# Identification of a wagging vibrational mode of water molecules at the water/vapor interface

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An improved time correlation function description of sum frequency generation (SFG) spectroscopy was applied to theoretically describe the water/vapor interface. The resulting spectra compare favorably in shape and relative magnitude to extant experimental results in the O—H stretching region of water. Further, the SFG spectra show a well-defined intermolecular mode at 875 cm$^{-1}$ that has significant intensity. The resonance is due to a wagging mode localized on a single water molecule. It represents a well-defined population of water molecules at the interface that, along with the free O—H modes, represent the dominant interfacial species.

Liquid water interfaces are ubiquitous and important in chemistry and the environment. Thus, with the advent of interface specific nonlinear optical spectroscopies, such interfaces have been intensely studied, both theoretically [1–6] and experimentally [7–9]. Sum frequency generation (SFG) spectroscopy is a powerful experimental method for probing the structure and dynamics of interfaces. SFG spectroscopy is dipole forbidden in isotropic media and interfaces serve to break the symmetry and produce a dipolar second-order polarization signal. The SFG experiment employs both a visible and infrared laser field overlapping in time and space at the interface, and in the absence of any vibrational resonance at the infrared laser frequency, a structureless signal due to the static hyperpolarizability of the interface is obtained [1,3,7,8]. When the infrared laser frequency corresponds to a vibration at the interface a resonant line shape is obtained with a characteristic shape that reflects both the structural and dynamical environment at the interface [10].

Here, classical molecular dynamics (MD) methods are used to model the dynamics of the water/vapor interface. Two complementary theoretical approaches—quantum-corrected time correlation function (TCF) and instantaneous normal mode (INM) methods—use the configurations generated by MD as input to describe the SFG spectrum of the interface and to ascertain the molecular origin of the SFG signal; both INM and TCF methods use a suitable spectroscopic (dipole and polarizability) model. This dual approach was demonstrated to be highly effective in understanding condensed phase spectroscopy of water, other liquids, and interfaces; classical mechanics, especially in the context of quantum-corrected TCF's, has proven to be surprisingly effective in modeling intramolecular vibrational spectroscopy [1,2,10–14].

An INM approximation to SFG spectroscopy is quantum mechanical by construction but offers a limited dynamical description. As a result, e.g., in bulk water, INM intramolecular resonances are broader than their TCF counterparts,

but with the same central frequency and integrated intensity. This suggests that the intramolecular INM spectra represent an underlying spectral density that is dynamically motionally narrowed in the actual line shape [10]. This is also found to be the case here for SFG spectra in all polarization conditions. This means that motional narrowing effects are important at interfaces and the dynamics is intermediate between the fast and slow modulation limits of motional narrowing. Most importantly this is a clear demonstration that SFG spectra contain both structural and dynamical signatures.

Previous TCF investigations of the water/vapor interface were limited to only following short time correlations and obtaining high-frequency spectra and used incorrect theoretical expressions [1–3]. In order to obtain better TCF results, especially at lower frequencies, long time correlations between the system dipole and polarizability need to be followed. Because molecular simulations of interfaces in Cartesian space necessarily produce two interfaces, simulation times were limited to the molecular diffusion time between interfaces so that molecules cannot contribute to signal at both interfaces during one MD run [1]. In this paper, a weak restraining potential is added that confines the molecules over time to the half of the simulation box they start in without significantly perturbing the relevant dynamics and the average structure of the liquid that contributes to the interfacial spectroscopy.

This modification permits the calculation of TCF's out to long times resulting in well-defined spectra that include intermolecular spectral line shapes. Surprisingly, a well-defined intermolecular mode was found to be prominent in the spectrum. It is centered at 875 cm$^{-1}$ and is comparable in (integrated) intensity to the rest of the intermolecular line shape. The line shape also has an intensity that is about a sixth of the magnitude of the intense free O—H stretching peak. Thus, a large and distinct population of interfacial water molecules has been identified. These modes, along with the well known free O—H oscillators are the dominant constituents of water/vapor interfaces and determine the physical and chemical properties of the interface.

Using INM methods the resonance is found to be due to a wagging mode localized on individual water molecules. The

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water molecules responsible are nearly parallel to the interface with their oxygen atoms anchored in the interface and the hydrogen atoms wagging normal to the interface. The hydrogens, pointing into the vapor phase, are hydrogen bonded to oxygen atoms at the interface. The presence of another distinct population of interfacial molecules, other than the free O—H stretch, was recently proposed [4,15,16]. That hypothesis is strongly supported by this paper. Here, a spectroscopically distinct species is directly observed and the vibrational mode responsible for the line shape is clearly identified. Thus, experimental SFG setups that permit taking spectra at relatively low wavelengths could probe this mode as a complement to the information contained in the free and donor O—H stretching modes.

The second-order response is given theoretically by a combination of resonant and nonresonant terms [2,3,7,17,18]. The resonant terms can be grouped to give a simple expression in terms of the systems polarizability and dipole. $\chi^{Res}(\omega)$ is given by [1,17,19]:

$$\chi^{Res}(\omega) = \frac{-i}{\hbar}\int_0^\infty dt e^{i\omega}\text{Tr}\{[\rho,\mu_i]\alpha_{jk}(t)\}. \quad (1)$$

In Eq. (1), $\rho = e^{-\beta H}/Q$ for a system with Hamiltonian $H$ and partition function $Q$ at reciprocal temperature $\beta = 1/kT$, and $k$ is Boltzmann's constant; $\mu$ is the system dipole, and $\alpha$ its polarizability tensor where the subscripts represent the vector and tensor components of interest, respectively. The operator evaluated at time $t$ is the Heisenberg representation of the operator $\alpha_{jk}(t) = e^{iHt/\hbar}\alpha_{jk}e^{-iHt/\hbar}$; Tr represents the trace of the operators. It is convenient to proceed by rewriting the Fourier-Laplace transform in Eq. (1) as the Fourier transform of a TCF that can then be interpreted in the classical limit and quantum corrected.

Equation (1) can be simplified, defining the real and imaginary parts of $\chi^{Res}(\omega) = \chi_R^{Res}(\omega) + i\chi_I^{Res}(\omega)$ gives [2]:

$$\chi_I(\omega) = \frac{2\pi}{\hbar}\tanh(\beta\hbar\omega/2)C_R(\omega) = \frac{2}{\hbar}\int_0^\infty \sin(\omega t)C_I(t)dt, \quad (2)$$

$$\chi_R(\omega) = \frac{2}{\hbar}P\int_{-\infty}^\infty \frac{\tanh(\beta\hbar\omega/2)C_R(\omega')}{\omega+\omega'}d\omega'$$

$$= \frac{2}{\hbar}\int_0^\infty \cos(\omega t)C_I(t)dt. \quad (3)$$

Note that previous expressions in the literature were mistaken although the expressions used did not significantly effect the modulus of the signal [1,3,19]. In Eq. (3), $P$ designates the principle part and the TCF, $C(t) = \langle\mu_i(0)\alpha_{jk}(t)\rangle = C_R(t) + iC_I(t)$, is defined in terms of its real and imaginary parts and their (real) Fourier transforms $C(\omega) = C_R(\omega) + C_I(\omega)$. The focus of SFG experiments is on high-frequency spectra where $(\hbar\omega \gg kT)$ and classical mechanics are clearly invalid.

The classical TCF result, $C_{Cl}(t)$ can be calculated using MD and TCF methods; $C_{Cl}(\omega)$ is the same as $C_R(\omega)$ in the classical limit. $C_R(\omega)$ is obtained for high frequencies via quantum correction using a "harmonic correction" factor: $C_R(\omega) = [(\beta\hbar\omega/2)\coth(\beta\hbar\omega/2)]\,C_{Cl}(\omega)$ [1,2]. This correction factor is exact in relating the (real part of the) classical harmonic coordinate correlation function to its quantum mechanical counterpart. $C_I(\omega)$ is then obtained using the exact result $C_I(\omega) = \tanh(\beta\hbar\omega/2)C_R(\omega)$. Thus the procedure is to calculate a classical TCF, $C_{Cl}(t)$, using MD and a suitable spectroscopic model, Fourier transform into frequency and quantum correct it to obtain $C_R(\omega)$ and then $C_I(\omega)$ that can be used in Eqs. (2) and (3).

To construct an INM approximation to Eq. (1) it is sufficient to evaluate the trace in Eq. (1) for a harmonic system, giving (in its classical form for consistency):

$$C_{Cl}(\omega) = \left\langle (\partial\mu_i/\partial Q_l)(\partial\alpha_{jk}/\partial Q_l)\delta(\omega-\omega_l)\frac{kT}{\omega^2} \right\rangle \quad (4)$$

In Eq. (4), $\omega_l$ is the frequency of mode $Q_l$ and the angle brackets here represent averaging over classical configurations of the system generated. $C_{Cl}(\omega)$ is then back transformed into the time domain and used in place of the classical TCF, in the procedure given above, to obtain an INM approximation to the spectroscopy.

The MD methods and spectroscopic model have been described previously [1]. Briefly, microcanonical MD was performed on an ambient water/vapor interface to generate a time ordered series of configurations (10 1.0-ns data sets)—a flexible simple point charge (SPC) model was used. The simulation consisted of 64 water molecules, and the spectra were checked for convergence by comparing with a 216-water-molecule simulation and the spectra were statistically indistinguishable. The interface was constructed using the standard MD geometry with vacuum (vapor) above and below the water. Unfortunately this produces two interfaces with average net dipoles in opposite directions and if molecules were allowed to diffuse from one interface to the other the SFG signal would be perturbed [1]; each interface is treated as a separate entity in calculating TCF's. This limited earlier investigations to relatively short time simulations and resulted in noisy spectra that were limited to the high frequency O—H stretching region [1,3].

To overcome this limitation, a weak (laterally isotropic) restraining potential in the direction normal to the interface was employed to keep a molecule in the half of the box that it started in for the length of the simulation [2,20]. The restraining potential becomes negligible near the interface and is only significant within $\approx 2.0$ Å of the box center. The interfacial density profile was unchanged by the restraining potential and it only significantly affects the long time diffusion constant in the normal direction [2].

The induced dipoles and polarizability tensor of each configuration is then calculated using a point atomic polarizability approximation (PAPA) polarizability model that includes many-body polarization effects explicitly and accounts for polarizability derivatives with bond-length-dependent point polarizabilities. The permanent dipoles are calculated based on *ab initio* data as described previously [1,3]. The TCF, $C_{Cl}(t)$, was calculated out to 50 ps where it has nearly de-
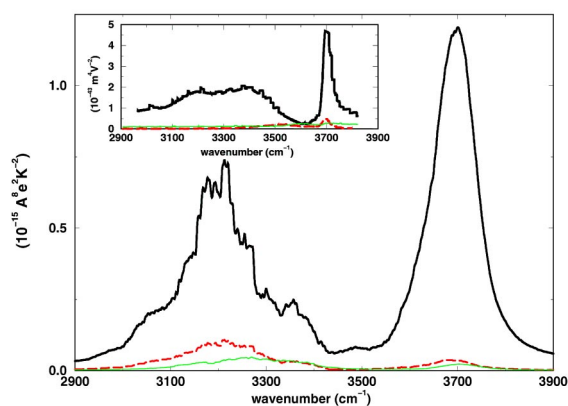
FIG. 1. (Color online) TCF SFG spectra in the O—H stretching region for three polarizations: *SSP* (thick, solid black line), *PPP* (dashed red line), and *SPS* (thin, solid green line). The inset is experimental data [7] for the same polarizations using the same color scheme.
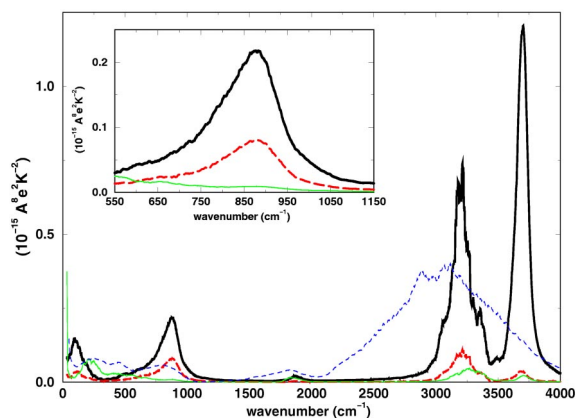


FIG. 2. (Color online) TCF SFG spectra for the entire water vibrational spectrum for three polarizations: *SSP* (thick, solid black line), *PPP* (thick, dashed red line), and *SPS* (thin, solid green line). The *SSP* INM SFG spectra is also shown (thin, dashed blue line). The inset highlights the intermolecular resonance at 875 cm$^{-1}$.

cayed to zero and is used to calculate the SFG spectra as described above.

Figure 1 displays the theoretical TCF SFG spectra in the O—H stretching region for the three independent polarization conditions that are possible in the electronically nonresonant experiment, i.e., *SSP*, *PPP*, and *SPS*. The theoretical spectra have been adjusted in relative intensity to account for the Fresnel factors that modify the experimental intensities [2,7]. The first two (last) index can be interpreted as the element of the system polarizability tensor (dipole) that is being probed, respectively—*S* denotes directions parallel to the surface and *P* perpendicular. In the data we have included the nonresonant contribution, $\chi^{N\,Res}(\omega)$, that is a small negative constant [3,8] and the full signal is given by $\chi^{(2)}_{SFG}(\omega) \propto |\chi^{Res}(\omega) + \chi^{N\,Res}(\omega)|^2$.

In Fig. 1, the free O—H peak is prominent at 3700 cm$^{-1}$ and the rest of the O—H stretching region has a more complicated shape. The inset of Fig. 1 displays experimental data for the O—H stretching region taken in the same polarization geometries [7]. The relative intensities agree nearly quantitatively between theory and experiment. The free O—H stretching line shape is captured very accurately by the theory and the rest of the O—H region has a similar shape. The ratio of relative intensities between the free O—H and the rest of the O—H stretching band are about 2:1 for both experiment and theory. Clearly the theory captures the essential features of the spectrum and its polarization dependence. To quantitate the polarization dependence, the ratio of the *SSP:PPP* intensities for the free O—H stretch, where the signal to noise is best, is 13:1 (10:1) for the theoretical (experimental) spectra, and the *SPS* is about a factor of three smaller than the *PPP* in both cases. The agreement is well within the relative error demonstrating the success of theoretical methods.

Figure 2 displays the theoretical SFG spectrum over the entire water vibrational spectrum. The theoretical INM spectrum (for the *SSP* geometry) is also shown. The INM and TCF spectra were found to integrate to the same value (over the entire 0–5000-cm$^{-1}$ range) and separately over the

O—H stretching region (2000–5000 cm$^{-1}$). This behavior is strong evidence for the interpretation of the INM line shape as an underlying spectral density that is motionally narrowed in the observed spectrum. This result also suggests that SFG spectra are sensitive to both structure and dynamics—the INM spectrum clearly exhibits the same resonances but is broader implying that the observed line shapes are motionally narrowed and dynamical contributions to SFG signals are important [2,7].

Most strikingly, Fig. 2 reveals an intense intermolecular resonance at 875 cm$^{-1}$. In contrast, the intermolecular spectrum of bulk water is relatively unstructured [10]. This symmetric line shape indicates a spectroscopically distinct species and represents—such as the free O—H stretch—a population of water molecules unique to the interface. It is roughly as intense as the rest of intermolecular spectrum and about a sixth of the intensity of the free O—H peak within our model (note that the bending line shape at higher frequency is much less intense). Recent experiments [15,16] and theory [4] indirectly inferred the presence of a surface species—a water molecule with two dangling hydrogens. Here we have directly identified the species and its spectroscopic signature. The spectrum is expected to be experimentally measurable using SFG but there has been a lack of intense infrared laser sources in this spectral region.

Figure 3 displays representative INM's from the O—H wagging region that give rise to the spectral signature. The mode is a wagging motion localized on a single water molecule, almost parallel to the interface, with two hydrogens displaced normal to the interface and the oxygen anchored in the interface. Further analysis revealed that, while the hydrogens appear to be freely oscillating into the vapor phase, they are both typically hydrogen bonded to an oxygen in the interface, based on standard hydrogen bonding criteria [4]. Indeed, it is the hydrogen bonding that provides the vibrational restoring force that results in a relatively high frequency intermolecular resonance.

The inset of Fig. 2 focuses in on the O—H wagging region and the polarization dependence of the signal is clear.
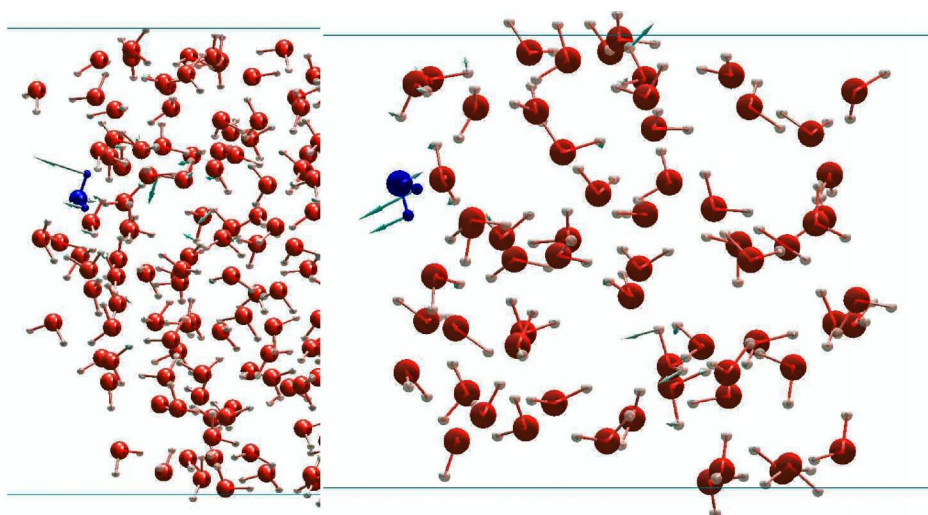
FIG. 3. (Color online) Two snapshots of a water/vapor interface containing 216 molecules and 64 molecules featuring INM's from the O—H wagging region at 864 and 950 cm$^{-1}$, respectively. The INM's are representative of a wagging motion localized on a single water molecule (shown in blue), almost parallel to the interface, with two hydrogens displaced normal to the interface and the oxygen anchored in the interface.

Both the *SSP* and *PPP* geometries show an intense line shape and are sensitive to motions (dipole derivatives) perpendicular to the interface. The *SPS* geometry shows only a hint of the signal consistent with its sensitivity to modes with dipoles changing parallel the surface. This analysis also highlights the ability of SFG spectra to infer intermolecular molecular geometries by examining the polarization dependence of the spectroscopy. Should appropriate infrared laser sources become available, this O—H wagging mode may represent another probe, in addition to O—H stretching, of interfacial structure and dynamics that couples to lower frequency dynamical processes.

In summary, a spectroscopically distinct interfacial species has been identified at the water/vapor interface via improved theoretical SFG spectra. The mode was found to be an O—H wagging motion localized on a single molecule and a similar species was suggested from earlier investigations [4,15,16]. The mode is currently difficult to detect using SFG spectroscopy. However, electronically and vibrationally doubly resonant second-order experiments may be able to detect the interfacial mode [21]. Lastly, this paper points out the power of theoretical spectroscopy in providing insight into MD simulations—many MD simulations of the water/vapor interface have been conducted but traditional analysis techniques do not easily reveal important interfacial subpopulations like the O—H wagging motions.

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