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Evidence for Long-lived Collision Complexes in Ion-Molecule Reactions: DO_2^+ from O_2^+ and D_2.

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Recently, there has been discussion concerning the importance of long-lived collision complexes in ion-molecule reactions.[1] Some collision complexes have lifetimes long enough ($>10^{-6}$ sec) to permit direct detection by mass spectrometry.[2] Such detection is impossible for those complexes which survive only a few rotational periods ($<10^{-10}$ sec). Measurement of the velocity vector distribution of the reaction products provides the least equivocal means of demonstrating the occurrence of these shorter-lived complexes. Such investigations[3-7] of the reactions N_2^+ (D_2,D) N_2D^+, Ar^+ (D_2,D) ArD^+, N_2^+ (CH_4,CH_3) N_2H^+ and other[8] exothermic hydrogen atom transfers have shown that products are distributed asymmetrically in the center-of-mass coordinate system. Consequently, these reactions proceed, in the energy range investigated, by direct or very short-lived interaction mechanisms in which collision partners remain close for less than one rotational period. We report here measurements of the velocity distribution of DO_2^+ from the endothermic (ΔE_o^o = 1.9 eV) reaction O_2^+ (D_2,D) DO_2^+

which strongly suggest that this process occurs via a collision complex which lasts several rotational periods.

Experiments were performed with the apparatus described earlier.[6] A microwave discharge in O_2 produced O_2^+, and the method of Turner et al[9] showed that the momentum analysed beam contained less than 3% O_2^+ in metastable excited electronic states. Reaction threshold measurements indicated that the average vibrational excitation of O_2^+ was approximately 0.5 eV.

Figure 1a shows a typical contour map of the intensity of DO_2^+ per unit velocity space volume. The distribution is very nearly isotropic, and the greatest intensity occurs at the center-of-mass velocity. While the symmetry of the intensity about the barycentric angles of $\pm$ 90° indicates the occurrence of a collision complex which lasts several rotational periods, the isotropy suggests that the angular momentum of the complex is relatively small, and its temperature, or internal energy per mode, is large.[10] This deduction is consistent with the relatively small total reaction cross section (< 1 Å^2) and with the relatively large binding energy (2.6 eV) of $D_2O_2^+$ with respect to O_2^+ and D_2. The high intensity of product near the center-of-mass velocity indicates substantial internal excitation of the DO_2^+, which is to be expected if energy is distributed statistically among internal and translational modes of a decaying complex.

Figure 1b shows profiles along the 0-180° line of the intensity distributions of HO_2^+ and DO_2^+ from collisions of O_2^+ with HD. The slight asymmetry about the center of mass velocity can be traced to interference of the O_2^+ beam with the detection

of the forward scattered products. The isotope effect, which favors DO_2^+ by a factor of eight, is opposite in sense to that found for products scattered in the ion beam direction from the reactions of N_2^+ with HD and isotopic methanes,[6,7] but is the one to be expected if the collision complex were decaying according to statistical or phase space considerations.[11] The greater density of vibrational levels of DO_2^+ and its lower zero point energy favor its formation.

Figure 1c shows profiles of the distribution of DO_2^+ formed from O_2^+-D_2 collisions of different relative energy. As the relative energy increases, the product distribution becomes asymmetric, and eventually displays the forward peaking characteristic of direct hydrogen atom abstractions. Transition from a long-lived complex to a direct interaction as the collision energy is increased is to be expected, since unimolecular reaction rate theory[12] shows that the lifetime with respect to dissociation of an excited molecule decreases and approaches 10^{-14} sec as the excitation in excess of the dissociation threshold increases.

We believe that there are two significant reasons why the O_2^+ (D_2,D) DO_2^+ reaction proceeds through a long-lived complex at lower energy. First, the $D_2O_2^+$ intermediate represents a potential well whose depth, excluding activation barriers, is 2.6 eV with respect to reactants. Second, the reaction is endothermic by 1.9 eV. Consequently, the lifetime of the complex for a given initial energy is lengthened since the threshold

for dissociation to products is correspondingly high. Moreover, the direct reaction processes which might proceed with large cross section are excluded, since, for example, in order for an endothermic reaction to proceed via the ideal stripping process, the projectile energy relative to one atom must be greater than the endothermicity. Clearly, this condition is met only at projectile energies relative to the target molecule that exceed the minimum necessary for reaction.

A more detailed account of this reaction and of formation of the other ionic products OH^+, O^+, and H_2O^+ will be published later.

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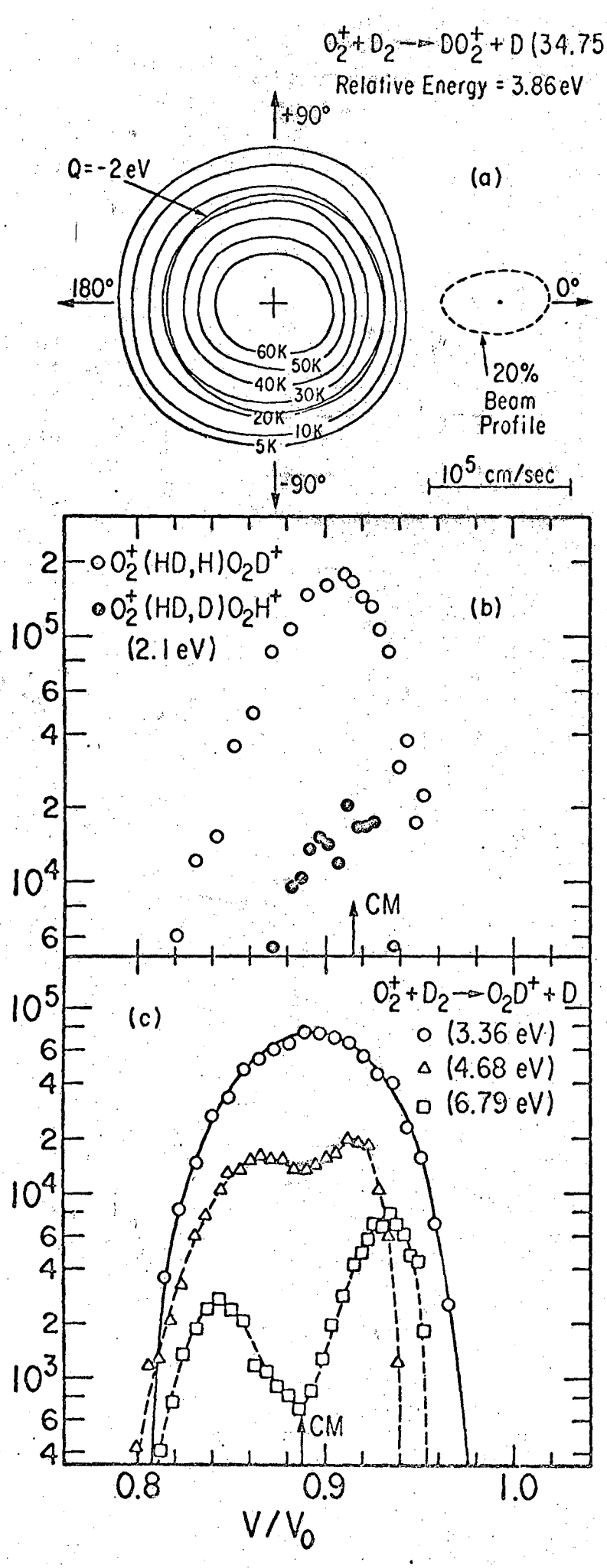
Fig. 1 (a) A contour map in the center-of-mass system of the intensity per unit velocity space volume of DO_2^+ from O_2^+-D_2 collisions at 3.86 eV initial relative translational energy. The scattering from a stationary target gas with no beam energy and angle spread, and no initial internal excitation should fall within the circle marked Q = -2.0. (b) Intensities at 0° LAB of DO_2^+ and HO_2^+ from 2.1 eV collisions of O_2^+ with HD, plotted as functions of v/v_o, the ratio of product to projectile laboratory velocity. (c) Intensities at 0°LAB cf DO_2^+ from O_2^+-D_2 collisions at three relative energies. The greater spread of the 3.36 eV experiment is due to the relatively greater importance of initial internal excitation of O_2^+.


$O_2^+ + D_2 \rightarrow DO_2^+ + D$ (34.75 eV)
Relative Energy = 3.86 eV
+90°
Q=-2 eV
(a)
180°
0°
60K
50K
40K
30K
20K
10K
5K
20% Beam Profile
-90°
10^5 cm/sec
$O_2^+(HD,H)O_2D^+$
$O_2^+(HD,D)O_2H^+$
(2.1 eV)
(b)
CM
$O_2^+ + D_2 \rightarrow O_2D^+ + D$
(c)
(3.36 eV)
(4.68 eV)
(6.79 eV)
CM
0.8
0.9
1.0
V/V0

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