

Isotopic Dilution Study of the Water/Vapor Interface by Phase-Sensitive Sum-Frequency Vibrational Spectroscopy

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There have been intensive theoretical and experimental studies of water/vapor interfaces in recent years. The focus is to understand the interfacial vibrational spectra obtained from sum-frequency vibrational spectroscopy (SFVS) and to relate them to the interfacial structure. (See recent review articles and references therein.^{1–4}) The interfacial molecules supposedly are linked to form a highly disordered hydrogen bonding network.³ Continuous variation of strength and geometry of the H-bonds leads to spectra of OH stretches that spread over a broad range between ~ 3000 and 3750 cm^{-1} and are rather difficult to interpret. Richmond and co-workers used isotopic dilution to simplify the spectra and their analysis.^{5,6} Bonn and co-workers later extended the study to the OD stretch region.⁷ There are however intrinsic difficulties in their works. The $\text{Im } \chi_S^{(2)}$ spectrum that explicitly characterizes the surface resonances was deduced from fitting of the $|\chi_S^{(2)}|^2$ spectrum with the assumption of discrete resonances, where $\chi_S^{(2)}$ is the surface nonlinear susceptibility of the interface. Such fitting, unfortunately, is often not unique and has created much confusion. We have recently developed a phase-sensitive (PS) SFVS technique that allows direct measurement of $\text{Im } \chi_S^{(2)}(\omega_{IR})$.^{8,9} In this paper, we employed the technique to obtain $\text{Im } \chi_S^{(2)}(\omega_{IR})$ for water/vapor interfaces of isotopic mixtures. We were able to deduce from the result the $\text{Im } \chi_S^{(2)}$ spectra of not only H_2O /vapor and D_2O /vapor interfaces but also the HDO/vapor interface. Analysis of the latter spectrum is expected to be much simpler because OH and OD of HDO are decoupled. The measured $\text{Im } \chi_S^{(2)}$ spectra are characteristically different from those deduced from fitting by Richmond's and Bonn's groups. In particular, in the bonded-OH (or OD) stretch region, a positive and a negative resonance bands at lower and higher frequencies, respectively, always appear in the measured spectra, in contrast to all resonances in the deduced spectra.

The experimental arrangement for PS-SFVS measurement on water/vapor interfaces has been described elsewhere.⁸ With $\chi_S^{(2)} = |\chi_S^{(2)}| \exp(i\phi)$ being complex, we measure both $\chi_S^{(2)}(\omega_{IR})$ and $\phi(\omega_{IR})$ and obtain the spectra of $\text{Re } \chi_S^{(2)}$ and $\text{Im } \chi_S^{(2)}$. For a resonance continuum, we have⁸

$$\vec{\chi}_S^{(2)}(\omega_{IR}) = \chi_{NR}^{(2)} + \int \frac{\vec{A}_q \rho(\omega_q)}{\omega_{IR} - \omega_q + i\Gamma_q} d\omega_q \quad \text{with} \quad \vec{\chi}_S^{(2)}(\omega_{IR}) = \vec{A}_q \rho_q / \pi$$

We have studied five isotopic mixtures, with molar ratios of H_2O /HDO/ $\text{D}_2\text{O} = 1/0/0, 4/4/1, 1/4/4, 1/8/16,$ and $0/0/1$. Their measured $|\chi_S^{(2)}|$ and $\text{Im } \chi_S^{(2)}$ spectra (taken with S-, S-, and P-polarized SF, visible input, and IR input, respectively) in the OH ($3000\text{--}3800$ cm^{-1}) and OD ($2200\text{--}2800$ cm^{-1}) stretch regions are presented in Figure 1A and 1B, respectively. The $|\chi_S^{(2)}(\omega_{IR})|^2$ spectra are nearly the same as those of Richmond's group⁵ for the OH stretches and Bonn's group for the OD stretches.⁷ For the pure H_2O and D_2O cases, the bonded-OH spectra exhibit the well-established double-peak feature. With sufficient isotopic dilution, this feature disappears

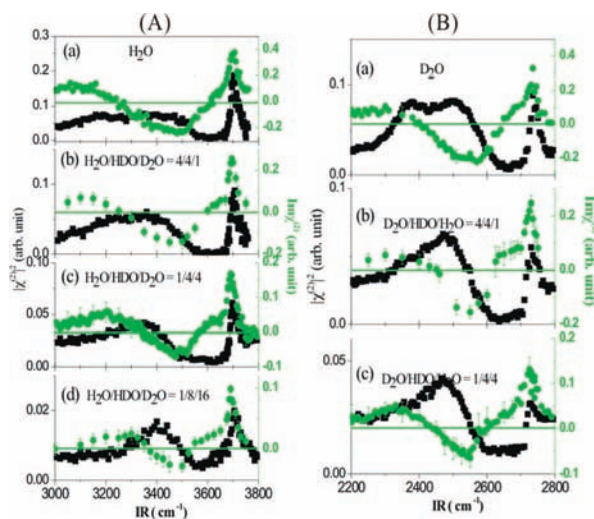


Figure 1. Spectra of $|\chi_S^{(2)}(\omega_{IR})|^2$ and $\text{Im } \chi_S^{(2)}(\omega_{IR})$ for water/vapor interfaces of isotopic mixtures in the (A) OH and (B) OD stretch regions.

and changes into a single broad band^{5–7} (Figure 1A(c) and 1B(c)). However, our $\text{Im } \chi_S^{(2)}(\omega_{IR})$ spectra in Figure 1, with one positive and one negative resonance band in the bonded-OH(OD) region, are obviously different from those obtained from fitting of $|\chi_S^{(2)}(\omega_{IR})|^2$ and from MD simulations,^{4,5,7,10,11} both of which yielded only negative resonances in the same region. Another feature in $\text{Im } \chi_S^{(2)}(\omega_{IR})$ that stands out is the positive shoulder below the relatively sharp OH (OD) peak.

The water interfacial structure is expected to be the same for all isotopic mixtures. This is supported by the observation that the $\text{Im } \chi_S^{(2)}$ spectra of OH and OD stretches for H_2O /vapor and D_2O /vapor interfaces, respectively, are nearly identical after a frequency rescaling of 1.35, shown in Figure 2. (The corresponding $|\chi_S^{(2)}|^2$ spectra are different because of different nonresonant contributions.) The same is true for spectra of water/vapor interfaces of H_2O /HDO/ $\text{D}_2\text{O} = 1/4/4$ and $4/4/1$ except that the positive shoulder is broader and more pronounced in the OD spectra. Therefore we would like to use the spectrum of the HDO/vapor interface to search for understanding of the water/vapor interface. Because OH and OD on HDO are decoupled, the OH(OD)-stretch spectrum is simply determined by how the OH(OD) bonds are arranged at the interface. Isotopic dilution was used in earlier attempts to deduce the spectrum of $|\chi_S^{(2)}(\omega_{IR})|^2$ for the HDO/vapor interface.^{5–7} With the limited amount of dilution, however, the spectrum obtained was contaminated by interfering contributions from the nonresonant background, $\chi_S^{(2)}$, and remnant H_2O in the diluted mixture, which could not be removed. This is not the case with direct measurement of $\text{Im } \chi_S^{(2)}(\omega_{IR})$. In the first approximation, $\text{Im } \chi_S^{(2)}(\omega_{IR})$ of an isotopic mixture can be regarded as the linear combination of $\text{Im } \chi_S^{(2)}(\omega_{IR})$ of the contributing isotopic components. By subtracting out the small contribution of H_2O to $\text{Im } \chi_S^{(2)}(\omega_{IR})$ for the H_2O /HDO/ D_2O

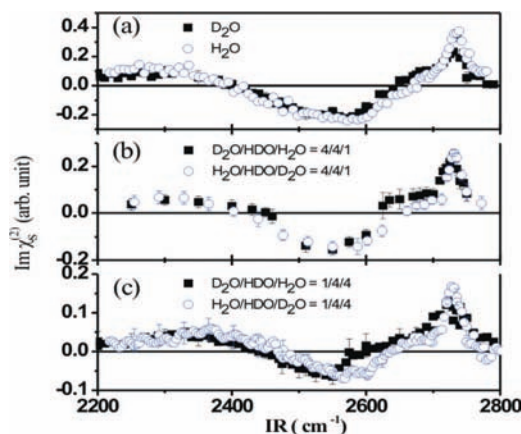


Figure 2. Comparison of $\text{Im } \chi_S^{(2)}(\omega_{IR})$ spectra for (a) $\text{H}_2\text{O}/\text{vapor}$ and $\text{D}_2\text{O}/\text{vapor}$ (with frequency rescaled by a factor 1.35) interfaces and for (b and c) water/vapor interfaces of two isotopic mixtures.

$=1/8/16$ case, we can obtain quite accurately the $\text{Im } \chi_S^{(2)}(\omega_{IR})$ spectrum of OH stretches for the HDO/vapor interface, shown in Figure 3 in comparison with that for the $\text{H}_2\text{O}/\text{vapor}$ interface. A

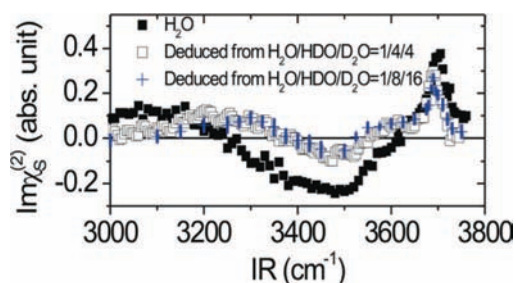


Figure 3. $\text{Im } \chi_S^{(2)}(\omega_{IR})$ for the HDO/vapor interface deduced from the spectra of the water/vapor interface of $\text{H}_2\text{O}/\text{HDO}/\text{D}_2\text{O} = 1/8/16$ (+) and $\text{H}_2\text{O}/\text{HDO}/\text{D}_2\text{O} = 1/4/4$ (□) in comparison with $\text{Im } \chi_S^{(2)}(\omega_{IR})$ for the $\text{H}_2\text{O}/\text{vapor}$ interface (■).

very similar spectrum (also presented in Figure 3) is obtained, although less accurately, from subtracting out the contribution of H_2O to $\text{Im } \chi_S^{(2)}(\omega_{IR})$ for the $\text{H}_2\text{O}/\text{HDO}/\text{D}_2\text{O} = 1/4/4$ case.

The SF spectrum of the water/vapor interface is dominated by contributions from roughly the first two molecular layers occupied by DAA, DDA, and DDAA molecules in a highly distorted H-bonding network.⁹ Here, D and A refer to donor and acceptor bonds through which the molecule connects with its neighbors. The broad $\text{Im } \chi_S^{(2)}(\omega_{IR})$ spectrum of the HDO/vapor interface in Figure 3 must come from the OH of HDO. The stretch frequency of OH is lower with stronger H-bonding (particularly donor bonding) and higher coordination on HDO. The sharp positive peak at 3690 cm^{-1} is readily assigned to the unbonded dangling OH stretch of DAA protruding at the surface. It is red-shifted by $\sim 10 \text{ cm}^{-1}$ from that of the $\text{H}_2\text{O}/\text{vapor}$ interface, also observed previously,⁵ suggesting

that coupling between the dangling OH and the donor-bonded OH in H_2O is not negligible. The positive band centered around 3300 cm^{-1} and the negative band around 3450 cm^{-1} appear at the same positions as the IR absorption bands of HDO in bulk ice and liquid (with bandwidths of ~ 100 and $\sim 300 \text{ cm}^{-1}$, respectively).^{12,13} Thus the OHs of the “ice-like” tetrahedrally bonded DDAA molecules with donor bonding to DAA and DDA in the topmost layer must have a dominating contribution to the positive band. This is consistent with the previous assignment of the positive “ice-like” band at 3200 cm^{-1} for the $\text{H}_2\text{O}/\text{vapor}$ interface.⁹ The red shift of the H_2O band results from coupling of the two OHs on H_2O that yields the downshifted symmetric stretch mode. (The antisymmetric mode is expected to be very weak in our SFVS geometry.) The OH of DDAA, DAA, and DDA more loosely donor-bonded to molecules below must have dominated over the negative “liquid-like” band. This is also consistent with the assignment of the H_2O case,⁹ but the band is narrower because OH and OD on HDO are decoupled. The positive shoulder below the sharp peak is broader and more prominent than in the H_2O case. Its spectral range suggests that it comes from weakly donor-bonded OH, but the positive amplitude indicates that the OH of DDAA pointing toward vapor must have dominated. Why the shoulder appears so different from that of the H_2O case is not clear, but presumably it is because the effect of the intramolecular coupling of OH is significant in the H_2O case. Why the shoulder in the OD stretch spectrum is more prominent is also not clear.

The $\text{Im } \chi_S^{(2)}$ spectrum we have deduced from PS-SFVS for the HDO/vapor interface is expected to be most helpful in our search for understanding of the water/vapor interfacial structure because of its relative simplicity. It is probably the first spectrum of water interfaces theorists should try to simulate.

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