Isotopic Dilution Studies of the Vapor/Water Interface as Investigated by Vibrational Sum-Frequency Spectroscopy

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Received: October 25, 2001; In Final Form: January 24, 2002

Vibrational sum-frequency spectroscopy (VSFS) studies of dilute HOD/H_2O/D_2O mixtures have been used to investigate the hydrogen-bonding interactions at the vapor/water interface. The decoupled nature of the HOD vibrations produces a less complex OH stretching band than the highly coupled OH stretches of H_2O, creating a clearer picture of the molecular environments present in the interfacial region. From the spectra of interfacial HOD, it is determined that the frequency of the uncoupled donor OH stretching mode is similar to what is observed in bulk HOD studies, leading to the conclusion that the hydrogen bonding environment at the surface is similar to that found in liquid H_2O. This conclusion is supported by the tetrahedrally coordinated region of the vapor/H_2O VSF spectrum, where the predominant resonant intensity is centered around 3300 cm^{-1}, consistent with bulk Raman and IR spectra of liquid water.

Introduction

Many key environmental and biological processes occur at aqueous interfaces. However, before adsorption and transport of molecules at vapor/water interfaces can be fully understood, a more detailed description is required of the structure and bonding occurring at the neat vapor/water interface. Due to water's extraordinary ability to hydrogen bond in a wide variety of environments, developing such an understanding is a continuing challenge for both experimentalists and theorists. In recent years, vibrational sum-frequency spectroscopy (VSFS) has been shown to be a powerful technique for probing liquid surfaces under ambient conditions.[1,2]

The first VSF spectrum of the OH stretch region of the vapor/water interface acquired by Du et al.[3,4] provided two important conclusions regarding the bonding and orientation of water at this interface. First, a significant portion (>20%) of the water surface is populated by water molecules with one hydrogen projecting into the vapor phase, the free or dangling OH bond. Second, although the broad nature of the response from tetrahedrally bonded water molecules made detailed assignments difficult, the spectral profile appeared more consistent with the strong hydrogen bonds of an ice-like surface phase, rather than the weaker, more disordered bonding character of liquid water.[2]

In this paper, we provide new insight into the VSF spectrum of the vapor/water interface through studies of vapor/HOD/D_2O interfaces. Isotopic dilution studies such as these are ideally suited for deconvolving complicated H_2O spectral features due to the energetically uncoupled nature of the OH and OD stretching modes in HOD.[5−10] For example, for those water molecules with one OH bond projecting into the air, isotopic dilution allows the measurement of the frequency and bandwidth of the uncoupled, hydrogen bonded OH oscillator, which is directed into the aqueous phase. Previous VSF studies of HOD at the CCl_4/D_2O interface have located this uncoupled donor mode at 3450 cm^{-1}.[11] Given that at least 20% of the molecules can adopt this configuration, and that the frequency of such a

bonded mode significantly overlaps OH modes of other hydrogen bonded water molecules,[9] such measurements can be very revealing. Also, the frequency of this mode when compared with temperature-dependent bulk studies can provide further insight into whether the surface region has more "ice-like" or "liquid-like" character.

SF Analysis. Vibrational sum-frequency spectroscopy (VSFS) is a second order nonlinear optical technique which is inherently surface specific due to the lack of inversion symmetry present at the interface between two isotropic media.[2,12,13] The second-order polarization induced in the surface molecules by the presence of the two input beams re-radiates at the sum of the two incident frequencies. The intensity of the SF response, I_{SF}, (equation 1) is proportional to the square of the second-order susceptibility of the medium, $\chi^{(2)}$, and to the incident intensity of the 800 and IR beams

$$\mathbf{I}_{SF} \propto |\mathbf{F}_{SF}\chi^{(2)}{:}\mathbf{f}_{800}\mathbf{E}_{800}\mathbf{f}_{IR}(\mathbf{n}_{H_2O})\mathbf{E}_{IR}|^2 \tag{1}$$

$\mathbf{f}_{800}$, $\mathbf{f}_{IR}(\mathbf{n}_{H_2O})$, and $\mathbf{F}_{SF}$, represent the linear and nonlinear Fresnel coefficients respectively, which account for the transmission and reflectance of the beams at the interface.

The second-order susceptibility $\chi^{(2)}$, (eq 2) has both resonant and nonresonant contributions

$$\chi^{(2)} = \chi^{(2)}_{NR} + \sum_\nu \chi^{(2)}_\nu \tag{2}$$

The nonresonant contribution (NR) to the SF intensity is relatively small for liquid surfaces, but due to the coherent nature of the SF process, cannot simply be subtracted from the spectrum to give the resonant contribution. The magnitude of the NR response in these studies is obtained from the VSF spectrum of the vapor/D_2O interface, which has no vibrational resonances in the frequency region probed. This NR value is assumed to be the same for the D_2O, H_2O, and HOD interfaces, and is used in the spectral fits of the HOD and H_2O spectra, allowing the separation and determination of the resonant response. The molecular interpretation of the VSF spectra

presented in this paper is based solely on the calculated resonant SF response.

The resonant contribution to the susceptibility, $\sum_\nu \chi_\nu^{(2)}$ is commonly assumed to arise from Lorentzian distributions of molecular energies. However, for molecules in the condensed phase, in particular molecules that experience a wide variety of bonding environments, such as water, the vibrational line widths are significantly inhomogeneously broadened. To account for both types of broadening, the resonant contribution to the susceptibility, $\chi_\nu^{(2)}$, assumes the following form (equation 3), first used for SF spectra by Bain[14]

$$\chi_\nu^{(2)} = \int_{-\infty}^{\infty} \frac{A_\nu e^{-[(\omega_L - \omega_\nu)/\Gamma_\nu]^2}}{\omega - \omega_L + i\Gamma_L} d\omega_L \qquad (3)$$

where Γ_L is the Lorentzian HWHM, ω_ν and A_ν are the center frequency and complex transition strength of the resonant mode, and Γ_ν is the Gaussian FWHM/$\sqrt{2\ln2}$.

The spectra presented here have been normalized by the SF spectrum of $\langle 100 \rangle$ GaAs to correct for temporal de-phasing of the IR beam, variation of I_{IR} as a function of frequency, and changes in IR and 800 overlap on the sample, a refinement over previous work.[15,16] The spectra have also been divided by the appropriate linear and nonlinear Fresnel coefficients, f_{800}, $f_{IR}(n_{H_2O})$, and F_{SF}. The Fresnel coefficient normalization is done to correct for the variation in intensity of the infrared beam transmitted through the interface due to the changing index of refraction of H_2O in the region studied. Previous Fresnel calculations published by Wei et al.[17] have assumed a constant index of refraction in this region. In our studies, due to the lack of data for the index of refraction of HOD, the indices of refraction of the HOD solutions as a function of frequency are approximated by weighting the indices of H_2O[18] and D_2O[19] by the initial mole fractions of H_2O and D_2O.

**Experimental Section**

The laser system used in these studies has been described previously.[16,20] The H_2O used is obtained from a Millipore Nanopure system (17.9 MΩ cm), whereas the D_2O is "ultralow conductivity" (0.4 MΩ cm), purchased from CDN Isotopes. The liquid samples are fully enclosed in a glass and Teflon cell with CaF_2 input and output windows. The cell is kept under a small positive pressure of dry $N_2(g)$, and all liquids are introduced to the cell via "gastight" syringes to minimize contaminants and maintain isotopic concentrations.

Results and Discussion

Figure 1, parts a−c, shows the VSF spectra of the vapor/H_2O, vapor/HOD, and vapor/D_2O interfaces, taken under SSP polarization conditions. The vapor/H_2O spectrum shows a sharp peak at $\sim$3700 cm^{-1}, indicative of free OH oscillators at the water surface. Also predominant in the neat H_2O spectrum is the broad band of intensity between 3100 and 3500 cm^{-1}, characteristic of the stretching of tetrahedrally coordinated water molecules.[9] Prior to division by the Fresnel coefficients, the vapor/H_2O spectrum presented here agrees well with the most recent vapor/H_2O spectrum published by the Shen laboratory.[17] The vapor/D_2O spectrum shown in Figure 1c is flat, consistent with the lack of vibrational resonances in the 2850−3900 cm^{-1} region.

From the series of concentration studies of HOD/H_2O/D_2O mixtures we have conducted, the spectrum with the lowest concentration of H_2O has been selected for display in Figure 1b. This spectrum of primarily HOD at the vapor/D_2O interface
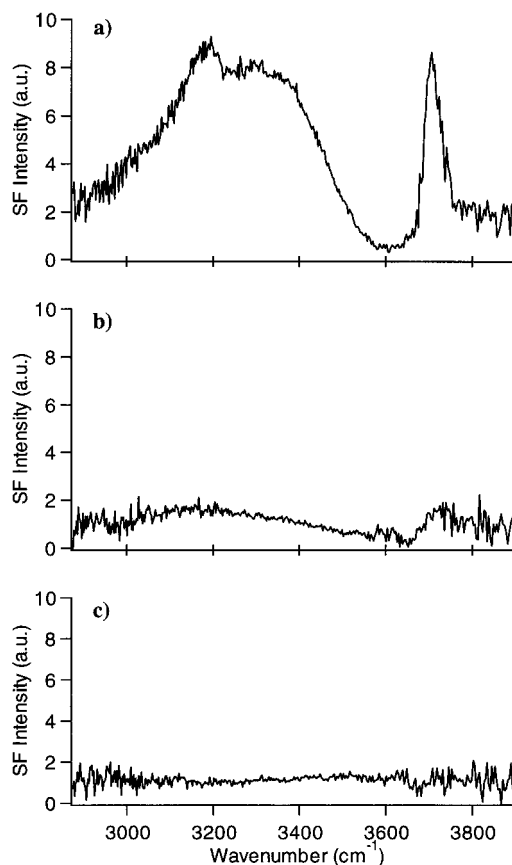

Figure 1. VSF spectra of the (a) neat vapor/water interface, (b) vapor/HOD interface (0.25 mf HOD, 0.02 mf H_2O, 0.73 mf D_2O), (c) neat vapor/D_2O interface. All three spectra are taken under SSP polarization conditions.

(0.25 mf HOD, 0.02 mf H_2O, 0.73 mf D_2O) shows very little amplitude above the NR level of neat D_2O in the 3000−3300 cm^{-1} region of the spectrum (Figure 1b). However, above $\sim$3350 cm^{-1}, the intensity pattern is characteristic of an interference between SF light arising from the NR response, and two resonant vibrational modes, one centered at $\sim$3420 cm^{-1} and another in the free OH mode region near 3700 cm^{-1}. By inspection, these two modes are of opposite phase. Spectra of additional HOD concentrations[21] show a similar intensity pattern above 3350 cm^{-1}, arising from this interference of the two resonant modes with the nonresonant sum-frequency signal.

To obtain a more quantitative measure of the spectral features in Figure 1, the analysis and spectral fitting method described by Brown et al.,[15] has been applied. Figure 2a shows the fit obtained for the simpler HOD spectrum of Figure 1b. Contributions include the nonresonant response and four resonant peaks corresponding to the interfacial HOD and residual H_2O molecules (Figure 2b). Figure 3 provides a simple cartoon of the HOD modes that contribute to the resonant peaks in Figure 2b. Although the nonresonant sum-frequency signal is significantly larger than the resonant response, for the HOD spectrum, the resonant spectrum (displayed in Figure 2b) is determined by removing the nonresonant level from the fit to the entire spectrum. This resonant response is dominated by peaks which we assign to the free OH at 3694 cm^{-1} (labeled as (1) in Figure 3) and the uncoupled donor OH at 3420 cm^{-1}. The opposite phases assigned to these two peaks are consistent with the molecular orientations depicted in Figure 3. The uncoupled donor OH peak is red shifted relative to the free OH because of bonding interactions in the aqueous phase, and can include
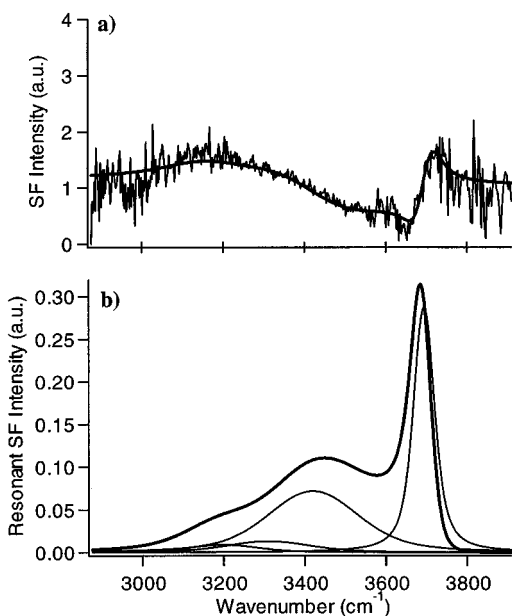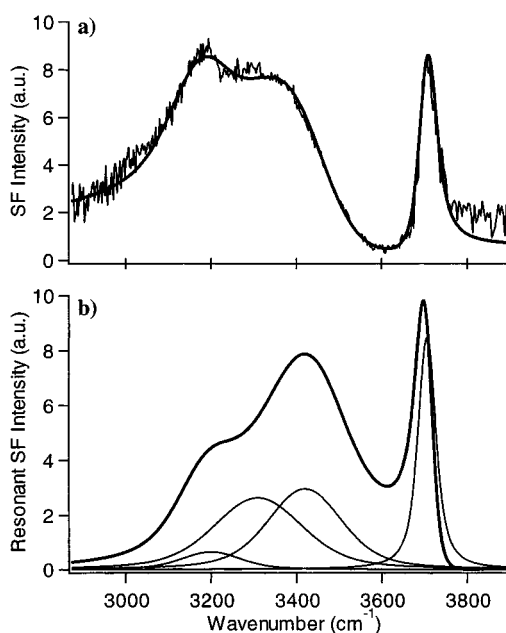
Figure 2. (a) Expanded HOD spectrum (0.25 mf HOD, 0.02 mf H_2O) and fit. (b) Resonant SF response from interfacial HOD (thick solid line). The squared contributions from the different molecular species, $|\chi_\nu^{(2)}|^2$, are shown with thin solid lines.
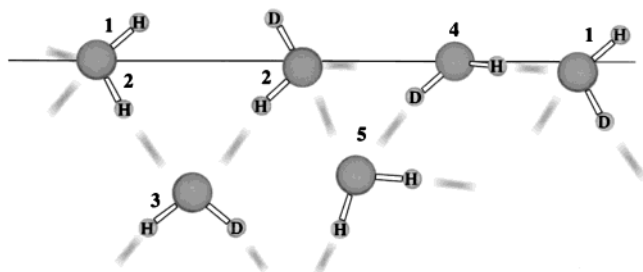
Figure 3. Pictorial representation of the species expected at the vapor/HOD interface. The OH bonds are labeled as follows: 1. Free OH in a H_2O or HOD molecule. 2. Uncoupled donor OH of a molecule containing a free OH or OD. 3. Uncoupled donor OH of a tetrahedrally coordinated HOD molecule. 4. Double donor HOD molecule. 5. Tetrahedrally coordinated H_2O molecule.

molecules that have one hydrogen which projects into the aqueous phase, (labeled as (2)) as well as those molecules in the interfacial region where both the OH and OD bonds interact with other water molecules (labeled as (3)). HOD molecules in the bulk will not contribute to the SF spectrum due to their isotropic orientation. Under the polarization scheme used here (SSP), SF intensity from any of these OH modes requires an average orientation of the OH dipole to have a component perpendicular to the surface plane.

The frequency and bandwidth of the bonded OH peak of surface HOD coincides with those observed for the uncoupled OH stretching mode in bulk infrared spectra of dilute HOD in D_2O. Surface studies of ice have been performed by Devlin et al.,[22] in which they observe the uncoupled donor OH stretch at ~3100 cm^{-1} which is considerably red shifted from the value of 3420 cm^{-1} observed here, as expected. Temperature studies of liquid HOD in H_2O have shown the frequency of the uncoupled OD bands to be temperature dependent, shifting to the red as the temperature is lowered, approaching the value observed for amorphous ice as the solution becomes super-cooled.[7] Our HOD results therefore indicate that the top surface layers have bonding interactions more consistent with a "liquid-like" surface than an "ice-like" surface.

Figure 4. (a) Expanded H_2O spectrum and fit. (b) Resonant SF response from the neat H_2O interface (thick solid line). The squared contributions from the different molecular species, $|\chi_\nu^{(2)}|^2$, are shown with thin solid lines.

The two smaller contributing resonant peaks shown in Figure 2b at 3200 and 3310 cm^{-1} are assigned to the stretching of tetrahedrally coordinated water molecules, from the 0.02 mf of H_2O present in the solution. Spectra of additional HOD concentrations are consistent with the conclusions drawn from Figure 2 and will be discussed in a longer publication,[21] along with quantitative analysis of the peak areas as a function of concentration.

The vapor/H_2O spectrum of Figure 1a has been treated in the same manner as the HOD data with the results shown in Figure 4. The overall fit to the data that includes the nonresonant and resonant components is shown in Figure 4a. Figure 4b shows the calculated resonant spectrum and the individual $|\chi_\nu^{(2)}|^2$ components. As with the HOD spectrum, the resonant contribution to the H_2O spectrum shows that a significant fraction of the VSF intensity in the spectrum arises from the uncoupled free and donor OH vibrations. The frequency of the free OH peak has shifted to the blue by ~12 cm^{-1} relative to the free OH of surface HOD, consistent with related studies.[6,23] The donor OH mode (3420 cm^{-1}) has maintained its frequency relative to the HOD spectrum, but has a higher overall intensity, consistent with the increased number of OH oscillators in the solution.

Surface H_2O (or HOD) molecules oriented such that hydrogen bonding occurs through both OH (or OD) bonds, but not through the lone pairs (designated as 4 in Figure 3), called "double donors" have been observed in clusters[22,24-26] at ~3550 cm^{-1}. Although is probable that such double donor molecules contribute to the sum-frequency spectra, there is no clear feature in either the HOD or H_2O spectra we can assign to this species.

Bulk Raman and IR spectra of liquid H_2O show strong intensity in the 3200−3450 cm^{-1} region. This broad intensity band is attributed to the stretching of tetrahedrally coordinated water molecules which experience a wide variety of hydrogen bonding environments.[9,27] In addition to the contributions from the free and donor OH modes, the resonant VSF H_2O spectrum (Figure 4(b)) also exhibits significant intensity arising from a peak at 3310 cm^{-1} and to a lesser extent, one at 3200 cm^{-1}.

On the basis of the frequencies of these peaks, we assign the intensity in this region to the OH stretches of tetrahedrally coordinated water molecules in liquid-like environments (labeled (5) in Figure 3). These two peaks were also present in the HOD spectra (due to the small amount of water present), but have increased significantly in intensity, in proportion to the increased amount of water in the solution. It is likely, given the bulk IR and Raman spectra of liquid water, that tetrahedrally coordinated molecules also contribute to the 3420 cm^{-1} peak, but the HOD spectra indicate that the dominant contribution to this peak is from uncoupled donor OH modes.

The lack of strong resonant intensity in the 3100−3250 cm^{-1} region in either the HOD or H$_2$O spectra, when combined with the peak position of the donor OH peak, leads to the conclusion that the water molecules comprising the vapor/water interface are in an environment much more similar to that of liquid water than of ice. The OH stretching bands observed in ice studies tend to be significantly shifted to the red, (3100−3250 cm^{-1} for both the tetrahedral and donor OH bands), and are narrower than those observed here.[8,9,22,28]

Conclusions

Measuring the VSF spectra of vapor/D$_2$O, HOD, and H$_2$O interfaces has allowed the development of a more detailed description of the broad OH stretching band of surface water. From the neat D$_2$O spectrum, the nonresonant SF response can be determined, allowing the separation of the resonant response for both the HOD and H$_2$O spectra. The resonant response from the vapor/HOD interface is dominated by the free OH stretch at 3694 cm^{-1} and the donor OH stretch at 3420 cm^{-1}. The frequency of the donor OH stretching mode peak is indicative of molecules in a room temperature or liquid-like environment. The molecules at the vapor/H$_2$O interface also exhibit this behavior, with the major contributions to the spectrum arising from the stretching of uncoupled donor OH oscillators and tetrahedrally coordinated molecules, both in environments more characteristic of liquid water than of ice.

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