Resonance Raman Studies of the Low-Lying Dissociative Rydberg-Valence States of H_2O, D_2O, and HDO

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A resonance Raman study of water has been performed with the use of excitation wavelengths ranging from 200 nm (6.20 eV) to 141 nm (8.78 eV). With excitation resonant with the dissociative $\tilde{A}$ state the spectra exhibit intensity exclusively in the symmetric stretching vibration, showing up to six quanta. There is no activity in the bending or antisymmetric stretching vibrations, showing that the dissociation of the $\tilde{A}$ state of water proceeds initially along the symmetric-stretch coordinate. Resonance with the second absorption band results in a spectrum exhibiting significant intensity in the bending vibration.

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Resonance Raman spectroscopy provides useful information about potential-energy surfaces of excited electronic states of polyatomic molecules. The recent application of this technique to the study of systems with repulsive excited-state surfaces[1,2] has provided a description of the early-time behavior of the photodissociation process. The dynamics of bond cleavage is reflected in the intensity pattern of the fundamental, overtone, and combination transitions seen in the Raman spectrum. Since this is, in effect, a "mapping" onto the ground-state surface, the degree to which the ground-state potential is characterized often determines the ultimate detail of the picture that can be obtained from the resonance Raman data.

Previous studies of this phenomenon for directly dissociative states[1,2] have involved relatively complex molecules. In the present study we take advantage of the recent extension of resonance Raman spectroscopy into the far ultraviolet region[3] to apply this technique to the water molecule and its isotopomers. Being a small molecule composed of low-atomic-number atoms, the calculation of water's low-lying excited-state potential-energy surfaces is possible with considerable accuracy.[4-6] The lowest excited state, which is assigned as the $\tilde{A}\,^1B_1$ $(1b_1, 3sa_1/\sigma^* 4a_1)$ Rydberg state, provides an example of a directly dissociative state of a small polyatomic molecule with no other nearby potential surfaces.

An *ab initio* surface has been developed for the $\tilde{A}$ state[4] and has been applied with success[7,8] to the experimental data for the absorption spectrum and the photolysis product-state distribution.[9-14] Our resonance Raman spectra provide another stringent test of the validity of the surface and of the dynamics of the photodissociation. The results to be presented show that the dissociation of water in the $\tilde{A}$ state proceeds with motion initially along the symmetric-stretching coordinate without involvement of the bending vibration. This information is unavailable from other experiments. These results also demonstrate that high-quality Raman spectra can be obtained in the far ultraviolet region from dissociating systems with use of existing laser technology.

The absorption spectrum of the $\tilde{X} \rightarrow \tilde{A}$ transition of water, shown in Fig. 1, is broad and essentially structureless.[15-17] Although this state is assigned as a Rydberg state, it is generally thought[6] to contain significant antibonding valence character as reflected in its dissociative nature; absorption results in the production of $H(^2S)+OH(^2\Pi)$. A purely Rydberg excited state should have properties similar to that of the limiting ion which is bound with a geometry very similar to the ground state.[18,19] As the absorption spectrum contains very little information on the excited-state potential-energy surface, most of the experimental studies of water photodissociation have involved examinations of the OH radical produced.[9-14] For incident wavelengths below 177 nm, the products $H_2(^1\Sigma_g^+)+O(^1D)$ are also accessible although there is a significant energy barrier (1 to 2 eV) along this reaction coordinate.[4,5,20]

The resonance Raman spectra of water vapor were

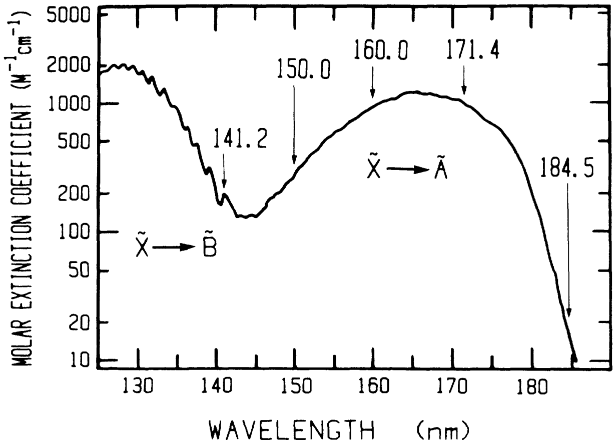

FIG. 1. The absorption spectrum of H_2O vapor in the spectral region 125 to 185 nm (Ref. 15). The arrows indicate the excitation wavelengths used in our Raman studies. The state assignments are those discussed in the text.

measured with an apparatus that we have recently developed for obtaining Raman spectra using excitation wavelengths in the purgeable vacuum ultraviolet.[3,21] The anti-Stokes Raman-shifted lines of the fourth harmonic of a high-power Nd-doped yttrium-aluminum-garnet laser provided the necessary excitation wavelengths. The water sample was a vapor stream near atmospheric pressure produced by the bubbling of nitrogen through a reservoir held at 90 °C. At this temperature the vapor pressure of water is 525 Torr. The wavelengths used are shown in Fig. 1. The Raman spectrum was also obtained off resonance at 200 nm. At this wavelength the only band observed was the fundamental transition of the symmetric stretch.

The resonance Raman spectra of H_2O and D_2O taken with 184-, 171-, and 160-nm excitation exhibit intensity exclusively in the symmetric stretching vibration, ν_1. A progression of six quanta of ν_1 is seen at 160 nm. This is shown in Fig. 2 for H_2O. The 171-nm spectrum is similar to the 160-nm spectrum. The pattern of overtone intensity observed for D_2O at 160 and 171 nm is very similar to that for H_2O. There is no activity in the bending vibration, and what activity is observed in the antisymmetric stretching vibration is due to resonance interactions in the ground state with nearby symmetric-stretching states.[22] This conclusion is supported by the comparison of the relative intensities of the pairs of bands [200] and [002], [300] and [102], [400] and [202], and [500] and [302]. These ratios are the same for both 171- and 160-nm excitation. This is the pattern expected if the intensity in each doublet is derived from a single active mode, and would not be expected if both the symmetric and antisymmetric stretches were active. If there were intrinsic activity in the antisymmetric stretching vibration we would also expect to observe bands corresponding to [004] and [104]. These bands are not seen.

In the spectrum of HDO the OD and OH stretching fundamentals have approximately equal intensities and the ratio of OD/OH band intensities remains approximately constant for the first few overtones. Combinations of these two bands are also observed. Again, no activity is seen in the bending-vibration transitions. We are currently studying these spectra to see if the data are consistent with the dynamics calculated from the *ab initio* potential.[8]

Being a symmetric triatomic molecule, water has both symmetric and antisymmetric vibrational degrees of freedom. The global potential surface of the $\tilde{A}$ state must be symmetric with respect to the antisymmetric displacement. Thus the slope of the surface along the antisymmetric-displacement coordinate will vanish at the point corresponding to the ground-state geometry (the "vertical" position). Progress of the molecule to the dissociation limit must involve bifurcation of the initial wave packet along the antisymmetric-stretch coordinate, which depends initially on the second derivative of the excited-state surface with respect to the antisymmetric-stretching coordinate. Before this occurs to any appreciable extent there may be considerable motion along one or both of the symmetric-stretching and bending coordinates. This motion depends initially on the slope of the surface along these coordinates at the vertical position. For example, in the resonance Raman spectrum of ozone the symmetric stretching vibration and even quanta of the antisymmetric stretching vibration have comparable intensities[1]; the [004], [104], and [006] bands of ozone are observed in its 266-nm resonance Raman spectrum. In this case the effect of the slope along the symmetric-stretching coordinate and the second derivative along the antisymmetric-stretching coordinate are comparable, with both motions contributing to the early-time motions of the wave packet. In cases where the vertical region of the potential-energy surface does

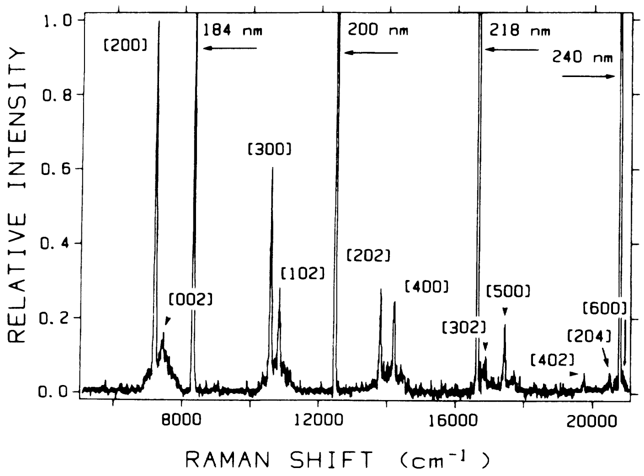

FIG. 2. The resonance Raman spectrum of H_2O obtained with 160-nm (7.75-eV) excitation. Although only the overtones are shown here, the fundamental of the symmetric stretching vibration has also been observed. The sample temperature was held at 90 °C ± 2 °C. The bands observed are identified in terms of quanta of the symmetric stretching vibration (ν_1), the bending vibration (ν_2), and the antisymmetric stretching vibration (ν_3), respectively. All transitions originate in the vibrationless level [000]. The [500] transition is anomalously intense in this particular spectrum because of a noise spike in one of the scans. More typically, this transition is only slightly stronger than the [302] transition. No attempt has been made to correct for the instrument response in this spectrum. However, we believe that this is fairly constant over the range shown here. The features labeled 184, 200, 218, and 240 nm are due to incomplete separation of the lower-order stimulated Raman shifts from the Raman-shifting cell. These lines are used for frequency calibration. The structure present near the first and second overtone transitions is also observed at the base of the fundamental of the symmetric stretch. This intensity pattern is identical in the 171- and 160-nm spectra, but is quite different far from resonance in the 200-nm spectrum. This is unresolved rotational-vibrational structure.

not have a significant slope along the symmetric coordinates, activity in the even overtones of the anitsymmetric stretching vibration is expected to predominate.

The resonance Raman spectrum of water can be combined with the recent *ab initio* calculations of the excited-state potential-energy surface[4] to provide a description of the dynamics of the photodissociation process.[7,8] At the vertical geometry, the excited state is so strongly antibonding that a steep gradient is calculated along the symmetric-stretching coordinate.[4] Our spectra demonstrate that this symmetric expansion, rather than motion along the dissociative antisymmetric-stretching coordinate, dominates the excited-state behavior at early times. According to the picture provided by these calculations, the distortions from C_{2v} symmetry which lead to the observed photoproducts begin when the molecule reaches a saddle point 0.38 eV below the vertical point where both OH bond lengths have expanded by 13%. The optimum bond angle in the $\tilde{A}$ state is close to the ground-state value of 104.5° for OH bond lengths near the ground-state equilibrium value. Thus no activity is expected in the bending vibration as is observed. This is consistent with the low rotational excitation of the OH product.[7-14]

The lack of activity in the bending vibration is in direct contradiction with the conclusions of Wang, Felps, and McGlynn,[17] who have reported several diffuse features in the absorption spectrum which they assign to a vibrational progression in the bending coordinate. These features are spaced by approximately 1840 cm^{-1} in H_2O and 1470 cm^{-1} in D_2O. However, Engel, Schinke, and Staemmler[7] find that the "vibrational" features can be explained by the $\tilde{A}$-state potential-energy surface without recourse to bending-vibrational activity. Our experimental results are in agreement with this conclusion.

We have also recorded the resonance Raman spectrum of H_2O at 141 nm. This excitation wavelength is in resonance with one of the first vibrational peaks of the $\tilde{X} \rightarrow \tilde{B}$ transition of water. The excited $\tilde{B}$ state is assigned as the ${}^1A_1$ $(3a_1, 3sa_1/\sigma^* 4a_1)$ Rydberg-valence state of water. In this case a clear vibrational progression with a frequency of approximately 800 cm^{-1} is observed in the absorption spectrum.[15,17,23] The active vibration is expected on theoretical and spectroscopic grounds to be the bending vibration.[5,17,23-25]

The 141-nm resonance Raman spectrum shown in Fig. 3 indeed exhibits activity in the bending vibration. The intensity ratio of the stretching vibration to the bending vibration in this spectrum is [100]:[010] = 3:1. For the 200-nm off-resonance spectrum, and the 160-nm spectrum resonant with the $\tilde{X} \rightarrow \tilde{A}$ transition, a lower limit for this ratio may be obtained from the signal-to-noise ratio in our data. At these wavelengths, this ratio is at least 30:1. Thus there is a clear indication of selective enhancement of the bending vibration in the 141-nm spectrum resonant with the $\tilde{X} \rightarrow \tilde{B}$ transition.

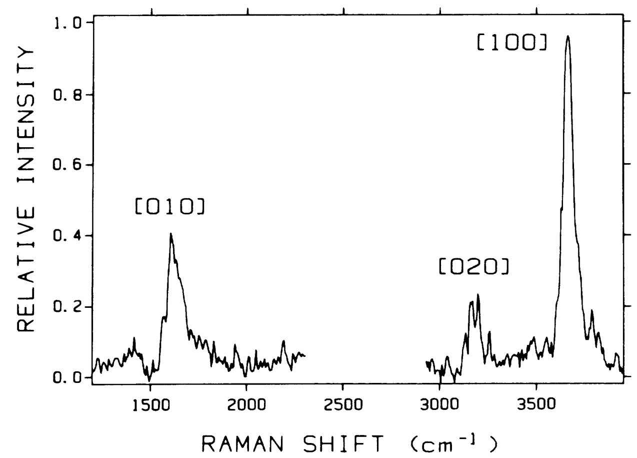

FIG. 3. The resonance Raman spectrum H_2O measured with 141-nm (8.78-eV) excitation. The bands observed are identified in terms of quanta of the symmetric stretching (ν_1), bending (ν_2), and antisymmetric stretching (ν_3) vibrations, respectively. All transitions originate in the vibrationless level [000].

We have reported here the first resonance Raman study of a hydride in a purely dissociative state. Resonance Raman spectroscopy has been demonstrated to be a useful technique for the investigation of the detailed dynamics of photodissociation processes.[1,2,26] Water appears to be a particularly fruitful molecule for investigations of this type. Reliable ground- and excited-state potential-energy surfaces are available. The $\tilde{A}$ state of water appears to be isolated from neighboring electronic surfaces, eliminating complications due to curve crossings. Furthermore, unresolved rotational structure is observed in the resonance Raman spectra of water (Fig. 2). Because of its small moment of inertia it is possible, in principle, to resolve the rotational-vibrational transitions even with ultraviolet excitation. This information may then be used to determine the effects of rotational motion on the dissociation dynamics.[26]

The results reported here for the $\tilde{A}$ and $\tilde{B}$ states of water, although preliminary, provide a direct experimental demonstration of the main features of the photodissociation of water that are in agreement with the conclusions drawn from recent theoretical studies. These results have stimulated additional theoretical effects.[27] A more extensive investigation of the $\tilde{B}$ state, as well as a full analysis of the spectra obtained in resonance with the $\tilde{A}$ state, will be the subject of a future publication.

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