State-to-State Dynamics for $O(^1D) + D_2 \rightarrow OD + D$: Evidence for a Collinear Abstraction Mechanism

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The $O(^1D) + D_2 \rightarrow OD + D$ reaction at two different collisional energies, 2.0 and 3.2 kcal/mol, is investigated by using the H(D) Rydberg "tagging" time-of-flight technique. Experimental results in this study indicate that the OD product is clearly more backward scattered relative to the $O(^1D)$ beam direction at the collisional energy of 3.2 kcal/mol. The extra backward scattered OD products are mostly in the highly vibrationally excited states ($v = 4, 5, 6$), which is typical of a collinear abstraction mechanism. The experimental results in this work also provide a good testing bed for quantitative theoretical investigations of this benchmark system.

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The $O(^1D) + H_2$ reaction plays an important role in both atmospheric [1] and combustion chemistry [2]. It is also a well-known benchmark system for an insertion type chemical reaction at low collisional energies. Extensive experimental and theoretical studies have been carried out in order to elucidate the dynamics of this reaction (and its isotope variants) [3–27]. An overview of the studies on this reaction during the last decade or so can be found in a recent review article by Casavecchia [28]. This reaction was regarded as a typical example of insertion reaction previously. Recently, Liu and coworkers [23–27] have measured the excitation function and the differential cross sections at different collision energies for the $O(^1D)$ + HD reaction using the Doppler-selected time-of-flight (TOF) method. Their experimental results show that at low collision energies (<1.8 kcal/mol), the reaction mainly proceeds via an insertion pathway that exhibits roughly a forward-backward symmetric product angular distribution. At higher collision energies (>1.8 kcal/mol), however, an "elusive" abstraction type channel is becoming apparent. Because of the limited resolution of the above experiments, however, quantum state-specific information on the radical products (OH/OD) has not been derived for this reaction. Therefore, this abstraction mechanism is not clearly characterized. The question of whether or not this mechanism appearing at higher collisional energies proceeds through a colinear geometry is unclear from previous experimental studies.

Recently, we have studied the $O(^1D) + H_2$ [29] and $O(^1D)$ + HD [30] reactions in our laboratory, using the H(D) atom Rydberg tagging TOF technique, which was pioneered by Welge and co-workers [31]. These experiments are carried out at collision energies of 1.3 and 1.7 kcal/mol, respectively, which are below the 1.8 kcal/mol barrier for the "elusive" abstraction mechanism inferred from previous experimental studies [25]. Interesting dynamics are observed for both reactions in these studies. The purpose of the present investigation is to look for experimental evidences of the abstraction mechanism by investigating the $O(^1D) + D_2$ reaction at different collisional energies. Preliminary experimental results on the $O(^1D) + D_2 \rightarrow OD + D$ reaction presented in this work show strong evidence for a colinear abstraction mechanism at higher collisional energies.

The excitation of the ground state D atom product ($n = 1$) is made by the following two-step excitation scheme:

$$D(n = 1) + h\nu(121.6\ \text{nm}) \rightarrow D(n = 2) \tag{1}$$

and

$$D(n = 2) + h\nu(365\ \text{nm}) \rightarrow D(n \sim 50)\,. \tag{2}$$

The 121.6 nm vacuum ultraviolet (VUV) light used in the first step excitation is generated by a two photon resonant ($2\omega_1$-ω_2) four wave mixing scheme in the Kr gas cell. In this scheme, $2\omega_1$(212.5 nm) is resonant with the Kr ($4p$-$5p$) transition [32]. The ω_1 light is generated by doubling the output of a dye laser pumped by a Nd:YAG (355 nm) laser, while the ω_2 (845 nm) light is the direct output of a dye laser pumped by the second harmonic of the same YAG laser. A few millijoules of 212.5 and 845 nm laser lights are used typically in the experiment. The efficiency of the VUV generation can be enhanced by adding the Ar gas as the phase matching medium in a 3:1 ratio between Ar and Kr. By generating about 50 μJ of the 121.6 nm laser light, the first step can be easily saturated since this transition has a huge excitation cross section (3.0×10^{-13} cm^2). Following the first step VUV excitation, the D atom product is then sequentially excited to a higher Rydberg state with $n \approx 50$ using a 365 nm light, which is generated by doubling a dye laser pumped

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by the same YAG laser. These two excitation laser pulses have to be overlapped well in space and synchronized in time in the detection region. The neutral Rydberg D atom then flies a certain TOF distance and reaches microchannel plate (MCP) detector with a fine metal grid (grounded) in the front. After passing through the grid, the Rydberg D atom products are then immediately field ionized by the electric field applied between the front plate of the Z-stack MCP detector and the fine metal grid. The signal received by the MCP is amplified by a fast preamplifier, and then counted by a multichannel scaler (MCS).

Two parallel molecular beams (D_2 and O_2) are generated with similar pulsed valves in this experiment. The $O(^1D)$ atom beam is produced by the photolysis of 157 nm of the O_2 molecule. The 157 nm laser light is produced by a F_2 laser (Lambda Physik LPX 2101). The $O(^3P)$ atom is also generated in the process, but plays no role in the reaction with D_2 since the reaction is endothermic. The $O(^1D)$ beam is then crossed at 90° with the D_2 molecular beam. The D_2 molecular beam is produced by expanding the D_2 sample through a pulsed nozzle. Two different conditions are used in this experiment: a liquid nitrogen cooled nozzle and a room temperature nozzle, which correspond to the two collisional energies, 2.0 and 3.2 kcal/mol, since the D_2 beam velocities of these conditions are different. The velocity of the $O(^1D)$ beam has been measured to be 2050 m/s with a very narrow velocity distribution ($v/\delta v > 50$), while the velocities of the liquid nitrogen cooled and the room temperature D_2 beams are 1036 and 2135 m/s, respectively. The cooled nozzle D_2 expansion has a much smaller spread in the beam velocity, and thus a much smaller energy spread in the collisional energy. In order to reduce the angle spread of the collision, a small aperture is placed between the O_2 and D_2 beams to better define the $O(^1D)$ beam. The D atom products were detected using the Rydberg "tagging" TOF method with a rotatable MCP detector. The Newton diagrams of the reaction investigated at the two collisional energies in this study are shown in Fig. 1.

Time-of-flight spectra of the D atom products have been measured at many laboratory angles at both collisional energies. Kinetic energy distributions can be derived by direct conversion of these TOF spectra. For the experiment carried out at 2.0 kcal/mol, Fig. 2(a) shows the total product angular distribution from $\Theta_L = -60°$ to 117.5°, which correspond to the forward (−60°), the sideward (30°), and the backward (117.5°) scattering directions. The direction of the D_2 beam is at $\Theta_L = 0°$, while the direction of the $O(^1D)$ beam is at $\Theta_L = 90°$. By definition in this work, the forwardness and backwardness of the D atom products are with respect to the D_2 beam direction, while those of the OD products are with respect to the $O(^1D)$ beam direction. Using this definition, the forwardness and backwardness are consistent when different products (D & OD) are discussed. From the angular distribution shown in Fig. 2(a), it is quite obvious that the angular distribution of the reaction product (D) is essentially forward and symmetric. That is not too surprising since 2.0 kcal/mol is only slightly above the barrier (1.8 kcal/mol) for the abstraction mechanism inferred from previous experimental studies. It is interesting that even though the total product distribution is forward and backward symmetric, the product kinetic energy distributions at the forward and backward directions in the CM frame are noticeably different. Figure 3 shows the product kinetic distributions at $\Theta_L = -60°$ and 117.5° for the $O(^1D) + D_2$ reaction at 2.0 kcal/mol collisional energy. Extensive sharp features are present in

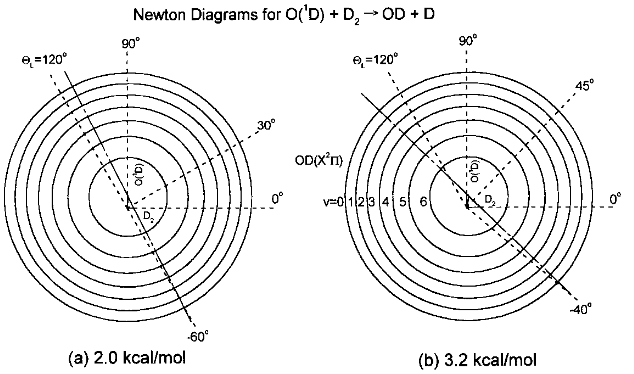

FIG. 1. The Newton diagram for the $O(^1D) + D_2 \rightarrow OD + D$ reaction at (a) 2.0 kcal/mol and (b) 3.2 kcal/mol.

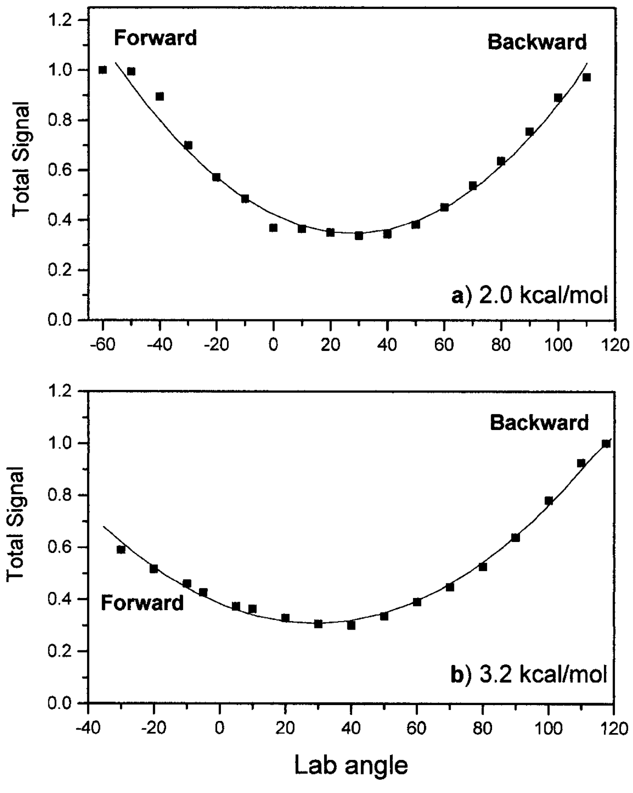

FIG. 2. Product angular distribution for the total D atom product for the $O(^1D) + D_2 \rightarrow OD + D$ reaction at (a) 2.0 kcal/mol and (b) 3.2 kcal/mol.

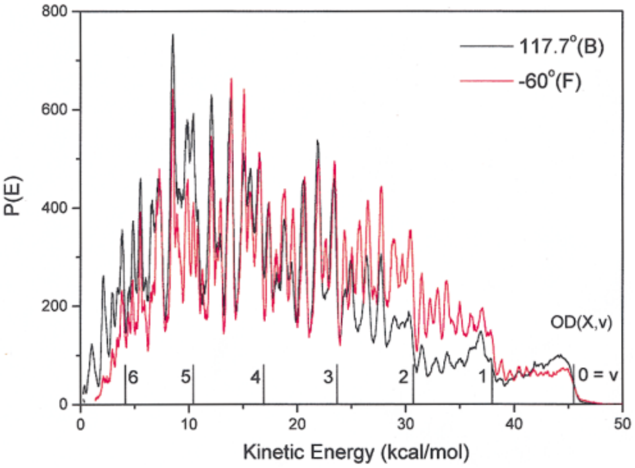

FIG. 3 (color). Kinetic energy distributions in the center-of-mass frame at the forward and backward scattering angles for the O(^{1}D) + D_2 → OD + D reaction at 2.0 kcal/mol.

these kinetic energy distributions. These sharp structures correspond to the ro-vibrational structures of the OD products since the D atom has no internal energy distribution. Most of these structures are overlapped structures of different OD ro-vibrational states from $v = 0$ to 6. Spin-orbit states of the OD product are not resolved in these TOF spectra. Upon examining the kinetic energy distributions, it is clear that most of the OD products are highly rotationally excited since the low rotational OD product at the onset of each vibrational state of OD is not significant in comparison with other regions. The two kinetic energy distributions possess similar shapes overall. However, the detailed structures of these two distributions are noticeably different, indicating that state-specific OD product is clearly not exactly forward and backward symmetric. This result is quite similar to that of the O(^{1}D) + H_2 reaction. The overall symmetric OD product distribution at 2.0 kcal/mol is indicative of an insertion type mechanism.

The O(^{1}D) + D_2 reaction is also studied at a higher collisional energy, 3.2 kcal/mol, with a room temperature D_2 beam, in order to better understand the reaction mechanisms involved at higher collisional energies. When the collisional energy of the reaction is increased from 2.0 to 3.2 kcal/mol, the total product angular distribution changes from a roughly forward-and-backward symmetric distribution to a clearly more backward distribution. Figure 2(b) shows the total product angular distribution. The increase in the backward scattering signal is quite obvious, which also agrees with previous experimental results. The nature of these backward scattered products is a very important issue, since that can provide important insight into the reaction mechanism responsible for these backward products. Figure 4 shows the two product kinetic energy distributions at the forward ($\Theta_L = -40°$) and backward ($\Theta_L = 117.5°$) directions in the CM frame. Apparently, the resolution of these kinetic energy distributions is worse than those at 2.0 kcal/mol, because the room temperature beam has a much larger beam velocity spread. Although the resolution is much lower at this collisional energy, the basic information is not all lost in these kinetic energy distributions. By comparing the two distributions (Fig. 4), it is quite obvious that the kinetic energy distribution at the backward direction is significantly different from that of the forward direction. At higher kinetic energy or lower OD internal energy, the distributions at the forward and backward directions are similar, which resembles the results at 2.0 kcal/mol. At lower kinetic energy or higher internal energy, the backward product is much more pronounced than that of the forward direction. These more backward products are likely the OD ($v = 4, 5, 6$) products (see Fig. 4). Clearly, these backward products are not rotationally hot. These results are quite different from those at the collisional energy of 2.0 kcal/mol, in which the forward and backward kinetic energy distributions are generally similar. From the above analysis, it is not difficult to draw the conclusion that the extra backward OD products appearing at higher collisional energy are likely vibrationally hot ($v = 4, 5, 6$) and rotationally cold, which is typical of a collinear abstraction mechanism [33].

In this study, the O(^{1}D) + D_2 → OD + D reaction at two collisional energies using the H(D) atom Rydberg "tagging" TOF technique was reported. The total product angular distributions, as well as the product kinetic energy distributions, were also measured. Even though a full analysis is not yet available on this system, clear dynamical information can still be derived on this system. It is obvious that the more backward scattered OD products, appearing at higher collisional energies, are vibrationally excited and rotationally cold. This result strongly supports that a typical collinear abstraction mechanism is responsible for the increased backward product scattering at higher collisional energies for this reaction. This mechanism should

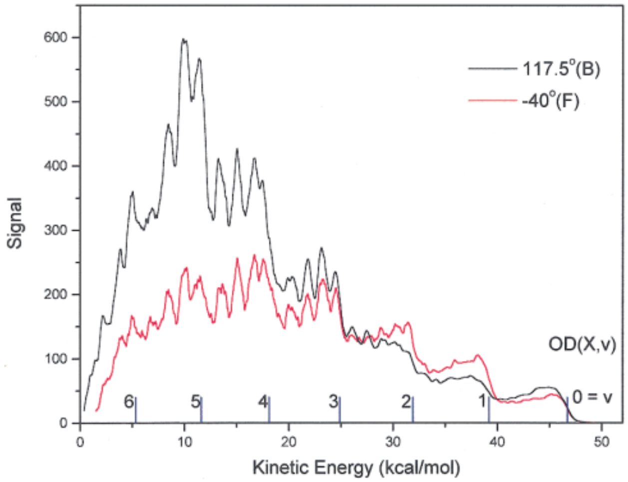

FIG. 4 (color). Kinetic energy distributions in the center-of-mass frame at the forward and backward scattering angles for the O(^{1}D) + D_2 → OD + D reaction at 3.2 kcal/mol.

also be responsible for the increase of the total reaction cross sections of this reaction at higher collisional energies, which is in agreement with theoretical predictions.

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