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Impulsive Inelastic Scattering of $O^+(^4S)$ by Isotopic Hydrogen Molecules

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We present experimental evidence that at relative energies above 10 eV the non-reactive inelastic scattering of O^+ by H_2, D_2, and HD arises from impulsive elastic scattering of O^+ by individual H or D atoms. The relation of this impulsive non-reactive scattering to the reactive scattering from these systems is briefly discussed.

The study of reactive and non-reactive scattering at relatively high energies offers a particularly attractive path to the understanding of collisional processes. For collisions at relative energies of the order of 10 eV and above we can expect that most frequently the results will be influenced only by the gross features of the potential energy surface, rather than by the subtle details. An understanding of dynamical processes in the high energy regime would provide the basis for the interpretation of lower energy collision phenomena with considerably more certainty than has heretofore been possible.

One of the most useful pictures of high energy scattering processes is the impulse model, in which a collision of an atom with a molecule is viewed as a sequence of independent binary atomic interactions. This model and its variations and extensions have been used to discuss and interpret both inelastic and reactive scattering, [1-6] and in some cases have produced quite acceptable agreement with experimental data. In this Letter we wish to report experimental results that explicitly display features which arise directly from the impulsive nature of certain high energy collisions. These phenomena appear in the non-reactive scattering of $O^+(^4S)$ by H_2, D_2, and HD. We have recently given an extensive report of the low energy reactive scattering in these systems [7].

The experiments were performed by allowing a collimated, energy selected beam of O^+ in its electronic ground state to impinge on the target gas (H_2, HD, or D_2) which was contained in a scattering cell at approximately 10^{-3} torr. The energy-angular distribution of the scattered O^+ was measured with a moveable electrostatic energy analyzer-quadrupole mass filter combination. The results can be displayed either as complete contour maps of the velocity vector distribution of scattered O^+, or as plots of O^+ intensity as a function of laboratory speed in the original direction of the O^+ beam. The source and characterization of the O^+ beam, as well as the details of the apparatus and the data reduction techniques have been described previously [7,8].

Figure 1 shows a contour map of the specific intensity of O^+ scattered from D_2 at an initial relative energy of 25.0 eV. The outermost circle labeled Q = 0 has its origin at the velocity of the center-of-mass of the complete O^+-D_2 system, and represents the locus of O^+ scattered elastically from D_2. In the small angle (< 45°) region, the contours indicate an intensity ridge which follows this elastic circle quite closely. At larger angles, however, the scattering lies well within the elastic circle, and therefore is very inelastic. In fact, this inelastically scattered O^+ forms a second, rather broad, ridge of intensity which closely follows the circle

labeled V_{KO}. This circle, which has its origin at the velocity of the center-of-mass of O^+ and one D atom, is the locus of O^+ scattered elastically from a free deuterium atom. The fact that the large angle scattering has its maximum intensity very close to this circle indicates that in many small impact parameter collisions, the interaction between O^+ and D_2 is to a good approximation a two-body impulsive force between O^+ and one D atom. During this interaction, the second D atom acts as a spectator.

While the location of the inelastic ridge suggests that much of the inelastic scattering is well described by the spectator or impulse model, the breadth of this ridge is noticeably greater than would be expected if O^+ were being scattered by a truly free D atom. This conclusion can be reached by comparing the inelastic O^+-D_2 scattering with the scattering of O^+ from He (not shown here) or with the small angle elastic ridge in Fig. 1. Thus, while the basically impulsive nature of the O^+-D_2 collision is clear, the effects of the third body are also manifested in the data.

While intensity contour maps such as Fig. 1 give valuable indications of the overall nature of the scattering processes, some of the detail available in the original data is lost. It is useful, therefore, to examine the intensity profiles of O^+ scattered at a laboratory angle of 0°, which corresponds to a cut along the 0°-180° axis in the projectile-

target molecule barycentric system. Samples of such velocity spectra are shown in Fig. 2. It is clear that O^+ backscattered from H_2 or D_2 reaches its maximum intensity at a velocity very near to that predicted by the impulse model.

The scattering of O^+ from HD at relative energies of 23.7 and 31.5 eV provides an even more spectacular demonstration of the basic validity of the impulse model. For this system, the high energy inelastic O^+ scattering shows <u>two</u> peaks, one corresponding to scattering from the H atom, the other to scattering from the D atom. While the higher velocity peak is well centered at the velocity expected for purely impulsive scattering from H, the lower velocity peak departs somewhat from the predictions of the impulse model. At lower initial relative energies, the two peaks coalesce into one, which is consistent with the departure from pure impulsive behavior expected at low relative energies.

Some evidence for this type of impulsive inelastic scattering has been found in an investigation of the Li^+-H_2 system by Schöttler and Toennies [9], and in very high energy (> 40 eV) collisions of K^+ with H_2 and D_2 by Van Dop, Boerboom and Los [10]. The latter authors mention having observed two peaks in the scattering of 10 keV Ar^+ from HD, but give no details. The present work is apparently the first complete angular distribution which clearly displays impulsive inelastic scattering, and the first demonstration

of the inelastic isotope effect from HD at moderate energies.

It is of interest to speculate on what features of the potential energy surface are responsible for the appearance of impulsive scattering in the O^+-H_2 at these energies, and what the other consequences of these features might be. The simplest requirement for impulsive scattering is [1]

$$\frac{\omega L}{\upsilon} \ll 1, \tag{1}$$

where ω is the circular frequency of vibration, υ is the relative speed, and L is a length parameter measuring the range of the repulsive forces between colliding atoms. Using the vibration frequency of D_2 ($\omega = 5.8 \times 10^{14}$ sec^{-1}) and taking L to be 0.25 Å, we get $\omega L/\upsilon = 4.2\ E^{-\frac{1}{2}}$, where E is the laboratory energy of O^+ in volts. Thus for the 125 eV experiment shown in Fig. 1, $\omega L/\upsilon = 0.37$, which is not much less than unity. However, the inequality (1) may be overly restrictive. In a potentially reactive system such as O^+-D_2, the effective frequency of the internal motion of D_2 when the three atoms are close will be significantly lower than the vibration frequency of the free D_2 molecule, thereby allowing the spectator D atom to experience only small forces in properly oriented O^+-D_2 collisions.

Some support for this point of view comes from our observation [7] that the small angle reactive scattering

in this system shows very strict adherence to the spectator stripping model at relative energies below 10 eV. This in itself indicates a potential surface in which certain motions of the deuterium atoms are significantly decoupled. At relative energies above 10 eV, the OD^+ reaction product formed by spectator stripping becomes unstable with respect to dissociation, and at the same time, impulsive non-reactive scattering of O^+ becomes prominent. We feel that this is a further indication that reactive spectator stripping and impulsive inelastic scattering have their origins in the same features of the potential energy surface.

The impulsive nature of the non-reactive scattering in this system suggests that the high energy reactive scattering at large angles might be well represented by a sequential impulse model (O^+ hits D, D hits D, O^+ picks up either D) of the type outlined by Bates, Cook, and Smith [3], and developed by George and Suplinskas [5,6]. We have investigated this point and will report the results fully a subsequent publication.

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Figure Captions

Figure 1. A contour map of the specific intensity of O^+ scattered from D_2 at an initial relative energy of 25.0 eV, plotted in the O^+-D_2 center-of-mass coordinate system. The circle labeled Q = 0 is the locus of O^+ elastically scattered from D_2. Scattering inside the circle labeled Q = -4.5 eV comes from collisions inelastic enough to dissociate D_2. The circle labeled V_{KO} is the locus of O^+ scattered elastically from one D atom.

Figure 2. Profiles of the intensity of O^+ scattered along the 0°-180° axis in the atom-molecule center-of-mass system. In each panel the abscissa is the laboratory velocity, increasing from left to right. The label B locates the beam velocity; CM, the center-of-mass velocity; V_{H_2}, the velocity of O^+ scattered elastically from H_2; V_H, the velocity of O^+ scattered from a free H atom, and similarly for V_{D_2} and V_D. (a) 150 eV (Lab) O^+ scattered from H_2, 16.7 eV relative energy. (b) 150 eV O^+ scattered from D_2, 30 eV relative energy. (c) 150 eV O^+ scattered from HD, 23.7 eV relative energy. (d) 200 eV O^+ scattered from HD, 31.5 eV relative energy. All curves are normalized to give a peak height of unity.

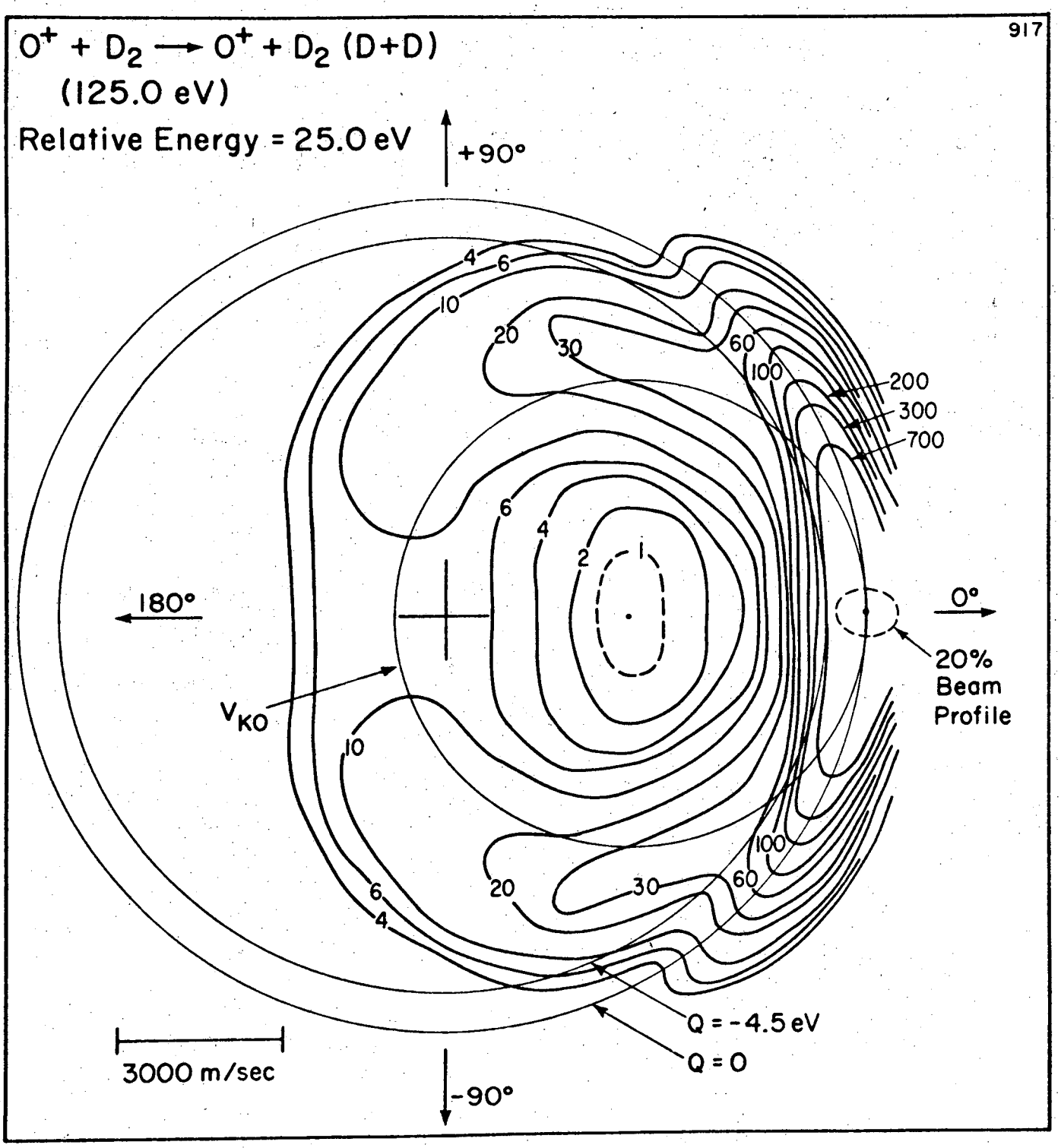

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Fig. 1

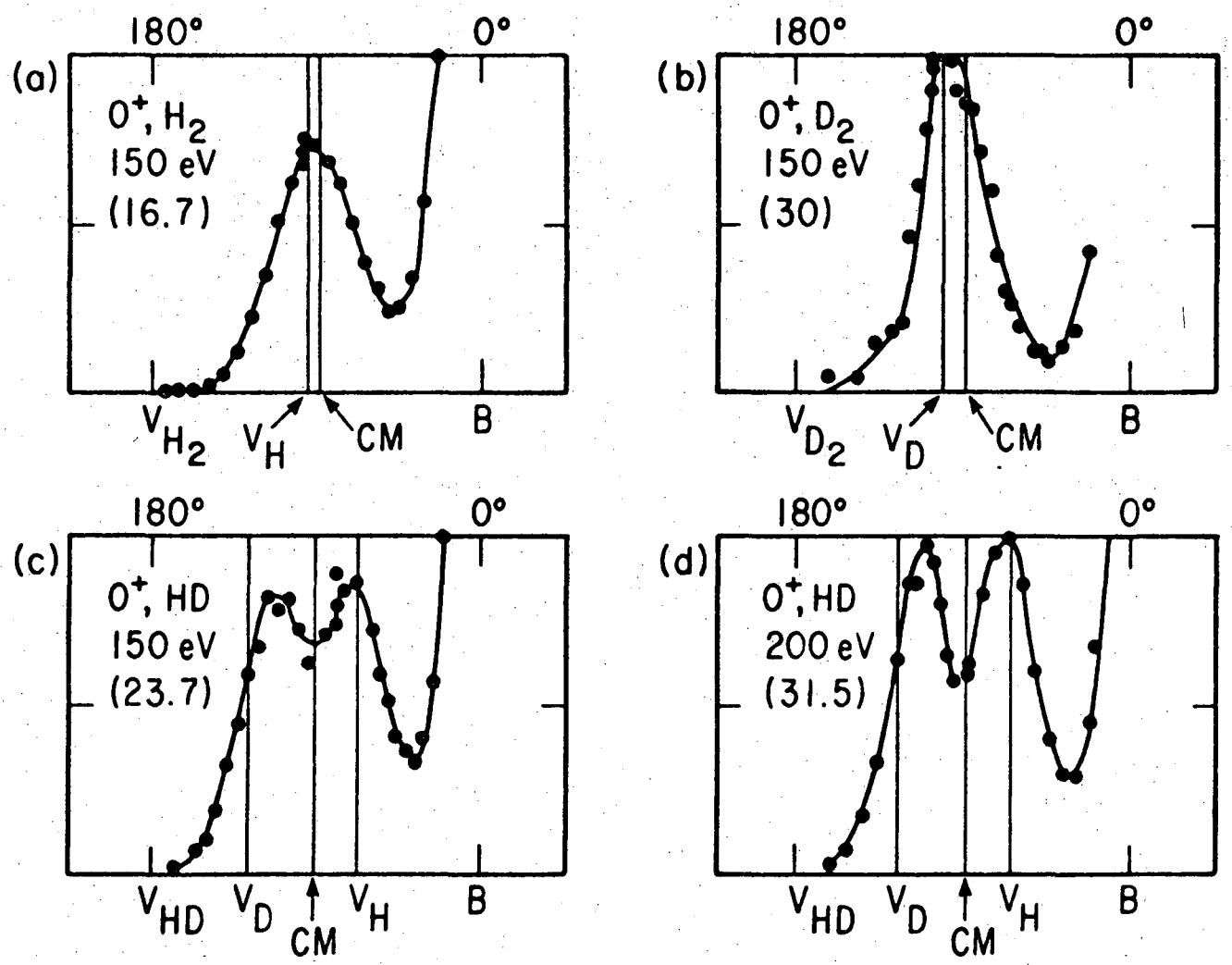

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Fig. 2

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