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Authors
Herschbach, D.R.
Kwei, G.H.
Norris, J.A.

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REACTIVE SCATTERING IN CROSSED MOLECULAR BEAMS: K ATOMS WITH CH_3I AND C_2H_5I.*

D. R. Herschbach, G. H. Kwei, and J. A. Norris
Department of Chemistry and Lawrence Radiation Laboratory,
University of California, Berkeley, California

Angular distributions of reactively scattered KI have been measured at the intersection of a K atom beam with beams of CH_3I and C_2H_5I. In these reactions kinematical features[1] are particularly favorable for a study of the recoil spectrum of the product molecules, and an analysis of the data which relies only upon conservation laws has shown: (1) the final relative velocity vector $\underset{\sim}{v}'$ has a quite anisotropic distribution, peaked about the direction of the initial relative velocity vector $\underset{\sim}{v}$; (2) the average magnitude of v' is only about 30% larger than v, and over 80% of the 25 kcal/mole energy of reaction goes into vibrational and rotational excitation of the products.

The beams are formed by thermal effusion from ovens mounted on a turntable which is rotated to sweep the angular distribution past surface ionization detectors. Vertical adjustment of the detector positions allows the scattering to be measured out of the plane as well as in the plane of the incident beams. The KI is distinguished from elastically scattered K by use of two detectors:[2] one a W filament, about equally sensitive to K and KI; the other a Pt-W alloy, about 50 times as effective for K as for KI. For these reactions, this differential detection was not crucial, however, since the KI distributions are displaced far enough from the K beam to be observable with the W detector alone.

Typical results for K + CH_3I are shown in Fig. 1; under the same conditions C_2H_5I gives similar results except that the KI distribution is shifted to larger Θ, by about 7°. For both reactions the collision yield (integrated intensity of KI divided by total K scattered from the parent beam) is found to be about 10^{-4},

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corresponding to a total reaction cross section[3] of roughly 10 A^2. Measurements at several temperatures of the incident beams indicate that the activation energy is negligibly small, less than 0.3 kcal/mole.

The qualitative features implied by the observed angular distributions may be seen in Fig. 1c. The recoil velocity which carries the KI away from the center of mass (vector denoted by $\underset{\sim}{c}$) can have any direction but conservation of momentum and energy determine its magnitude as $v_4' = [(M_3/M_4)(2/M)(E+Q)]^{1/2}$, where $M_4 \leftrightarrow$ KI and $M_3 \leftrightarrow CH_3$; E is the initial relative kinetic energy and Q the internal energy converted into translational energy of separation of the products. Thus the possible spectrum of recoil vectors for KI is represented by a set of spheres, one for each value of Q up to a maximum of about 25 kcal/mole (the difference in dissociation energy of the K-I and C-I bonds). It is seen that the broad peak observed near 83° in the laboratory corresponds to scattering in which an observer stationed at the center of mass would see the KI recoil backwards (and the CH_3 forwards) with respect to the incoming K beam. Large Q values can contribute to this peak only if the recoil velocity vector deviates considerably from the direction of $\underset{\sim}{v}$, as illustrated by the vector labeled $\underset{\sim}{a}$. The scattering must have cylindrical symmetry about $\underset{\sim}{v}$, since the incident beams contain all possible molecular orientations and impact parameters. Therefore, the angular deviation of $\underset{\sim}{v}_4'$ from $\underset{\sim}{v}$ can be studied directly by measurement of the out of plane scattering. The shaded region indicates where endpoints of $\underset{\sim}{v}_4'$ vectors must lie in order to contribute to the observed peak, as derived by combining the in plane and out of plane data and allowing for the influence of the velocity distributions in the reactants. These results demonstrate that the dominant contributions to the recoil spectrum have Q values less than 5 kcal/mole. Velocity selection is essential if the resolution is to be improved. Much of the observed width of the KI peaks is due just to velocity averaging, as shown by the dashed curve in Fig. 1b,

calculated for zero activation energy, $\underset{\sim}{v}'_4$ collinear with $\underset{\sim}{v}$, and Q = 1.6 kcal/mole.

The observed small shift in the KI distribution for the C_2H_5I reaction is expected from the mass change. Another check of the interpretation has been found in results for the analogous reactions of Rb atoms.[4]

One other reaction, K + HBr $\longleftrightarrow$ H + KBr, has previously been studied in crossed molecular beams.[2,5] The angular distribution observed is not comparable with those studied here, however. It yields information about only the total reaction cross section, as the conservation laws confine the KBr to such a small sphere that the recoil spectrum is entirely smeared out by the initial velocity distributions.[1,6]

Footnotes

1. D. R. Herschbach, J. Chem. Phys. 33, 1870 (1960); further details are given in UCRL Report 9379 (University of California Radiation Laboratory, April, 1960).

2. E. H. Taylor and S. Datz, J. Chem. Phys. 23, 1711 (1955); 25, 395 (1956).

3. Elastic scattering hides any reactive scattering that might appear in the region $-30° < \theta < 30°$.

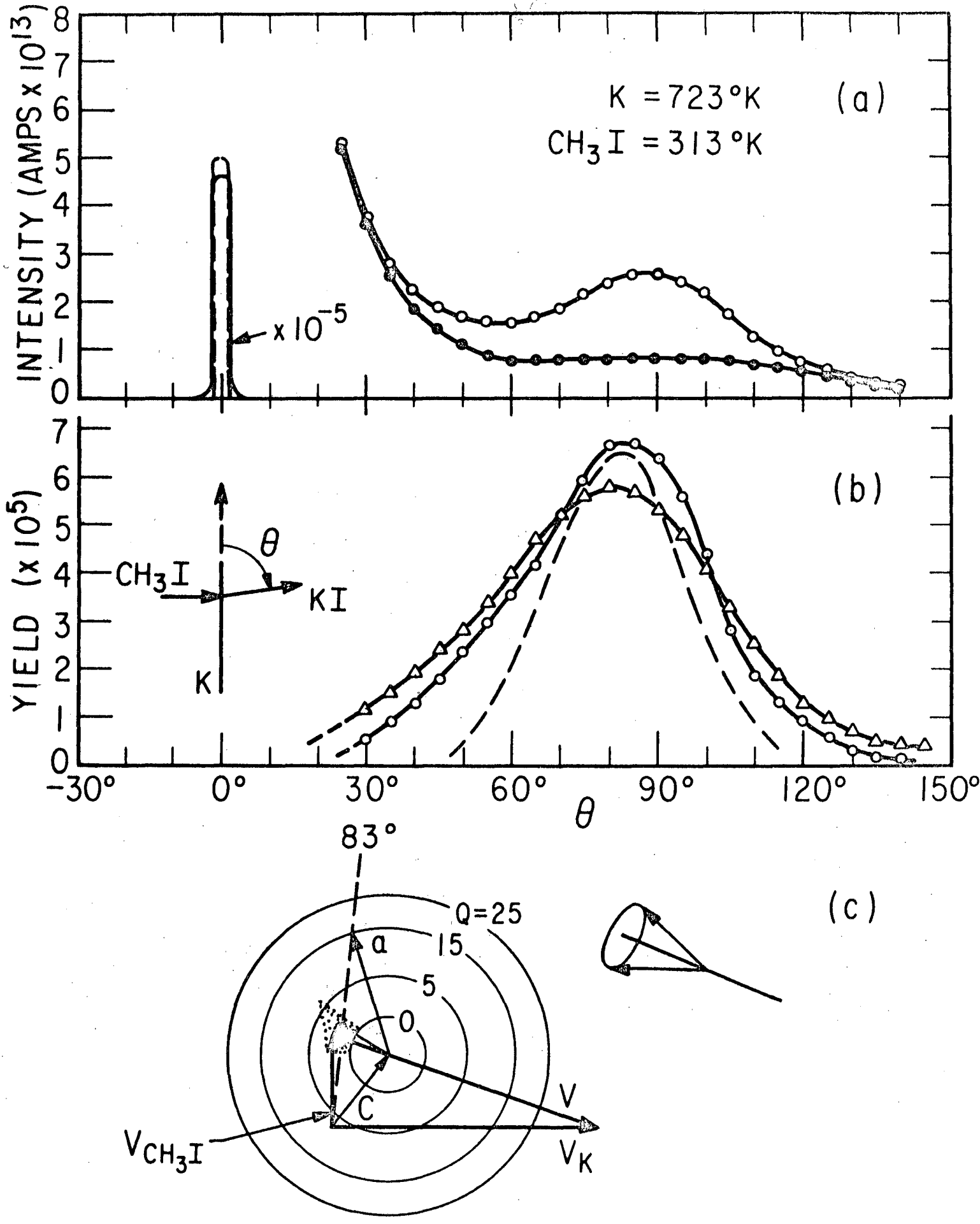
4. J. L. Kinsey, G. H. Kwei, and D. R. Herschbach, J. Chem. Phys. (to be published).

5. E. F. Greene, R. W. Roberts, and J. Ross, J. Chem. Phys. 32, 940 (1960).

6. S. Datz, D. R. Herschbach, and E. H. Taylor, J. Chem. Phys. (to be published).

Caption for figure

Fig. 1 Typical data and analysis: (a) Parent K beam 0.7° wide attenuated 7% by perpendicularly crossed CH_3I beam. Readings on Pt detector (solid circles) normalized to W (open circles) at parent beam peak. (b) KI distributions; circles derived from (a), triangles from a replicate experiment (four months later) using a parent K beam 2° wide and 40% attenuated. Ordinate scale chosen so that area under curves gives collision yield. (c) Vector diagram for most probable velocities of reactants, for which initial E = 1.3 kcal/mole.


INTENSITY (AMPS x 10^13)
K = 723°K
CH3I = 313°K
(a)
x 10^-5
YIELD (x 10^5)
(b)
θ
CH3I
KI
K
-30°
0°
30°
60°
90°
120°
150°
83°
Q=25
15
5
0
a
C
V
VCH3I
VK
(c)