

GENERAL PHYSICS

I. MOLECULAR COLLISIONS*

Academic and Research Staff

Prof. J. L. Kinsey
Dr. J. S. Kittelberger
Dr. E. K. Parks

Graduate Students

R. P. English
C. H. Fisher

D. O. Ham

M. H. Klumpp
J. R. Lawter

A. SCATTERING OF ALKALI METALS BY OXYGEN-CONTAINING MOLECULES IN CROSSED MOLECULAR BEAMS

This is a preliminary report of some crossed molecular beam scattering experiments related to the general field of chemical kinetics. Experiments have been done with beams of K scattered by SO₂, CO₂, and NO, and Cs scattered by SO₂, CO₂, and NO₂. Further experiments and analysis are in progress.

The most significant result of these experiments is a clear demonstration of collision complexes with lifetimes long compared with a rotation time of the complex. For three decades, theories of chemical kinetics have concentrated on statistical calculations, based on the assumption of complex formation. Until now, however, all of the systems studied in crossed molecular beams have been shown to stick together no longer than a typical vibration period.¹ Since the molecular-beam method is the only unambiguous means of demonstrating complex formation in a single collision, it is important to verify that such processes do occur in some cases.

The apparatus used in these experiments consisted of three differentially pumped vacuum chambers in which pressures $\approx 10^{-7}$ Torr were maintained during the course of an experiment. Two of the chambers contained the sources of the two beams which intersected approximately perpendicularly in the third chamber. In this chamber a surface ionization detector was rotated about the intersection of the two beams in the plane of the crossed beams. The intensity of scattered alkali-metal atoms was measured directly as a function of angle.

A mechanical velocity selector of the slotted-disk type was used to eliminate all of the alkali atoms from the beam except those within a small range (triangular distribution with 8% full width at half-height) around a desired velocity. This improves not only the velocity resolution of the crossed beams but also the angular resolution for the scattered products. It was possible to vary the incident relative kinetic energy over a threefold range.

*This work is supported in part by the Joint Services Electronics Programs (U.S. Army, U.S. Navy, and U.S. Air Force) under Contract DA 28-043-AMC-02536(E).

(I. MOLECULAR COLLISIONS)

The results obtained for SO_2 are shown in Figs. I-1 and I-2. The peak at large angles is clear evidence for a collision complex which lasts long enough to rotate several turns before breaking up. In the case of SO_2 chemical reaction is energetically not allowed, so the complex breaks into the reactant species, an alkali atom and an SO_2

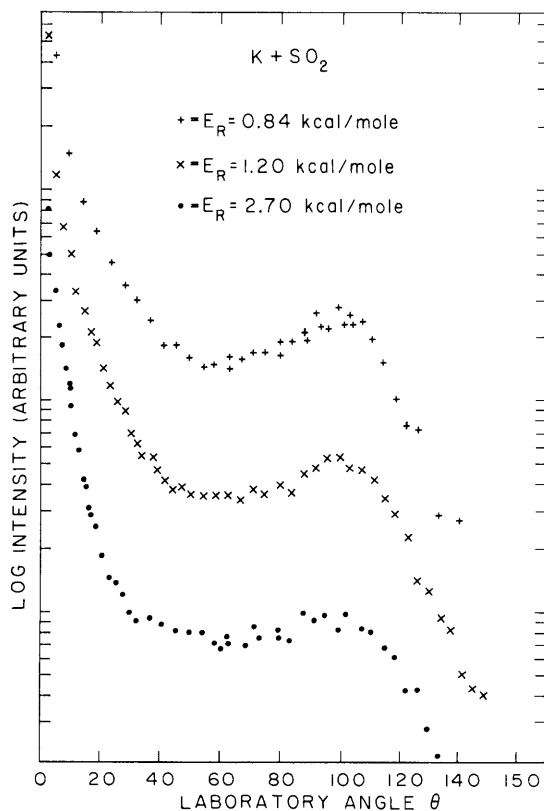


Fig. I-1.

$\text{K} + \text{SO}_2$: Angular distribution of scattered K versus laboratory angle in degrees for three initial relative translational energies.

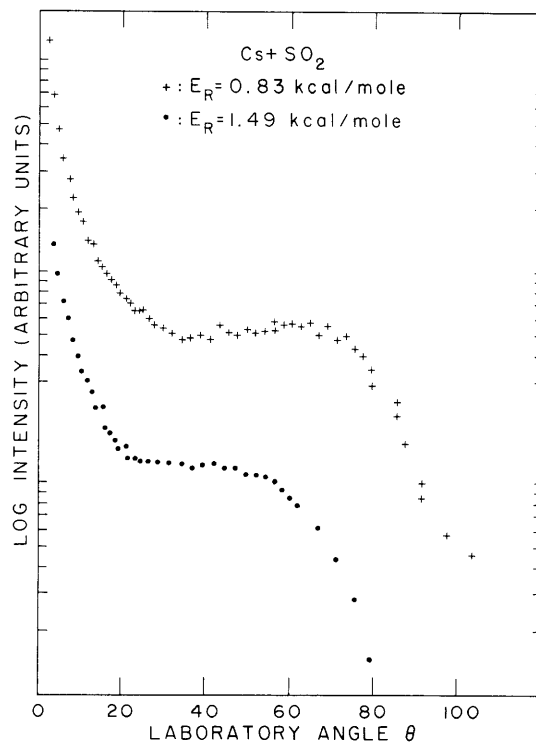


Fig. I-2.

$\text{Cs} + \text{SO}_2$: Angular distribution of scattered Cs versus laboratory angle in degrees for two initial relative translational energies.

molecule. If the complex lasts for many rotations, the angular distribution becomes isotropic in the center of mass (c. m.) coordinate system. An isotropic distribution in the c. m. system yields a peak in the laboratory distribution at the laboratory angle corresponding to a scattering angle of 180° in the c. m. system, owing to the properties of the c. m.-to-laboratory transformation.² No peak would appear for a collision whose duration is shorter than a rotation time, since the differential scattering cross section goes sharply to zero at 180° in the c. m. system in this case.

The position of the laboratory peak is sensitive to the inelasticity of the collision

(I. MOLECULAR COLLISIONS)

(the amount of translational energy transferred into rotation and vibration of the SO_2 for this non-reactive case). The width of the peak results from the distributions in initial velocities, angles of intersection, and the amount of inelasticity. The appearance of the peak at smaller angles in the Cs experiments is a purely kinematic effect associated with the larger mass of the Cs atoms. That the peak appears at the angles predicted by kinematic analysis based on the results of the K experiments constitutes verification of the explanation given above for the observed peak.

The qualitative conclusions, in addition to the existence of the long-lived complex, which can be drawn from these data are: (i) the inelasticity varies from ~20% to 50% of the initial relative kinetic energy, E_R , in the range of E_R studied and is essentially linear with E_R ; (ii) the distribution of inelasticities is very broad; and (iii) vibrational excitation seems to occur with very small probability – the inelasticity is all rotational excitation.

The other systems studied form an interesting range of the various possibilities for interaction in systems which form long-lived collision complexes. The total cross section for formation of the complex is so small in the case of NO that no peak is observed. A peak is observed with CO_2 , but it is not as prominent as with SO_2 . NO_2 yields further possibilities for comparison with theories because reaction is known to occur in this case. Further experiments and quantitative evaluation and comparison of these results with theoretical predictions are in progress.

D. O. Ham

References

1. D. R. Herschbach, "Molecular Beams," Advances in Chemical Physics, Vol. X, John Ross (ed.) (John Wiley and Sons, Inc., New York, 1966).
2. F. A. Morse and R. B. Bernstein, J. Chem. Phys. 37, 2019 (1962).

