Crossed beam studies of fouratom reactions: The dynamics of OH+D2

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COMMUNICATIONS

Crossed beam studies of four-atom reactions: The dynamics of OH+D$_2$

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The reaction OH+D$_2$→HOD+D was studied in a crossed beams experiment at a collision energy of 6.3 kcal/mol. Center-of-mass translational energy and angular distributions were determined. The HOD product shows a very pronounced backward scattering. Thirty-two percent of the available energy is released as product translational energy.

In the last few years there has been an impressive progress in both experiment and theory towards the solutions of the atom+diatom reactive scattering problem.[1] Benchmark systems in the comparison between experiments and theory have been the H(D)+H$_2$ (Refs. 2 and 3) and F+H$_2$(D$_2$) (Ref. 4) reactions, for which very detailed dynamical observables were measured within the space of the 1980s and early 1990s. The solution of the quantum mechanical problem of reactive scattering involving four atoms can be considered as the challenge of the 1990s. In this respect, the reaction OH+H$_2$ will play a primary role because it involves three hydrogen atoms, and therefore offers favorable possibilities for *ab initio* studies using quantum methods.

In addition to its theoretical interest, the reaction

$$OH+H_2 \rightarrow H_2O+H \quad \Delta H_0^0 = -14.8 \text{ kcal/mol} \quad (1)$$
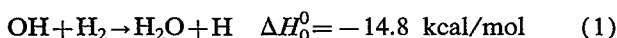
is of considerable practical importance, since it is the chain propagation step in hydrogen combustion.[5] As a consequence, it has been the object of many experimental and theoretical investigations. Kinetic bulk experiments have measured rate constants over an extended range of temperatures.[6] At room temperature the reaction is very slow ($k_{298}=6.1\times10^{-15}$ cc mol^{-1} s^{-1}, corresponding to a cross section of 3.6×10^{-4} Å^2), but exhibits a nonlinear Arrhenius behavior with a pronounced upward curvature at high T.[6] The experimental activation energies are 4.0 kcal/mol for OH+H$_2$ and 5.3 kcal/mol for OH+D$_2$.[6(b)] The effect of initial vibrational excitation of the OH and H$_2$ molecules on the reaction rate was also explored.[7]

The importance and prototypical nature of this reaction has also encouraged a variety of state-of-the-art dynamical experiments in recent years. All of them, however, have focused on the reverse endothermic reaction H+H$_2$O→OH+H$_2$. By exploiting the hot H-atom technique, absolute reactive cross sections and OH internal state distributions were measured in the energy range from 1.43 to 2.52 eV.[8] Recently, a series of experiments involving selective initial excitation of the local OH stretching mode of H$_2$O (HOD) have also been carried out.[9] Elegant as these dynamics experiments are, they do not provide a

sensitive probe of the details of the potential energy surface (PES) along the minimum energy path. Very recently inelastic rovibrational excitation of H$_2$O by 2.2 eV H atoms was also investigated.[10] Very limited experimental information is instead available on the dynamics of the direct process. The only information available comes from early flash photolysis studies[11] coupled to time resolved infrared detection, which did not observed any infrared emission from H$_2$O formed in reaction (1). Therefore, from these studies only upper bounds to the fraction of available energy released into vibrational excitation could be inferred.

High-quality *ab initio* calculations have also been performed on the PES of this prototypical four-atom reaction.[12] The calculated barrier height is 6.2 kcal/mol and the saddle point is found to have a coplanar geometry and to be located in the entrance channel. Quasiclassical trajectory computations[13] of the reactive scattering of OH+H$_2$ have been carried out using a PES based on a fit to the *ab initio* points. Transition state theory[14] has also been applied to this reaction and several other trajectory calculations were also performed.[15] Recently, quantum mechanical scattering calculations of integral cross sections and rate constants were performed for the first time by Clary[16] on both OH+H$_2$ and OH+D$_2$. Very recently, Clary[17] has also computed differential cross sections for OH+D$_2$ at several energies, so that direct detailed comparison between experiments and theory is now becoming possible.

In this Communication, we report the first direct experimental investigation of the dynamics of reaction (1). The crossed molecular beams scattering method with mass spectrometric detection is used. For obvious reasons of simpler detection, we have looked at the isotopic variant

$$OH+D_2 \rightarrow HOD+D.$$
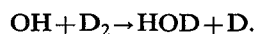
We report here measurements of the angular and velocity distributions of the HOD product at a relative collision energy, E_c, of 6.3 kcal/mol. At this energy the integral reactive cross section is about 0.4 Å^2.[16(b)] These studies were made possible by the development of a continuous supersonic beam source of OH radicals.

The experiment was carried out on a crossed molecular beams apparatus which is the optimized version[18] of the high-resolution machine previously used for measuring elastic and total differential cross sections for atom–atom and atom–molecule collisions.[19] Briefly, a doubly differentially pumped supersonic beam of OH radicals is crossed at 90° with a singly differentially pumped supersonic beam of D_2 molecules in a large scattering chamber kept in the 10^{-7} mbar range in operating conditions. The continuous supersonic beam of OH was generated by a high-pressure radio-frequency (RF) discharge source similar to that used for generating beams of atomic oxygen.[18,20] By discharging a few percent water seeded in helium at 300 mbar total pressure and 260 W of RF power and expanding it through a 240 μm diameter quartz nozzle cooled with low electrical conductivity water, supersonic beams of OH radicals with peak velocities above 3000 m/s and with velocity spread of about 20% were attained. Besides OH, other species are present in the beam, such as undissociated water, H atoms, $O(^1D)$, $O(^3P)$, and H_2: However, they do not interfere in the present experiments. The OH radicals are in the lowest $^2\Pi$ electronic state, since possible electronically excited OH will radiatively cascade to the ground state in much less than 1 μs.[21] The OH beam is also expected to be rotationally cold, since rotational relaxation of OH by H_2O is known to be gas kinetic ($k=2.2\times10^{-10}$ cc mol^{-1} s^{-1}).[22] Vibrational relaxation of OH by H_2O is known to be also rather fast ($k=1.3-2.6\times10^{-11}$ cc mol^{-1} s^{-1})[23] and by H and O atoms even faster (of the order of 10^{-10} cc mol^{-1} s^{-1}).[7(a),(c)] Although we have some indication from our scattering results that OH in the beam is predominantly in the $v=0$ level (see below), a detailed characterization of its internal quantum states is desirable and will be carried out in the near future by spectroscopic techniques. The D_2 beam was produced by a supersonic expansion of 4.5 bar of pure D_2 through a 75 μm orifice kept at about 600 K. The peak velocity was 2640 m/s with a FWHM spread of 15%. The D_2 molecules are estimated to be in the lowest few rotational ($j=0$, 1, 2) levels. The HOD product was detected with a rotatable ultrahigh-vacuum electron impact ionization quadrupole mass spectrometer detector, kept at 10^{-11} mbar. To improve the signal-to-background ratio, experiments were carried out using isotopically labeled $H_2^{18}O$. This permitted us to detect HOD product at $m/e=21$, which has a very low inherent background in the detector. Angular distributions were measured by modulating the D_2 beam at 160 Hz for background subtraction. Product velocity distributions were obtained at five selected laboratory angles by the cross-correlation time-of-flight technique using four identical pseudo-random sequences of 127 elements each and operating at 5 μs/channel.

The laboratory angular distribution for the HOD product at $E_c=6.3$ kcal/mol is shown in Fig. 1, together with the most probable velocity vector ("Newton") diagram. The lab angle Θ is measured from the OH beam. In the center-of-mass (c.m.) coordinate system, $\vartheta=0°$ is the direction of the OH beam and represents the forward direction with respect to OH, while $\vartheta=180°$, which is the di-
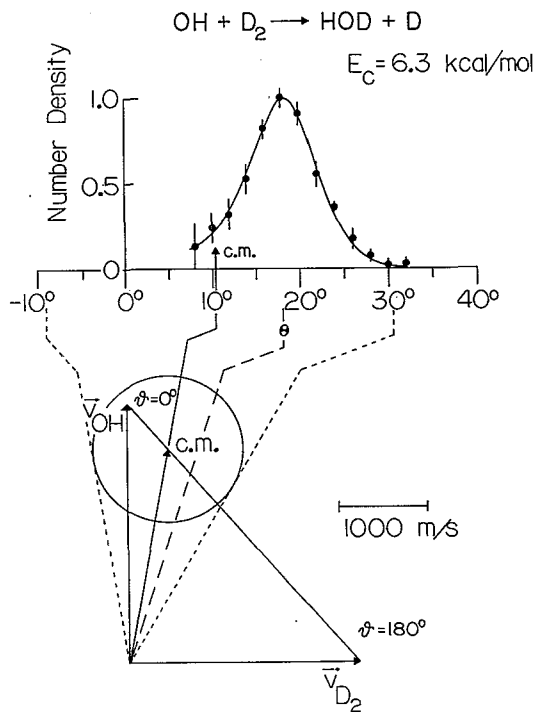

FIG. 1. HOD product laboratory angular distribution from the OH+D_2 reaction at a collision energy of 6.3 kcal/mol. The circle in the Newton diagram [drawn for OH ($v=0$)] delimits the maximum HOD speed when all the available energy is assumed to go in translation. The solid line represents the calculated angular distribution with best-fit c.m. angular and translational energy distributions.

rection of the D_2 beam, represents the backward direction with respect to the OH beam. The circle in the Newton diagram (see Fig. 1) represents the maximum c.m. speed for HOD product assuming that the OH reactant is in $v=0$ and that all the available energy goes into product translational energy. The HOD angular distribution peaks dramatically to the right of the c.m. angle, indicating that the product is thoroughly backscattered. However, its space distribution is completely confined within the angular range predicted assuming that OH is in $v=0$. The presence of OH($v=1$) in the beam would originate in Fig. 1 a significantly larger Newton circle available for the product, corresponding to a lab angular range from $\Theta=-15°$ until $\Theta=36°$.

In order to recover the translational energy and angular distributions in the c.m. system, the time-of-flight measurements of the HOD velocity distribution were used, together with the lab angular distribution, in a forward convolution trial-and-error best-fit analysis. The continuous line in Fig. 1 is the lab angular distribution generated by the best-fit c.m. functions. The best-fit c.m. angular distribution is depicted as solid line in Fig. 2. One can immediately see how the HOD product c.m. angular distribution peaks in the backward direction ($\vartheta=180°$). This is the expected results for a direct chemical reaction dominated by collinear, or nearly collinear, geometries. The product c.m. angular distribution observed bears strong similarities with that measured for the isoelectronic F+D_2 reaction[4(b)]
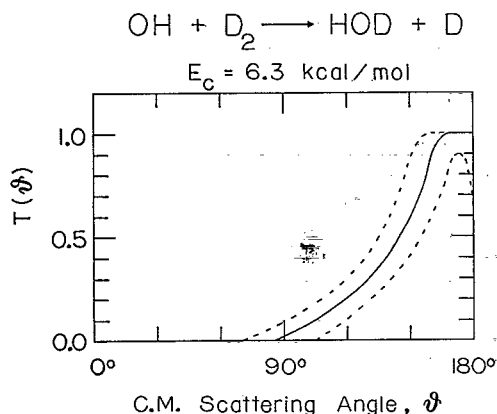
OH + D$_2$ ⟶ HOD + D

E$_c$ = 6.3 kcal/mol

FIG. 2. Center-of-mass angular distribution (continuous line) of the HOD product from the OH+D$_2$ reaction at E_c=6.3 kcal/mol. The area within dashed lines represent the limits of c.m. angular functions which still give acceptable fits to the data.

and for D+H$_2$,[2] and with that calculated for Cl+H$_2$,[24] suggesting that the PES of these systems have a similar topology. All the above abstraction reactions appear to proceed dominantly through collinear, or nearly collinear, geometries, and the nearly collinear *transition state* gives rise to a pronounced rebound dynamics, at least at low collision energies.

It is possible to infer the geometry of the transition state directly from the marked anisotropy of the c.m. angular distribution.[25] In fact, in a direct H-displacement reaction the light H leaves very quickly virtually without perturbing the transition state geometry. Theoretical *ab initio* calculations[12] predict that the preferred geometry of the transition state is that shown in Fig. 3. If this is true, as a consequence of a direct collision the D atom is expected to depart in a direction lying in the HOD plane[26] and forming an angle of about 15° with respect to the incoming OH. As a consequence of linear momentum conservation, the detected heavier HOD product will recoil in the opposite direction, forming an angle of about 165° with respect to the incoming OH (see Fig. 3). This is very much like what we observe experimentally. As can be seen in Fig, 2, the experimental c.m. angular distribution is not sharply peaked at ϑ=180°, but extends almost flat within 160° and 180°, being centered around 170°.

About 32% of the total available energy is found to be

channeled into translation. This suggests that a large fraction of the available energy is released into vibrational excitation, since large rotational excitation is not expected for this nearly collinearly dominated reaction. Similar effects were also observed in the related F+D$_2$ reaction.[4(b)]

It is interesting to compare the present results with those of dynamical calculations on the *ab initio* surface. Quasiclassical trajectory calculations[27] of the c.m. angular distribution of the H$_2$O product from OH+H$_2$ at a translational energy of 0.2 and 0.3 eV, show good qualitative agreement with the HOD distribution measured in the present experiment at 0.273 eV. The calculated distribution is also completely confined between 90° and 180° in the c.m. frame, and about 35% of the available energy is found as translational energy. Calculations for the OH+D$_2$ reaction at the energy of the present experiment would be desirable and would permit a direct quantitative comparison.[28]

Clary[16(b)] has carried out *approximate* quantum mechanical calculations of state selected cross sections and rate constants for OH+D$_2$ in which, however, no c.m. angular and translational energy distributions were generated. We have just learned that using the latest version of his quantum method, Clary[17] has just completed calculations of the differential cross section for the reaction OH+D$_2$ at several energies including the energy of our experiment. He finds a completely backward scattered HOD product at E_c=6.3 kcal/mol. His calculated c.m. angular distribution is similar to that determined experimentally in the present work, falling within the experimental error (dashed lines in Fig. 2) of our determination. The calculated fraction of energy released in translation is 0.30, which also compares well with our results.

Currently, experiments at other collision energies and on the isotopic OD+H$_2$ variant are under way. Ultimately, these differential cross section measurements will provide a detailed test of the theory, i.e., of *ab initio* PES and scattering calculations, for this fundamental four-atom elementary reaction. *Exact* quantum dynamical calculations of the double differential cross sections for OH+H$_2$ may shortly be within reach of modern computer capabilities.
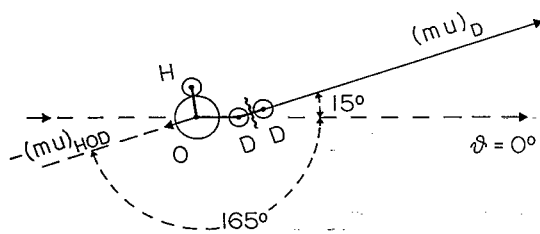
FIG. 3. The geometry of the *ab initio* transition state is shown schematically. The incoming direction of OH, indicated by an arrow, defines ϑ=0°. The velocity vectors of the departing D and HOD products are also represented. *m* and *u* stand for mass and c.m. velocity, respectively.

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