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The O_2^+-HD Reactions at High Energy: A New Type of Isotope Effect

by

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The effect of isotopic substitution on reaction rate constants has been a valuable aid in deducing both reaction mechanisms and the properties of transition states.[1] Recently, very large hydrogen-deuterium isotope effects have been found in ion beam studies of exothermic hydrogen atom transfer reactions carried out at relative energies of collision which were rather high on the usual chemical energy scale.[2-4] The most detailed of these investigations[3] showed that in the N_2^+-HD reaction, abstraction of hydrogen to form N_2H^+ is as much as twenty times more probable as deuterium atom abstraction, in grazing collisions which lead to the prevalent forward scattering of the ion product. While the general shapes of the angular distributions of N_2H^+ and N_2D^+ are similar, the nearly head-on collisions which lead to large angle scattering preferentially produce N_2D^+.

We have also demonstrated[5] that a rather different isotope effect occurs in the O_2^+-HD reaction at low (< 5 eV) relative collision energies. In this instance, reaction occurs through

formation of a long-lived HDO_2^+ complex which decays to give isotropic distributions of both HO_2^+ and DO_2^+. The total intensity of the DO_2^+ product greatly exceeds (~8×) that of the HO_2^+, just as one would expect from zero point energy and density of states considerations.

In this note we report the occurrence of a novel isotope effect in O_2^+-HD collisions at high (> 6 eV) relative energies. Figure 1 shows intensity contour maps of the distribution of HO_2^+, DO_2^+, and O_2^+ from O_2^+-HD collisions at 8.59 eV relative energy. Both the HO_2^+ and DO_2^+ distributions are asymmetric about ±90° in the barycentric system, which is consistent with our observation[5] that these reactions proceed by a direct interaction mechanism at relative energies above 5 eV. The angular distributions of HO_2^+ and DO_2^+ are of totally different form, with the HO_2^+ almost exclusively in the small angle, grazing collision region, and the DO_2^+ predominantly in the large angle, rebound collision region. We have found that the OH^+ and OD^+ products also display asymmetric distributions of a much less extreme type, with OH^+ falling principally at angles smaller than 90°, and OD^+ predominating at angles greater than 90°.

There are two simple explanations which may account for these angular dependent isotope effects. On the basis of geometrical factors alone, the $HOOD^+$ collision complex will tend to be formed with O_2^+ and HD roughly parallel to each other, and approximately perpendicular to the direction of flight of O_2^+.

The center of mass of the resulting $HOOD^+$ complex is closer to the D atom than the H atom, while the center of force is midway between these atoms. Therefore, the motion of the O_2^+ projectile will, on the average, tend to cause the complex to start rotating with the OH end moving in the flight direction of the O_2^+ projectile, and the OD end moving in the opposite direction. If the complex decomposes in less than one rotation, as it does in this high energy regime, any OH^+ or HO_2^+ would tend to be scattered into the forward or small angle region, while deuterated products would appear at large angles.

A second explanation for the HO_2^+-DO_2^+ isotope effect involves the fact that HO_2^+ formed by the spectator stripping process from HD at 8.6 eV relative energy is stable with respect to decomposition to H and O_2^+. In contrast, DO_2^+ formed by stripping from HD at this relative energy has sufficient internal excitation to decompose to D and O_2^+. Thus, DO_2^+ should appear only as a product of rebound collisions in which some of the internal energy of the molecule-ion can be dissipated as relative translation of H and DO_2^+. Some support for this picture is found in the nonreactive scattering of O_2^+ from HD shown in Fig. 1C. The inelastically scattered O_2^+ has an intensity peak close to the velocity which DO_2^+ form by spectator stripping would have. This feature of the O_2^+ distribution may, therefore, arise from the dissociation of the unstable forward scattered DO_2^+.

We feel that product stability may be the principal factor causing the very different angular distributions of HO_2^+ and DO_2^+ at these higher relative energies. In the formation of OH^+ and

OD^+, the problem of product stability does not arise, and the smaller differences in the distributions of OH^+ and OD^+ may be caused by preferential tumbling of the short-lived collision complex to give forward scattered OH^+ and back scattered OD^+.

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Figure Caption

Fig. 1. (a) Contour map of the specific intensity of HO_2^+ from the O_2^+-HD reaction at 8.59 eV relative energy. The small cross marks the velocity of HO_2^+ formed by the ideal stripping process, and the circle labelled Q = -2.0 eV is the approximate locus of product with no internal excitation. (b) The specific intensity of DO_2^+. Note the low intensity in the vicinity of the spectator stripping velocity of DO_2^+. (c) The specific intensity of O_2^+ scattered from HD. The intensity maximum in the inelastic region falls very near to the velocity of DO_2^+ formed by the spectator stripping process, which is marked by a cross.

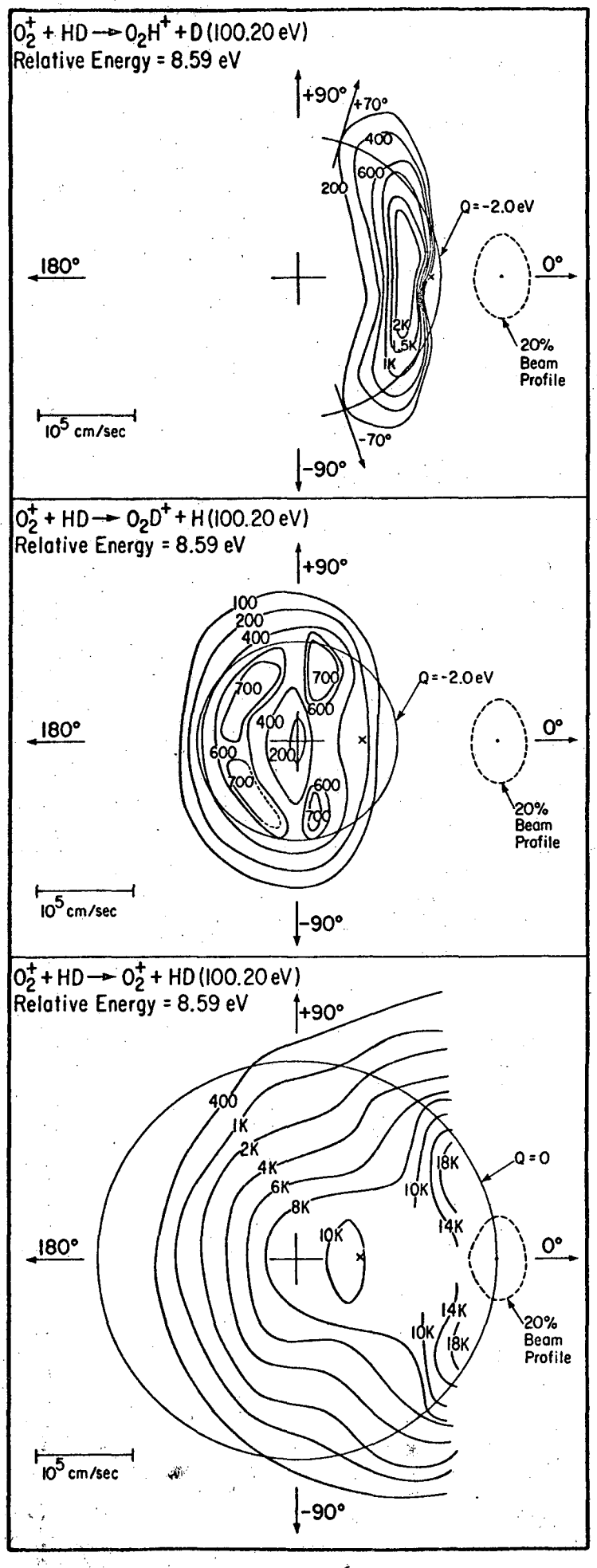
$O_2^+ + HD \rightarrow O_2H^+ + D$ (100.20 eV)
Relative Energy = 8.59 eV
+90°
+70°
400
600
200
Q=-2.0 eV
180°
0°
2K
1.5K
1K
20% Beam Profile
10^5 cm/sec
-70°
-90°
$O_2^+ + HD \rightarrow O_2D^+ + H$ (100.20 eV)
Relative Energy = 8.59 eV
+90°
100
200
400
700
700
600
400
600
200
700
600
700
Q=-2.0 eV
180°
0°
20% Beam Profile
10^5 cm/sec
-90°
$O_2^+ + HD \rightarrow O_2^+ + HD$ (100.20 eV)
Relative Energy = 8.59 eV
+90°
400
1K
2K
4K
6K
8K
10K
18K
10K
14K
Q=0
180°
0°
14K
10K
18K
20% Beam Profile
10^5 cm/sec
-90°

Fig. 6.

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