

## State- and Bond-Selected Photodissociation and Bimolecular Reaction of Water [and Discussion]

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# State- and bond-selected photodissociation and bimolecular reaction of water

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It is possible to exploit the isolation of the O–H stretching vibration in H<sub>2</sub>O and HOD to control the photodissociation and reaction dynamics in water molecules excited in the region of the third overtone ( $4\nu_{\text{OH}}$ ) of the O–H stretch. In vibrationally mediated photodissociation of H<sub>2</sub>O, the selection of different initial stretching states having roughly the same energy leads to drastically different populations of the vibrational states of the OH photolysis product. By exciting the O–H stretching overtone in HOD, we can selectively photolyze that bond. In bimolecular reaction experiments, we react H<sub>2</sub>O ( $4\nu_{\text{OH}}$ ) with H atoms to produce H<sub>2</sub> and OH. The reaction, which is endothermic, proceeds at an undetectable rate in our room temperature measurements. Vibrationally excited water, however, reacts at roughly the gas kinetic collision rate. Applying this technique to HOD ( $4\nu_{\text{OH}}$ ) allows us to demonstrate bond selected bimolecular chemistry in which the reaction produces only OD. This observation suggests a general approach to assessing bond controlled reactions in a variety of systems.

## 1. Introduction

Intramolecular dynamics controls many aspects of chemical reactivity. For state-selected reactions of polyatomic molecules, in which a specific excitation prepares an initial quantum state that subsequently reacts, intramolecular processes control the retention of the excitation in the initially energized degree of freedom. An alternate, but equivalent, point of view is that intramolecular interactions determine the nature of the initially excited eigenstate or combination of eigenstates. Our goal is to prepare highly vibrationally excited molecules by a very selective excitation scheme and to monitor their subsequent behaviour to discover the operative intramolecular interactions. If we prepare an initial state that survives long enough to interact with a photon or a reactive species, the results of that interaction may reveal the character of the initially prepared state and illuminate the intramolecular dynamics. In addition, if the subsequent interaction is sufficiently specific, we can exploit this selectivity to control the course of the reaction.

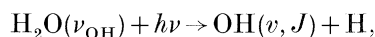
We have used vibrationally mediated photodissociation, in which the subsequent interaction of the highly vibrationally excited molecule is with a photon, to demonstrate that the initially prepared state strongly influences the population of the quantum states of the dissociation products (Likar *et al.* 1988, 1989; Sinha *et al.* 1987, 1989; Ticich *et al.* 1987; Vander Wal & Crim 1989). One of the clearest examples of the influence of the initial state is a recent experiment on water (Vander

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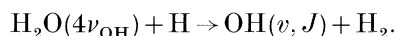
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Wal & Crim 1989) in which the identity of the initially excited eigenstate determines the population of the vibrational states of the OH dissociation product. In fact, it is even possible to control the breaking of a particular chemical bond in HOD (Vander Wal *et al.* 1990) through the specificity of the interaction of the initially excited states with the dissociating photon. We have also observed bimolecular reactions of water (in which the subsequent interaction of the highly vibrationally excited molecule is with a hydrogen atom) that show an enormous enhancement over the reaction rate for unexcited molecules. The specificity of the interaction between the vibrationally excited water molecule and the hydrogen atom allows us to control the reaction of a particular bond. This reaction of HOD is a first example of bond selected bimolecular chemistry (Sinha *et al.* 1990).

Direct excitation of an overtone vibration with a pulsed dye laser creates the highly vibrationally-excited molecules in our experiments. In the case of water, we excite a single rovibrational state with a transition that derives its oscillator strength from the O–H bond stretching vibration. The experiments described here use the third overtone ( $4\nu_{\text{OH}}$ ) of the O–H stretching vibration. In the vibrationally mediated photodissociation measurements, we excite the vibrationally energized water molecules  $\text{H}_2\text{O}(4\nu_{\text{OH}})$  to an unbound electronically excited state with a photon from an ultraviolet laser and finally detect the OH dissociation product,



by laser induced fluorescence (LIF) (Vander Wal & Crim 1989). In the bimolecular reaction studies, we react the vibrationally excited water with hydrogen and also detect the OH product of the reaction by laser induced fluorescence (Sinha 1990),



In both cases, the LIF detection provides the relative populations of individual rovibrational states of OH.

## 2. Vibrationally mediated photodissociation of $\text{H}_2\text{O}$ and HOD

Vibrationally mediated photodissociation of water relies on the extension of the O–H bond in the vibrationally excited molecule to promote transitions to a dissociative electronic surface. Figure 1 illustrates the situation in  $\text{H}_2\text{O}$ , where extension of the O–H bond allows a transition with a photon of wavelength  $\lambda_2$  that could not occur from the equilibrium geometry. The vibrational excitation allows the molecule to explore a greater portion of the ground electronic state potential energy surface than would be possible otherwise and thus produces good Franck–Condon factors for transitions to normally inaccessible parts of the excited state potential. The particularly important aspect for the vibrationally mediated photodissociation of HOD is that vibrational excitation of the O–H bond constrains the second step to leave the dissociating molecule in the exit channel on the excited state surface that corresponds to cleavage of only the O–H bond. This is the key to bond selectivity in vibrationally mediated photodissociation.

The relatively large rotational constant of water separates the rovibrational transitions sufficiently for us to excite a single rotational state in the region of the third O–H overtone vibration. Figure 2 shows a part of the photoacoustic spectrum of pure water and of a mixture of  $\text{H}_2\text{O}$ , HOD and  $\text{D}_2\text{O}$  in the region of  $4\nu_{\text{OH}}$ . Because the rotational spectrum of water is assigned (Baumann & Mecke 1933), we are able

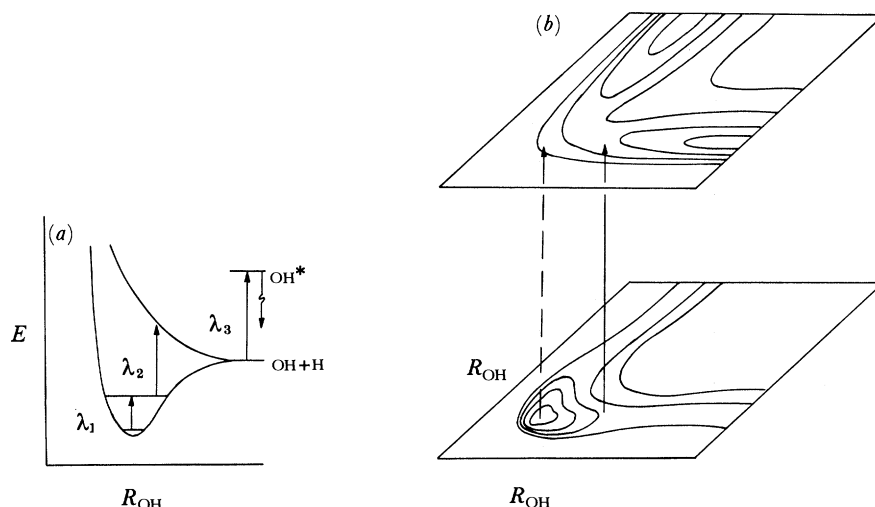


Figure 1. Qualitative potential energy surfaces for the ground and first electronically excited states of water. (a) A cut through the surfaces along the O–H stretching coordinate. (b) Energy contours for the two potential energy surfaces at a fixed bending angle. The broken arrow illustrates excitation from the equilibrium geometry, and the solid arrow shows excitation for an extended O–H bond.

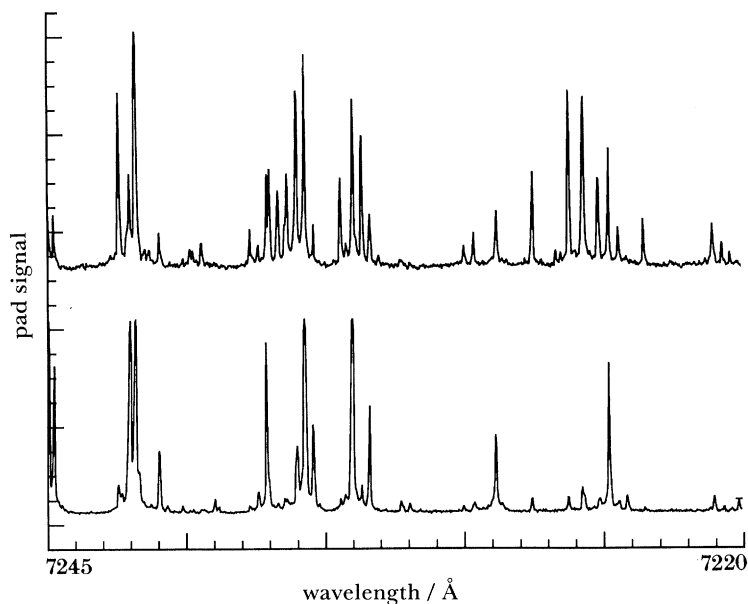


Figure 2. Photoacoustic spectra of  $\text{H}_2\text{O}$  (lower trace) and of a mixture of  $\text{H}_2\text{O}$ ,  $\text{HOD}$  and  $\text{D}_2\text{O}$  (upper trace) in the region of the  $4\nu_{\text{OH}}$  transition. The features that appear in the spectrum of the mixture but not in that of the sample of pure  $\text{H}_2\text{O}$  are from excitation of  $4\nu_{\text{OH}}$  in  $\text{HOD}$ .

to prepare  $\text{H}_2\text{O}$  molecules in a known single angular momentum state  $J_{K_a K_c}$  with four quanta of O–H stretching vibration. The total angular momentum quantum number is  $J$ , and  $K_a$  and  $K_c$  are its projection on the  $a$  and  $c$  axes in the prolate and oblate symmetric top limits respectively. Comparing the spectrum of  $\text{H}_2\text{O}$  alone with that of  $\text{HOD}$  and  $\text{H}_2\text{O}$  together shows that there are rovibrational transitions in  $\text{HOD}$

that are isolated from those of water or to which the H<sub>2</sub>O transitions makes a very small contribution. These are the transitions that we use to excite HOD.

(a) *Rotations*

The vibrationally mediated photodissociation of single rotational states of H<sub>2</sub>O( $4\nu_{\text{OH}}$ ) produces structured distributions of the resulting OH fragments among their rotational states (Vander Wal & Crim 1989). The pattern of the distribution depends strongly on the initially selected rotational state in H<sub>2</sub>O. This result agrees with pioneering experiments of Andresen and coworkers (Andresen *et al.* 1985; Schinke *et al.* 1985; Häusler *et al.* 1987), in which 193 nm photons dissociate water molecules prepared in individual rotational states having one quantum of asymmetric stretching excitation. The distributions in that experiment and in ours on H<sub>2</sub>O( $4\nu_{\text{OH}}$ ) agree quantitatively within the uncertainties of both measurements. In addition, both measurements agree well with quantal calculations (Andresen *et al.* 1985; Schinke *et al.* 1985; Häusler *et al.* 1987) using an *ab initio* excited state potential energy surface. Our experiments on two different vibrational states and the measurements on the first vibrationally excited state show that the initially prepared rotational state in H<sub>2</sub>O controls the relative populations of the product rotational states, as predicted by theory. The indifference of the product rotational state distribution to the amount of initial stretching excitation and to the photolysis wavelength reflects the small anisotropy of the excited state potential in the regions explored by these measurements.

(b) *Vibrations*

(i) *Vibrational eigenstates*

The distribution of four quanta of excitation between the two stretching vibrations of water gives several local mode states (Child 1984). If one O–H stretching vibration contains  $a$  quanta and the other  $b$  quanta, the possible states, designated  $|ab\rangle$ , are  $|04\rangle$ ,  $|40\rangle$ ,  $|13\rangle$ ,  $|31\rangle$  and  $|22\rangle$ . Because the two oscillators are equivalent, the actual eigenstates in this pure local mode representation are the symmetric (+) and antisymmetric (–) combinations of the states differing only by the location of the excitation in the two oscillators,

$$|ab\rangle^{\pm} = 2^{-\frac{1}{2}}(|ab\rangle \pm |ba\rangle).$$

Interbond coupling separates these degenerate states, which have the same symmetry as the corresponding symmetric and asymmetric normal mode vibrations. Child & Halonen (1984) have developed these ideas generally, and Lawton & Child have discussed the specific application to water (Lawton & Child 1979; Child & Lawton 1982) in detail. Mills & Robiette (1985) provide a particularly informative discussion of the correlation between the local and normal mode pictures as well. We also excite combination states containing one or two quanta of bending excitation, and here we label these as  $|ab\rangle^{\pm}|c\rangle$  where  $c$  is the number of bending quanta in the state. We generally omit the third quantum number when its value is zero. Our vibrational overtone excitation scheme prepares a single molecular eigenstate of water H<sub>2</sub>O( $|ab\rangle^{\pm}|c\rangle|JK_aK_c\rangle$ ).

(ii) *Stretching vibrations*

The two local mode states  $|04\rangle^-$  and  $|13\rangle^-$  differ in energy by only about 500 cm<sup>-1</sup> but correspond to rather different nuclear motions. Classically the unsymmetrized

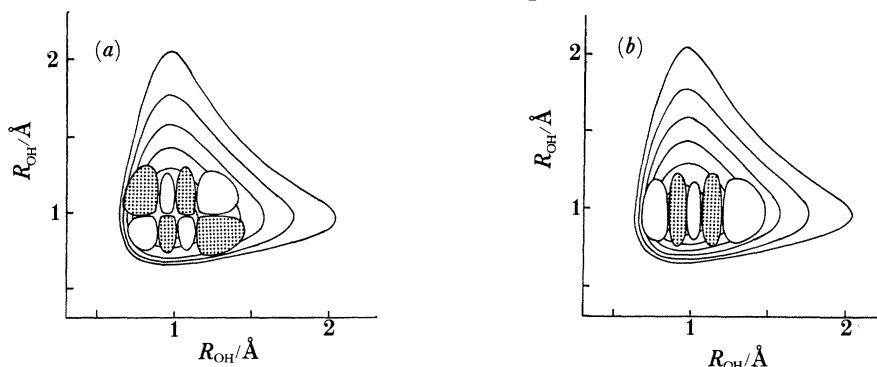


Figure 3. Unsymmeterized local mode wavefunctions for water in the region of four quanta of O–H stretching vibration. The  $|13\rangle$  state (a) has excitation in both O–H stretching coordinates but the  $|04\rangle$  state (b) has excitation in only one coordinate.

$|04\rangle$  state has no vibrational excitation in one oscillator while the  $|13\rangle$  state has excitation in both. Figure 3 illustrates this by showing the two unsymmeterized local mode wavefunctions for water. The crucial feature in the present context is the node along the coordinate for the less excited oscillator in the  $|13\rangle$  state. In the fully symmeterized wavefunction (see for example, Weide *et al.* 1989), the nodal pattern is more complicated, but the simple behaviour illustrated in the figure remains at large O–H bond distances.

We excite either the  $|04\rangle^-$  or  $|13\rangle^-$  local mode state with 40 mJ pulses of light ( $\lambda_1 \approx 700$  nm) from a Nd–YAG, pumped dye laser and dissociate the highly vibrationally excited molecule 30 ns later with photon from a second laser at  $\lambda_2 = 218.5, 239.5$  or 266 nm. We determine the populations in individual quantum states of the OH fragment from the photodissociation by partly saturated laser induced fluorescence at  $\lambda_3 \approx 308$  nm (Vander Wal & Crim 1989). The energy of the photolysis photon ( $\lambda_2$ ) is too small to dissociate  $\text{H}_2\text{O}$  from its equilibrium geometry. As illustrated in figure 1, the dissociation samples the portion of the ground electronic state wavefunction that corresponds to an extended O–H bond.

The initial vibrational state from which the photodissociation occurs potentially controls the final vibrational state of the O–H fragment. We can picture the vibrationally mediated photodissociation as being the projection by a Franck–Condon transition of the wavefunction for the initially prepared vibrational overtone state onto the electronically excited state potential energy surface. The molecule subsequently dissociates on that surface. The vibrational excitation in the unbroken bond, as determined by the vibrational overtone wavefunction, controls the vibrational state of the OH product. The unsymmeterized wavefunctions in figure 3 suggest that dissociation from the  $|04\rangle^-$  state should produce little vibration in the OH product since there is no node in the wavefunction along the coordinate of the surviving bond. On the other hand, photodissociation of the  $|13\rangle^-$  state is likely to produce vibrationally excited OH fragments by preservation of the initial excitation of the unbroken bond. This corresponds to the retention of one quantum of vibrational excitation in the less excited bond while the other bond breaks.

The vibrational overtone excitation spectra in figure 4, which were obtained monitoring different vibrational states of the OH product, support this simple model. We find that dissociating  $\text{H}_2\text{O}$  molecules from the  $|04\rangle^-$  state with 239.5 nm light produces less than 1% of the OH fragments in  $v = 1$  while dissociation from the

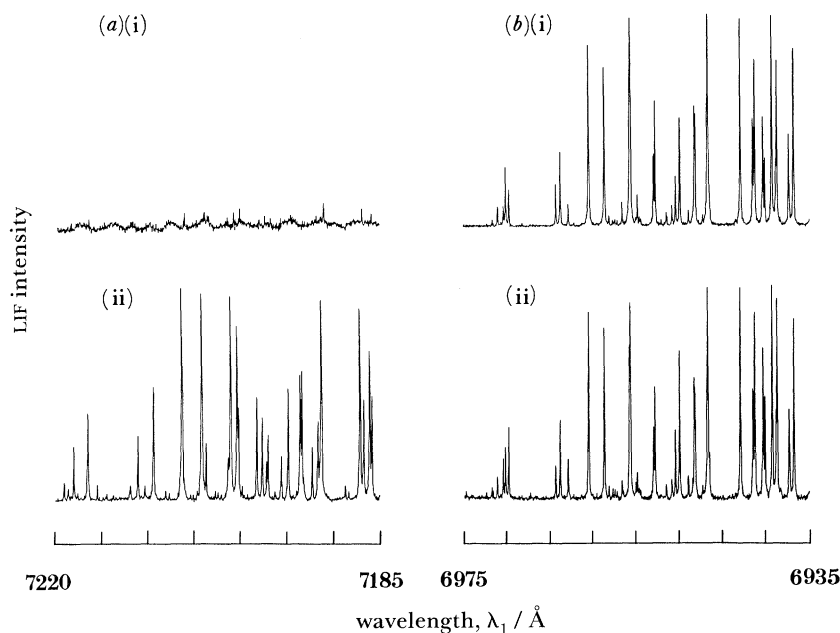


Figure 4. Vibrational overtone excitation spectra for transitions to the (a)  $|04\rangle^-$  and (b)  $|13\rangle^-$  states of water obtained probing (i)  $\text{OH}(v=1)$  and (ii)  $\text{OH}(v=0)$  products. The photolysis wavelength is  $\lambda_2 = 239.5$  nm. Photolysis of the  $|04\rangle^-$  state produces essentially no detectable  $\text{OH}(v=1)$ , in contrast to the results for the  $|13\rangle^-$  state.

Table 1. Product OH vibrational state populations for the photodissociation of water  $|04\rangle^-$  and  $|13\rangle^-$

wavelength $\lambda_2$ (nm)	initial vibrational state of $\text{H}_2\text{O}$			
	$ 04\rangle^-$ $\text{OH}(v=0)$	$ 04\rangle^-$ $\text{OH}(v=1)$	$ 13\rangle^-$ $\text{OH}(v=0)$	$ 13\rangle^-$ $\text{OH}(v=1)$
218.5	$0.91 \pm 0.03$	$0.09 \pm 0.03$	$0.06 \pm 0.05$	$0.94 \pm 0.05$
239.5	$0.99 \pm 0.01$	$0.01 \pm 0.01$	$0.16 \pm 0.06$	$0.84 \pm 0.06$
266	$> 0.98$	$< 0.02$	<sup>a</sup>	<sup>a</sup>

<sup>a</sup> No OH detected.

$|13\rangle^-$  state produces a fivefold excess of  $\text{OH}(v=1)$  over  $\text{OH}(v=0)$ . As figure 4 shows, the amount of  $\text{OH}(v=1)$  formed in the photolysis of the  $|04\rangle^-$  state is near the detection limit, but that formed in the photodissociation of the  $|13\rangle^-$  state is substantial. Conversion of the LIF signals to relative populations produces the quantitative results summarized in table 1, which also includes the results of the photodissociation of these states with  $\lambda_2 = 218.5$  and 266 nm photons.

The data shown in table 1 for two other wavelengths support our simple picture as well. Dissociation of the  $|13\rangle^-$  state with  $\lambda_2 = 266$  nm photons is so inefficient that we detect no OH fragments, but, in contrast, we obtain substantial amounts of OH from the 266 nm dissociation of the  $|04\rangle^-$  state. This reflects the greater extension of the wavefunction for the  $|04\rangle^-$  state along the O–H stretching coordinate, as shown in figure 3. It reaches a region where the ground and electronic state surfaces approach each other more closely than they do in the configurations accessible to the  $|13\rangle^-$  state wavefunction. Consequently, a 266 nm photon gives negligible excitation

to the dissociative surface from the  $|13\rangle^-$  state compared to dissociation from the  $|04\rangle^-$ .

Similarly, a more energetic photolysis photon,  $\lambda_2 = 218.5$  nm, can reach a large portion of the electronically excited potential energy surface from both the  $|04\rangle^-$  and the  $|13\rangle^-$  states. In this case, even photolysis of the  $|04\rangle^-$  state produces 9%  $\text{OH}(v = 1)$  since the excitation is near the barrier on the upper electronic surface, where the simple separation of the vibrations no longer holds. Recent quantitative calculation using wave-packet propagation on an *ab initio* potential energy surface (Weide *et al.* 1989) reproduce all of these observations.

### (iii) Bending vibrations

The role of bending vibrations in the vibrationally mediated photodissociation is rather different to that of stretching vibrations. In the simplest picture, stretches correlate with translation and vibration of the OH product, but bending vibrations correlate with rotations. Schinke & Engel (1985) have calculated the effect of bending excitation in the direct photodissociation of water and shown that it produces a signature in the rotational state populations of the OH fragment. Unlike the situation with stretching vibrations, the rotations of the product molecules are not indifferent to the initial bending state from which the dissociation occurs. Our two-step dissociation scheme can dissociate water molecules with different amounts of bending excitation. We excite rotationless molecules,  $J_{K_a K_b} = 0_{00}$ , with three quanta of OH stretching vibration and either one or two quanta of bending vibration and dissociate them using  $\lambda_2 = 218.5$  nm photons.

Figure 5 shows the OH product rotational state distributions for vibrationally mediated photodissociation of the  $|04\rangle^-|0\rangle$ ,  $|03\rangle^-|1\rangle$ , and  $|03\rangle^-|2\rangle$  vibrational states of water. (We use the  $|04\rangle^-$  state for the comparison since it lies closer in energy to the bending states than the  $|03\rangle^-$  state. We have shown that the initial stretching vibrational state has little influence on the rotational state distribution.) The rotational state distributions for the photolysis of molecules with excited bending vibrations (middle and upper panels) extend to higher rotational quantum numbers than does that for the molecule with only zero-point bending motion (lower panel). This qualitative behaviour reflects the transformation of the initial bending excitation into rotation of the fragments.

Schinke & Engel (1985) have speculated that bending excitation brings portions of the excited state potential into play that are more anisotropic than the region accessed from an initial state with no bending excitation. Quantitative comparison of their recent preliminary time-independent quantal calculations with our measurements tests this notion. Their calculated rotational state distributions for photolysis of the  $|04\rangle^-|0\rangle$  and  $|03\rangle^-|1\rangle$  states agree nearly quantitatively with our measurements, and the inclusion of the anisotropy of the potential in the calculation makes only a minor difference. For the  $|03\rangle^-|2\rangle$  state the comparison is poorer although the trend toward increasing rotational energy disposal, seen for the other two states, continues. Including the anisotropy in the calculation for the  $|03\rangle^-|2\rangle$  state changes the prediction noticeably and brings it into better, but not perfect, agreement with the measurement.

### (iv) Bond selective photolysis of HOD

The isolation of the O–H stretching vibration in water and the ability of vibrationally mediated photodissociation to excite the molecule from a configuration



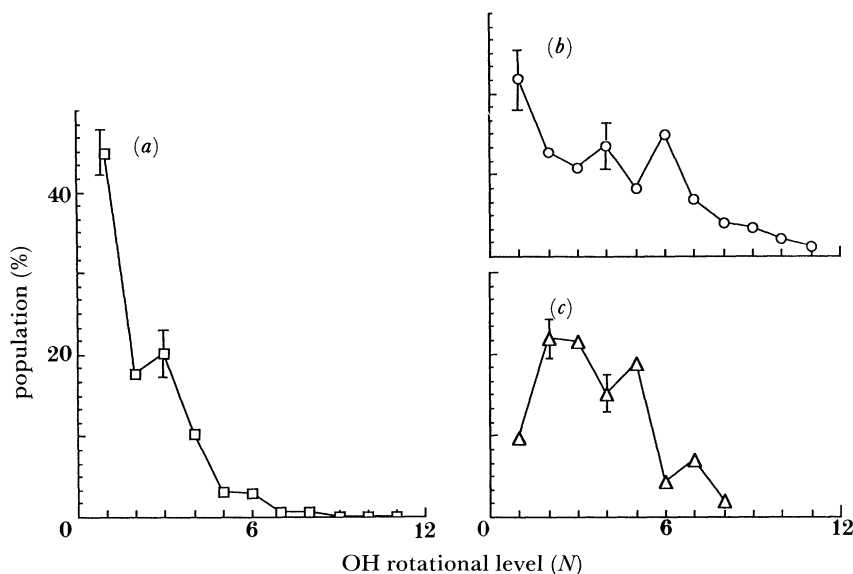
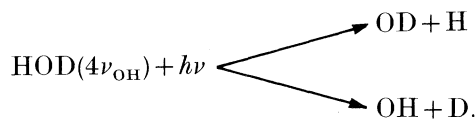


Figure 5. Rotational state distributions of  $\text{OH}(v=0)$  from the 218.5 nm photolysis of rotationless water molecules ( $J_{K_a K_c} = 0_{00}$ ) with different amounts of bending excitation. (a) shows the distribution from a state with no bending excitation ( $|04\rangle\text{-}|0\rangle$ ). (b) and (c) show the results for photolysis of states with one quantum ( $|03\rangle\text{-}|1\rangle$ ) and two quanta ( $|03\rangle\text{-}|2\rangle$ ) of bending excitation respectively.

that is well into the exit channel make it possible to control the bond cleavage. We demonstrate (Vander Wal *et al.* 1990) this by selectively cleaving the O–H bond of HOD. The two possible decomposition pathways in the photolysis of  $\text{HOD}(4\nu_{\text{OH}})$  are



Preparing  $\text{HOD}(4\nu_{\text{OH}})$  by vibrational overtone excitation and dissociating it with a 239.5 nm or 266 nm photon produces almost exclusively OD, since the excitation to the excited state surface is in the exit channel for breaking the O–H bond. Table 2 summarizes these results along with those for the 218.5 nm photolysis. The situation is substantially different for the shorter wavelength dissociation. The 218.5 nm photolysis of  $\text{HOD}(4\nu_{\text{OH}})$  produces comparable amounts of OH and OD. This again reflects the accessible regions of the excited state potential energy surface. With the higher energy photolysis photon, regions of the potential surface on both sides of the barrier that separates the OD and OH product channels become accessible and both products appear, as shown in table 2.

Theoretical calculations by Schinke and by Imre using wave-packet propagation and an *ab initio* surface agree with the qualitative picture and reproduce the observations quantitatively, as shown in the last column of the table 2. Another point of comparison is between our two-photon dissociation and a single-photon dissociation experiment using 157.5 nm photons (Shafer *et al.* 1989) Theoretical calculations agree well with the observations that the production of OD is four times more likely than the production of OH in the dissociation from the vibrationally

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Table 2. Relative yields of OD and OH fragments in the photodissociation of HOD

$\lambda_2$ nm	$E^a$ cm $^{-1}$	$f_{OD}$	experiment		theory
			$f_{OH}$	$f_{OD}/f_{OH}$	$f_{OH}/f_{OH}$
vibrationally mediated photodissociation ( $4\nu_{OH}$ )					
266	10150	$0.93 \pm 0.09$	$< 0.07$	$> 15$	—
239.5	14310	$0.94 \pm 0.09$	$< 0.06$	$> 15$	$> 40^{b,c,d}$
218.5	18320	$0.50 \pm 0.09$	$0.50 \pm 0.09$	$1.0 \pm 0.2$	$1.1^b 0.9^c$
direct dissociation					
157.5	22215			$4 \pm 1^e$	$4.2^f$

<sup>a</sup> Excess energy over bond dissociation energy. The excitation energy for the vibrationally mediated photodissociation is the sum of the energy of the band centre of the vibrational overtone transition ( $E_0 = 13430$  cm $^{-1}$ ) and that of the photolysis photon ( $h\nu_2$ ). The excess energy is  $E = E_0 + h\nu_2 - \Delta H_0^0$  where  $\Delta H_0^0$  is the bond dissociation energy of  $5.118$  eV =  $41\,280$  cm $^{-1}$ .

<sup>b</sup> J. Zhang (personal communication).

<sup>c</sup> R. Wiede (personal communication).

<sup>d</sup> These calculations predict essentially no OH production for  $\lambda_2 = 239.5$  and  $266$  nm photolysis.

<sup>e</sup> Shafer *et al.* (1989).

<sup>f</sup> Zhang *et al.* (1989).

unexcited molecule at this wavelength. The vibrationally mediated photodissociation at lower total energy produces ratios that are larger (for  $\lambda_2 = 239.5$  and  $266$  nm) and smaller (for  $\lambda_2 = 218.5$  nm) depending on the photolysis wavelength. Thus we are not observing a simple energetic effect but are rather seeing the control that the vibrationally excited intermediate state exerts over the decomposition.

### 3. Vibrationally enhanced and controlled bimolecular reaction

The extreme local mode character of the stretching vibrations in water, which permits bond selective vibrationally mediated photodissociation, allows us to control the rate and pathway of a bimolecular reaction as well. The reaction of water with hydrogen atoms,  $H_2O + H \rightarrow OH + H_2$ , is  $62$  kJ mol $^{-1}$  endothermic and has a calculated barrier of  $90$  kJ mol $^{-1}$  that agrees with thermal reaction results (Schatz *et al.* 1984). The diagram in figure 6 shows these energetics schematically. Kleinermanns & Wolfrum (1984) have used translationally energized hydrogen atoms from the photolysis of HBr to overcome the reaction barrier. They have measured the state distribution of the OH product and the reaction cross-section ( $0.24 \text{ \AA}^2 \dagger$ ) at an average total energy of about  $240$  kJ mol $^{-1}$ . Quasiclassical trajectory calculations (Schatz *et al.* 1984) predict that vibrational excitation of  $H_2O$  should enhance the rate of the thermal reaction by factors of between  $10^3$  and  $10^7$  depending on the details of the excitation. These calculations also predict product rotational state distributions and cross-sections for the reaction with energetic hydrogen atoms that agree qualitatively with the measurements.

Sinha (1990) has recently demonstrated a technique for observing the effect of vibrational excitation on hydrogen atom abstraction. This approach creates vibrationally energized molecules by vibrational overtone excitation and reacts them in a low pressure flow with H atoms from a microwave discharge of  $H_2$  and He. In the experiments described here, we apply this technique to both  $H_2O$  and HOD to

$$\dagger 1 \text{ \AA} = 10^{-10} \text{ m} = 10^{-1} \text{ nm.}$$

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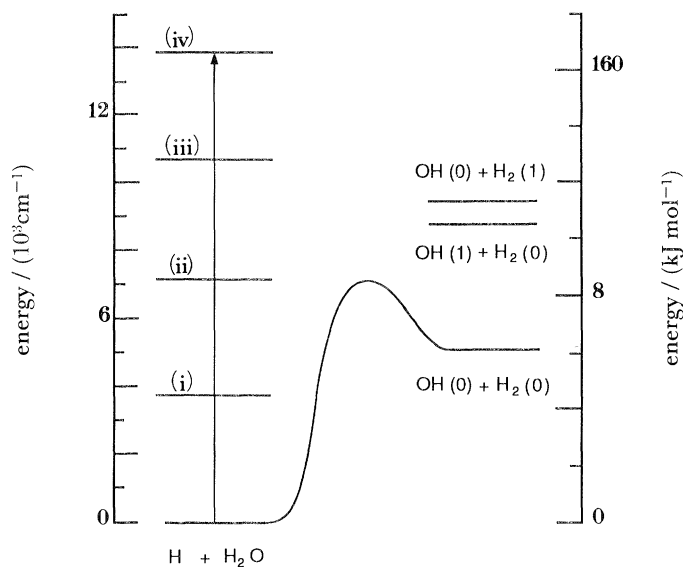


Figure 6. Energy level diagram for the reaction of water with hydrogen atoms. The energy levels on the right refer to several different O–H stretching states in  $\text{H}_2\text{O}$ . The horizontal lines on the right indicate the energies of the  $\text{H}_2$  and OH products in different vibrational states: (i)  $|01\rangle^-$ ; (ii)  $|02\rangle^-$ ; (iii)  $|03\rangle^-$ ; (iv)  $|04\rangle^-$ .

observe the acceleration of the reaction by vibrational excitation and to cleave the O–H bond in HOD selectively in a bimolecular reaction. The vibrational overtone excitation to produce  $\text{H}_2\text{O}(4\nu_{\text{OH}})$  or  $\text{HOD}(4\nu_{\text{OH}})$  and the LIF detection of the OH or OD products are exactly as described above. The total pressure of about 100 mTorr† in the reaction cell is mostly He from the discharge, and the partial pressure of water is typically 20 mTorr. We estimate that roughly 20% of the 20 mTorr of  $\text{H}_2$  in the discharge dissociates to produce about 8 mTorr of H atoms.

We observe no reaction between H and  $\text{H}_2\text{O}$  in the absence of light from the vibrational overtone excitation laser. The rate for room temperature reaction is well below that required to exceed our detection limit of about  $5 \times 10^5 \text{ molecule cm}^{-3} \text{ state}^{-1}$  for the OH product. Figure 7 shows a vibrational overtone excitation spectrum of  $\text{H}_2\text{O}$  obtained by monitoring the OH product of the reaction (upper panel) and a photoacoustic absorption spectrum of water in the same region (lower panel). As the figure illustrates, we detect no products above the background level when the vibrational overtone excitation laser does not coincide with a vibrational overtone transition in  $\text{H}_2\text{O}$ , but we do observe products when the laser excites a vibrational overtone state. Every absorption feature in the photoacoustic spectrum has a corresponding feature in the reaction spectrum.

Varying the time delay between the vibrational overtone excitation laser and the probe laser allows us to make a very rough estimate of the rate of the reaction. At a delay of 100 ns, the signal exceeds the detection limit by about a factor of 20. By using this time delay, our estimated density of H, and the excitation efficiency of the vibrational overtone transition in water (*ca.*  $10^{-5}$ ), we find a rate constant of  $10^{-10} \text{ molecule}^{-1} \text{ cm}^3 \text{ s}^{-1}$ . This rate corresponds to the reaction occurring within a few gas kinetics collisions, in agreement with the enhancements and cross-sections from

† 1 Torr  $\approx$  133 Pa.

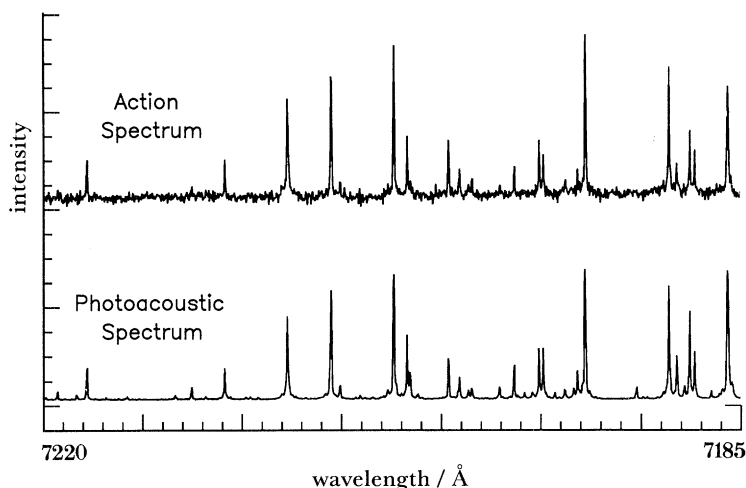
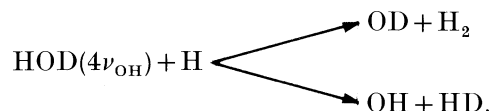


Figure 7. The vibrational overtone excitation spectrum of  $\text{H}_2\text{O}(|04\rangle^-)$  obtained monitoring the OH product (upper trace) and the corresponding photoacoustic spectrum (lower trace). Every feature in the photoacoustic (absorption) spectrum appears in the action spectrum.

the quasiclassical trajectory calculations (Schatz *et al.* 1984). Clearly, the vibrational excitation in water increases the rate of the reaction dramatically.

The vibrational enhancement of the reaction rate in water and the localized character of the vibrational overtone excitation allow us to produce the first example of a bond selected bimolecular reaction. We excite the third overtone of the O–H stretching vibration in HOD using the photoacoustic spectrum as a guide, exactly as described above for vibrationally mediated photodissociation, and we detect both the OH and OD products by laser induced fluorescence. The two possible reaction pathways are



We detect no OH product above the background signal when exciting  $\text{HOD}(4\nu_{\text{OH}})$  but do observe substantial amounts of OD. Figure 8 shows the signal for a portion of the LIF excitation spectrum in which both OD and OH transitions occur. There is no net OH production compared with OD. From the limiting noise in the spectrum, we determine that the reaction produces at least a 100 fold excess of OD over OH. This enhancement of the reactivity agrees with quasiclassical trajectory calculations (Schatz *et al.* 1984) that find vibrational excitation of the reacting bond enhances the cleavage of that bond by a factor of 10 to  $10^3$ . We are currently conducting more detailed experiments and plan to observe the partitioning of energy for both fragments and to explore the role of other initial excitations.

#### 4. Conclusion

Vibrational overtone excitation in water produces a highly localized state that is nearly a pure O–H stretching state. The vibrationally mediated photodissociation and bimolecular reaction experiments described here show that it is possible to

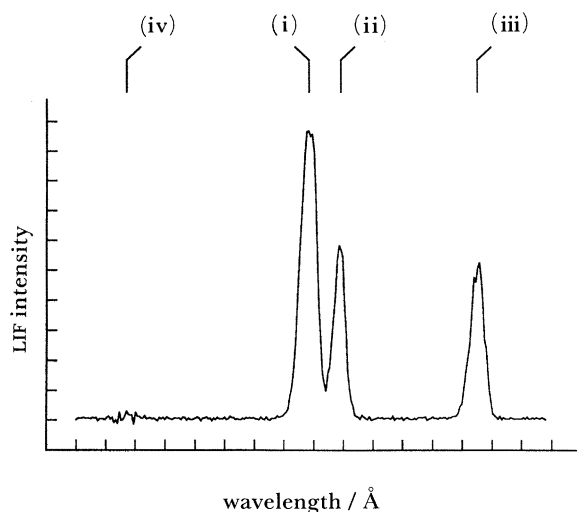


Figure 8. Laser induced fluorescence excitation spectrum of the products of the reaction  $\text{H} + \text{HOD}(4\nu_{\text{OH}})$ . The vertical lines mark the locations of transitions for both the OD ((i)  $\text{Q}_1(4)$ , (ii)  $\text{Q}_{21}(4)$  and (iii)  $\text{R}_2(4)$ ) and OH ((iv)  $\text{R}_2(4)$ ) fragments, but only transitions for OD appear in this spectrum. This 'net' signal comes from subtracting the OH background signal that is present even without light from the vibrational overtone excitation laser. (Minor contamination in the microwave discharge produces the background OH.)

control the dissociation or reaction of this highly energized molecule. In both cases, the great specificity in the subsequent reaction, as signalled by the selective cleavage of the O–H bond in HOD, arises from the preservation of excitation in the initially prepared state. Viewing the eigenstates in water as good local mode states provides a conceptual framework for the bond selectivity. It also points to the requirements for bond selectivity in photodissociations and bimolecular reactions of highly vibrationally excited molecules.

The molecular eigenstate prepared by vibrational overtone excitation is a linear combination of zero-order states. Typically, the states corresponding to excitation of the internal coordinates, such as bond lengths and angles, are particularly convenient zero-order states that appeal to chemical intuition. As usual (see, for example, Stannard & Gelbart 1981), we can express the highly vibrationally excited molecular eigenstate  $|n\rangle$  as a linear combination of the zero-order states  $|s\rangle$  and  $\{|l\rangle\}$ ,

$$|n\rangle = C_s^m |s\rangle + \sum C_l^n |l\rangle.$$

The state  $|s\rangle$  is the bright zero-order state, in our case the O–H stretching state, that carries the oscillator strength for the vibrational overtone transition, and the states  $\{|l\rangle\}$  are the dark zero-order states that have no oscillator strength. The transition probability in the vibrational overtone excitation step depends on the coefficient of the bright state, but, more important in the present context, it influences the second, bond selective, step as well.

The outcome of the subsequent interaction of eigenstate  $|n\rangle$  with a photon, in a vibrationally mediated photodissociation, or with an H atom, in a bimolecular reaction, depends on the amount of the zero-order O–H stretching state in the molecular eigenstate. In water, both the photodissociation and the reaction requires excitation of the O–H stretch. We can write the cross section for the subsequent interaction as  $\sigma \propto \langle f|P|n\rangle|^2$ , where  $P$  is the operator for the transition from state  $|n\rangle$

to the final state  $|f\rangle$ . The final state corresponds to the separated products, and the operator contains either the photodissociation transition probability or the reaction probability, depending on the process under consideration. If this transition or reaction probability depends only on the amount of pure O–H stretching excitation, all of the  $\langle f|P|l\rangle = P_{f\leftarrow l}$  are zero. In this case, the cross-section is

$$\sigma \propto |\langle f|P|n\rangle|^2 = |C_s^n \langle f|P|s\rangle + \sum_l C_l^n \langle f|P|l\rangle|^2 = |C_s^n|^2 |P_{f\leftarrow s}|^2.$$

This expression emphasizes that the requirement for large bond selectivity or rate enhancement, such as we observe in the vibrationally mediated photodissociation and bimolecular reaction of  $\text{HOD}(4\nu_{\text{OH}})$ , is that  $C_s^n$  be large. We know this is the case for water since it is a very good local mode state. In the language of intramolecular dynamics, a large  $C_s^n$  corresponds to an isolated state that closely resembles the zero-order state. For such a molecule, the zero-order state, if it were prepared, would largely retain its excitation and not transfer it to other zero-order states extensively. The key to predicting this selectivity for reactions of other molecules is to assess the magnitude of  $C_s^n$ . Vibrational overtone spectroscopy can provide this information and should be a guide to identifying likely candidates for bond selective photodissociation or reaction. Conversely, the observation of these selective processes reveals the nature of the initially prepared state.

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#### Discussion

N. C. HANDY (*University Chemical Laboratory, Cambridge, U.K.*). Dr Crim has introduced the concept of the molecular eigenstate as the wavefunction for the state of molecule after the action for the first laser which excites the molecule from the ground state. For  $\text{H}_2\text{O}$  the molecular eigenstate is either  $[40]^-$  or  $[31]^-$ , representing excited OH stretch vibrations. Can Dr Crim give me a precise definition of this state. I understand that the laser finds this state precisely, and therefore the molecular eigenstate is a stationary state.

At this meeting we have heard a lot about the progress of the variational method for the determination of the stationary states for given potential energy surfaces. We have seen that states such as those mentioned above can be found almost exactly by this approach. For those familiar with this approach it therefore does not seem appropriate to decompose the molecular eigenstate into ‘bright’ and ‘dark’ states; we have the wavefunction for this state and that is all that is required. Properties may be deduced by calculating appropriate overlap integrals (such as Franck–Condon factors).

F. F. CRIM. Professor Handy is of course correct in stating that once one knows the wavefunction, one knows everything about the molecular system and can calculate properties by calculating overlap integrals or other appropriate quantities. A different consideration motivates our using the language of dark and bright states in discussing vibrationally mediated photodissociation and bimolecular reaction. These zero-order states often correspond to our chemical intuition about bond stretches and vibrations, and when a zero-order motion such as bond stretching promotes reaction or photodissociation, as it seems to in water, this picture is particularly informative.