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Publication Date
1962-05-01

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CONTRIBUTIONS TO THE FARADAY SOCIETY

DISCUSSION ON INELASTIC COLLISIONS

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May, 1962

CONTRIBUTIONS TO THE FARADAY SOCIETY DISCUSSION
ON INELASTIC COLLISIONS[*]

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The following three comments have been sub-
mitted as part of the "General Discussion on In-
elastic Collisions of Atoms and Simple Molecules,"
held by the Faraday Society at Cambridge University,
April 10-12, 1962. As usual, the "official" form
of these comments only vaguely resembles what was
said at the meeting. We have also contributed a
paper, "Reactive Collisions in Crossed Molecular
Beams" (UCRL-10096, February, 1962), to the
Discussion. The complete collection of papers and
comments will be published (probably in October,
1962) as Volume 33 of Discussions of the Faraday
Society.

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1. Comment on excitation of products and the calculations of Bunker and Blais.

Vibrationally excited products have now been detected in about thirty exothermic atomic exchange reactions. However, as yet there are only a few studies which indicate what fraction of the products are excited. From a theoretical viewpoint this information is essential. Without it, we cannot tell whether the excited products represent the main course of the reaction or merely an interesting but practically negligible side effect. The reactions for which there is such information have all been mentioned at this Discussion. For the alkali reactions

$$M_2 + X \rightarrow MX + M \tag{1a}$$

and

$$M + RI \rightarrow MI + R \tag{1b}$$
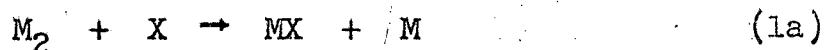
there is evidence that most of the products are highly excited, whereas for some H atom reactions

$$H + BC \rightarrow HB + C \tag{2a}$$

and

$$H + BCD \rightarrow HB + CD, \tag{2b}$$
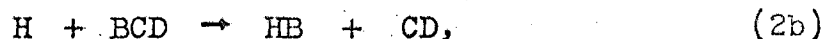
with $BC = Cl_2$, $BCD = O_3$, $ClNO$, NO_2, it is now established that the products are formed predominantly in low vibrational states.

Perhaps the most fundamental motivation for the study of product excitation is that it may contribute to the experimental characterization of the potential surfaces for reactions. The pronounced difference between the reactions (1) and (2) is thus an encouraging sign, and presumably it can be interpreted along lines indicated in early qualitative discussions of potential surfaces.[1,2] The angular distribution of products provides

another and in principle a quite direct approach to the study
of these surfaces. However, the theory of scattering from a
multidimensional potential surface has until now remained
swaddled in formal theorems and so has been unable to offer
much practical guidance in the interpretation of experiments.

Recently an extensive program of calculations on reactive
scattering has been undertaken by Bunker and Blais,[3] who use
Monte Carlo methods to integrate the classical equations of
motion. They have begun with a study of reaction (1b), based
on a surface constructed so that most of the fall in potential
energy is associated with attraction between the reactants, and
not repulsion between the products. This feature was suggested
as a necessary condition for vibrational excitation by Evans
and Polanyi, in their analysis[2] of reaction (1a), and has been
discussed more recently by Smith.[4] In the calculations of Bunker
and Blais, the three interacting particles (CH_3 is treated as a
single atom) are not restricted to be collinear. For the sake
of economy in computing time, however, it did prove necessary
to restrict the trajectories to a plane. Each collision is
initiated with a randomly chosen impact parameter and angular
orientation of the CH_3I molecule. The thermal distributions of
relative velocity and rotation and vibration of CH_3I are also
included.

The results obtained indicate that the assumed potential can
indeed account for all of the qualitative features inferred from
the molecular beam experiments. The predicted distribution of
product excitation is broad but shows a pronounced peak which
puts most of the energy of reaction into vibrational excitation

of the MI molecule. The angular distribution in the plane, $d\sigma/d\chi$, falls off more or less linearly from a maximum near $\chi = 0°$ to a value about one-tenth the maximum at $\chi = 180°$. Thus the intensity per unit solid angle (derived by averaging $d\sigma/d\chi$ over azimuthal angles) is predicted to be strongly peaked along the direction of the initial relative velocity vector and quite asymmetric about $\chi = 90°$, just as observed. (It should be noted, however, that restricting the trajectories to a plane automatically imposes the glory effect, regardless of how the angular momentum is partitioned between orbital and rotational motion.) In virtually all the successful collisions the trajectories "turn the corner" smoothly, and the complex proceeds to decompose within a vibrational period. This is not found to be the case when the calculation is limited to head-on collisions (i.e., $b = 0$ only); a large fraction of the collisions then lead to complicated, "snarled" trajectories, and $d\sigma/d\chi$ has a maximum in the vicinity of $\chi = 90°$. Bunker and Blais are now extending these calculations to different potential surfaces and to other reactions.

[1] Eyring, Gershinowitz, and Sun, J. Chem. Physics 1935, 3, 786; Glasstone, Laidler and Eyring, Theory of Rate Processes (McGraw-Hill, New York, 1941).

[2] Evans and Polanyi, Trans. Faraday Soc. 1939, 35, 178.

[3] Private communication from Dr. Bunker (Los Alamos Scientific Laboratory, New Mexico, March, 1962), who has kindly permitted me to describe this work here.

[4] Smith, J. Chem. Physics 1959, 31, 1352.

2. Reply to a question from Dr. H. O. Pritchard (Manchester University).

Unfortunately the direct experiment suggested by Dr. Pritchard would be extremely difficult. If velocity selectors (with resolution[1] of 10%) were placed in both beams, the yield of product would be reduced by a factor of about 10^{-5} or 10^{-6}; at the peak of the angular distribution only 10^3 to 10^4 product molecules sec^{-1} cm^{-2} would arrive at the detector (a monolayer in 10^4 years). Signals this weak have been detected in beam experiments,[2] but elaborate instrumentation is required. There is the further handicap that even at 1200°K practically all of the HBr would still be in the ground vibrational state.

It is possible to select a particular vibrational and rotational state of a beam by means of an electric resonance Stark-effect spectrometer.[3] In favorable cases several of the lowest states can be resolved, and the fraction of the original intensity transmitted in a selected beam is as much as 10^{-4}. Again the apparatus required is quite complicated, however.

In a shock tube experiment, Schott and Kinsey[4] have obtained results which indicate that the rate of the reaction $H + O_2 \rightarrow O + OH$ is enhanced when the O_2 is vibrationally excited.

[1]Hostettler and Bernstein, Rev. Sci. Instr. 1960, 31, 872.
[2]Ramsey, Molecular Beams (Clarendon Press, Oxford, 1956), p.387.
[3]Moran and Trischka, J. Chem. Physics 1961, 34, 923.
[4]Schott and Kinsey, J. Chem. Physics 1958, 29, 1177.

3. Comment on remarks of Dr. J. C. Polanyi (University of Toronto).

From the conservation laws alone it is not possible to establish a maximum fraction of W' that can appear as rotational excitation. The products are allowed to have any values of $\underset{\sim}{L}'$ and $\underset{\sim}{J}'$ consistent with energy conservation as long as the <u>vector sum</u>, $\underset{\sim}{L}' + \underset{\sim}{J}'$, equals the total angular momentum supplied by the reactants, $\underset{\sim}{L} + \underset{\sim}{J}$. In a reaction $A + BC \longrightarrow AB + C$, the rotational energy of AB is proportional to

$$J'^2 = \left|\underset{\sim}{L} + \underset{\sim}{J}\right|^2 + L'^2 - 2\left|\underset{\sim}{L} + \underset{\sim}{J}\right| L' \cos \psi$$

where ψ is the angle between $\underset{\sim}{L}'$ and $\underset{\sim}{L} + \underset{\sim}{J}$. When $\psi > \pi/2$, the $\underset{\sim}{L}'$ and $\underset{\sim}{J}'$ vectors can both have much larger magnitude than $\underset{\sim}{L} + \underset{\sim}{J}$. Thus the conservation laws allow all of the energy released in the reaction to go into rotation of AB; what fraction actually does cannot be predicted without assuming something about the forces involved in reactive collisions.

These forces are expected to become effective only in sufficiently close collisions. This permits a rough estimate of the maximum initial impact parameter, b, and the total angular momentum that can contribute significantly to reaction [as indicated already under eqn. (17) of our paper]. The range of the final impact parameter, b', is likewise expected to be limited by the short range of the forces. Here we define b' as the distance of closest approach of a pair of product molecules when their asymptotic straight-line trajectories are extrapolated backwards. The maximum values of b and b' in a reactive collision probably cannot be much greater than bond lengths in the reactants and product molecules.

The restriction which this assumption imposes on the orbital angular momentum of the products, $L' = \mu'v'b'$, has been discussed elsewhere.[1,2] It also implies an upper limit on the rotational momentum, J', given by

$$J' < |\underset{\sim}{L} + \underset{\sim}{J}|_{max} + L'_{max} \tag{1}$$

This limit is determined with $\underset{\sim}{L}'$ oriented oppositely to $\underset{\sim}{L} + \underset{\sim}{J}$. Another rough bound, probably more representative of the average rotational excitation, may be obtained by assuming $\underset{\sim}{L}'$ is distributed isotropically with respect to $\underset{\sim}{L} + \underset{\sim}{J}$; an average over all orientations then yields

$$\langle J'^2 \rangle < |\underset{\sim}{L} + \underset{\sim}{J}|^2_{max} + L'^2_{max} . \tag{2}$$

If L' is assumed to be negligibly small, (1) and (2) are equivalent and we obtain the bound considered by Polanyi,

$$J' < |\underset{\sim}{L} + \underset{\sim}{J}|_{max} \tag{3}$$

Eqn. (3) may also be derived from the less stringent assumption that $L' < 2|\underset{\sim}{L}+\underset{\sim}{J}|\cos\psi$ for the dominant contributions to reaction; this requires $\psi < \pi/2$ and $L' < 2|\underset{\sim}{L}+\underset{\sim}{J}|$, however. These various bounds are compared in Table 1. For the

TABLE 1

Reaction	Assumed b'_{max}(Å)	Bound to Rotational Excitation (kcal/mole)		
		(1)	(2)	(3)
$Na_2 + Cl$	2.5	43	30	2
$H + Cl_2$	any	36	36	36
$K + CH_3I$	4.0	10	5	3
$Rb + CH_3I$	4.0	5	3	2
$Cs + CH_3I$	4.0	3	2	2

examples treated by Polanyi, we used the same parameters and
assumed that the probability of reaction is negligible unless
$b \lesssim 2.5$ Å. For the M + RI reactions we used values of the final
relative velocity, v', derived from the observed angular distri-
butions and took $b \lesssim 4.0$ Å. The results given in the table refer
to the rotational excitation of MI and do not include any
excitation of CH_3. Since the small moment of inertia of the CH_3
radical enables it to carry away large amounts of rotational
energy with relatively low angular momentum (e.g., 10 kcal/mole
for $J_3 = 20$ $h/2\pi$, in contrast to KI, which has only 1.7 kcal/mole
for $J_4 = 100$ $h/2\pi$), the observation that in reactions involving
larger R groups the internal excitation does not decrease (but
rather increases somewhat) suggests that CH_3 must have little
rotational momentum, probably no more than 10 $h/2\pi$.

Table 1 and other calculations[1,2] lead to the rule stated
by Polanyi, with two amendments which recognize the role of $\underset{\sim}{L}'$.
First, even for a product with a large moment of inertia, we can
set a low limit on the rotational excitation only when we have
evidence that L'_{max} is not too large. The reason the M + RI
reactions conform to the rule is that the v' estimated from
experiment is rather small, and thus L'_{max} is less than $|\underset{\sim}{L} + \underset{\sim}{J}|_{max}$.
For the $Na_2 + Cl$ example this is no longer the case because the
value of v' used is much larger. Also, the moment of inertia of
NaCl is considerably smaller than that of the MI molecules.
Second, for H atom reactions as well as others, we must expect the
actual distribution of rotational excitation (in contrast to the
upper bound) to be sensitive to the distribution of both b and b'.
In the $H + Cl_2$ example, we note that up to 36 kcal/mole (100% of

w') may go into rotational excitation regardless of the value
of b'. However, in H atom reactions there is usually a large
increase in reduced mass on formation of the products ($\mu \ll \mu'$).
Angular momentum therefore can be readily taken up in orbital
motion, even for rather small values of v' and b'. Thus, the
upper bound to the rotational excitation will always be high when
a product has a very small moment of inertia, but the actual
excitation produced in the main course of the reaction may be far
below the bound (as in the CH_3 example) and will be strongly
affected by the forces that govern the break-up of the collision
complex.

There is a case, exemplified by the reactions

$$M + HX \rightarrow MX + H,$$

in which a high level of rotational excitation in a product is
required by the postulated bounds on the impact parameters.
On the reactant side, $L \gg J$, whereas on the product side we
expect $L' \ll J'$ and consequently $L \approx J'$. That is, here we
expect $\mu v b \gg \mu' v' b'$, since the reduced mass of the products
(approximately just the mass of H) is far smaller than that of
the reactants (26 times smaller for K + HBr, 66 for Cs + HI).
Because the reaction is only slightly exothermic, v' cannot
become large enough to offset more than a fraction of the mass
ratio. The velocity dependence of the scattering of K + HBr
beams does indeed indicate that KBr is formed with high ro-
tational momentum.[2] An interesting consequence of $L \approx J'$ is
that the angular momentum of MX is predicted to be strongly
polarized, with J' nearly perpendicular to the direction of
the initial relative velocity vector. In a beam experiment

this polarization should have a pronounced effect on the deflection pattern obtained when the MX molecules are made to pass through an inhomogeneous electric field.[1] Such an experiment is being attempted at Berkeley. In principle it should give information about the distribution of L in those collisions which lead to reaction.

[1]Herschbach, The Vortex 1961, 22, 348.

[2]Beck, Greene, and Ross, J. Chem. Physics (to be published) and private communication.