Motional Effect in Surface Sum-Frequency Vibrational Spectroscopy

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Fast orientational motion of molecules at a surface can affect the sum-frequency vibrational spectra of the surface. Calculation shows that the effect is significant if the molecular orientation varies over a broad range within the vibrational relaxation time. The stretch vibration of the free OH bonds at the vapor/water interface is used to illustrate the importance of the effect.

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Surface vibrational spectroscopy via infrared-visible sum-frequency generation (SFG) has been developed into a powerful tool to study structures of surfaces and interfaces [1]. It is highly surface specific and sensitive in media with inversion symmetry since the process is electric dipole allowed at the surface or interface but not in the bulk. With various input/output polarization combinations, the SFG vibrational spectra can yield detailed information about orientational distributions of selected atomic groups at a surface or interface [2–4].

In all quantitative SFG studies reported so far, the effects of rotational or librational motion of molecules on their vibrational spectra have been neglected. This, however, may not be a good approximation if the molecules move rapidly. In the latter case, two types of effects can be envisioned. One is the well-known motional narrowing effect, which reduces the inhomogeneous linewidth of a vibrational resonance [5]. The other is motional averaging, which may affect the strength of a vibrational resonance with a given input/output polarization combination. To our knowledge, this effect in vibrational spectroscopy has not been discussed before. In this paper we show that the motional averaging effect on SFG spectra can be significant and present an experimental case to demonstrate the effect.

Surface SFG results from a second-order nonlinear polarization $\mathbf{P}^{(2)}$ induced at a surface or interface by two input fields $\mathbf{E}_1$ and $\mathbf{E}_2$ at visible and infrared frequencies, respectively. In the time domain, we can write

$$\mathbf{P}^{(2)}(t) = N_S \langle \mathbf{p}^{(2)}(t) \rangle, \tag{1}$$

and (note [6])

$$p_\lambda^{(2)}(t) = -i\epsilon_0 \sum_q \sum_{\mu\nu} a_{q,\lambda\mu\nu} E_{1\mu}(t) \times \int_0^{+\infty} E_{2\nu}(t-\tau) e^{-i(\omega_q - i\Gamma_q)\tau}\, d\tau, \tag{2}$$

where N_S is the surface density of molecules, the angle brackets denote an ensemble average, $a_{q,\lambda\mu\nu}$, ω_q, and Γ_q are the amplitude, resonant frequency, and damping constant of the qth molecular vibrational mode, respectively, and the indices λ, μ, ν refer to the molecular coordinates. Here we assume that the visible input is far from resonance. We also neglect inhomogeneous broadening and nonresonant contributions in our discussion. Transformed into the lab coordinates i, j, k, Eq. (2) becomes

$$p_i^{(2)}(t) = -i\epsilon_0 \sum_q \sum_{jk} \sum_{\lambda\mu\nu} a_{q,\lambda\mu\nu} E_{1j}(t) D_{i\lambda}(t) D_{j\mu}(t) \times \int_0^{+\infty} D_{k\nu}(t-\tau) E_{2k}(t-\tau) e^{-i(\omega_q - i\Gamma_q)\tau}\, d\tau. \tag{3}$$

Here $D_{l\xi}(t) = \hat{l} \cdot \hat{\xi}(t)$ is a time-dependent direction cosine matrix with $l = i, j, k$ and $\xi = \lambda, \mu, \nu$, assuming that the molecular orientation varies with time. Fourier transformation into the frequency domain gives

$$\tilde{p}_i^{(2)}(\omega_s) = \frac{\epsilon_0}{2\pi} \sum_q \sum_{jk} \sum_{\lambda\mu\nu} \int_{-\infty}^{+\infty} dt \times \int_{-\infty}^{+\infty} d\omega_1 \int_{-\infty}^{+\infty} d\omega_2\, a_{q,\lambda\mu\nu} \times \Theta_{q,ijk}^{\lambda\mu\nu}(\omega_2, t) \tilde{E}_{1j}(\omega_1) \tilde{E}_{2k}(\omega_2) e^{i(\omega_s - \omega_1 - \omega_2)t}, \tag{4}$$

where

$$\Theta_{q,ijk}^{\lambda\mu\nu}(\omega_2, t) = -iD_{i\lambda}(t) D_{j\mu}(t) \times \int_0^{+\infty} D_{k\nu}(t-\tau) e^{i(\omega_2 - \omega_q + i\Gamma_q)\tau}\, d\tau. \tag{5}$$

Then, with Eqs. (4) and (5) and the relation

$$\tilde{P}_i^{(2)}(\omega_s) = N_S \langle \tilde{p}_i^{(2)}(\omega_s) \rangle = \epsilon_0 \sum_{jk} \int_{-\infty}^{+\infty} d\omega_1 \int_{-\infty}^{+\infty} d\omega_2 \times \delta(\omega_s - \omega_1 - \omega_2) \chi_{ijk}^{(2)}(\omega_2) \tilde{E}_{1j}(\omega_1) \tilde{E}_{2k}(\omega_2) \tag{6}$$

defining the surface nonlinear susceptibility $\chi_{ijk}^{(2)}(\omega_2)$, we find

$$\chi_{ijk}^{(2)}(\omega_2) = N_S \sum_q \sum_{\lambda\mu\nu} a_{q,\lambda\mu\nu} \langle \Theta_{q,ijk}^{\lambda\mu\nu}(\omega_2) \rangle. \tag{7}$$

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Being an ensemble average, $\langle \Theta_{q,ijk}^{\lambda\mu\nu}(\omega_2) \rangle$ in Eq. (7) is time independent.

If the molecular orientations are fixed in time, then

$$\Theta_{q,ijk}^{\lambda\mu\nu}(\omega_2) = \frac{1}{\omega_2 - \omega_q + i\Gamma_q} D_{i\lambda} D_{j\mu} D_{k\nu} , \tag{8}$$

which leads to

$$\chi_{ijk}^{(2)}(\omega_2) = N_{\mathrm{S}} \sum_q \sum_{\lambda\mu\nu} \frac{a_{q,\lambda\mu\nu}}{\omega_2 - \omega_q + i\Gamma_q} \langle D_{i\lambda} D_{j\mu} D_{k\nu} \rangle . \tag{9}$$

Equation (9) is the expression that has been commonly used for the analysis [2–4,7] and simulation [8] of SFG vibrational spectra. As the derivation shows, however, Eq. (9) is not necessarily correct if $D_{l\xi}(t)$ varies in time. It is still a good approximation, though, if $D_{l\xi}(t)$ varies much more slowly than the vibrational relaxation time $1/\Gamma_q$ (the slow-motion limit). In the other extreme, however, if the molecular orientation fluctuates very rapidly around the average orientation within the time scale $1/\Gamma_q$ (the rapid-motion limit), with

$$-i \int_0^{+\infty} D_{k\nu}(t - \tau) e^{i(\omega_2 - \omega_q + i\Gamma_q)\tau} \, d\tau \approx \frac{1}{\omega_2 - \omega_q + i\Gamma_q} \times \langle D_{k\nu}(t) \rangle \tag{10}$$

and the equivalence of temporal and ensemble averages, we find

$$\langle \Theta_{q,ijk}^{\lambda\mu\nu}(\omega_2) \rangle \approx \frac{1}{\omega_2 - \omega_q + i\Gamma_q} \langle D_{i\lambda} D_{j\mu} \rangle \langle D_{k\nu} \rangle , \tag{11}$$

and

$$\chi_{ijk}^{(2)}(\omega_2) \approx N_{\mathrm{S}} \sum_q \sum_{\lambda\mu\nu} \frac{a_{q,\lambda\mu\nu}}{\omega_2 - \omega_q + i\Gamma_q} \langle D_{i\lambda} D_{j\mu} \rangle \langle D_{k\nu} \rangle . \tag{12}$$

This is obviously different from Eq. (9). For the intermediate case between the two limits, we must refer to the more general expression for $\chi_{ijk}^{(2)}(\omega_2)$ [Eq. (7)].

A typical molecular vibrational damping coefficient $\Gamma_q/(2\pi c) \approx 10\ \mathrm{cm}^{-1}$ corresponds to a relaxation time $1/\Gamma_q \approx 0.5$ ps. The orientational fluctuations of molecules of liquids may occur on a comparable or shorter time scale and therefore could have an observable effect on the SFG surface vibrational spectra. We take the free (or dangling) OH bonds at the vapor/water interface as an example. The free OH stretch mode appears as a sharp peak at $\sim 3700\ \mathrm{cm}^{-1}$ in the SFG spectra [8,9]. Femtosecond pump-probe spectroscopy has found that the orientational relaxation time of HDO molecules in bulk D_2O is on a scale of 1 ps and decreases as the hydrogen bond strength decreases [10,11]. Therefore, we expect the orientational relaxation time of the free OH bonds at the vapor/water interface to be significantly smaller than 1 ps. To see how the SFG spectra can be affected by the OH orientational fluctuation, which may occur rapidly over a large solid angle, we calculate the resonant mode amplitudes for different polarization combinations in both slow- and rapid-motion limits. As seen from Eqs. (9) and (12), the mode amplitudes are given by

$$A_{q,ijk} = N_{\mathrm{S}} \sum_{\lambda\mu\nu} a_{q,\lambda\mu\nu} \langle D_{i\lambda} D_{j\mu} D_{k\nu} \rangle \tag{13}$$

for the slow-motion limit, and

$$A_{q,ijk} = N_{\mathrm{S}} \sum_{\lambda\mu\nu} a_{q,\lambda\mu\nu} \langle D_{i\lambda} D_{j\mu} \rangle \langle D_{k\nu} \rangle \tag{14}$$

for the rapid-motion limit. As in Ref. [9], we assume the only nonvanishing elements of $a_{q,\lambda\mu\nu}$ for a free OH bond are $a_{\zeta\zeta\zeta}$ and $a_{\xi\xi\zeta} = a_{\eta\eta\zeta}$, where $\hat{\zeta}$ is along the OH bond direction and $\hat{\xi}$ and $\hat{\eta}$ are perpendicular to $\hat{\zeta}$. From Raman measurements it was found that $a_{\xi\xi\zeta} = 0.32 a_{\zeta\zeta\zeta}$ [9,12]. To calculate the ensemble averages, we assume for the free OH bonds at the interface a step function orientational distribution

$$f(\theta) = \mathrm{const} \quad \text{for } 0 \le \theta \le \theta_{\mathrm{M}} ,$$

$$f(\theta) = 0 \quad \text{for } \theta > \theta_{\mathrm{M}} ,$$

in the bond tilt angle θ from the surface normal $\hat{z}$ (the azimuthal distribution is isotropic). We could also assume $f(\theta)$ to take other forms (e.g., a Gaussian distribution) without changing our general conclusion.

The SFG output from a surface is proportional to the square of the effective surface nonlinear susceptibility [3]

$$\chi_{\mathrm{eff}}^{(2)}(\omega_2) = \sum_q \frac{A_{q,\mathrm{eff}}}{\omega_2 - \omega_q + i\Gamma_q} , \tag{15}$$

with

$$A_{q,\mathrm{eff}} = [\mathbf{L}(\omega_s) \cdot \hat{\mathbf{e}}_s] \cdot \mathbf{A}_q \colon [\mathbf{L}(\omega_1) \cdot \hat{\mathbf{e}}_1][\mathbf{L}(\omega_2) \cdot \hat{\mathbf{e}}_2] , \tag{16}$$

where $\hat{\mathbf{e}}_i$ is the unit polarization vector of the field at ω_i and $\mathbf{L}(\omega_i)$ is the tensorial Fresnel factor [3]. The values of the Fresnel factors are listed in Table I (note [13]). We can then use Eq. (16) to calculate $A_{q,\mathrm{eff}}(\hat{\mathbf{e}}_s, \hat{\mathbf{e}}_1, \hat{\mathbf{e}}_2)$ and compare with experimentally deduced values.

TABLE I. Calculated Fresnel factors for the air/water interface. z is along the sample surface normal, with the xz plane being the light incidence plane. β is the incidence angle of the input or output beam. ϵ' is the effective dielectric constant of the surface monolayer.

	ω_s	ω_1	ω_2
λ	444 nm	532 nm	2.7 μm
n	1.34	1.34	1.18
β	46.7°	45°	57°
L_{xx}	0.95	0.95	1.04
L_{yy}	0.76	0.77	0.79
L_{zz}	$1.05/\epsilon_s'$	$1.05/\epsilon_1'$	$0.96/\epsilon_2'$
$e_x L_{xx}$ (p)	−0.66	0.67	0.57
$e_y L_{yy}$ (s)	0.76	0.77	0.79
$e_z L_{zz}$(p)	$0.76/\epsilon_s'$	$0.75/\epsilon_1'$	$0.80/\epsilon_2'$

We have calculated $A_{q,\mathrm{eff}}$ for three different polarization combinations ssp (denoting s-, s-, and p-polarized sum-frequency output, visible input, and infrared input, respectively), ppp, and sps in both slow- and rapid-motion limits. The results as functions of θ_{M} are presented in Fig. 1. For ssp and ppp, the difference between the two limits is appreciable only at large θ_{M}, which is understandable because the motional effect is important only if the motion covers a very broad range. For $A_{q,\mathrm{eff}}(sps)$, it vanishes in the rapid-motion limit for all θ_{M} because, from Eqs. (14) and (16), $A_{q,\mathrm{eff}}(sps) \propto A_{q,yzy} \propto \langle \hat{y} \cdot \hat{\zeta} \rangle = 0$, since $\langle \hat{\zeta} \rangle$ is along the surface normal $\hat{z}$. On the other hand, in the slow-motion limit, $A_{q,\mathrm{eff}}(sps)$ contains terms proportional to $\langle (\hat{y} \cdot \hat{\zeta})(\hat{z} \cdot \hat{\zeta})(\hat{y} \cdot \hat{\zeta}) \rangle$ and $\langle (\hat{y} \cdot \hat{\eta})(\hat{z} \cdot \hat{\eta})(\hat{y} \cdot \hat{\zeta}) \rangle$ that do not vanish for finite θ_{M}.

We have obtained experimentally the SFG spectra from the vapor/water interface with the polarization combinations specified above. The experimental setup has been described elsewhere [1]. In this experiment, a 1.5 mJ visible laser pulse at 532 nm and a 100 μJ infrared pulse tunable from 2900 to 3850 cm^{-1} (with a linewidth $\approx 6\ \mathrm{cm}^{-1}$) were overlapped at the sample surface with incidence angles of 45° and 57°, respectively. Both input pulses had a beam diameter of ~ 1 mm, a pulse width of ~ 15 ps, and a repetition rate of 20 Hz. The SFG output was detected in the reflected direction.

The measured spectra are depicted in Fig. 2. The SFG intensities have been calibrated with a reference z-cut quartz crystal [3], yielding the spectra of $|\chi_{\mathrm{eff}}^{(2)}(\omega_2)|^2$ in MKS units. The solid curves are fits using Eq. (15) with the addition of a nonresonant contribution to $\chi_{\mathrm{eff}}^{(2)}$. The free OH stretch mode appears at $\omega_q/(2\pi c) = 3698\ \mathrm{cm}^{-1}$, with $\Gamma_q/(2\pi c) = 14.5\ \mathrm{cm}^{-1}$ (including the finite infrared linewidth) and the following mode amplitudes:

$$A_{q,\mathrm{eff}}(ssp) = 1.70 \pm 0.15 \times 10^{-9}\ \mathrm{m}^2\,\mathrm{V}^{-1}\,\mathrm{sec}^{-1},$$
$$A_{q,\mathrm{eff}}(ppp) = 4.8 \pm 0.5 \times 10^{-10}\ \mathrm{m}^2\,\mathrm{V}^{-1}\,\mathrm{sec}^{-1},$$
$$A_{q,\mathrm{eff}}(sps) = 9 \pm 3 \times 10^{-11}\ \mathrm{m}^2\,\mathrm{V}^{-1}\,\mathrm{sec}^{-1}.$$

The two broad peaks at ~ 3200 and $\sim 3400\ \mathrm{cm}^{-1}$ in the ssp spectrum have been assigned to the more ordered and less ordered hydrogen-bonded OH stretch modes, respectively [14]. The resonant feature at 3500–3600 cm^{-1} in the ppp and sps polarization combinations, which has not been reported before for the vapor/water interface, is presumably associated with OH bonds that are only weakly perturbed by hydrogen bonding to neighbors. In this paper, our focus is on the free OH bonds only.

To compare the theory with experiment, we notice that from the experiment,

$$A_{q,\mathrm{eff}}(ssp){:}\,A_{q,\mathrm{eff}}(ppp){:}A_{q,\mathrm{eff}}(sps) = 1{:}0.28 \pm 0.04{:}0.05 \pm 0.02\,.$$

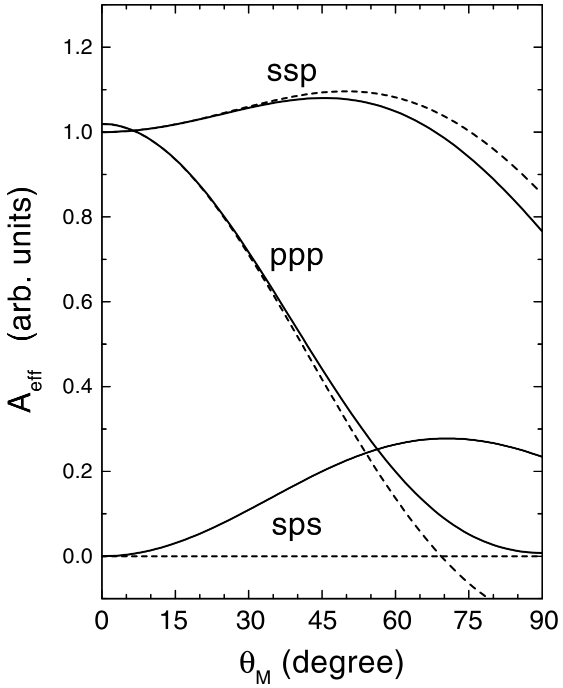

FIG. 1. Theoretical prediction of the mode amplitudes $A_{q,\mathrm{eff}}$ for the free OH bonds on the water surface. The solid lines are calculated for the slow-motion limit, and the dashed lines are for the rapid-motion limit. All values are normalized with respect to $A_{q,\mathrm{eff}}(ssp)$ at $\theta_{\mathrm{M}} = 0$.

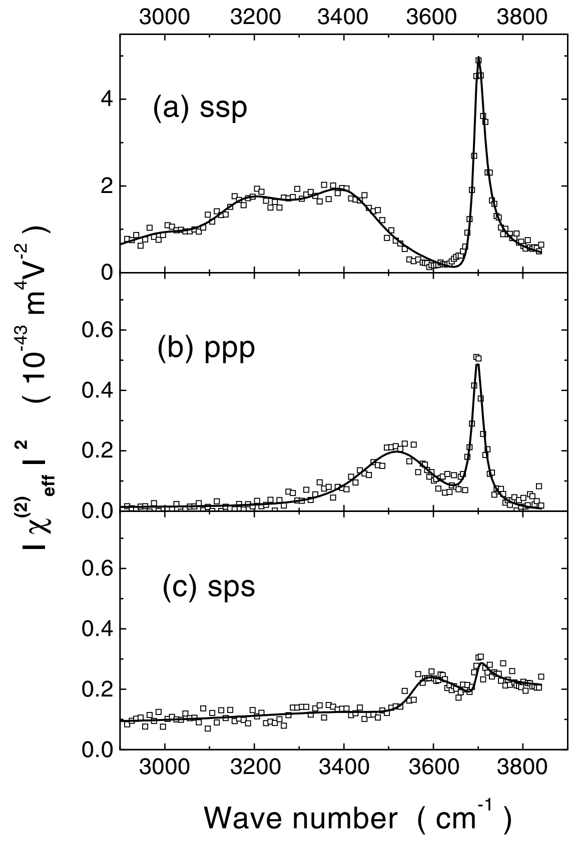

FIG. 2. OH SFG spectra of the water surface at 20 °C with three different polarization combinations ssp, ppp, and sps.

This does not agree with the ratio for any value of θ_M obtained from the set of curves for the slow-motion limit in Fig. 1. In other words, with the motional effect neglected, we cannot find a reasonable orientational distribution for the free OH bonds to explain the experimental results. The very small value of $A_{q,\mathrm{eff}}(sps)$ in comparison with $A_{q,\mathrm{eff}}(ssp)$ and $A_{q,\mathrm{eff}}(ppp)$ indicates that the motional effect is significant and that the rapid-motion limit is actually a better approximation. The theoretical curves for the rapid-motion limit in Fig. 1 predict that an orientational distribution with $\theta_\mathrm{M} = 51°$ should yield a ratio $A_{q,\mathrm{eff}}(ssp){:}A_{q,\mathrm{eff}}(ppp){:}A_{q,\mathrm{eff}}(sps) = 1{:}0.28{:}0$, which matches the experimental ratio better than the theoretical prediction based on the slow-motion limit.

We note that the theoretical result described here does not depend critically on the assumptions made for $a_{q,\lambda\mu\nu}$, ϵ', and $f(\theta)$. The motional effect is largely manifested by the unexpectedly weak mode strength in the sps SFG spectrum. This has been observed on other liquid surfaces as well. For example, the absence of the N-H stretch mode in the sps SFG spectrum of the surface of an ammonia-water solution [4] could also be the result of motional averaging. On the other hand, for larger molecules with slow orientational fluctuations, we can observe reasonably large values of $A_{q,\mathrm{eff}}(sps)$. One such example is the C-N stretch mode of pentylcyanoterphenyl (5CT) molecules on water, from which a ratio $\frac{A_{q,\mathrm{eff}}(sps)}{A_{q,\mathrm{eff}}(ssp)} \approx 0.4$ has been reported [2].

In summary, we have considered here an effect from the rotation or libration of molecules on surface sum-frequency vibrational spectroscopy. The free OH stretch mode at the vapor/water interface is used as an example to illustrate the significance of the effect. Difficulty in the interpretation of the SFG spectra would arise if the effect is neglected. In general, the effect of motional averaging should also be observable in infrared and Raman spectroscopy.

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$$\tilde{p}_\lambda^{(2)}(\omega_s) = \epsilon_0 \sum_q \sum_{\mu\nu} \int_{-\infty}^{+\infty} d\omega_1 \int_{-\infty}^{+\infty} d\omega_2\, \delta(\omega_s - \omega_1 - \omega_2) \times \frac{a_{q,\lambda\mu\nu}}{\omega_2 - \omega_q + i\Gamma_q} \tilde{E}_{1\mu}(\omega_1)\tilde{E}_{2\nu}(\omega_2)\,.$$

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