

# Comparison of Reagent Stretch vs Bend Excitation in the H + D<sub>2</sub>O Reaction: An Example of Mode-Selective Chemistry

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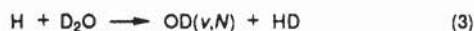
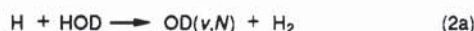
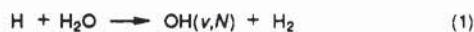
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Received: August 14, 1992; In Final Form: October 1, 1992

A state-to-state study of the reaction  $\text{H} + \text{D}_2\text{O}(\nu_1, \nu_2, \nu_3) \rightarrow \text{OD}(\nu, N) + \text{HD}$  was carried out to compare the effects of reagent stretch and bend excitation. D<sub>2</sub>O was prepared by infrared excitation in either the asymmetric stretch fundamental state, denoted D<sub>2</sub>O(0,0,1), or the bend–asymmetric stretch combination state, denoted D<sub>2</sub>O(0,1,1). Fast H atoms are generated by photolysis of HI at 266 nm, and the OD product is probed quantum-state-specifically by laser-induced fluorescence (LIF). This system exhibits mode-selective chemistry; excitation of the asymmetric stretch in D<sub>2</sub>O enhances the reaction rate by at least a factor of 5 (and possibly a factor of 20), whereas excitation of the D<sub>2</sub>O bend does not affect the reaction rate within experimental uncertainty. For both D<sub>2</sub>O(0,0,1) and D<sub>2</sub>O(0,1,1) the OD product is produced with little vibrational excitation [OD( $\nu=1$ ): OD( $\nu=0$ )  $\approx$  1:20]. This observation suggests that the D<sub>2</sub>O asymmetric stretch state is best thought of as a linear combination of local mode stretches, with the H atom reacting preferentially with the stretched OD bond. The measured OD rotational distributions from vibrationally excited D<sub>2</sub>O are nearly the same as the distribution from ground-state D<sub>2</sub>O.  $\Lambda$ -doublet ratios are also reported.

## Introduction

An intriguing question is whether different vibrational motions of a polyatomic reactant affect in different ways a bimolecular reaction of this reagent. Does the reaction rate or product state distribution depend on how internal energy is put into the reaction? Past work has shown that such behavior is the exception rather than the rule.<sup>1–3</sup> Particularly amenable to this type of study are the reactions of hydrogen atoms with water and its isotopically substituted analogs:



This reaction family constitutes a simple system in which a polyatomic reactant may be prepared in any of several different vibrational modes. It may be the simplest such system that is tractable both theoretically and experimentally.

Many groups have studied reactions 1 and 2 experimentally and theoretically.<sup>4–23</sup> Based on quasiclassical trajectory calculations on an H–H<sub>2</sub>O potential energy surface constructed by Schatz and Elgersma<sup>4</sup> from ab initio calculations of Walch and Dunning,<sup>5</sup> Schatz, Colton, and Grant<sup>6</sup> predicted in 1984 that reaction 1 would show mode selectivity. The effects of vibrational excitation on reactions 1 and 2 have been investigated experimentally by Crim and co-workers<sup>7–10</sup> and in this laboratory.<sup>11,12</sup> These reactions are believed to occur by an H-atom abstraction mechanism; the nonreacting OH group acts as a “spectator”, which couples only weakly to the other atoms in the collision complex and receives little of the energy available to the products. Crim and co-workers<sup>8</sup> investigated the rate of reaction 1 as a function of the vibrational state of the H<sub>2</sub>O molecule. They found that this rate was considerably larger for H<sub>2</sub>O prepared in the local-mode state |03><sup>–</sup> (3 quanta of stretch in one of the OH bonds) than in either the |12><sup>–</sup> state, with 2 quanta in one bond and 1 in the other, or the |02><sup>–</sup> |2<sup>–</sup> state, with 2 quanta each of stretch and bend. These three high-overtone local mode states

have nearly the same energy, but that energy is distributed differently for the different states. The much higher reactivity of the state with all the vibrational energy in the reaction coordinate (i.e., in one bond) is an example of mode-selective chemistry. In these experiments, most of the available energy was provided by H<sub>2</sub>O vibration. Crim and co-workers also showed<sup>8</sup> that vibrational excitation of the spectator group is preserved as hydroxyl product vibrational excitation: preparation of H<sub>2</sub>O in the state |13><sup>–</sup> leads predominantly to formation of OH( $\nu=1$ ), whereas preparation of the |04><sup>–</sup> state leads predominantly to OH( $\nu=0$ ).

In this paper we present a detailed comparison of the effects of polyatomic reagent stretch and bend vibrational excitation on the reaction rate and product energy disposal for reaction 3, in which the D<sub>2</sub>O molecules are prepared with low levels of vibrational excitation and the extra energy needed for reaction is provided by H-atom kinetic energy. D<sub>2</sub>O is prepared by infrared excitation in either of two vibrational states with differing amounts of stretch and bend excitation: the asymmetric stretch fundamental mode, denoted D<sub>2</sub>O(0,0,1), and the bend–asymmetric stretch combination mode, denoted D<sub>2</sub>O(0,1,1). We use D<sub>2</sub>O instead of H<sub>2</sub>O because the infrared (IR) radiation for excitation of the latter is absorbed by atmospheric water vapor. The reaction cross section is estimated for both modes. Vibrational, rotational, and electronic fine-structure state populations of the OD products are measured for each D<sub>2</sub>O mode to determine how the vibrational motions of the D<sub>2</sub>O molecule “map into” the motions of the OD product. For comparison, we also investigate the reaction of H atoms with ground-state D<sub>2</sub>O.

## Experimental Section

Our experiment is described in detail elsewhere.<sup>12</sup> Our studies are carried out in a flowing mixture of HI (Matheson, >98% purity) and D<sub>2</sub>O (Aldrich, 99.9% D atom purity) in the ratio 5:4, maintained at a total pressure of 50 mTorr. D<sub>2</sub>O is prepared in either the asymmetric stretch state D<sub>2</sub>O(0,0,1), at  $\sim$ 2800 cm<sup>–1</sup> (3.57  $\mu\text{m}$ ), or the bend–asymmetric stretch combination state D<sub>2</sub>O(0,1,1), at  $\sim$ 4000 cm<sup>–1</sup> (2.50  $\mu\text{m}$ ), by IR excitation using the output of a tunable optical parametric oscillator (OPO, 5–10-mJ pulse energy) pumped by the 1.064- $\mu\text{m}$  fundamental from a Nd:YAG laser (Quanta-Ray DCR-1). H atoms are generated by photolysis of HI molecules at 266 nm, the fourth harmonic

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of a Nd:YAG laser (Quantel 581-10, 10–15-mJ pulse energy). The pump and photolysis lasers are fired simultaneously, and their beams propagate collinearly into the reaction chamber. After a short, well-defined time delay (100 ns) a third tunable UV laser pulse, generated by frequency doubling the output of a Nd:YAG-pumped dye laser (Quantel TDL-50 pumped by a Quanta-Ray DCR-2A), counterpropagates through the chamber and probes the nascent OD by laser-induced fluorescence (LIF) using the  $A^2\Sigma^+ - X^2\Pi$  ultraviolet band system in the spectral region 305–315 nm. The fluorescence is detected perpendicular to the laser beam axis by a photomultiplier tube (PMT; RCA C31034). Signals from the PMT are captured by a gated charge integrator (LeCroy 2249SG ADC, CAMAC modular data bus) during a time gate of 1.5  $\mu$ s (which corresponds to approximately twice the radiative lifetime of the OD  $A^2\Sigma^+$  state), delayed by 10–30 ns from the probe pulse to discriminate against scattered laser light. The digitized data are passed to a personal computer (IBM PC-XT) for storage and analysis.

The total pressure  $P$  and the pump–probe delay  $\Delta t$ , the time between firing of pump and probe lasers, are chosen to assure single-collision conditions: the product rotational distributions were observed to be invariant for  $P\Delta t < 10^{-8}$  Torr s. Our data were collected with  $P\Delta t = 5 \times 10^{-9}$  Torr s (50 mTorr total pressure, 100 ns pump–probe delay). Care was also taken to work at pressures low enough to avoid effects caused by quenching of the OD  $A$  state during its fluorescence lifetime (approximately 700 ns<sup>24</sup>).

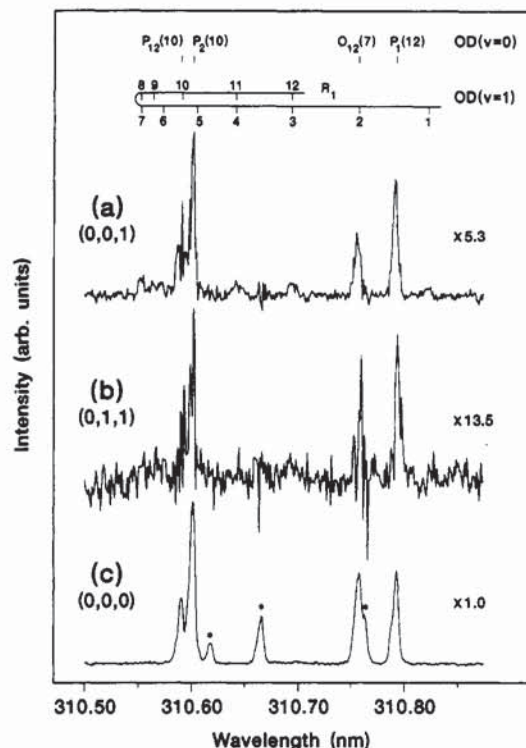
Reaction 3 is endothermic by 0.66 eV (5320  $\text{cm}^{-1}$ )<sup>25</sup> and has an estimated barrier of 0.94 eV (7580  $\text{cm}^{-1}$ ).<sup>13</sup> Photolysis of HI at 266 nm gives H atoms with two possible energies, 1.5 eV and 0.65 eV, in the H–D<sub>2</sub>O center-of-mass frame in the ratio 1.8:1.<sup>26</sup> These two energies stem from the two possible spin–orbit states of the resulting I atom [ $I(^2P_{3/2})$  and  $I(^2P_{1/2})$ ]. The 1.5-eV H atoms have sufficient energy to react with both vibrationally excited and ground-state D<sub>2</sub>O. The OD product signal that arises from reaction of H atoms with vibrationally excited D<sub>2</sub>O is separated from that of ground-state D<sub>2</sub>O using a shot-by-shot subtraction procedure. Both photolysis and probe lasers operate at a repetition rate of 20 Hz, while the OPO fires at 10 Hz (i.e., on every other probe laser shot). By scanning slowly over OD lines and subtracting LIF signals from alternate probe laser shots, we separate OD signals resulting from vibrationally excited D<sub>2</sub>O and ground-state D<sub>2</sub>O. The subtraction procedure was checked by verifying that no difference signal was produced when the OPO was blocked.

The OPO was tuned to pump various vibrational transitions of D<sub>2</sub>O using an optoacoustic cell to locate features in the D<sub>2</sub>O IR excitation spectrum. A monochromator (1-m length with a 300 grooves/mm grating; Spex, Model 1704) was used to verify the IR wavelength. D<sub>2</sub>O absorption features were assigned using the D<sub>2</sub>O line position data of Papineau et al.<sup>27</sup> and of Benedict et al.<sup>28</sup> Strong peaks for exciting D<sub>2</sub>O were chosen to avoid overlap with HOD lines.<sup>29,30</sup> Typical features used for D<sub>2</sub>O excitation consisted of approximately eight unresolved rotational lines of one vibrational band, spanning two or three  $J$  values (in the range  $J = 4$ –6, the peak of the room temperature D<sub>2</sub>O Boltzmann distribution), with a variety of  $K_A$  and  $K_C$  quantum numbers.

The vibrational band strength of the (0,1,1) band of D<sub>2</sub>O is approximately an order of magnitude less than that of the (0,0,1) band.<sup>31,32</sup> Consequently, we excite fewer D<sub>2</sub>O molecules when pumping the (0,1,1) transition than (0,0,1). This difference was apparent in the much lower signal-to-noise ratio obtained in the D<sub>2</sub>O(0,1,1) experiments.

## Results and Discussion

**Data Acquisition and Analysis.** OD internal state distributions were obtained by recording fluorescence intensity vs probe laser wavelength excited and detected on the A–X (0,0) and (1,1)



**Figure 1.** Segments of OD A–X LIF excitation spectra showing the OD products for the following reactions: (a) H + D<sub>2</sub>O(0,0,1), (b) H + D<sub>2</sub>O(0,1,1), and (c) H + D<sub>2</sub>O(0,0,0). These spectra include lines of the OD(0,0) band, which probes OD( $v=0$ ), and the OD(1,1) band, which probes OD( $v=1$ ). The lines marked with asterisks are Q<sub>1</sub>(12), P<sub>1</sub>(6), and P<sub>2</sub>(5) of OH( $v=0$ ), arising from the reaction H + HOD where HOD is a small contaminant in the D<sub>2</sub>O.

bands. Rotational lines in these spectra were assigned using the spectroscopic line position data of Clyne, Coxon, and Woon Fat.<sup>33</sup> Figure 1 shows representative spectra, which contain portions of the (0,0) band P<sub>1</sub> and P<sub>2</sub> branches and (1,1) band R<sub>1</sub> branch of the OD products of the reaction of translationally hot H atoms with (a) D<sub>2</sub>O(0,0,1), (b) D<sub>2</sub>O(0,1,1), and (c) D<sub>2</sub>O(0,0,0). The spectra shown in Figure 1 parts a and b were obtained using shot-by-shot subtraction. Figure 1 shows that vibrationally excited D<sub>2</sub>O gives a small amount of OD( $v=1$ ), whereas ground-state D<sub>2</sub>O yields no OD( $v=1$ ).

Rotational distributions of the OD( $v=0$ ) product from H + D<sub>2</sub>O(0,0,1) and H + D<sub>2</sub>O(0,1,1) were obtained from the integrated intensities of the lines of the P<sub>1</sub> branch of the OD(0,0) band. The distribution for H + D<sub>2</sub>O(0,0,0) was obtained using the OD(0,0) band R<sub>1</sub> branch, without the use of the OPO or the subtraction procedure. OD product vibrational excitation was investigated for all D<sub>2</sub>O vibrational modes studied: population of OD( $v=1$ ) was measured by scanning the probe laser over the R<sub>1</sub> branch of the OD(1,1) band. This wavelength region also contains several high- $N$  P<sub>1</sub> branch lines of the OD(0,0) band, as shown in Figure 1, which allow comparison of OD( $v=1$ ) and OD( $v=0$ ) signals and determination of the ( $v=1$ ):( $v=0$ ) branching ratio.

Integrated rotational line intensities were converted to relative populations by correcting for variations in probe laser power, rotational line strength, and the (wavelength-dependent) interference filter transmission. The Einstein  $A$  and  $B$  coefficients used were those calculated by Dimpfl and Kinsey.<sup>24</sup> Small corrections for the polarization of the probe laser, required when exciting LIF with linearly polarized light,<sup>34</sup> were applied as appropriate.

**Reaction Cross Sections.** Comparison of the relative LIF signal intensities that result from excited vs unexcited D<sub>2</sub>O molecules provides information on the relative reactive cross sections for vibrationally excited D<sub>2</sub>O. Based on the ratio of the optoacoustic signals, we pump approximately  $2.3 \pm 0.8$  times as much D<sub>2</sub>O–

**TABLE I: Percent Yields of OD( $v=1$ )**

precursor	percent yield	( $v=0$ ):( $v=1$ ) ratio
D <sub>2</sub> O(0,0,0)	<0.55	>180:1
D <sub>2</sub> O(0,0,1)	5.3(+2.8, -1.0)	19(+4, -7)
D <sub>2</sub> O(0,1,1)	4.2(+4.2, -2.1)	24(+24, -12)

(0,0,1) as D<sub>2</sub>O(0,1,1). The absolute magnitude of the D<sub>2</sub>O(0,0,1) fraction is uncertain, but it is estimated to be approximately 0.02 by taking into account the rotational partition function and an estimate of the pumping efficiency. Taking into account the fraction of the D<sub>2</sub>O molecules excited, we find that excitation of either mode increases the reaction cross section by at least a factor of 5, with no significant difference observed between the (0,0,1) and (0,1,1) modes. This enhancement factor is the same as that observed for cleavage of an excited OD bond in HOD.<sup>12</sup> Because of uncertainties in the pumping efficiency, this value should be regarded as a crude estimate that probably significantly underestimates the true cross section enhancement.

Our measurements show that the reactive cross section for D<sub>2</sub>O(0,1,1) is not significantly different from that for D<sub>2</sub>O(0,0,1); an extra quantum of bend excitation (1200 cm<sup>-1</sup>) does not enhance the reactivity significantly. This observation is rather remarkable. In our study of the H + HOD reaction,<sup>12</sup> we found that the reactive cross section was approximately 4 times larger for HOD prepared with 1 quantum of OH stretch than for HOD with 1 quantum of OD stretch (the energy difference is ~1000 cm<sup>-1</sup>). In the H + D<sub>2</sub>O reaction, a larger amount of extra energy present as bend does not affect the reaction rate. Clearly, stretch excitation promotes the reaction much more efficiently than bend excitation, and thus we find that this system exhibits mode-selective chemistry. This behavior can be understood by noting that stretch excitation puts energy into motion along the reaction coordinate (the breaking of the OD bond), whereas bend excitation involves motion perpendicular to the reaction coordinate.

Our results, when combined with those of Kessler and Kleiner<sup>14</sup> also show that stretch excitation increases reactivity much more than an equivalent amount of extra translational energy. Kessler and Kleiner<sup>14</sup> showed that the cross section for H + H<sub>2</sub>O increases by only about 40% when the H atom translational energy is increased from 1.4 eV to 2.6 eV. In contrast, the present work shows that 0.35 eV of energy in D<sub>2</sub>O stretch vibration increases the cross section by at least 400%. This behavior was also observed for the H + HOD reaction.<sup>12</sup> It is consistent with the picture developed by Polanyi and co-workers<sup>35,36</sup> for the effects of vibrational vs translational energy on reaction cross sections: vibrational energy is more effective at overcoming late barriers, whereas translation is more effective at overcoming early barriers. The H + D<sub>2</sub>O reaction has a late barrier,<sup>4,5</sup> and thus the higher efficiency of vibration in promoting reaction is as expected.

We find, then, that OD stretch energy increases the H + D<sub>2</sub>O reaction rate much more than either D<sub>2</sub>O bend excitation or translational energy. In simplest terms, this difference occurs because OD stretch excitation moves the system along the reaction coordinate in the direction of the barrier, whereas the other motions do not. Our results show most importantly that the manner in which internal energy is put into a reaction can significantly affect the reaction rate.

**OD Vibrational Excitation.** Analysis of multiple probe laser scans over the OD(1,1) R<sub>1</sub> branch region gave OD product vibrational branching ratios for the three D<sub>2</sub>O vibrational modes studied. These results are summarized in Table I. No OD( $v=1$ ) was detected for the reaction of H with D<sub>2</sub>O(0,0,0) whereas a small amount was observed for both excited-state reactions. We did not check for OD( $v=2$ ) or higher vibrational levels; the relatively small population of OD( $v=1$ ) suggests that no significant amounts of OD are formed with higher vibrational excitation.

At first glance, the ratios for the products from vibrationally excited D<sub>2</sub>O might seem surprising. The D<sub>2</sub>O vibrations excited

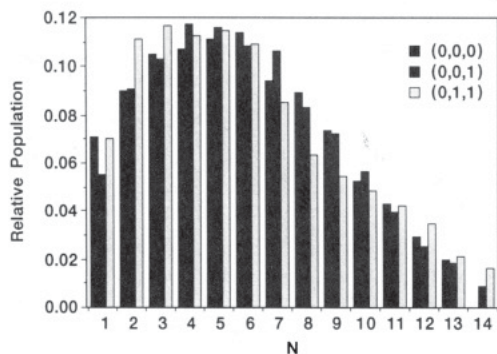
are normal modes that involve equal motion of each of the two D atoms with 1 quantum of stretch excitation "distributed" between the two bonds. If, as the spectator model predicts, the nonreacting OD does not gain or lose significant energy in the course of the reaction, the OD product might be expected to be formed with approximately equal amounts of  $v=0$  and  $v=1$ . Instead, we find only about 5% of the OD product in the state  $v=1$  for both the (0,0,1) and (0,1,1) modes. We are not sure of the reason why so little OD( $v=1$ ) product is observed. Perhaps, this is simply a consequence of some Franck-Condon-type argument, but we would like to suggest the possibility of another picture, based on the nonreacting OD bond acting as a noninteracting spectator that receives little of the available energy.

The nature of the vibrational eigenstates of the D<sub>2</sub>O molecule can be described by linear combinations of local mode vibrations even at low levels of excitation.<sup>37</sup> For example, the first excited state of the asymmetric stretch mode consists of 99% of the wavefunction  $\Psi = (2)^{-1/2}(|01\rangle - |10\rangle)$  (i.e., the square of the coefficient for  $\Psi$  in the expansion of this D<sub>2</sub>O eigenstate is 0.99),<sup>37</sup> where  $|10\rangle$  and  $|01\rangle$  denote the local mode basis functions for the stretch of each of the two bonds. The wavefunction  $\Psi$  describes a single quantum of localized OD stretch excitation with its probability amplitude distributed between the two bonds. Measurement of the location of this 1 quantum of stretch would find it in either bond with 50% probability, that is, measurement of which bond was vibrationally excited would find each bond excited 50% of the time, on average, *but such a measurement would always yield all the excitation in only one of the two bonds*, provided that the measurement were carried out on a time scale faster than the coupling time between the two degenerate stretches. For a 1.5-eV H atom the interaction time with a D<sub>2</sub>O molecule is on the order of 10 fs, whereas the time scale for energy transfer between the two local stretches, as given by the energy splitting between the symmetric and antisymmetric linear combinations of these stretches, is ~300 fs. Fast H atoms are known to cleave preferentially the vibrationally excited bond of HOD.<sup>11,12</sup> For D<sub>2</sub>O, then, a higher probability of reaction would be expected if the H atom struck the excited OD bond than if the nonexcited OD bond were struck.

As mentioned previously, Crim and co-workers<sup>8</sup> have shown that vibrational excitation of the spectator group is preserved as hydroxyl product vibrational excitation in the H + H<sub>2</sub>O reaction when H<sub>2</sub>O is prepared in high-overtone states. If this behavior holds for the reaction of H with D<sub>2</sub>O prepared with 1 quantum of stretch excitation, cleavage of the OD bond containing the excitation should leave the other OD group in its vibrational ground state, whereas reaction of the unexcited bond should give OD product in  $v=1$ . This result implies that the ratio of ground-state OD( $v=0$ ) product to excited OD( $v=1$ ) product is equal to the ratio of the reactive cross section of a vibrationally excited OD bond (of D<sub>2</sub>O) to the cross section of a bond in its vibrational ground state. From Table I we infer that 1 quantum of vibrational stretch excitation increases the reactive cross section of an OD group in D<sub>2</sub>O by approximately a factor of 20, which is consistent with the enhancement of greater than a factor of 5 given in the previous section. The low yield of vibrationally excited OD product is thus readily understood.

The OH( $v=0$ ):OD( $v=1$ ) ratio (and thus the inferred cross section enhancement) was also found to be approximately 20:1 for the reaction of HOD prepared with 1 quantum of (localized) OD stretch.<sup>12</sup> This similarity is as expected. The vibrational energy of the excited OD bond is about the same for D<sub>2</sub>O and HOD, so the cross section enhancements should be similar.

**OD Rotational Distributions.** Figure 2 shows the rotational state distributions for the OD( $v=0$ ) products of the reaction of fast H atoms with D<sub>2</sub>O(0,0,0), D<sub>2</sub>O(0,0,1), and D<sub>2</sub>O(0,1,1). The OD( $v=1$ ) product observed for the reactions of excited D<sub>2</sub>O appeared to have approximately the same rotational distribution



**Figure 2.** Rotational state populations of the OD( $v=0$ ) products from the reaction of 1.5-eV H atoms with D<sub>2</sub>O(0,0,0), D<sub>2</sub>O(0,0,1), and D<sub>2</sub>O(0,1,1). Shown are the relative populations of the A'  $\Lambda$ -doublet of the <sup>2</sup> $\Pi_{3/2}$  spin-orbit component as a function of  $N$ . All distributions have been normalized to have a total population of unity.

**TABLE II: Rotational Temperatures of OD Products**

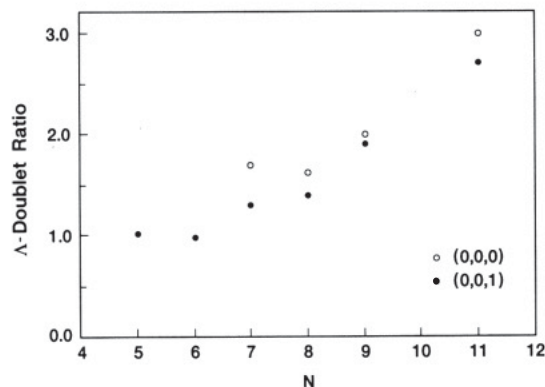
precursor	OD rotational temp (K)
D <sub>2</sub> O(0,0,0)	850 ± 75
D <sub>2</sub> O(0,0,1)	790 ± 40
D <sub>2</sub> O(0,1,1)	900 ± 100

as the OD( $v=0$ ) product, but signal levels for  $v=1$  were too low to obtain a detailed population distribution. Rotational distributions from vibrationally excited D<sub>2</sub>O were derived from intensities of P<sub>1</sub> branch members, most of which were free from overlap. The distribution for ground-state D<sub>2</sub>O was derived from intensity data taken on the R<sub>1</sub> branch because many of the P<sub>1</sub> lines were overlapped with OH rotational lines (which arise from the reaction of H with contaminant HOD and are not present in the OPO-induced difference spectra).

The rotational distributions of Figure 2 are "cold"; average rotational energies are 500–650 cm<sup>-1</sup>, or 0.06–0.08 eV, compared with available reaction product energies of 0.84–1.34 eV. This observation is consistent with the results of many previous investigations<sup>7,9,12,14–16,39</sup> and further supports the picture of the nonreacting OD fragment as a spectator. All rotational distributions could be well fit by Boltzmann distributions, as was found for the rotational distributions of the OH and OD products of the reaction H + HOD.<sup>12</sup> Table II gives the best fit rotational temperatures for all observed distributions.

Within the respective error bars of the different measurements, all three D<sub>2</sub>O vibrational modes give OD product with the same temperature. Clearly, neither stretch nor bend excitation of the D<sub>2</sub>O molecule has a large effect on the OD product rotational distribution. This result is somewhat surprising, especially for the D<sub>2</sub>O(0,1,1) mode. Bending motion of the D<sub>2</sub>O reactant would be expected to translate into rotation of the OD product. Specifically, 1 quantum of D<sub>2</sub>O bend provides ~1200 cm<sup>-1</sup> of energy, and since D<sub>2</sub>O bend motion involves both bonds, each OD group should have half of this energy in angular motion. Thus, the average OD product rotational energy might be expected to be approximately 600 cm<sup>-1</sup> higher for (0,1,1) mode excitation than for (0,0,1) excitation. Table II shows that this expectation is not correct. Taking into account the uncertainties in both measurements, we find that the difference in average OD product rotational energy between these modes is at most 130 cm<sup>-1</sup> ( $E_{\text{ave}} \approx 520$  cm<sup>-1</sup> for  $T = 750$  K;  $E_{\text{ave}} \approx 650$  cm<sup>-1</sup> for  $T = 1000$  K), or 22% of the expected value.

Based on examination of trajectories, QCT calculations of Schatz<sup>6</sup> found the origin of hydroxyl rotation to be a combination of product repulsion and reagent excitation. Product repulsion excites hydroxyl rotation by impulsive forces between the O atom and the departing hydrogen molecule in the breakup of the transition state. On the other hand, stripping trajectories produce rotational excitation by mapping the reagent bend excitation onto rotation. Clary<sup>38</sup> performed quantum scattering calculations on



**Figure 3.**  $\Lambda$ -doublet population ratios,  $\Pi(A')/\Pi(A'')$ , as a function of  $N$ , for the OD( $v=0$ ) product of the reaction of 1.5-eV H atoms with D<sub>2</sub>O(0,0,0) and D<sub>2</sub>O(0,0,1).

this system and found that increased bend excitation increases the rotational angular momentum of the hydroxyl product, although the effect was small for excitation of 1 quantum of bend. In our investigations of the reaction H + HOD,<sup>12</sup> the observation that more rotational energy appears in the OD than OH led us to conclude that most of the hydroxyl product rotational excitation arose from product repulsion. Jacobs, Volpp, and Wolfrum<sup>39</sup> carried out experiments of H + D<sub>2</sub>O and H + H<sub>2</sub>O at 2.5 eV collision energy and found that more energy appears in the rotation of OH than OD. This result was interpreted as evidence of the mapping of bend into hydroxyl product rotation. Possibly the mechanism of rotational excitation switches from impulsive at our 1.5-eV collision energy to stripping at 2.5-eV collision energy. To the extent that the product rotational distribution is dominated by product repulsion, a small effect of reagent bend excitation should be expected. For the reaction H + D<sub>2</sub>O(0,1,1), the torque  $\tau$  exerted on the forming OD product by the departing HD molecule (and the resulting OD angular momentum  $J_r$ ) would add vectorially with the angular momentum  $J_b$  contributed to that OD group from D<sub>2</sub>O bending motion. Depending on the motion of the nonreacting OD at the time of reaction (i.e., the phase of the bend motion),  $J_r$  and  $J_b$  could be parallel, antiparallel, or at any angle. The magnitude of the vector sum of these two contributions could thus have any value between  $J_r + J_b$  and  $|J_r - J_b|$ . Averaged over many collisions at many angles, the effect may largely cancel, which would explain the lack of significant enhancement in the rotational excitation of the OD product from D<sub>2</sub>O(0,1,1) over that from D<sub>2</sub>O(0,0,1).

Slight differences do appear to be present in the product temperatures for the different D<sub>2</sub>O vibrational modes. The considerable uncertainty in some of the measured temperatures leads us to caution that these differences may not be significant, but the temperatures do suggest several trends. The OD from stretch-excited D<sub>2</sub>O(0,0,1) may be slightly colder than that from ground-state D<sub>2</sub>O, as was observed for HOD.<sup>12</sup> The OD from D<sub>2</sub>O(0,1,1) may be slightly hotter than that from D<sub>2</sub>O(0,0,1), which suggests that bend excitation may result in a small amount of additional product rotational excitation.

**$\Lambda$ -Doublet Distributions.** By measuring the intensities of pairs of P<sub>1</sub>( $N$ ) and Q<sub>1</sub>( $N$ ) lines, we have determined the  $\Pi(A')/\Pi(A'')$   $\Lambda$ -doublet ratio for several rotational states of the OD product of the reactions H + D<sub>2</sub>O(0,0,1) and H + D<sub>2</sub>O(0,0,0). In OD the  $\Lambda$ -doublet components are defined by the orientation of the singly occupied  $p\pi$  orbital on the O atom with respect to the plane of rotation of the molecule: for the A' component, this orbital lies in the plane of rotation, while in the A'' component the  $p\pi$  orbital is perpendicular to this plane. Our results are shown graphically in Figure 3. We find that, for both D<sub>2</sub>O vibrational states, the A':A'' ratio of the OD product increases monotonically with rotational quantum number to a maximum of about 3 for the highest  $N$  probed. These results are similar to those observed

in our laboratory<sup>12</sup> for H + HOD and by Honda et al.<sup>15</sup> and Kleinermanns and Wolfrum<sup>16</sup> for H + H<sub>2</sub>O. In our studies of H + HOD,<sup>12</sup> we concluded that hydroxyl product rotational excitation is caused primarily by repulsive forces on the O atom during the breaking of the other hydroxyl bond. These forces also give rise to a strong preference for the in-plane A'  $\Delta$ -doublet because the resulting hydroxyl plane of rotation necessarily contains the breaking bond (and hence the singly occupied  $p\pi$  orbital). These effects probably also hold for the H + D<sub>2</sub>O reaction.

### Conclusion

We have presented a detailed comparison of the effects of vibrational stretch vs bend excitation on the title reaction. The reaction cross section is increased considerably (by at least a factor of 5) by 1 quantum of D<sub>2</sub>O stretch excitation. It is not increased, however, by either 1 quantum of bend excitation (because bending motion is perpendicular to the reaction coordinate) or extra translational energy (because this reaction has a late barrier). Thus, the mode-selectivity observed by Crim and co-workers<sup>8</sup> is preserved even at low levels of vibrational excitation. D<sub>2</sub>O stretch excitation leads to formation of approximately 5% of the OD product in the state  $v = 1$ . This observation can be explained by viewing the D<sub>2</sub>O stretch states as superpositions of localized stretches: the vibrational branching ratio then simply reflects the relative reactivities of the excited vs unexcited OD bonds in D<sub>2</sub>O. The OD rotational distribution is largely unaffected by D<sub>2</sub>O vibrational excitation. In particular, bend excitation does not significantly increase the OD product rotational energy. The  $\Delta$ -doublet distributions suggest that, as with H + HOD, repulsion in the cleavage of the broken OD bond may be largely responsible for OD product rotational excitation. We hope this work stimulates further theoretical efforts to model the reaction of H atoms with water molecules, which is certainly among the simplest reactions involving an atom and a triatomic molecule.

**Acknowledgment.** We thank B. Girard and R. Zhang for valuable technical assistance in the early stages of this work. We also appreciate the useful comments of one of the reviewers. M.J.B. gratefully acknowledges a GAANN graduate fellowship from the U.S. Department of Education. W.R.S. thanks the National Science Foundation for a graduate fellowship. This work was supported by the National Science Foundation under Grant No. NSF CHE 89-21198.

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