Effect of a Single Quantum Rotational Excitation on State-to-State Dynamics of the $O(^1D)+H_2 \rightarrow OH + H$ Reaction

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Crossed molecular beams scattering experiments on the $O(^1D)+H_2$ reaction have been carried out in order to study the effect of the reagent (H_2) rotational excitation on the detailed dynamics of this benchmark insertion reation. Experimental results indicate that a single quantum rotational excitation of H_2 has a significant impact on the product state distributions at the forward and backward scattering directions, while very little effect has been found in the sideway scattering direction. No clear patterns of this effect are found in the OH-product state distributions, indicating that the single quantum excitation on the dynamics is rather complicated.

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Quantum state resolved differential cross section measurements provide the most detailed mechanistic information on a chemical reaction through reactive scattering and also provide the most stringent test for a quantitatively accurate theoretical picture for this process. So far only a handful of reactive systems have been studied with quantum-state resolution in a scattering experiment [1–3]. In this Letter, we report a detailed experimental study of the reagent rotational excitation effect in a typical insertion chemical reaction, $O(^1D)+H_2$, at the quantum-state-to-state level.

The reaction of $O(^1D)+H_2$ plays a significant role in atmospheric [4] and combustion chemistry [5]. This reaction is also a well-known benchmark system for an insertion-type chemical reaction at low collision energies. Extensive experimental and theoretical studies have been carried out in order to elucidate the dynamics of this reaction (and its isotope variants [6–28]. Previous experimental studies indicated that this reaction is dominated by the insertion mechanism. Recently, Liu and co-workers [23–27] have shown that the reaction is dominated by the insertion pathway only at low collisional energies, while at higher collision energies ($>$ 1.8 kcal/mol) an additional abstraction channel is coming into play. Very recently, a quantum-state-resolved scattering study was reported on the $O(^1D)+H_2(J=0)$ reaction at 1.3 kcal/mol [29]. Even though extensive theoretical studies on this reation have been performed, the effect of rotational excitation on the dynamics of this insertion reaction is still not understood quantitatively.

In this work, the $O(^1D)+H_2(J=0/1) \rightarrow OH(^2\Pi, v, N) + H$ reaction at 1.3 kcal/mol was studied using the high H-atom Rydberg "tagging" time-of-flight (HRTOF) technique, which was pioneered by Schnieder *et al.* [30]. Details of the Rydberg tagging TOF machine used in this work have been described previously [29,32]. In this work, two parallel molecular beams (H_2 and O_2) were generated with similar pulsed valves in this experiment. The $O(^1D)$ atom beam was produced by the 157 nm photolysis of the O_2 molecule. The $O(^1D)$ beam was then crossed at 90° with the H_2 molecular beam. The H_2 molecular beam is generated by expanding the H_2 sample through a pulsed nozzle, which is cooled to the liquid nitrogen temperature. The collisional energy for this reaction is 1.3 kcal/mol. The H-atom products were detected using the HRTOF technique with a rotatable multichannel plate detector. TOF spectra of H-atom product at different laboratory (LAB) angles were measured. In order to study the difference of the reactivities of the H_2 molecule in the $J=0$ and $J=1$ states, two different H_2 samples are used in the experiment: a normal H_2 sample and a para-H_2 sample ($>98.5\%$). Since the H_2 beam is produced by expanding the H_2 sample via a cooled nozzle at the liquid nitrogen temperature, the H_2 molecules in the beam are populated only in the lowest rotational states [30]. Therefore para-H_2 in the molecular beam is populated only in the $J=0$ state, while normal H_2 is populated in both $J=0$ and 1 with a ratio of $1(J=0):3(J=1)$. In this experiment, TOF spectra at eight LAB scattering angles were measured for both H_2 samples with exactly the same experimental conditions. These spectra were measured by switching the two H_2 samples back and forth many times to reduce the systematic errors in the measurements. Since the numbers of density for the two H_2 samples in the beam are controlled to be exactly the same, the TOF spectra (TOFS) of the H-atom products from the $O(^1D)$ reactions with H_2 at both $J=0$ and 1 can be obtained from these two samples using a simple arithmetic. From the above discussions, the TOFS for the p-H_2 and n-H_2 reactions can be described in terms of that from H_2 at $J=0$ and $J=1$,

$$\mathrm{TOFS}(p\text{-}H_2) = \mathrm{TOFS}(J = 0), \quad (1)$$

$$\mathrm{TOFS}(n\text{-}H_2) = 0.75 \times \mathrm{TOFS}(J = 1) + 0.25 \times \mathrm{TOFS}(J = 0). \quad (2)$$

Therefore, the TOFS for the H_2 reactions at the pure $J = 0$ and 1 states can be determined from the experimentally measured TOFS for the p-H_2 and n-H_2 reactions:

$$\mathrm{TOFS}(J = 0) = \mathrm{TOFS}(p\text{-}H_2), \quad (3)$$

$$\mathrm{TOFS}(J = 1) = (\mathrm{TOFS}(n\text{-}H_2) - 0.25^{*}\mathrm{TOFS}(p\text{-}H_2))^{*}4/3. \quad (4)$$

After these TOF spectra were obtained, they were converted into the product kinetic energy distributions. Figure 1 shows the product kinetic energy distributions at the LAB angles of 117.5°, 30°, and −50° for the $O(^1D)$ reaction with H_2 at both $J = 0$ and 1 rotational levels. These angles correspond dynamically to the backward, sideway, and forward scattering directions for the OH product relative to the $O(^1D)$ atom beam direction or H-atom products relative to the $O(^1D)$ beam direction. The relative distributions for the $O(^1D)$ reaction with H_2 at $J = 0$ and $J = 1$ were therefore determined at the eight scattering angles. The ratios of the total products from $H_2(J = 0)$ and $H_2(J = 1)$ at eight different LAB angles were also determined. By integrating the differences in all eight LAB angles including the $\sin\theta$ weighting factor for the spherical integration, the ratio between the total cross sections of the $O(^1D)$ reaction with H_2 at $J = 0$ and $J = 1$ are determined to be $\sigma(J = 1)/\sigma(J = 0) = 0.95 \pm 0.02$. This shows that the H_2 molecule at $J = 0$ is slightly more reactive than that at $J = 1$, which agrees quite well with quantum theoretical calculations [32].

Clearly, the single quantum H_2 rotational excitation effect on the integral cross section of the $O(^1D) + H_2$ reaction seems quite small though detectable. The more interesting question is how the single quantum rotational excitation of the H_2 reagent affects the OH-product state resolved differential cross sections. From Fig. 1, the product translational energy distributions of the $O(^1D) + H_2(J = 1)$ reaction are slightly shifted to higher energy with respect to that of the $O(^1D) + H_2(J = 0)$ reaction. This is because the total energy of the $O(^1D) + H_2(J = 1)$ reaction is slightly more than that of the $O(^1D) + H_2(J = 0)$ reaction by $2B_{\mathrm{rot}}(H_2)$, i.e., 120 cm^{-1}. If we shift the product translational energy distributions of the $O(^1D) + H_2(J = 1)$ reaction by 120 cm^{-1}, all the peak positions in the distributions will be exactly aligned to those of the $O(^1D) + H_2(J = 0)$ reaction.

From the translational energy distributions shown in Fig. 1, the distributions at the backward (117.5°) and forward (− 50°) directions show some significant differences for the $H_2(J = 0)$ and $H_2(J = 1)$ reactions even though the distributions at the sideway scattering direction (30°) are very similar to each other for the two reactions. Since the rovibrational states of the OH radical are well known through previous spectroscopic studies, the translational energy distributions observed can be simulated quite conveniently. From the simulations, state-specific differential cross sections can be determined for the eight LAB angles measured. Figure 2 shows the rovibrational state distributions of the OH radical at the backward scattering direction with an LAB angle of 117.5°. Note here that OH products at different rovibrational states correspond to slightly different center-of-mass angles, but all near the backward scattering direction. From the state distributions obtained, it is clear that a single quantum rotational excitation in the H_2 reagent has a rather significant effect on the OH. Generally no regular pattern is observed for this effect. It seems that the rotational excitation seems to have a rather irregular effect on a specific OH state product, indicating that whether a single rotational excitation would enhance or reduce the state-specific

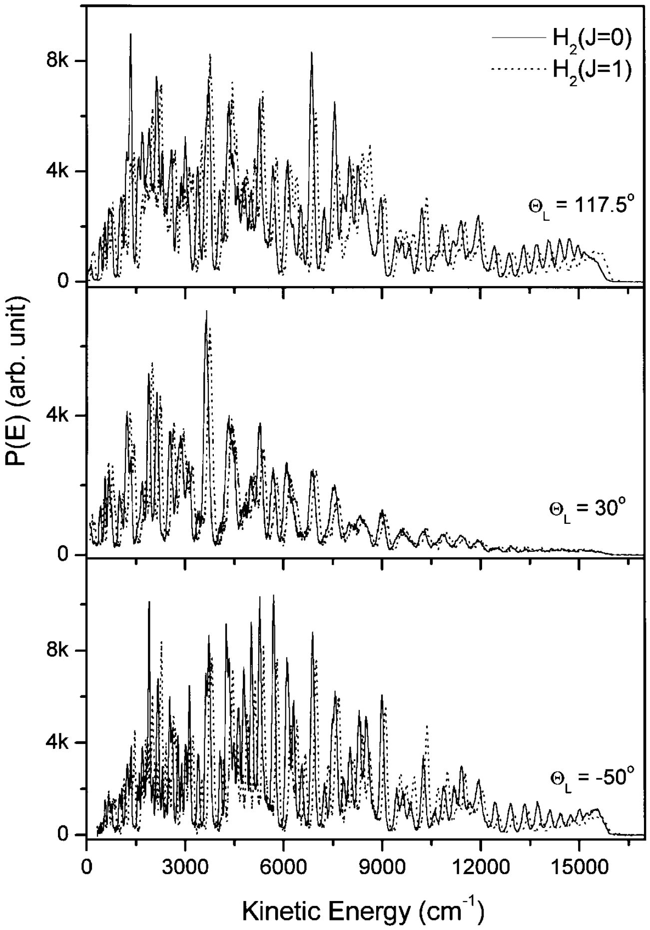

FIG. 1. Product kinetic energy distributions for the $O(^1D)$ reaction with $H_2(J = 0)$ and $H_2(J = 1)$ at three different laboratory angles: 117.5° (B), 30° (S), and −50° (F).

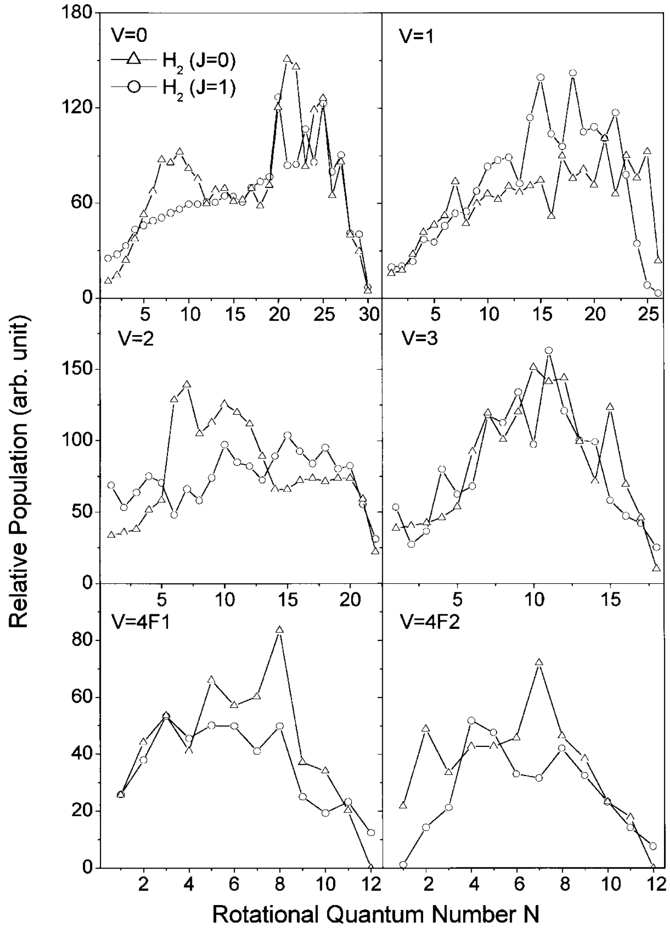

FIG. 2. Comparisons of the rovibrational state distributions obtained from the O(^{1}D) reaction with H_2 at the $J = 0$ and $J = 1$ levels at the backward scattering 117.5° LAB angle.

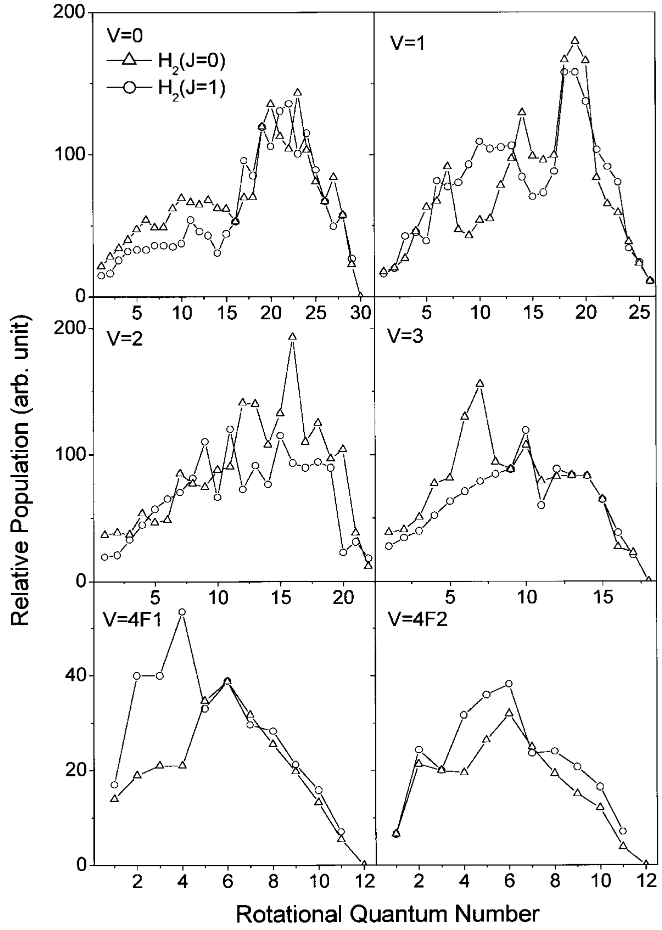

FIG. 3. Comparisons of the rovibrational state distributions obtained from the O(^{1}D) reaction with H_2 at the $J = 0$ and $J = 1$ levels at the forward scattering −50° LAB angle.

differential cross sections for a specific state seems to be very unpredictable. These observations are also true for the forward scattering direction (see Fig. 3) even though the effects are very quite different from that of the backward scattering direction. For the sideway scattering, however, the single quantum rotational excitation in H_2 seems to have a very limited effect on the OH-product state distributions, though noticeable (see Fig. 4). This is very different from that of the forward and backward scattering products.

Qualitatively, this phenomenon can be understood that the sideway scattering products are normally produced through larger impact parameter (b) collisions, i.e., larger orbital angular momentum, $L = \mu v b$, while forward/backward scattering products are produced via relative smaller impact parameter (b) collisions, i.e., smaller orbital angular momentum. Therefore, a single quantum rotational excitation (j) in H_2 should have a larger effect at the forward and backward directions because the total angular momentum $\boldsymbol{J} = \boldsymbol{L} + \boldsymbol{j}$ for the small $\boldsymbol{L}$ collisions is significantly changed relatively with a single rotational quantum excitation in H_2. However, relatively speaking, the total angular momentum $\boldsymbol{J} = \boldsymbol{L} + \boldsymbol{j}$ is altered only slightly by a single rotational quantum excitation in H_2 for larger impact parameter (larger $\boldsymbol{L}$) collisions which is mostly responsible for the sideway scattering products. The specific effect of the single quantum rotational excitation on the differential cross sections is also very interesting. The lack of the specific patterns for the forward and backward directions in this effect is probably due to the nature of this insertion reaction, which has a large number of reaction resonance states. Interestingly, in a similar experiment in our laboratory, it was found that a rotational quantum excitation in D_2 does not have any noticeable effect in the O(^{1}D) + D_2 reaction. Further detailed theoretical studies on this specific issue would certainly help us to better understand the nature of the rotational excitation effect on this benchmark insertion reaction.

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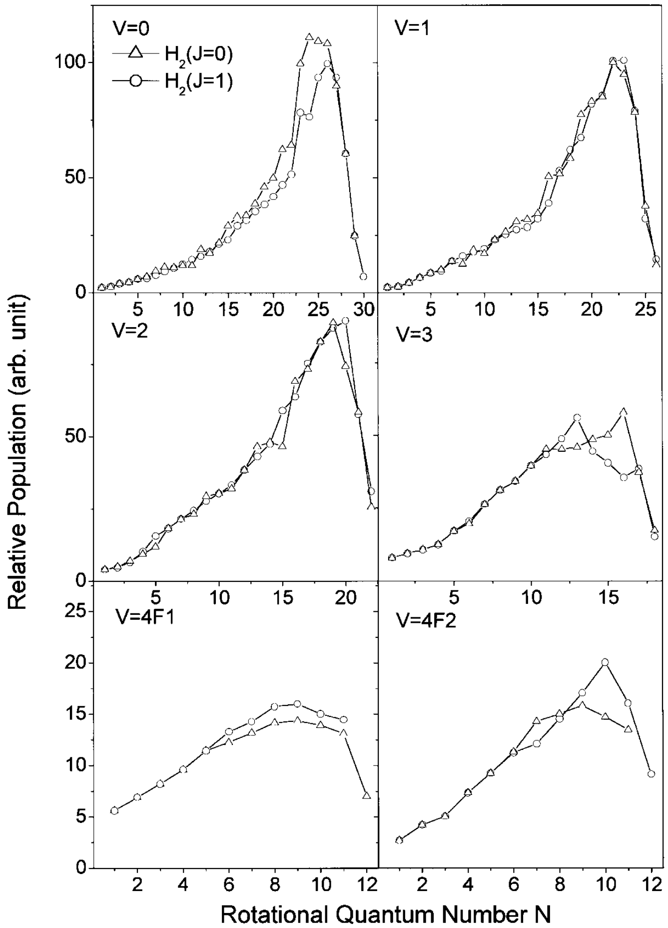

FIG. 4. Comparisons of the rovibrational state distributions obtained from the O(^{1}D) reaction with H_2 at the $J = 0$ and $J = 1$ levels at the sideway scattering 30° LAB angle.

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[1] L. Schnieder *et al.*, Science **269**, 207 (1995); L. Schnieder, K. Seekamp-Rahn, E. Wrede, and K. H. Welge, J. Chem. Phys. **107**, 6175 (1997).

[2] D. M. Neumark, A. M. Wodtke, G. N. Robinson, C. C. Hayden, and Y. T. Lee, J. Chem. Phys. **82**, 3045 (1985); D. M. Neumark, A. M. Wodtke, G. N. Robinson, C. C. Hayden, K. Shobatake, R. K. Sparks, T. P. Schafer, and Y. T. Lee, J. Chem. Phys. **82**, 3067 (1985).

[3] M. Faubel, B. Martinez-Haya, L. Y. Rusin, U. Tappe, and J. P. Toennies, Chem. Phys. Lett. **232**, 197 (1995); M. Faubel, B. Martinez-Haya, L. Y. Rusin, U. Tappe, J. P. Toennies , F. J. Aoiz, and L. Banares, J. Phys. Chem. A **102**, 8695 (1998); M. Baer, M. Faubel, B. Martinez-Haya, L. Y. Rusin, U. Tappe, and J. P. Toennies, J. Chem. Phys. **110**, 10 231 (1999).

[4] G. Anderson, Annu. Rev. Phys. Chem. **38**, 489 (1987), and references therein.

[5] G. Dixon-Lewis and D. J. Williams, Comprehensive Chem. Kinet. **17**, 1 (1977).

[6] P. A. Whitlock, J. T. Muckerman, and E. R. Fisher, J. Chem. Phys. **76**, 4468 (1982).

[7] R. Schinke and W. A. Lester, Jr., J. Chem. Phys. **72**, 3754 (1980).

[8] S. W. Ransome and J. S. Wright, J. Chem. Phys. **77**, 6346 (1982).

[9] P. J. Kuntz, B. I. Niefer, and J. J. Sloan, J. Chem. Phys. **88**, 3629 (1988).

[10] G. C. Schatz, A. Paioannou, L. A. Pederson, L. B. Harding, T. Hollebeck, T.-S. Ho, and H. Rabitz, J. Chem. Phys. **107**, 2340 (1997).

[11] J. E. Butler, R. G. Macdonald, D. J. Donalson, and J. J. Sloan, Chem. Phys. Lett. **95**, 183 (1983).

[12] J. E. Butler, G. M. Jursich, I. A. Watson, and J. R. Wiesenfeld, J. Chem. Phys. **84**, 5365 (1986).

[13] R. J. Buss, P. Casavecchia, T. Hirooka, S. J. Sibener, and Y. T. Lee, Chem. Phys. Lett. **82**, 386 (1981).

[14] K. Tsukiyama, B. Katz, and R. Bersohn, J. Chem. Phys. **83**, 2889 (1985).

[15] Y. Matsumi, K. Tonokura, M. Kawasaki, and H. L. Kim, J. Phys. Chem. **96**, 10 622 (1992).

[16] M. S. Fritzcharles and G. C. Schatz, J. Phys. Chem. **90**, 3634 (1986).

[17] L. J. Dunne, Chem. Phys. Lett. **158**, 535 (1989).

[18] A. J. Alexander, F. J. Aoiz, M. Brouard, and J. P. Simons, Chem. Phys. Lett. **256**, 561 (1996).

[19] K. Badenhoop, K. Koizumi, and G. C. Schatz, J. Chem. Phys. **91**, 142 (1989).

[20] T. Peng, D. M. Zhang, J. Z. H. Zhang, and R. Schinke, Chem. Phys. Lett. **248**, 37 (1996).

[21] M. Alagia, N. Balucani, L. Cartechini, P. Casavecchia, G. G. Volpi, F. J. Aoiz, P. J. Kuntz, and J. J. Sloan, J. Chem. Phys. **108**, 6698 (1998).

[22] M. Ahmed, D. S. Peterka, and A. Suits, Chem. Phys. Lett. **310**, 372 (1999).

[23] D.-C. Che and K. Liu, J. Chem. Phys. **103**, 5164 (1995).

[24] Y. T. Hsu and K. Liu, J. Chem. Phys. **107**, 1664 (1997).

[25] Y. T. Hsu, J. H. Wang, and K. Liu, J. Chem. Phys. **107**, 2351 (1997).

[26] Y.-T. Hsu, K. Liu, L. A. Pederson, and G. C. Schatz, J. Chem. Phys. **111**, 7921 (1999).

[27] Y.-T. Hsu, K. Liu, L. A. Pederson, and G. C. Schatz, J. Chem. Phys. **111**, 7931 (1999).

[28] P. Casavecchia, Rep. Prog. Phys. **63**, 355 (2000).

[29] X. Liu, J. J. Lin, S. A. Harich, G. C. Schatz, and X. Yang, Science **289**, 1536 (2000).

[30] L. Schnieder *et al.*, J. Chem. Phys. **92**, 7027 (1990).

[31] F. J. Aoiz *et al.*, J. Chem. Phys. **116**, 10 692 (2002).

[32] S. K. Gray, G. G. Balint-Kurti, G. C. Schatz, J. J. Lin, X. Liu, S. Harich, and X. Yang, J. Chem. Phys. **113**, 7330 (2000).