions can be explained as arising from large impact parameter collisions.   Our interpretation is that the

[1] J. P. Sung, R. J. Malins and D. W. Setser, *J. Phys. Chem.*, 1979, **83**, 1007.
[2] R. J. Malins and D. W. Setser, *J. Chem. Phys.*, 1979, to be submitted.

favoured approach geometry changes from end-on to more nearly side-on without much change in potential barrier as the halogen becomes heavier. This is consistent with the trends in angular distribution observed for reactive scattering for the homonuclear halogens and with the rate constants in table 1. The variation in approach geometry from end-on to side-on correlates with increasing importance of hydrogen migration from the less to the more electronegative halogen atom as one of the halogens becomes heavier for the interhalogen series.

Dr. H. U. Lee (*Stuttgart*) said: Polanyi *et al.*[1] have raised the intriguing concept of alternative direct and migratory reaction dynamics. Although such competing mechanisms appear to be manifested in the H + XY reactions, the question remains whether an extension to heavier and more complex systems can be found to occur in nature. Recently, Smith *et al.*[2] have reported an investigation of the Ba + CF_3I reaction. Here macroscopic branching[1] is not observed, for reasons already suggested;[2] the only product detected is BaI. But the possibility might exist for microscopic branching.[1] Indeed, laser-induced fluorescence has initially shown a vibrational distribution in the BaI product that appears to be bimodal;[2] however, more refined studies[3] have subsequently cast doubt on these results.

We take this opportunity to communicate our investigations on the analogous reactions involving ytterbium, Yb. Our previous studies[4] indicate that the dynamics of Yb + halogenomethane reactions exhibit features that essentially parallel those of the group IIA metal atoms. This should not be perplexing, since Yb has the electronic configuration $[Xe]4f^{14}6s^2$ and a moderately low ionization potential of 6.2 eV. Several factors suggest that bimodality could be more easily detected in the Yb than in the Ba reactions. Firstly, the exothermicities of the Yb + CH_3I and CF_3I reactions amount to ≈ 4.6 and ≈ 6.8 kcal mol^{-1}, respectively; thus, a maximum of only 15 vibrational levels in YbI can be populated. Furthermore, the vibrational bands within the $\Delta v = 0$ sequence are so widely spaced (≈ 5 Å) that definitive assignments can be made. One serious drawback, however, is the lack of rotational constants for YbI. In this case, one may confidently assume that for low v the Franck–Condon factors decrease monotonically within the $\Delta v = 0$ sequence, by analogy with YbF[5,6] and the Group IIA monohalides.[7] In all, a comparison of Yb encounters with CH_3I and CF_3I would be interesting because any hint at a YbI bimodal distribution in the former reaction would reveal itself unequivocally in the latter. That is, the F atoms on CF_3I provide a much more attractive site for Yb attack than the H atoms on CH_3I, thus accentuating the competition between direct and migratory mechanisms.

The reactions of Yb with CH_3I and CF_3I were investigated in a molecular beam apparatus. C.w. laser-induced fluorescence was used to probe the vib-rotational distribution of the nascent YbI products. The signal was modulated by chopping the halogenomethane gas beam, instead of the laser light, in order to suppress spurious signals arising from oven reactions, scattering off walls, etc. The results are striking. No YbF product could be detected. Exhibited in fig. 10 are the YbI vibrational distributions, assuming, for simplicity, constant Franck–Condon factors within the

[1] J. C. Polanyi, J. L. Schreiber and W. J. Skrlac, *Faraday Disc. Chem. Soc.*, 1977, **67**, 66.
[2] G. P. Smith, J. C. Whitehead and R. N. Zare, *J. Chem. Phys.*, 1977, **67**, 4912.
[3] R. N. Zare, communicated at this Discussion.
[4] R. Dirscherl and H. U. Lee, to be published.
[5] R. F. Barrow and A. H. Chojnicki, *J.C.S. Faraday II*, 1975, **71**, 728.
[6] H. U. Lee and R. N. Zare, *J. Mol. Spectr.*, 1977, **64**, 233.
[7] H. W. Cruse, P. J. Dagdigian and R. N. Zare, *Faraday Disc. Chem. Soc.*, 1973, **55**, 277.

$\Delta v = 0$ sequence. Each case exhibits a unimodal distribution; however, the fraction of energy released into YbI vibration differs notably, namely, >20% in Yb + CH_3I and >50% in Yb + CF_3I. By analogy with the reactions of K and Ba with CH_3I, where the salt products are found to scatter predominantly into the backward hemisphere,[1,2] the Yb + CH_3I system probably follows a rebound mechanism. Scattering
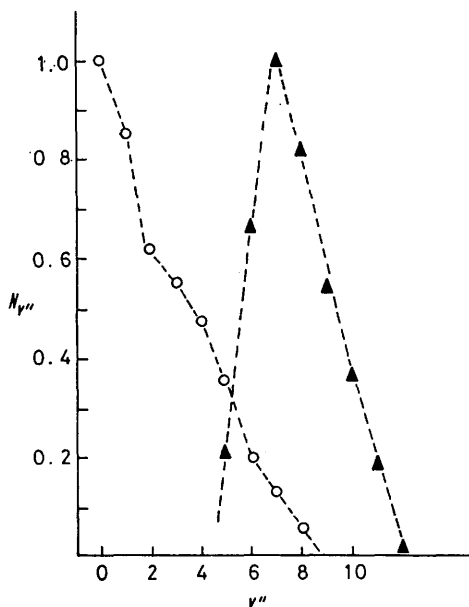

FIG. 10.—Relative vibrational population distributions, N_v'', of YbI formed in the reaction Yb + CH_3I (open circle) and YB + CF_3I (shaded triangles). The distributions are deduced from the LIF spectra, assuming constant Franck–Condon factors within the $\Delta v = 0$ sequence of YbI ($A^2\Pi_{\frac{1}{2}} + X^2\Sigma^+$).

data from the Ba + CF_3I reaction are also available,[2] but the conclusions are less clear-cut, so that an analogy for the Yb + CF_3I system will not be drawn here. We note, however, that the YbI vibrational distribution from the latter reaction (cf. fig. 10) is inverted, thus suggesting that the mechanism is also direct. Unfortunately, our results by no means prove that bimodal or n-modal distributions cannot be observed in other systems.

Dr. R. G. Macdonald and Dr. J. J. Sloan (*National Research Council, Canada*) said: We have recently studied several further examples of the " alternate site " branching reactions referred to in the paper of Polanyi *et al.*, and have obtained evidence that a migration step may be involved in the reaction F + HCOOH → HF + HCOO which was mentioned in that paper. Our evidence rests on a comparison between the detailed rate constants, $k(v')$, measured *via* arrested relaxation chemiluminescence experiments on the reactions:

F + DCOOH → HF(v') + DCOO and F + CH_3OD → DF(v') + CH_3O.
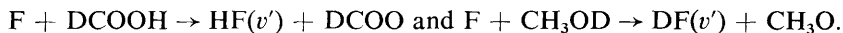
[1] A. M. Rulis and R. B. Bernstein, *J. Chem. Phys.*, 1972, **57**, 5497; *Faraday Disc. Chem. Soc.*, 1973, **55**, 293.
[2] S. M. Lin, C. A. Mims and R. R. Herm, *J. Phys. Chem.*, 1973, **77**, 569.

The $k(v')$ for both reactions are shown in fig. 11, plotted as a function of f'_v, the fraction of the total energy available to the products which enters vibration in the diatomic. Details of the experiments and data reduction are being published.[1,2] The product vibrational distributions shown in fig. 11 indicate that the reactions proceed *via* substantially different pathways. The inversion in the DF distribution from the CH_3OD reaction is characteristic of many similar cases,[3] which are believed to proceed *via* direct abstraction in a single collision. In contrast, the preferential population
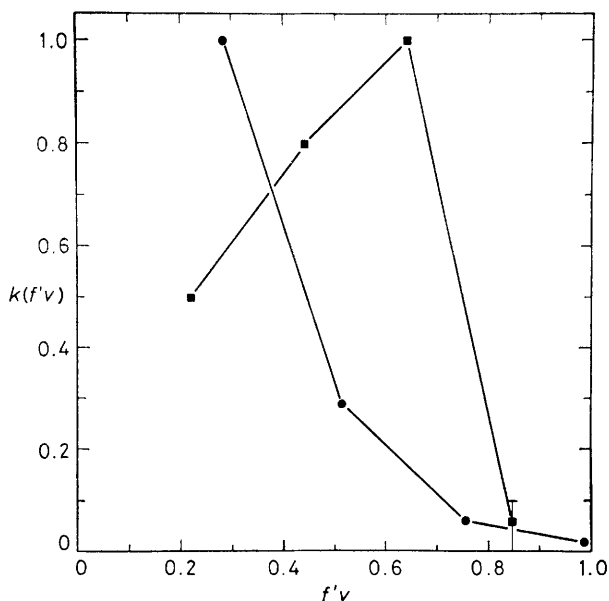

FIG. 11.—Detailed rate constants, $k(v')$, measured for the reactions $F + DCOOH \rightarrow HF(v') + DCOO$ (■) and $F + CH_3OD \rightarrow DF(v') - CH_3O$ (●), plotted against the fraction of the total energy available to the products for each vibrational state (f'_v).

of lower HF vibrational levels by the DCOOH reaction suggests an indirect mechanism having a relatively longer-lived intermediate.[1] Since the major difference in the two reactions is the presence of the carbonyl group near the reactive site in the latter case, we have suggested that this reaction may proceed *via* addition of the fluorine atom at the carbonyl group, followed by a migration of either the F or the H atom, leading to decomposition into the observed products. This mechanism would allow the distribution of part of the reaction exoergicity among the internal modes of the (long-lived) intermediate. Decomposition of the latter would result in a nearly-statistical distribution over product levels, in agreement with our measurement.

Prof. J. C. Polanyi (*Toronto*) (*communicated*): DeVries *et al.*'s calculations[4] present a novel scenario for the interaction of laser fields with reacting systems.[5,6] This flourishing field of theory has, however, yet to find its counterpart in experimental

[1] R. G. Macdonald and J. J. Sloan, *Chem. Phys.*, 1978, **31**, 165.
[2] R. G. Macdonald, J. J. Sloan and P. T. Wassell, *Chem. Phys.*, in press.
[3] D. Bogan and D. W. Setser, *A.C.S. Symp. Ser.*, 1978, **66**, 237.
[4] P. L. DeVries, T. F. George and J.-M. Yuan, *Faraday Disc. Chem. Soc.*, 1979, **67**, 90.
[5] See footnote (4), next page.
[6] See footnote (5), next page.

studies of reacting systems, such as the prototype of exchange reactions, A + BC → AB + C.[1,2]

Lasers have already transformed our ability to identify the states of excitation of reaction products and also to excite reactants selectively; both these innovations are illustrated strikingly in the opening paper of this Discussion.[3] Reaction dynamicists have (for twenty years) been using the information that they garner concerning product motions, reactant motions, and the links between the two, in order to infer the nature of the forces that govern the reacting system's journey from reactant to product. The present Discussion is, as would be hoped, replete with examples of such inferences. For some time to come this will continue to constitute our best hope of unravelling the dynamics of reaction.

The theoretical discussions, exemplified by DeVries et al.'s paper,[1] raise the question whether we could now be standing at the threshold of what one might characterise as the last frontier of reaction dynamics, in which we move from spectroscopy of reactants and products to the spectroscopy of the collocation of particles that really interests us, the reactive intermediate. The feature that is common to much of the contemporary discussion of the effects of intense laser fields is that the interaction between light and matter occurs while the particles, in our case the reacting particles, are at a sufficiently close range that the spectroscopic parameters are neither those of reactants nor those of products; this is, therefore, " spectroscopy of the transition state " (using the term " transition state " in its broadest sense to denote the range of configurations encountered en route from reactant to product).

What are the prospects for achieving a spectroscopy of the transition state in the coming few years? The fact that computations of required power levels for cases studied until now most often fall in the gigawatt to terawatt range[1,2,4,5] (powers that we associate with the electrical breakdown of gases) has produced a mood of discouragement, reflected in informal discussions at this meeting. These remarks are made in order to urge a contrary view, namely that the spectroscopy of the transition state should now be within reach of experiment.

The best sign that something is within reach in science (since we generally advance by infinitesimals) is that, from a selected vantage point, it can already be regarded as having been achieved. This is the case, it seems to me, in regard to the spectroscopy of the transition state.

For the common case of direct reaction the transition state involves a single encounter between particles which come together and then recoil in a time period of 10^{-13}-10^{-12} s. Spectroscopy of the transition state requires in the first place that

[1] P. L. DeVries, T. F. George and J. M. Yuan, Faraday Disc. Chem. Soc., 1979, 67, 90.
[2] Further effects of intense laser radiation on reactions A + BC → AB + C are computed by (a) A. E. Orel and W. H. Miller, Chem. Phys. Letters, 1978, 57, 362; (b) A. E. Orel and W. H. Miller, 1979, to be published.
[3] R. N. Zare, Faraday Disc. Chem. Soc., 1979, 67, 7.
[4] For a review of the work of the Rochester group see T. F. George, I. H. Zimmerman, P. L. DeVries, J. M. Yuan, K. S. Lam, J. C. Bellum, H. W. Lee, M. S. Slutsky and J. T. Liu, in Chemical and Biochemical Applications of Lasers, ed. C. B. Moore (Academic Press, New York, 1979), vol. IV.
[5] Early theoretical studies of the combined effects of collisional and optical excitation (up to 1976) include (a) L. I. Gudzenko and S. I. Yakovlenko, Sov. Phys. J.E.T.P., 1972, 35, 877; (b) N. F. Perel'man and V. A. Kovarskii, Sov. Phys. J.E.T.P., 1973, 36, 436; (c) A. A. Mikhailov, Optics and Spectroscopy, 1973, 34, 581; (d) N. M. Kroll and K. M. Watson, Phys. Rev. A, 1976, 13, 1018; (e) A. M. F. Lau, Phys. Rev. A., 1976, 13, 139; (f) A. M. F. Lau, Phys. Rev. A, 1976, 14, 279; (g) J. L. Gersten and M. H. Mittleman, J. Phys. B, 1976, 9, 383; (h) J. M. Yuan, T. F. George and F. J. McLafferty, Chem. Phys. Letters, 1976, 40, 163; (i) S. Geltman, J. Phys. B, 1976, 9, 569.

new spectral features stem from such a collision, and secondly that these features be interpretable in terms of the forces operative during the encounter.   Spectral features of this sort have been observed in both emission and absorption since the turn of the century, and have been interpeted with increasing sophistication since the classic paper on pressure-broadening by Lorentz.[1]

The prospects for measuring pressure broadening due to the collision which is chemical reaction appear to be good.   Beautiful studies of broadened emission lines of alkali metal atoms have been performed over the past few years, particularly by Gallagher and co-workers.[2]   The excited atoms $M^*(^2p)$ were formed from M, using a commercial alkali metal resonance lamp.   With a pressure of alkali metal atoms p_{M^*} $\leqslant p_M = 10^{-6}$ Torr and a pressure of added inert gas $p_{IG} \geqslant 1$ Torr, a concentration of M*IG was achieved that permitted observation of emission as far as several hundred ångström from the resonance line.   In the case of the blue-shifted emission this was interpreted, as a result of a series of studies,[2] as being due to binary M*IG collisions of 10^{-13}-10^{-12} s total duration, in which the colliding pair, $M^* + IG$, rides up a
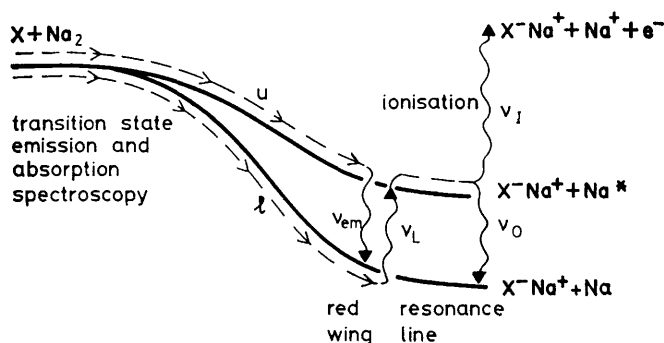

FIG. 12.—The reaction $X + Na_2 \rightarrow NaX + Na$.

repulsive $B^2\Sigma_{\frac{1}{2}}$ potential and, thereafter, emits to the repulsive $X^2\Sigma_{\frac{1}{2}}$ ground state. The maximum extent to which M*IG rides up the $B^2\Sigma_{\frac{1}{2}}$ curve to small r_{M^*-IG} depends on the gas temperature.   The emission intensity as a function of frequence $I_{em}(v)$, depends on the distribution over r_{M^*-IG}, i.e., $N_u(r)$.   (For strong resonance lines the transition dipole moment may be assumed independent of r_{M^*-IG}.)

In an analogous reacting system $M^*(^2p)$ would be formed directly as a product of chemical reaction, e.g., $X + M_2 \rightarrow MX + M^*(^2p)$;[3] fig. 12.   The formation of M* by this means is extremely efficient; the reactive cross-section for this path is $S^*_r =$ 10-100 Å^2.   The experimental problems in observing emission from the wings of the resonance line emission due to M*MX repulsion, with reagent pressures $P_X \approx P_{M_2}$ $\geqslant 10^{-3}$ Torr (collision rate comparable to that cited above) should not be insurmountable.   The experiment can be performed under bulb conditions.   Since all M* is formed via a strong collision, M*MX, it is unlikely that secondary encounters of thermal collision energy between M* and background gas will seriously obscure the

[1] H. A. Lorentz, Proc. Acad. Sci. Amsterdam, 1915, **18**, 154.

[2] (a) R. E. M. Hedges, D. L. Drummond and A. Gallagher, Phys. Rev. A, 1972, 6, 1519; (b) D. L Drummond and A. Gallagher, J. Chem. Phys., 1974, **60**, 3426; (c) C. G. Carrington and A. Gallagher, Phys. Rev. A, 1974, **10**, 1464; (d) C. G. Carrington and A. Gallagher, J. Chem. Phys., 1974, **60**, 3436; (e) G. York, R. Scheps and A. Gallagher, J. Chem. Phys., 1975, **63**, 1052; (f) W. P. West, P. Shuker and A. Gallagher, J. Chem. Phys., 1978, **68**, 3864.

[3] W. S. Struve, J. R. Krenos, D. L. McFadden and D. R. Herschbach, J. Chem. Phys., 1975, **62**, 404 and references therein.

primary broadening (one can anyway discriminate against this by modulating the reactant sprays).   The assumption of constant transition moment for M*, irrespective of $r_{M^{*}-MX}$, may well be inadequate in view of the strong electric field gradient from $M^{+}X^{-}$; nonetheless the intensity distribution in the wings of the resonance line, $I_{em}^{+}(\nu)$, will provide information regarding $N_{u}^{+}(r)$, which in turn depends on the (inverse of) the time the system spends in that interval of configurations, $i.e.$, $\tau_{u}^{+}(r)$.   This is the desired dynamical information.   [It should be noted that $\tau_{u}^{+}(r)$ need not be markedly less for the reactive case than for thermal encounters, since product translational energy, T', scales with v^{+} and, furthermore, the exothermicity is only partially converted to T'].   For emission experiments the dynamical information refers to the trip across the upper potential surface [hence $\tau_{u}^{+}(r)$].

So far no mention has been made of lasers for spectroscopy of the reaction intermediate.[1] They play a vital role, however, in the absorption analogue of the above experiment, which would have as its objective the determination of dynamics on the ground potential surface, $i.e.$, $\tau_{l}(r)$ for the non-reactive case, and $\tau(\frac{1}{2}r)$ for the reactive case.   A c.w. or pulsed laser[2] can be used to excite in the pressure-broadened wings of an atomic resonance line.   The absorbing species in experiments reported until now[2] was SrIG (strontium + inert gas) with a lifetime of 10^{-13}-10^{-12} s.   Laser absorption transfers SrIG to an upper electronic state in which it dissociates (again in 10^{-13}-10^{-12} s) to give Sr*; the emission intensity of the Sr* resonance line then gives a measure of the extent of SrIG absorption; $I_{abs}(\nu)$.   This latter quantity gives information concerning $\tau_{l}(r)$, the time spent on the lower potential curve at configuration r_{SR-IG} [So long as resonance line emission is used as the index of the amount of absorption, it will be difficult to scale up the pressures, without severe entrapment. Ref. (2) nonetheless, used Sr at up to 10^{-2} Torr.   Alternative methods of monitoring Sr*($^{1}P_{1}^{0}$) could be used, in place of resonance radiation, thereby eliminating entrapment (see below)].

In the analogous reactive case a reaction forming ground state M with large cross-section, $e.g.$, H + Na$_{2}$ → (HNaNa)$_{+}^{+}$ → NaH + Na(^{2}s),[3] or X + Na$_{2}$ as before (see fig. 12), could provide the source of collisionally-perturbed Na.   These reactions both have $S_{r} \approx 100$ Å^{2}.   With thermal reagents H + Na$_{2}$ gives only ground-state Na.[4] If, for the sake of discussion, we consider a crossed-beam rather than a bulb experiment, then (with supersonic reagent flows and a reactive cross-section of ≈ 100 Å^{2}) one can expect a steady-state density $\approx 10^{9}$ Na atom cm^{-3} ($\approx 10^{-7}$ Torr) at the crossing point.   The rate of removal of Na atoms is $\approx 10^{5}$ s^{-1}.   Since the rate of removal of the transition state is $10^{8} \times$ greater (10^{13} s^{-1}), the steady-state concentration is ≈ 10 particle cm^{-3}.

Numbers of atomic particles an order of magnitude less than this have been measured in recent years[5] (a) by c.w. laser-induced fluorescence at the resonance line[5a] and (b) by two-photon ionization using pulsed lasers of ≈ 1 mJ pulse^{-1}.[5b]   Referring to fig. 12, method (a) would correspond to absorption of ν_{L} followed by fluorescence of ν_{0} [$cf.$ ref. (2)].   Method (b) would correspond to absorption of ν_{L} followed by

[1] Recently advantages of a 10 mW c.w. laser for excitation of M → M* in M*IG emission experiments (as compared with the traditional resonance lamp) have been demonstrated; see W. P. West, P. Shuker and A. Gallagher, $J. Chem. Phys.$, 1978, **68**, 3864.

[2] J. L. Carlsten, A. Szöke and M. G. Raymer, $Phys. Rev. A$, 1977, **15**, 1029.

[3] Y. T. Lee, R. J. Gordon and D. R. Herschbach, $J. Chem. Phys.$, 1971, **54**, 2410.

[4] W. S. Struve, J. R. Krenos, D. L. McFadden and D. R. Herschbach, $J. Chem. Phys.$, 1975, **62**, 404 and references therein.

[5] (a) W. M. Fairbank Jr., T. W. Hänsch and A. L. Schlawlow, $J. Opt. Soc. Amer.$, 1975, **65**, 199, and references therein; (b) G. S. Hurst, M. H. Nayfeh and J. P. Young, $Appl. Phys., Letters$, 1977, **30**, 229.

absorption of v_1. The latter method avoids complications of resonance-radiation entrapment and lends itself to bulb experiments at higher densities (one atom cm^{-3} has been detected in an environment of 10^{19} atoms plus molecules cm^{-3}). For the case used as an example v_L and v_1 could conveniently come from dye lasers pumped synchronously by the 532 and 353 nm lines of a single Nd:YAG laser; v_L would be tuned in the region to the red of the 589 nm sodium D-line, whereas v_1 would be tuned to 410 nm near threshold for ionisation of Na*(^2p) and hence at a maximum of the photoionisation cross-section curve for this species.[2] For these experiments the absorption $\tau_1^*(r)$, leads to information regarding $N_1^*(r)$ and hence $\tau_1^*(r)$, the time that the system spends at successive configurations on the lower potential curve.

It is a pleasure to thank Stephen Bly, Tom George, John Hepburn, Dan Klimek, Albert Lau, Kopin Liu, Glen Macdonald, Stephen Wallace and John Weiner for helpful discussions.

Prof. K. F. Freed (*Chicago*) said: There is a simple but realistic, analytically solvable model to predict energy distributions in products of bimolecular reactions.[3] Consider the conventional plots of the potential energy as a function of reaction coordinates as presented by the solid line in fig. 13. The activation barrier arises by
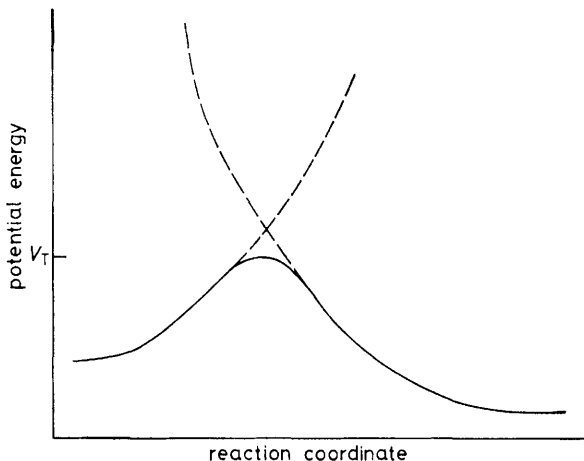

FIG. 13.—Schematic representation of potential energy as a function of reaction coordinate (solid curve) for a typical activated chemical reaction. Dashed curves depict a cut through the diabatic surfaces which is taken along the reaction coordinate.

virtue of an orbital energy crossing[4] associated with the two dashed diabatic surfaces in fig. 13. Follow the adiabatic electronic wavefunctions in going from reactants to products. If this electronic wavefunction is changing rapidly enough from reactant character to product character, then a sudden approximation is expected to be useful for this transition. This sudden approximation is merely a Franck–Condon description for transitions from one diabatic surface to another, where elastic scattering can take place on the reactant and product diabatic surfaces. The criteria for the validity of a sudden approximation would appear to be optimal at higher energies,

[1] G. S. Hurst, M. H. Nayjeh and J. P. Young, *Appl. Phys. Letters*, 1977, **30**, 229.
[2] R. D. Hudson, *Phys. Rev. A*, 1964, **135**, 1212; J. Chang and H. P. Kelly, *Phys. Rev. A*, 1975, **12**, 92.
[3] K. H. Fung and K. F. Freed, *Chem. Phys.*, 1978, **30**, 249.
[4] R. B. Woodward and R. Hoffmann, *The Conservation of Orbital Symmetry* (Academic Press, New York, 1970).

so consequently we have considered a Franck–Condon theory of reactive scattering at low energies in which only tunnelling processes can occur.[1] This pushes the theory to perhaps the least favourable possible conditions.

Other workers have investigated Franck–Condon approaches to the descriptions of reactive scattering,[2,3] but they have encountered a number of difficulties in evaluating the continuum–continuum two dimensional Franck–Condon factors associated with the collinear atom–diatomic reactions. The source of these difficulties is readily seen as follows: On the reactant surface we have a continuum function along the reaction coordinate, $S_{E_r}(R_r)$, and as oscillator function, $\varphi_{n_r}(r_r)$, along the remaining coordinate orthogonal to the reaction coordinate. A similar situation prevails for the product diabatic surface. However, the reactant and product surface coordinate systems are totally different from each other and are related through a transformation,

$$R_p = R_p(R_r, r_r), \quad r_p = r_p(R_r, r_r). \tag{1}$$

Thus, the two dimensional continuum–continuum, (reactant–product) Franck–Condon factors are of the form

$$\int dR_r \int dr_r S_{E_p}^*[R_p(R_r, r_r)]\varphi_{n_p}^*[r_p(R_r, r_r)]S_{E_r}(R_r)\varphi_{n_r}(r_r). \tag{2}$$

Eqn (2) presents a two-dimensional totally non-separable continuum–continuum integral.

Previous workers have simplified this by introducing approximations where continuum functions are replaced by those appropriate to free particles or only the amplitude of the continuum function at the classical turning point on the repulsive diabatic potentials are introduced rather than the full function, *etc.*[2,3] We have shown, however, that for the case of the A + BC → AB + C reaction, where A, B, and C may all be polyatomic species, the many dimensional non-separable continuum–continuum integrals [with a product of bound oscillator functions replacing the single oscillator function in eqn (2)] may exactly[1] be reduced to a two-dimensional integral along the non-orthogonal reactant and products surface reaction coordinates,

$$\int dR_r \int dR_p S_{E_p}^*(R_p)S_{E_r}(R_r)g(R_p, R_r), \tag{3}$$

where g is obtained analytically as a bivariate gaussian multiplied by a polynomial. This two-dimensional integral can be expressed in terms of one-dimensional bound–continuum integrals of a form which is identical in character to those occurring in our theory of photodissociation processes.[4] The resultant one-dimensional integrals may readily be evaluated numerically or be calculated with accurate analytical approximations.[4]

The actual wavefunctions on the two diabatic surfaces are linear combinations of the types of reactant and product functions appearing in eqn (2). Our calculations[1] approximate the linear combinations by the use of simple forced oscillator models. A model potential energy surface has been chosen to mimic the reaction of D + HI → H + DI isotope exchange, but the potential has been modified to increase the barrier height to a value of 1.51 eV. The Franck–Condon calculations are compared with exact quantum calculations on the adiabatic surface as kindly provided to us by Dr. R. Walker. The EQ refers to the exact quantum prediction and NI refers to full Franck–Condon treatment in fig. 14 and 15. (The other curves represent different

[1] K. H. Fung and K. F. Freed, *Chem. Phys.*, 1978, **30**, 249.
[2] V. Halavee and M. Shapiro, *J. Chem. Phys.*, 1976, **64**, 2826.
[3] G. C. Schatz and J. Ross, *J. Chem. Phys.*, 1977, **66**, 1021, 1037.
[4] K. F. Freed and Y. B. Band, *Excited States*, 1978, **3**, 109.

analytical approximations.) The case in fig. 14, involving HI initially in the $v = 0$ level, is for a total energy of 1 eV, very far below the top of the barrier. Fig. 15 involves HI in the $v = 4$ level initially with a collision energy of 1.5 eV, almost at the top of the barrier. The predicted distributions in product state vibrational energy are very good from the Franck–Condon analysis.[1-3] The peak in the product distribution is
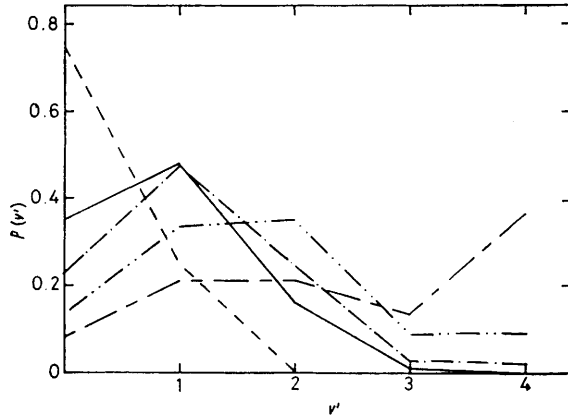

FIG. 14.—Comparison of exact quantum (EQ) and Franck–Condon (NI) product vibrational distributions for a total energy of 1 eV. (————) EQ, (— — —) AIRY, (— — — —) DELTA, (— ·· —) AIRY + S + MR, (— · —) NI.
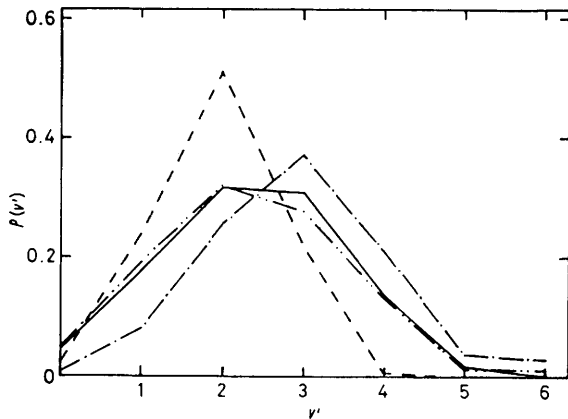

FIG. 15.—As for fig. 14 but for a total energy of 1.5 eV (Barrier height on adiabatic surface is 1.51 eV)

obtained correctly to within one vibrational unit. The predicted vibrational energy distribution is fairly insensitive to how the diabatic potentials are chosen within reasonable limits, but predicted absolute reaction probabilities are quite sensitive to the choice of diabatic surfaces.[1] Further study is needed of the criteria for choosing diabatic surfaces so as to obtain accurate total reaction probabilities.

The theory may also be applied to reactions which proceed through complexes as illustrated in fig. 16. Here the (solid line) adiabatic surface is decomposed into three diabatic (dashed) surfaces. The Franck–Condon description may be used for both

[1] K. H. Fung and K. F. Freed, *Chem. Phys.*, 1978, **30**, 249.
[2] U. Halavee and M. Shapiro, *J. Chem. Phys.*, 1977, **64**, 2826.
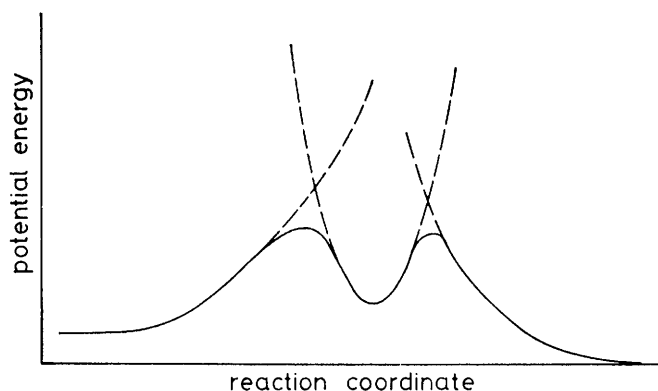[3] G. C. Schatz and J. Ross, *J. Chem. Phys.*, 1977, **66**, 1021, 1037.

FIG. 16.—Potential energy plotted against reaction coordinate (solid curve) for reaction proceeding through an intermediate. Dashed curves represent the diabatic surfaces plotted against reaction coordinate.

transitions between diabatic surfaces. Because we evaluate state-to-state relative transition probabilities, the method is useful provided the number of channels on each diabatic surface is readily enumerable. Hence, systems with very stable intermediates would involve too many states of the intermediate, so some type of averaging process should be employed.

Prof. M. Menzinger, Dr. A. Tanin and Dr. J. C. Wong (*Toronto*) said: While a rapidly growing body of information exists today regarding the relative effectiveness of reagent translation and vibration in inducing simple adiabatic A + BC reactions, the related problem of mode specificity in electronically non-adiabatic processes has hitherto received little attention.

The simplest and, since the work of Tully and Preston[1] (TP) also the best understood, non-adiabatic reaction is

$$H^+ + H_2 \rightarrow H_2 + H^+ \qquad \text{adiabatic} \qquad (1a)$$
$$\rightarrow H_2 + H \quad \text{non-adiabatic.} \qquad (1b)$$
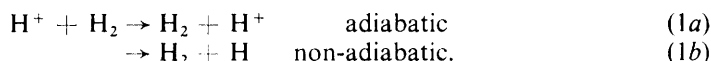
The agreement between theory[1] and experiment[2] is considered to be very good. The conclusion of TP regarding the mode specificity in process (1b) were based on the explicit but disputable neglect of so-called mass-polarization terms (*i.e.*, cross-terms between particle coordinates in the molecular Hamiltonian). TP's work, which has guided previous qualitative thinking about diabatic mode-specificity in general, requires the modifications outlined below.

The non-adiabatic coupling matrix element[1] $\langle 1|\nabla_{R2}|2\rangle$ calculated by the DIM method is shown in fig. 17 ($R1$ and $R2$ are the internuclear distances in the collinear H_3^+). The asymmetry of the coupling $\langle 1|\nabla_{R2}|2\rangle \nabla_{R2}$ with respect to the bisecting line $R1 = R2$ disagrees however, as a brief reflection reveals, with the symmetry of the physical system. Motion across the ridge (fig. 17) should be equally effective in the entrance channel as it is in the exit channel. This is what one observes (fig. 18) when the " nuclear–nuclear mass polarization " term (*i.e.*, the off-diagonal element $\langle 1|\nabla_{R1}|2\rangle$ in the nuclear kinetic energy) is properly included in the coupling $[\langle 1|\nabla_{R2}|2\rangle + \langle 1|\nabla_{R1}|2\rangle]\nabla_{R2}$ induced by motion along $R2$ [*i.e.*, vibration across the (vertical)

[1] J. C. Tully and R. K. Preston, *J. Chem. Phys.*, 1971, **55**, 562.
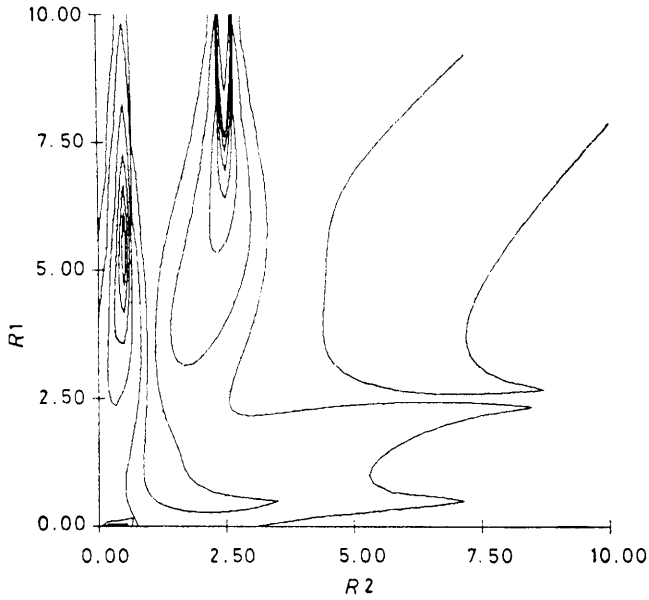[2] G. Ochs and E. Teloy, *J. Chem. Phys.*, 1974, **61**, 4920.

Fig. 17.—Coupling matrix element $\langle 1 | \nabla_{R2} | 2 \rangle_{\nabla_{R2}}$ for collinear H_3^+ in $\{R1, R2\}$ coordinates, excluding " mass polarization ". Note the unphysical asymmetry w.r.t. $R1 = R2$.
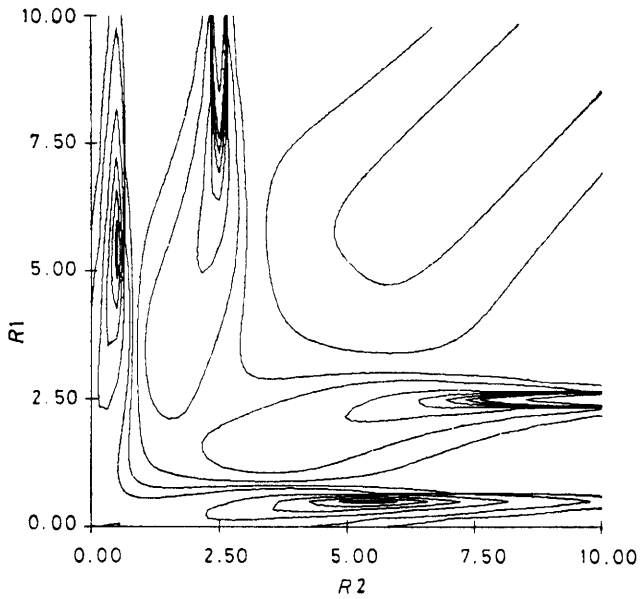

Fig. 18.—Complete coupling $[\langle 1 | \nabla_{R2} | 2 \rangle + \langle 1 | \nabla_{R1} | 2 \rangle]_{\nabla_{R2}}$ including the " mass polarization " cross term. The contour values are (in a.u.): 0.1, 0.3, 1.0, 2.0, 3.0, 4.0, 5.0, 10.0.

exit and translation along the (horizontal) entrance channel]. For symmetry, the coupling elements $[\langle 1|\nabla_{R1}|2\rangle + \langle 1|\nabla_{R2}|2\rangle]\nabla_{R1}$ for $R1$ motion (translation in the exit and vibration in the entrance channel) are of equal magnitude. In other words: translational motion along a seam of avoided PES intersection may couple state $|1\rangle$ and $|2\rangle$ very strongly.

Dynamical calculations are usually done in (r, R) coordinates which diagonalize the kinetic energy operator or eliminate nuclear–nuclear mass polarization terms (here $r = R1$ is the target vibrational coordinate and R is the distance between projectile and the c.m. of the target molecule). However, the matrix element $\langle 1|\nabla_R|2\rangle$ responsible for translational coupling in the entrance channel is still about one half of the $\langle 1|\nabla_r|2\rangle$ vibrational term! A simple calculation (integration of the semiclassical equations along two two-dimensional model PE surfaces) has shown that the single pass transition probability is indeed significantly altered by translation along the seam of avoided intersection, in contrast to TP's conclusions.

The cross-sections for the processes (1a) and (1b) are, however, only little affected by translational coupling since multiple crossing of the seam averages over the individual transition probabilities as TP have discussed in some detail.[1] Coupling by motion along a seam is expected to play a more prominent role in cases of single crossings of seams that lie transverse to a PES-valley, e.g. in harpooning reactions.

Dr. A. Gonzalez Ureña, Mr. V. J. Herrero and Mr. F. Aoiz Moleres (*Madrid*) said:
This remark is concerned with the report of Wren and Menzinger[2] on the Ba + NO$_2$ → BaO + NO reaction cross-section minimum and it is also related to the weak minimum in the Rb + CH$_3$I → RbI + CH$_3$ and the Sm + N$_2$O → SmO + N$_2$ reaction cross-section evidenced by Bernstein and co workers[3,4] and Yokozeki and Menzinger,[5] respectively.

It can be shown[6] that for the atom–diatom reaction case (*i.e.*, in our approach we regard the CH$_3$; N$_2$ and NO as single particles), the high energy reaction cross-section takes the form:

$$\sigma_R = A\langle I'_v\rangle \left(1 + \frac{Q_{max.}}{E_T}\right) \tag{1}$$

where A is an energy independent factor, $Q_{max.}$ the maximum reaction exergicity, $\langle I'_v\rangle$ the overall moment of inertia of the diatom formed and E_T the collision energy. When an empirical relation such as $\langle I'_v\rangle = I'_e(1 - \gamma E)$, which is similar to that of $\langle B'_v\rangle = B'_e - \alpha\langle v + \frac{1}{2}\rangle$, is introduced to account for the energy dependence of $\langle I'_v\rangle$, then eqn (1) reduces to

$$\sigma_R = AI'_e \left(1 + \frac{Q_{max.}}{E_T}\right)\left(\frac{1}{1 - \gamma E}\right). \tag{2}$$

In the above expressions $B'_e(I'_e)$ is the equilibrium rotational constant (moment of inertia) of the products' diatom, $\langle B'_v\rangle$ and $\langle I'_v\rangle$ the corresponding vibrational averaged values, v the vibrational quantum number, α and γ empirical constants related to the vibrational–rotational energy coupling (among other factors) and E, the total energy available to the products, *i.e.*, $E = E_T + Q_{max}$.

Eqn (2) predicts a minimum in σ_R at $E_T = E_{min}$ from whence the γ value obtained

[1] J. C. Tully and R. K. Pretson, *J. Chem. Phys.*, 1971, **55**, 562.
[2] See D. J. Wren and M. Menzinger, *Faraday Disc. Chem. Soc.*, 1979, **67**, 97.
[3] H. E. Litvak, A. González Ureña and R. B. Bernstein, *J. Chem. Phys.*, 1974, **61**, 4091.
[4] S. A. Pace, H. F. Pang and R. B. Bernstein, *J. Chem. Phys.*, 1977, **66**, 3675.
[5] A. Yokozeki and M. Menzinger, *Chem. Phys.*, 1977, **20**, 9.
[6] A. González Ureña, V. J. Herrero and F. J. Aoiz, unpublished.

is $\gamma = Q_{max}/(E_{min} + Q_{max})^2$. Substituting this γ value in eqn (2) we can easily see that the cross-section functionality is only governed by the two parameters Q_{max} and E_{min} and once they are known the kinetic energy dependence of the reaction cross-section can be obtained straightforwardly. On the other hand, once the E_{min} value is known, eqn (2) can be used to fit the excitation function data by varying only the Q_{max} value, and therefore approximate values for the products' diatom dissociation energy can be obtained, provided that the reactant one is known. Indeed this procedure can be useful for those reactions where the products' diatom is formed in an excited state for which the dissociation energy value is not well known.

The application of our model to the Rb $+ CH_3 I \rightarrow RbI + CH_3$ and Ba $+ NO_2$ (hot) $\rightarrow BaO + NO$ system is shown in fig. 19 and 20, respectively, including previous
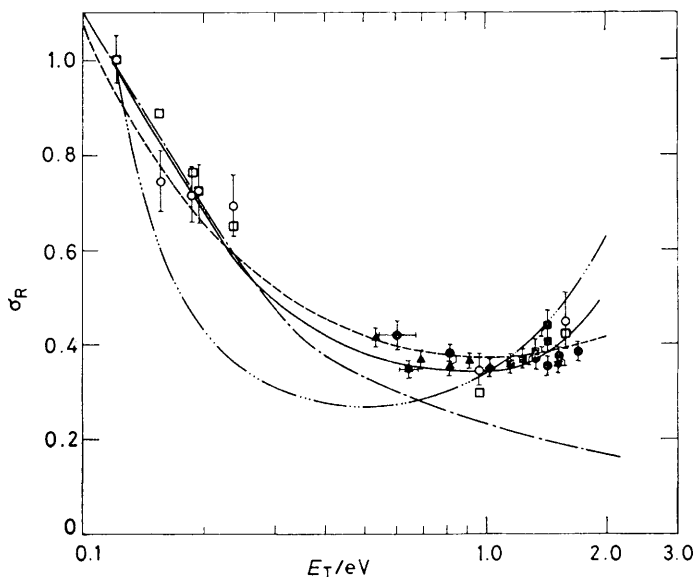

FIG. 19.—$\sigma_R(E_T)$ for the Rb + CH₃I reaction. Symbols represent the experimental values reported in ref. (4). (— — —) Modified [ref. (1)] equation of Eu, ref. (1*b*); (— · —) ref. (1*c*); (— · · · —) ref. (1*a*); (———) the present treatment represented by eqn (2) (see text).

theoretical treatments.[1] The representation is satisfactory and gives a good fit to the data, in particular for the shallow minimum. The present model gives for RbI and BaO dissociation energies $D(RbI) = 85 \pm 8$ kcal mol⁻¹ and $D(BaO) = 82 \pm 12$ kcal mol⁻¹. The respective values recommended by Gaydon[2] are $D(RbI) = 80$ kcal mol⁻¹ and $D(BaO, ^3\Pi) = 115$ kcal mol⁻¹. In spite of the low $D(BaO)$ value the agreement seems to be satisfactory. It should be noted, besides the semi-empirical nature of our model, that for many cases dissociation energies of excited species can only be determined within very wide limits.

It should be pointed out that the minimum in the reaction cross-section only

[1] (*a*) H. Kaplan and R. D. Levine, *Chem. Phys.*, 1976, **18**, 103; (*b*) B. C. Eu, *J. Chem. Phys.* 1974, **60**, 1178; *Chem. Phys.*, 1974, **5**, 95; (*c*) H. K. Shin, *Chem. Phys. Letters*, 1975, **34**, 546; *Chem. Phys. Letters*, 1976, **38**, 253.

[2] A. G. Gaydon, *Dissociation Energies and Spectra of Diatomic Molecules* (Chapman and Hall, London, 1968).

[3] S. A. Pace, H. F. Pang and R. B. Bernstein, *J. Chem. Phys.*, 1977, **66**, 3675.

[4] H. E. Litvak, A. González Ureña and R. B. Bernstein, *J. Chem. Phys.*, 1974, **61**, 4091.

appears when the E-dependence of $\langle I'_v \rangle$ is considered; thus it seems to be an anharmon-
city effect in the products' valley of the potential energy surface and, within the
framework of the present model, it is basically related to the increase in the internal
number of products' diatom states (*i.e.*, non-rigid-rotor–harmonic-oscillator approxi-
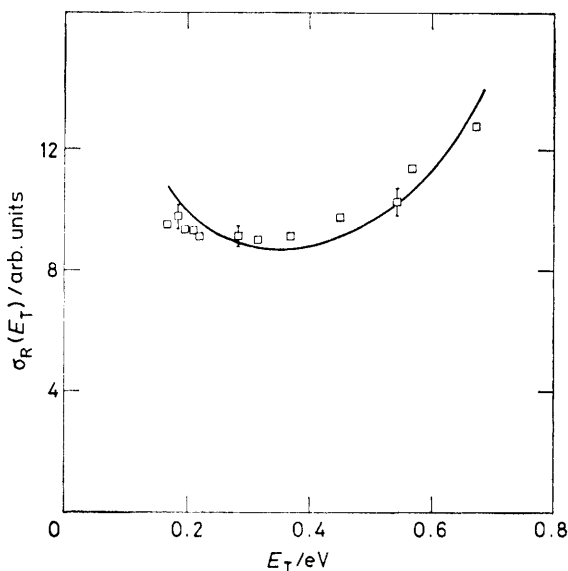mation) as the collision energy increases.

FIG. 20.—Same as fig. 19 but for the Ba + NO_2 → BaO → NO reaction.   Symbols: experimental
values from ref. (1).   Solid line represents model calculation.

A similar satisfactory representation is obtained for the chemiluminiscent Sm +
N_2O → SmO + N_2 reaction and a full account, with applications to other families
of reactions, is in preparation.
We thank Prof. Menzinger for helpful discussions.

Prof. G. C. Schatz (*Northwestern University*) said: Prof. Menzinger's study of the
mode specificity of vibrational energy consumption in Ba + N_2O indicates that even
though the vibrational mode v_1 appears to displace the molecule along the reaction co-
ordinate, it might in fact *not* be the promoting mode in this reaction.   One explana-
tion for this, and also why it is the bending mode v_2 in this system which appears to
enhance the reaction rate more efficiently, is provided by our recent theoretical studies
on how mode frequencies determine the specificity of the vibrational enhancement pro-
cess in atom–triatom reactions. As will be demonstrated below, we have found that
often the lowest frequency modes of a polyatomic (such as Menzinger's v^2) couple
efficiently into motion along the reaction coordinate, while high frequency modes
tend to be vibrationally adiabatic at energies close to threshold.   This occurs even
when the saddle point lies in the " direction " of a high frequency mode displacement,
provided that the frequency difference between the low and high frequency modes is
appreciable (as it appears to be in N_2O) and that the symmetry of the reaction coordin-
ate does not prevent the low frequency mode from coupling into motion along it
(*i.e.*, the v_2 mode could not be active if the Ba + N_2O transition state were linear).
Our theoretical studies refer to quasiclassical trajectory calculations on a collinear

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[1] D. J. Wren and M. Menzinger, *Faraday Disc. Chem. Soc.*, 1979, **67**, 97.

model of the $O + CS_2 \rightarrow CS + SO$ system. Unique to these trajectory studies is the use of good action-angle variables to determine accurately the semiclassical stationary vibrational states of the triatomic before each collision. This avoids the problem of intramolecular energy flow caused by anharmonic coupling, as we have discussed in detail elsewhere.[1,2] The collinear model of $O + CS_2$ uses a LEPS-type potential surface adapted[3] from one used in an earlier study by Smith,[4] the saddle point for which is located at $r_{OS} = 3.007$, $r_{SC} = 3.338$, and $r_{CS} = 2.914$ (all in bohr). Since the equilibrium CS distance in CS_2 is 2.937 bohr, it appears that this saddle point configuration corresponds to an asymmetric stretch deformation. Since the asymmetric stretch frequency here is substantially higher ($hv_3 = 0.20$ eV) than the symmetric stretch ($hv_1 = 0.08$ eV), this system is appropriate for testing our arguments concerning the effects of vibrational adiabaticity and nonadiabaticity on mode specificity.

The calculated reaction probabilities for $O + CS_2(000, 100, 001, 201, 500$ and $002)$ as a function of the relative translational energy E_0 are plotted in fig. 21. (The bending
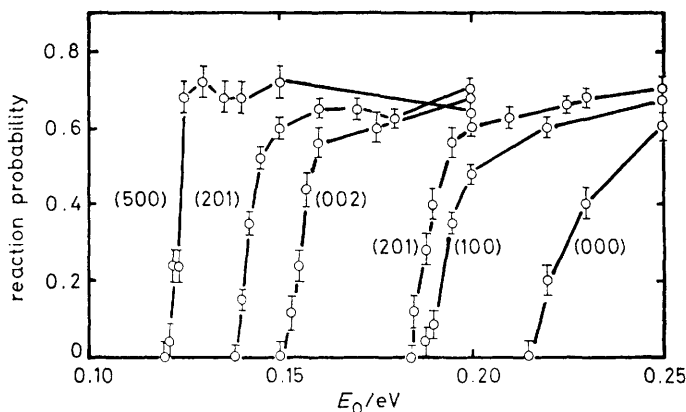

FIG. 21.—Total reaction probability as a function of reagent translational energy E_0 for collinear $O + CS_2$ with CS_2 initially in the (000), (100), (001), (201), (500) and (002) vibrational states. The relative energies of these states are 0.0, 0.08, 0.20, 0.36, 0.40 and 0.40 eV, respectively.

quantum number here is arbitrarily regarded as being zero for notational purposes.) Fig. 21 shows that the lowering in threshold for excitation of the (100) state is comparable to that for the (001) state, despite the fact that $v_3 \gg v_1$. Also, the threshold for (500) is substantially lower than for (002), even though these states are nearly degenerate. Thus we find that symmetric stretch excitation more efficiently lowers the reaction threshold than asymmetric stretch excitation for this reaction. An analysis of trajectory behaviour reveals[3] that this occurs because the asymmetric stretch is vibrationally adiabatic during the reaction (correlating to CS vibration in the products), while the symmetric stretch is highly nonadiabatic, mixing substantially into motion along the reaction coordinate, and thus promoting the reaction.

Prof. M. H. Alexander (*Maryland*) **and Prof. P. J. Dagdigian** (*Johns Hopkins*) said: We were most interested in the discussion of Wren and Menzinger. It is gratifying

[1] G. C. Schatz and T. Mulloney, *J. Phys. Chem.*, 1979, **83**, 989.
[2] G. C. Schatz and M. D. Moser, *Chem. Phys.*, 1978, **35**, 239; *J. Chem. Phys.*, 1978, **68**, 1992.
[3] G. C. Schatz, *J. Chem. Phys.*, 1979, **71**, 542.
[4] I. W. M. Smith, *Disc. Faraday Soc.*, 1967, **44**, 194.

that they were able to make use of some of our earlier ideas[1-3] concerning the diabatically preferred decay of the singly-charged ion-pair intermediates, formed in reactions of alkaline earth atoms with molecular oxidants, to yield electronically excited alkaline earth oxide products, which correspond to singly-charged M^+O^- ion pairs. We also would like to point out that an interesting complement to the concluding remarks of Wren and Menzinger is provided by our paper[3] dealing with the application of statistical theories to the prediction of electronic branching ratios and internal energy distributions in the reactions of alkaline earth atoms, in both ground and electronically excited states, with molecular oxidants.

Recently, we have been involved in developing semi-empirical potential surfaces for the $M^+O_2^-$ ion-pairs which are the primary intermediates in the reaction of the alkaline earth atoms with molecular oxygen. We have adapted our previous work[4] on LiO_2 and NaO_2 to the MgO_2 system, using available matrix isolation spectroscopic data.[5]

We are currently extending our earlier studies[1,6] of the chemiluminescent reactions of metastable $Ca(^3P)$ and $Sr(^3P)$ atoms with N_2O to the $Ba(^3D)$ and $Mg(^3P)$ reactants. These metastable atoms are produced by a discharge within an effusive high temperature oven in an experimental configuration similar to that described previously.[1,2,6] As in the case of Ca and Sr, under single collision conditions the reaction of metastable Ba with N_2O yields metal oxide products in highly excited electronic states. As evidence we see a substantial degree of banded emission in the near u.v. whose features correspond roughly to the BaO $C \rightarrow X$ bands seen by Field and coworkers[7] and Torres-Filho and Pruett[8] in laser-induced fluorescence studies of the products of the N_2O + ground state $Ba(^1S)$ reaction.

In contrast to these studies and to our reported preliminary findings,[6] in the reaction $Mg(^3P) + N_2O$ we see virtually no chemiluminescence over the spectral range $300 < \lambda/nm < 600$, even though many of the highly excited MgO states $[Mg(3p\pi)O (2p\sigma^2 2p\pi^3)]$ are energetically accessible. Possibly, efficient non-radiative decay of these nascent product states occurs by means of curve crossing into the $^3\Sigma^-$ state, itself a member of the $\pi^3\pi$ manifold. Because of the weak MgO bond energy, this state, which correlates directly with the ground state $Mg(^2S) + O(^3P)$ dissociation products, is predissociative or purely repulsive.[9] These results should be compared to the higher pressure experiments of Benard et al.[10] where the observed emission in the MgO $^3\Delta(\pi^3\pi) \rightarrow a^3\Pi$ system was attributed[11] to the direct product of the $Mg(^3P) + N_2O$ reaction.

Prof. M. Menzinger and Dr. D. J. Wren (*Toronto*) said: The Ba + $NO_2 \rightarrow$ BaO* CL reaction has been frequently studied together and compared with the Ba + N_2O system.[12,13] Though superficially similar the two differ substantially with respect to

[1] P. J. Dagdigian, *Chem. Phys. Letters*, 1978, **55**, 239.
[2] L. Pasternack and P. J. Dagdigian, *Chem. Phys.*, 1978, **33**, 1.
[3] M. H. Alexander and P. J. Dagdigian, *Chem. Phys.*, 1978, **33**, 13.
[4] M. H. Alexander, *J. Chem. Phys.*, 1978, **69**, 3502.
[5] L. Andrews, E. S. Prochaska and B. S. Ault, *J. Chem. Phys.*, 1978, **69**, 556.
[6] B. E. Wilcomb and P. J. Dagdigian, *J. Chem. Phys.*, 1978, **69**, 1779.
[7] R. A. Gottscho, B. Koffend, R. W. Field and J. Lombardi, *J. Chem. Phys.*, 1978, **68**, 4110.
[8] A. Torres-Filho and J. G. Pruett, *J. Chem. Phys.*, 1979, **70**, 1427.
[9] J. Schamps and H. Lefebvre-Brion, *J. Chem. Phys.*, 1972, **56**, 573.
[10] D. J. Benard, W. D. Slafer and J. Hecht, *J. Chem. Phys.*, 1977, **66**, 1012.
[11] D. J. Benard and W. D. Slafer, *J. Chem. Phys.*, 1977, **66**, 1017.
[12] Ch. Ottinger and R. N. Zare, *Chem. Phys. Letters*, 1970, **5**, 243.
[13] C. D. Jonah, R. N. Zare and Ch. Ottinger, *J. Chem. Phys.*, 1972, **56**, 263.

energetics, electronic structure, overall reaction rate, photon yield, energy partitioning and, as this note is intended to show, energy consumption.

We have studied the Ba + NO_2 system by the two beam techniques described in the preceding Ba + N_2O paper and obtained the following results:

The reaction is characterized by a total cross-section $\bar{\sigma}_T = 210 \pm 40$ Å^2 (at $T_{N_2O} = 291$ K) ≈ 8 times greater than that for the N_2O counterpart. The photon yield Φ is only 0.1 relative to that of the Ba + N_2O system. The activation energies $E_a^{CL} = 3.8 \pm 0.8$ kJ mol^{-1} and $E_a^T = 2.1 \pm 0.6$ kJ mol^{-1} are small, in accord with the absence of a substantial barrier in an initiating harpooning step.

Fig. 22 shows the CL excitation functions $\sigma_{CL}(\bar{E}|T_0)$ for two nozzle temperatures.

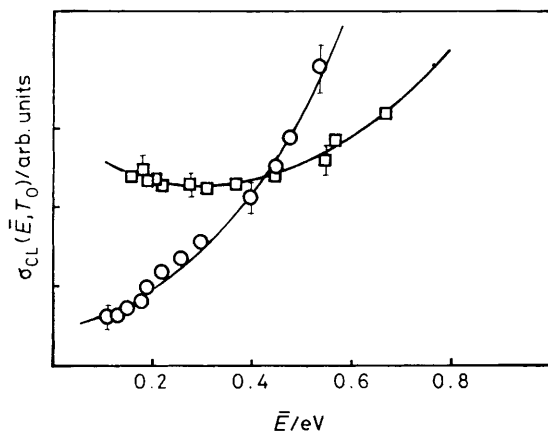FIG. 22.—CL excitation functions $\sigma_{CL}(E|T_0)$ of the Ba − NO_2 → BaO* reaction for two nozzle temperatures, T_0: ○, 281; □, 623 K. The energy scale corresponds to Ba + NO_2 (monomers: □) for $T_0 = 681$ K and to Ba + $(NO_2)_2$ (dimers: ○) for $T_0 = 281$ K.

Most noteworthy is again the strong dependence on T_0: The $T_0 = 623$ K curve extrapolates to a finite value for $\bar{E} \to 0$, and exhibits a shallow minimum,[1,2] while the $T_0 = 281$ K curve tends to zero as $\bar{E} \to 0$.

Our explanation for this effect differs from that in the N_2O system. Expansion from low T_0 nozzles favours formation of the strongly bound $(NO_2)_2$ dimers ($D_0 = 54$ kJ mol^{-1}) as well as larger clusters. Heating the nozzle inhibits cluster formation and favours NO_2 monomer beams.[3] Mass spectrometric detection following electron impact ionization unfortunately proves unsuitable for analysing the cluster content due to the dominant role of dissociative ionization. The NO_2^+ ion is the principal species under all nozzle conditions. Estimates of the cluster content using the kinetic model of Knuth[3] predicts ⩾90% clusters (dimers) at $T_0 = 281$ K and ⩾90% monomers at $T_0 = 623$ K. Vibrational excitation, although undoubtedly present (monomers are assumed to be characterized by a vibrational temperature $T_v = T_0$, and clusters will be vibrationally hot due to the cluster binding energy) appears to play a subordinate role in the T_0-dependence.

In brief, the high temperature nozzle generates NO_2 monomers and the room tem-

[1] A. Yokozeki and M. Menzinger, Chem. Phys., 1977, 20, 9.
[2] H. E. Litvak, A. González-Ureña and R. B. Bernstein, J. Chem. Phys., 1974, 61, 4019; S. A. Pace, H. F. Pang and R. B. Bernstein, J. Chem. Phys., 1977, 66, 3675.
[3] E. L. Knuth, J. Chem. Phys., 1977, 66, 3515.

perature nozzle $(NO_2)_n$ cluster beams.   The energy scale for the latter in fig. 22 corresponds to the dimer reaction

$$Ba + (NO_2)_2 \rightarrow BaO^* + (NO \cdot NO_2)$$

The decreased reactivity of dimers at low energies follows from the paired electron nature of $(NO_2)_2$ and its decreased electron affinity compared with the $NO_2(^2A_1)$ radical monomer.   The cross-over at $\bar{E} \approx 36$ kJ probably reflects the more rapid growth of product phase space for clusters.   The finite cross section of the monomer reaction at low energies is in accord with a harpooning mechanism.   The intriguing minimum in $\sigma_{CL}(E)$ is similar to features observed in other systems.[1,2]

ADDITIONAL REMARKS

Prof. P. E. Siska (*Pittsburgh*) **and Prof. D. R. Herschbach** (*Harvard*) said: It may be desirable to indicate more explicitly the derivation of the energy transfer formula given in eqn (7) of our paper. In the impulsive limit, we follow the kinematic treatment of Mahan.[3] Repulsive energy E_0' released between B and C results in elastic momentum transfer to the B atom.   This transferred momentum persists as internal motion of the AB product.   The initial B-atom velocity is given by

$$u_B^0 = (m_C/m_{BC})(2E_0'/\mu_{AB,C})^{\frac{1}{2}}, \tag{1}$$

where $\mu_{AB,C}$ is the reduced mass of the products and other notation is defined in our paper.   The elastic momentum transfer thus leads to a change in the B-atom velocity given by

$$\Delta u_B = 2u_B \sin (\theta_p^0/2) \tag{2}$$

and the resulting internal excitation of the AB molecule is then

$$\Delta E'_{int} = \tfrac{1}{2}\mu_{AB}(\Delta u_B^0)^2 = 2\mu_{AB}(u_B^0)^2 \sin^2 (\theta_p^0/2). \tag{3}$$

Thus, we obtain

$$\Delta E_{nt}/E' = 4 \sin^2 \beta \cos^2 \beta \sin^2 (\theta_p^0/2). \tag{4}$$

This result becomes identical to eqn (1) in the paper of Fluendy *et al.* in the small-angle regime, where $\sin (\theta/2) \simeq \theta/2$.   Since the impulsive limit is expected to provide the maximum energy transfer, multiplication by the adiabaticity function $H(\rho)$, with $0 \leqslant H \leqslant 1$, allows a greater range of validity and yields our eqn (7).   Note that in a " half-collision " the maximum change in velocity (which occurs for $\theta = \pi$) is exactly half (corresponding to $\Delta u_B = u_B^0$), and the maximum energy transfer is reduced by a factor of 4.   In the eclectic model, however, the products usually undergo a nearly " full-collision ", while the reagents experience less than a " half-collision ".   For all

[1] A. Yokozeki and M. Menzinger, *Chem. Phys.*, 1977, **20**, 9.
[2] H. E. Litvak, A. González-Ureña and R. B. Bernstein, *J. Chem. Phys.*, 1974, **61**, 4019; S. A. Pace, H. F. Pang and R. B. Bernstein, *J. Chem. Phys.*, 1977, **66**, 3675.
[3] B. H. Mahan, *J. Chem. Phys.*, 1970, **52**, 5221.

the systems thus far treated with this model, the exit scattering angle θ_p^0 is well approximated by a hard-sphere deflection function, for which

$$\sin^2 (\theta_p^0/2) = 1 - (b'/R')^2, \tag{5}$$

where b' is the exit impact parameter and R' the effective sphere radius.[1] In this limit, eqn (7) corresponds to a classical breathing sphere model.

Dr. K. H. Bowen, Dr. G. W. Liesegang and Prof. D. R. Herschbach (*Harvard*) said: Prof. Menzinger has reported evidence for a marked effect of $(NO_2)_n^-$ clusters in chemiluminescent reactions with Ba atoms. In recent studies of electron attachment to molecular clusters, we have obtained some results which may be pertinent to his work. In our experiment, the molecular clusters are generated from a supersonic nozzle and the electron transfer occurs from a seeded alkali atom beam produced in a second supersonic nozzle. By scanning the alkali velocity, we detect the threshold for ion pair formation *via*

$$A + X_n \rightarrow A^+ + X_n^-,$$
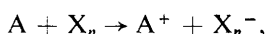
from which the electron affinity of the molecular clusters can be derived. Measurements have been carried out for clusters of Cl_2, SO_2, NO_2, and a number of other systems. For the NO_2 case, we find a result that is so far unique: the observed negative cluster ions $(NO_2)_n^-$ contain only an *odd* number of molecules corresponding to $n = 1, 3, 5 \ldots$ Even in the positive ion mass spectrum,[2] the observed cluster ions $(NO_2)_n^+$ for *odd* $n = 1, 3 \ldots$ are much stronger than for *even* $n = 2, 4 \ldots$ but the disparity is not nearly so marked as for the negative cluster ions.

[1] G. H. Kwei and D. R. Herschbach, *J. Phys. Chem.*, 1979, **83**, 1550.
[2] S. E. Novick, B. J. Howard and W. Klemperer, *J. Chem. Phys.*, 1972, **57**, 5619.