MOLECULAR DYNAMICS OF ELEMENTARY CHEMICAL REACTIONS

Nobel Lecture. 8 December 1986

by

DUDLEY R. HERSCHBACH

Department of Chemistry, Harvard University, Cambridge, Massachusetts 02138, U.S.A.

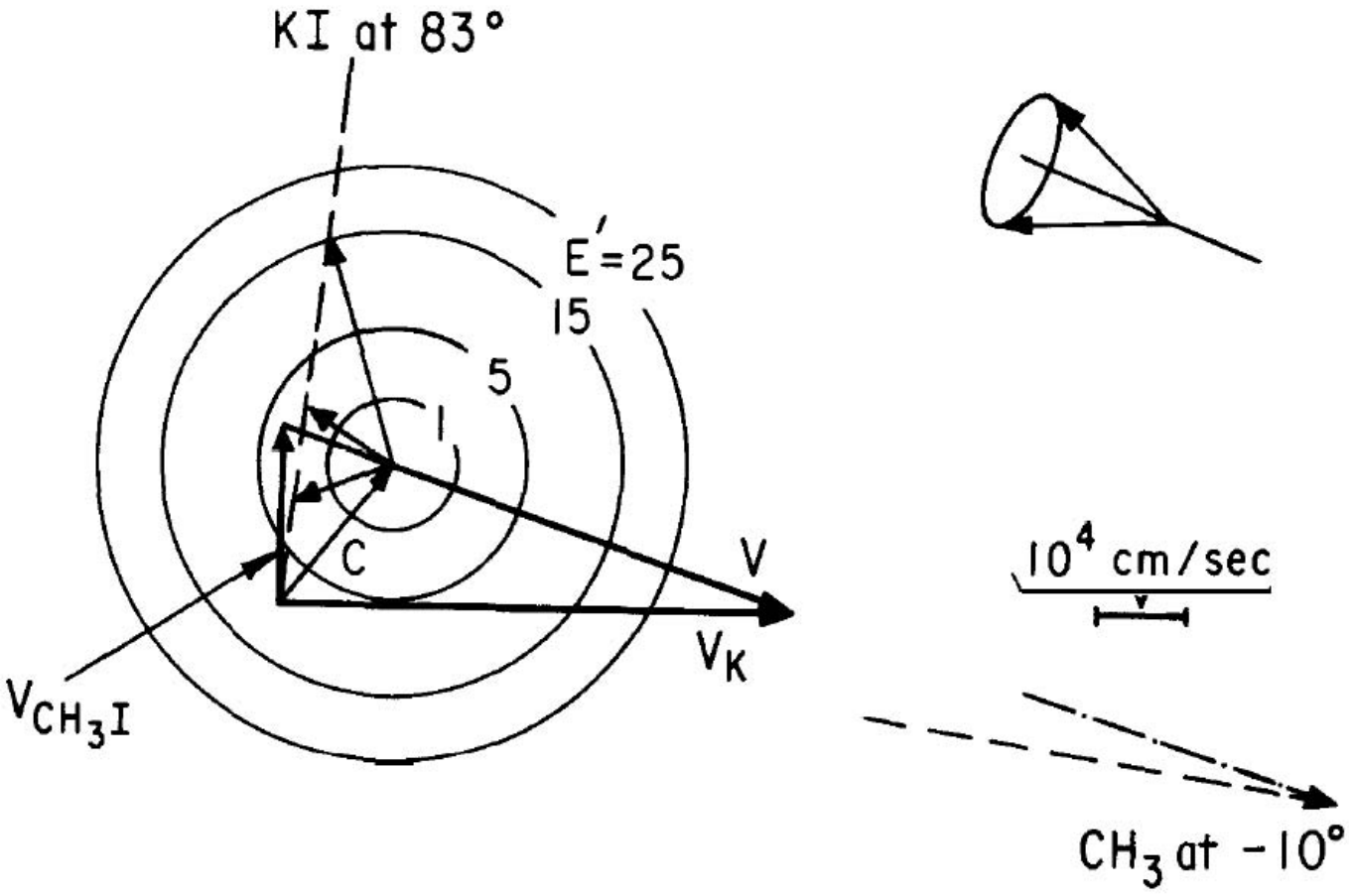

Fig. 5. Newton diagram corresponding to most probable velocitites of reactants in Fig 4. Spheres indicate range of KI recoil vectors allowed by conservation of energy and linear momentum; each is labelled by value of E'(kcal/mol), the final relative translational kinetic energy. Distribution of recoil vectors must have cylindrical symmetry about initial relative velocity vector, by virtue of "dart board" randomness of collisions. Three sample recoil vectors are shown that correspond to the KI observed at the peak of the angular distribution. Also shown is estimate of most probable recoil vector for CH_3 product.

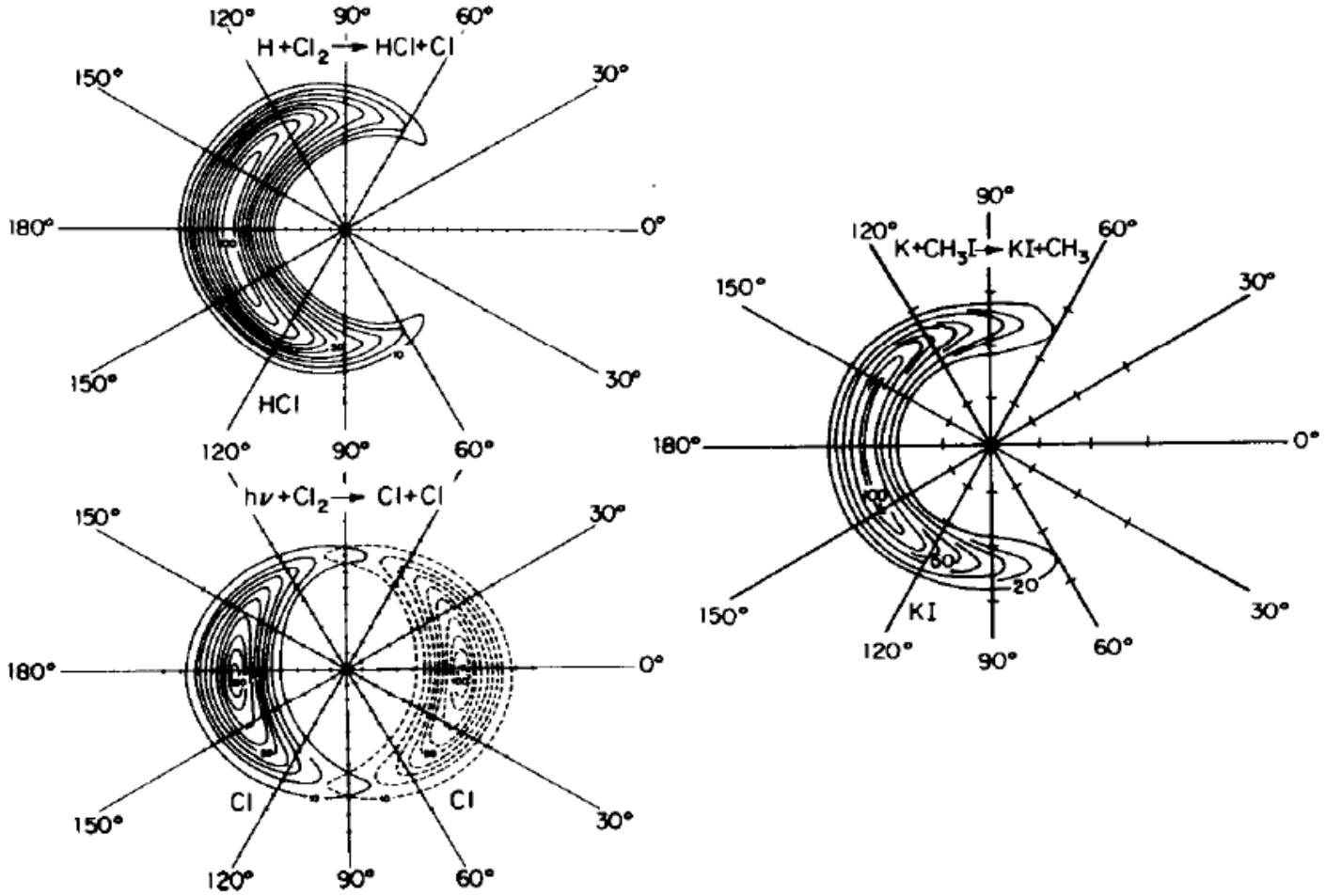

Fig. 16. Comparison of contour maps for photodissociation of the Cl_2 molecule and for reactive scattering of H + Cl, and K + CH_3I. Map for the latter case from work of A.M. Rulis and R.B. Bernstein [3]. For each map, origin is at center-of-mass and horizontal axis is along reactant relative velocity vector, with direction of incident atom or photon designated $\theta = 0^o$. Tic marks along radial lines indicate velocity internals of 200 m/sec.

Molecular beam studies of the $F+H_2$ reaction

D. M. Neumark,[a] A. M. Wodtke, G. N. Robinson, C. C. Hayden,[b] and Y. T. Lee
Materials and Molecular Research Division, Lawrence Berkeley Laboratory and Department of Chemistry, University of California, Berkeley, California 94720

(Received 27 August 1984; accepted 13 November 1984)

The dynamics of the $F + H_2$ reaction have been investigated in a high resolution crossed molecular beam study. Differential cross sections and kinetic energy distributions were obtained for each HF vibrational state. The $v = 1$ and $v = 2$ states were predominantly backward scattered, but substantial forward scattering was observed for HF ($v = 3$) over the range of collision energies accessible in our apparatus, from 0.7 to 3.4 kcal/mol. The results strongly suggest that dynamical resonances play a significant role in the reaction dynamics of $F + H_2$ and that resonance effects are most prominent in the $v = 3$ product channel. Quantal reactive scattering calculations on $F + H_2$ predict that the $v = 2$ channel should be most strongly affected by resonances. This discrepancy is attributed to inadequacies in the potential energy surface used in the calculations, and several modifications to the surface are proposed based on the experimental results. Other features of the reaction are also discussed, including the integrated partial cross sections, the effect of H_2 rotation, and the reactivity of $F(^2P_{1/2})$.

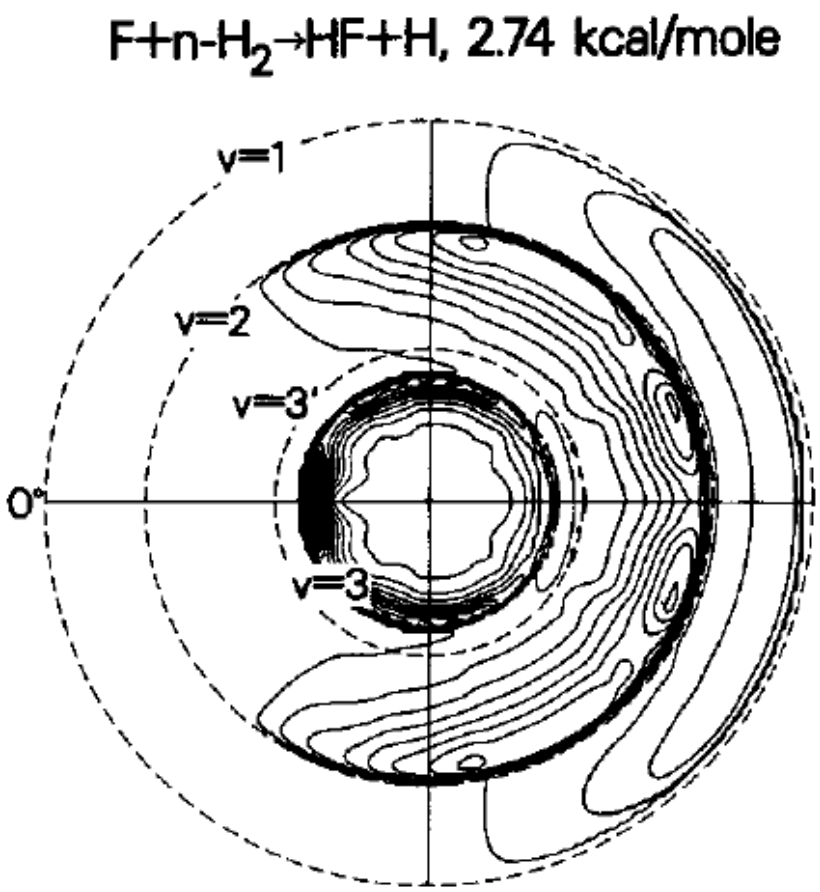

FIG. 20. Center-of-mass velocity flux contour map for F + n-H_2, 2.74 kcal/mol, with three-dimensional perspective.