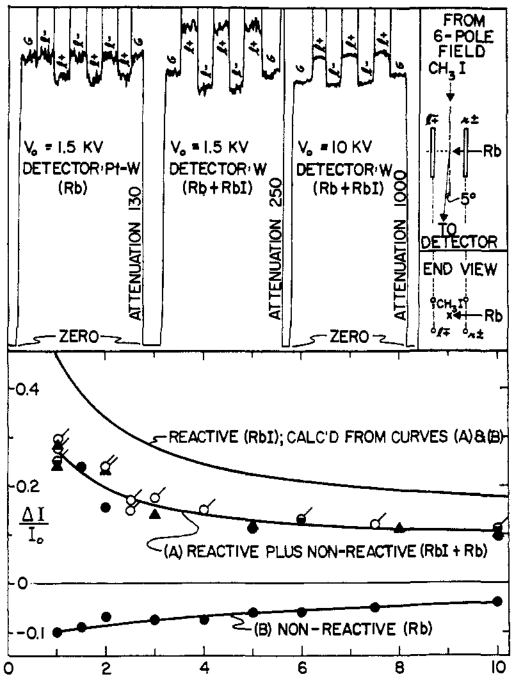

Figure 1.

field. From the fractional change, $\Delta I/I_0$, in the intensity of the RbI product (detected at 85° with respect to the Rb beam[5]) upon reversal of the polarity of the orienting field, the ratio of the reactive cross sections, σ_f/σ_u, may be obtained. Since the degree of alignment of the CH_3I in an orienting field is a function[6] of the hexapole rod voltage, V_0, the results require extrapolation to the limit of "perfect" alignment, *i.e.*, $V_0 \rightarrow \bar{V}_{th}$.

The apparatus was that of ref 3, with the following changes. The velocity selector was removed; a crossed-beam system and a goniometer mount for the detector assembly were introduced. A horizontal, flat-beam system was used, with horizontal, flat, in-plane detection. The CH_3I beam was modulated at 25 Hz; the Rb and RbI were detected by differential surface ionization. The electron-multiplier output from the quadrupole mass spectrometer was passed through a narrow-band amplifier and phase-sensitive detector to a recorder. The focused beam of CH_3I intersected the Rb beam within the "orienting field," placed immediately following the six-pole field. Voltages symmetrical around ground were applied; normally about 100 v was used (*e.g.*, $l = \pm 50$, $r = \mp 50$). The results were independent of the orienting voltage from 20 to 180 v.

Auxiliary experiments were carried out to establish the validity of the orientation effects observed. For an unfocused beam of CH_3I ($V_0 = 0$, direct-beam obstacle removed) there was no effect of reversal of the orienting field upon either the Rb or RbI current (*i.e.*, $\Delta I/I_0 \lesssim 0.01$).

A tracing of a sample recorder chart is shown (Figure 1). The symbol G indicates a grounded orientation field (I_0). The asymmetry data are plotted. It is of interest to note the significant "reverse asymmetry" of the nonreactive scattering, partly compensatory to the reactive effect. The upper curve is the asymmetry deduced for the pure reactive scattering (RbI), based on curves A and B and a reactive:nonreactive partitioning ratio of 2:1 (determined by auxiliary experiments).

Since all experimental imperfections would tend to reduce the observed reactive orientational anisotropy, the present results must be considered to yield a lower limit: $\sigma_f/\sigma_u \geq 1.5$. With a more nearly perfect "unfavorable" alignment (Rb–H_3CI), the reactive cross section may well be only a small fraction of the orientation-averaged cross section. Further work in this direction is in progress. Details of the experiments and analysis of results will be published elsewhere.

Acknowledgments. This work received its principal financial support from the U. S. Atomic Energy Commission, Division of Research, with some assistance from the National Aeronautics and Space Administration, Grant NsG-275-62. The authors wish to thank Mr. T. G. Waech for his assistance and acknowledge valuable discussions with Professors M. Karplus and D. R. Herschbach.

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(5) Herschbach and co-workers (*e.g.*, see D. R. Herschbach, *Discussions Faraday Soc.*, **33**, 149 (1962), and ref 2b) have shown that for the present reaction (a "rebound" type) the product is concentrated in the broad angular range 40–90° from the Rb beam.

(6) The degree of alignment[3] is ⟨cos θ⟩, where θ is the angle between the dipole moment and the electric field: $-\langle\cos\theta\rangle = \bar{V}_{th}/V_0$, where $\bar{V}_{th}$ is the velocity-averaged "threshold" voltage (here *ca.* 0.5 kv). Note that for $\langle\cos\theta\rangle = -1$, the negative end of the dipole is directed toward the negatively charged orienting plate.

Quasiclassical Trajectory Analysis for the Reaction of Potassium Atoms with Oriented Methyl Iodide Molecules[1]

Sir:

Beuhler, Bernstein, and Kramer[2] have recently reported preliminary results from a crossed beam study of the reaction of rubidium atoms with partially oriented methyl iodide molecules. They found that, in collisions with the I atom of CH_3I directed toward the incoming Rb, the reaction cross section for the formation of RbI is significantly greater than that in collisions with the reverse orientation of CH_3I. Since this observation represents the first microscopic determination of a "steric effect," its relation to our knowledge of the potential energy surface for the reaction is of considerable interest. In this communication we present some results obtained on this point by an extension to oriented molecules of quasiclassical trajectory calculations performed previously for the K–CH_3I exchange reaction[3] in the unoriented case.[4,5]

Prior to the work of Bernstein, *et al.*, the $M + CH_3I \rightarrow CH_3 + MI$ reaction in crossed beams composed of

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(1) Supported in part by a contract with the U. S. Atomic Energy Commission.

(2) R. J. Beuhler, Jr., R. B. Bernstein, and K. H. Kramer, *J. Am. Chem. Soc.*, **88**, 5331 (1966).

(3) Corresponding results to those of ref 2 are expected to hold for the K–CH_3I reaction. This expectation is confirmed by the work of P. R. Brooks and E. M. Jones on the K-oriented–CH_3I system (to be published); they used the method described in K. H. Kramer and R. B. Bernstein, *J. Chem. Phys.*, **42**, 767 (1965), and in ref 2.

(4) H. C. Blais and D. L. Bunker, *J. Chem. Phys.*, **37**, 2713 (1962); **39**, 315 (1963); **41**, 2377 (1964).

(5) (a) M. Karplus and L. M. Raff, *ibid.*, **41**, 1267 (1964); (b) *ibid.*, **44**, 1212 (1966).

alkali atoms M and *unoriented* CH_3I molecules had been intensively studied by Herschbach and co-workers.[6] Comparison of their conclusions concerning the center-of-mass differential cross section and reaction-energy partitioning with those from trajectory calculations for the K–CH_3I system on a number of different potential energy surfaces showed that an unequivocal distinction between the surfaces could not be made. For two of the surfaces (V_{MB} and V_S of ref 5b) we have now performed supplementary calculations with the same method as that employed previously[5] except that the initial conditions for each collision trajectory are altered: (a) rather than averaging over random initial orientations of CH_3I, only molecules with their axis parallel or antiparallel to the initial K–CH_3I relative velocity vector are included, and (b) instead of averaging of a CH_3I rotational state population corresponding to a Boltzmann distribution at the beam temperature, only $J = 0$ molecules are selected. This choice of initial conditions provides a very simple approximate simulation of CH_3I molecules perfectly oriented by an external electric field. It does not prevent reorientation of the CH_3I molecules due to the interaction with the incoming K atom. However, this has been shown by trajectory analyses to be unimportant for the system under consideration, in agreement with the observation of Bernstein, *et al.*,[2] that their results are independent of the orienting voltage.

The most direct comparison of the scattering calculations is in terms of the total reaction cross section S_r. Table I gives the results obtained with surface V_{MB} and V_S for unoriented CH_3I molecules and for the two initial orientations (K → CH_3I and K → ICH_3). It is clear from the table that there is a sharp distinction between the surfaces in the orientation dependence of S_r: for V_{MB}, S_r is very sensitive to the initial orientation, while for V_S there is no correlation between the initial orientation and the magnitude of S_r. This is not to say that V_S scattering is independent of orientation; *e.g.*, the form of the differential cross section is altered by the orientation, with the sharp peaking in the backward direction for K → ICH_3 reactive collisions shifted forward somewhat for K → CH_3I reactive collisions. Such a change is not surprising in view of the larger impact parameter collisions that contribute in the latter case. The final molecular rotational state distribution is correspondingly affected by the CH_3I orientation.

Table I. Total Cross Sections (A^2) for Oriented and Unoriented Collisions[a]

	V_{MB}	V_S[b]
Unoriented[c]	25	13
K → CH_3I	0	14
K → ICH_3	35	11

[a] Results based on 500 trajectories with maximum impact parameter of 8 au. [b] The differences among the various V_S results are not significant. [c] The present experimental estimate of the total cross section for K–CH_3I is 30 A^2; see ref 6.

Comparison of the above results with the measurements[2,3] requires prior consideration of a number of factors. First, a hopefully trivial point is that the orientation depends on the sign of the CH_3I dipole moment and all of the interpretation is based on the assumed choice $CH_3^+I^-$. Second, the state selection of the CH_3I molecules in the six-pole field achieves only a partial orientation, whose exact magnitude it is difficult to determine accurately. Thus, further work will be required to attempt to extrapolate the results to perfect orientation.[7] Third, measurements over only a small range of laboratory angles have been made, the angles being chosen to correspond to the maximum yield for the unoriented molecules. Thus, only an indication of the change in the total cross section is available, and there is left the possibility that part of the observed difference between the two initial orientations is due to a change in the center-of-mass angular distribution of the type found in the V_S collisions.[8]

In spite of the necessary cautions, the data appear to be sufficient to show that potential V_S is eliminated by the experimental asymmetry and to suggest that potential V_{MB} has the more appropriate form.[9,10] The essential difference between the two potential surfaces is that V_{MB} includes a K–CH_3 repulsion which makes the surface strongly dependent on the CH_3I orientation relative to the incoming K, while V_S lacks such a repulsion and is much closer to being spherically symmetric than V_{MB}. Thus, even these preliminary investigations clearly demonstrate that crossed beam experiments with oriented molecules provide an important new tool in the study of potential energy surfaces for reacting atoms and molecules.

Acknowledgment. We wish to thank Dr. R. B. Bernstein for stimulating our study by informing us of his exciting project prior to its completion. We are grateful to Dr. L. M. Raff for helpful discussions and for assistance with the computer programs used in this work.

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(6) For a review and references, see D. R. Herschbach, *Advan. Chem. Phys.*, **10**, 319 (1966).

(7) See also footnote 4 of ref 2.

(8) Bernstein, *et al.* (private communication), have also done measurements at somewhat smaller laboratory angles and find a lower asymmetry; the direction of the change is that indicated by the V_S results.

(9) To establish whether V_{MB} is too asymmetric will require more complete experimental alignment and more detailed calculations on partly oriented molecules. The calculations in ref 5b suggest a $\sin^2 (s/2)$ dependence as a crude approximation, where s is the angle between the I–K line and the I–CH_3 line.

(10) A recent analysis (D. R. Herschbach, private communication) of K–CH_3I elastic scattering in terms of an effective two-body potential (E. F. Greene, A. L. Morsund, and J. Ross, *Advan. Chem. Phys.*, **10**, 135 (1966)) indicates that the probability of reaction *vs.* impact parameter obtained from V_{MB} is more nearly correct than that from V_S (see ref 5b).

(11) Much of the work reported in this paper was done while both authors were in the Department of Chemistry, Columbia University, New York, N. Y.

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Received October 24, 1966

Comparison of Field Ionization and Chemical Ionization Mass Spectra of Decane Isomers

Sir:

Recently, a series of papers on a new mass spectrometric technique, called chemical ionization mass