Title
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ANALYSIS OF REACTIVE SCATTERING IN CROSSED MOLECULAR BEAMS

Dudley R. Herschbach

August 1960
In their recent paper, "Variation of a Chemical Reaction Cross Section with Energy," Greene, Roberts, and Ross\(^1\) report a study of the \(\text{K} + \text{HBr} \rightarrow \text{H} + \text{KBr}\) reaction in crossed molecular beams. This is the first reaction study in which the blurring due to velocity distributions has been substantially reduced, as the K velocity was selected mechanically and the HBr velocity spread diminished by holding the source at a low temperature. The ratio of the scattered intensity of KBr to elastically scattered K, observed at a laboratory angle of 35°, appeared to rise sharply above the background at a relative initial kinetic energy (RIKE, in kcal/mole) of 1.4, reach a maximum at 3.3, and thereafter decline. Several discussions\(^1,2\) of these results have interpreted them as a rather direct measurement of the variation of the reaction probability with relative energy. Therefore it seems necessary to point out that such information cannot be obtained from this experiment.

We consider three effects, the first two of which appear even if the intersecting beams are regarded as entirely monochromatic in speed and direction. The reaction probability as expressed in the differential cross section, \(\sigma(v,v',\chi)\), depends upon\(^3\) the magnitude of the initial and final relative velocity vectors, \(v\) and \(v'\), and the angle between them, \(\chi\). If the collision yield is measured at a fixed laboratory angle while the speed of one of the beams is varied, the

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orientation of $\chi$ and the center of mass vector $\mathbf{c}$ with respect to the
direction of observation will be continually changing. This causes
the dependence on $v$ and the dependence on $\chi$ to be superposed in the
results ("Problem I"). Calculations show the effect is quite serious:
for the example of Fig. 1a, the two values of $\chi$ that contribute to the
yield at $35^\circ$ in the laboratory undergo large changes, to $38^\circ$ and
$123^\circ$, when the RIKE is raised 25% by increasing $v_K$.

The recoil velocity of KBr relative to the center of mass is
small: $(M_H/M)v' \approx (1/120)v'$. From energy balance, $v' = [2(E+Q)/\mu']^{1/2}$,
where $E$ is the RIKE and $Q$ is the internal energy converted into trans-
lational energy of separation of the products. The maximum possible
value of $Q$ is only about 6 kcal/mole in this reaction. Thus one finds
that the recoil velocity vector of the KBr is confined within the small
sphere indicated in Fig. 1a. Even for completely specified initial
conditions there will always be some distribution of internal excita-
tion in the product molecules (i.e., distribution of $Q$-values), and
a corresponding distribution in values of $\chi$ that contribute at a given
laboratory angle ("Problem II"). However, if the strong correlation
between $v$ and $\chi$ introduced by "Problem I" could be eliminated (using
observations at other laboratory angles), it would be feasible to
derive the energy dependence of the cross section averaged over a range
of $\chi$ (and $Q$), because it turns out this range would not vary much as
RIKE is changed.

Figs. 1b,c,d and Table I demonstrate that the RIKE scale used in
Ref. 1 must be modified ("Problem III"). This scale ("nominal" in
Table I) was calculated for perpendicular collisions, using the most
probable $v_{HBr}$ at $152^\circ K$ and $v_K$ at the center of the triangular intensity
distribution transmitted by the selector. As shown by the diagrams,
KBr from such collisions could not appear at $35^\circ$ in the laboratory
when RIKE is above about 3 (since then spheres for $Q \geq 6$ no longer intercept the 35° line). The shaded areas (single shading for $Q = 6$; double for $Q = 0$) indicate the range of $v_{HBr}$ vectors which could yield KBr at 35°. Conservation of momentum and energy requires $v_{HBr}$ to fall between lines roughly parallel to the 35° line; the areas are further delimited by the partial collimation of the HBr ($\pm 30°$, a rather wide spray$^1$) and by the 1% intensity level. The contour lines give the percentage of the peak intensity as computed from the Maxwellian and the cosine distributions. Table I lists the derived ranges in RIKE. These are conservative estimates, based on the 10% contour and $Q = 0$ rather than the maximal $Q = 6$; allowance is made for the remaining spread in $v_K$ and the contribution of out-of-plane scattering (not included in Fig. 1). It will be noted that at a nominal RIKE of 1.4, a substantial number of collisions have RIKE as high as 2.8, near the activation energy determined from the temperature variation,$^5$ so the appearance of the threshold in this experiment at a low nominal RIKE is perhaps not surprising. Furthermore, the systematic shift of the shaded areas relative to the contour lines shows that as RIKE increases, the yield at 35° must be increasingly attenuated and eventually will disappear, regardless of the actual form of the energy dependence of the cross section.

We wish to thank E. F. Greene, R. W. Roberts, and J. Ross for helpful correspondence.
Footnotes


4. Obtained from the difference in dissociation energies of KBr and HBr, \( D^0 = 4.2 \pm 1.1 \) kcal/mole [A. G. Gaydon, Dissociation Energies (Chapman and Hall, London, 1953)] plus three times the most probable rotational energy of HBr, 0.15 kcal/mole at 152°K.

Table I. Analysis of energy variation

<table>
<thead>
<tr>
<th>Nominal RIKE</th>
<th>Central $v_K \times 10^4$ cm/sec</th>
<th>KBr Recoil Velocity $Q = 0$</th>
<th>KBr Recoil Velocity $Q = 6$</th>
<th>Range and Most Probable RIKE, $Q = 0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>3.65</td>
<td>0.18</td>
<td>0.62</td>
<td>0.2 - 1.0; 0.4</td>
</tr>
<tr>
<td>1.4</td>
<td>6.48</td>
<td>0.29</td>
<td>0.66</td>
<td>0.6 - 2.8; 1.6</td>
</tr>
<tr>
<td>3.3</td>
<td>10.21</td>
<td>0.44</td>
<td>0.75</td>
<td>2.7 - 5.7; 4.2</td>
</tr>
<tr>
<td>5.0</td>
<td>12.48</td>
<td>0.54</td>
<td>0.81</td>
<td>3.9 - 7.7; 6.1</td>
</tr>
<tr>
<td>7.0</td>
<td>14.73</td>
<td>0.65</td>
<td>0.88</td>
<td>6.0 - 10.6; 8.1</td>
</tr>
</tbody>
</table>
Fig. 1. Constructions to find (a) \( x \) values that contribute to 35° yield for given \( Q \) (radius of sphere); (b,c,d) effect of remaining spread in beam speeds and intersection angles.
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