

Supplementary Information for Sum frequency generation, calculation of absolute intensities, comparison with experiments, and two-field relaxation-based derivation

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Supplementary Information

A. Projection from the molecule coordinates onto the lab coordinates. The averaging in Eq. 33 is over the phase space, Γ , including the coordinates in Q and the molecular orientations in the D s, and indeed over all coordinates other than the OH vibrational coordinate q . The product of the various D s with $\omega(Q[t])$ serves to distinguish the surface molecules from the molecules in the bulk, when ensemble averaged, since it will give rise to a zero SFG signal from the interior molecules. The exponential in Eq. 32 containing $\omega(Q)$ serves, in effect, to single out the contributions to the dangling OH peak, in the case of a water surface, from the contributions from the motion of the other H₂O vibrational coordinates.

$D_{l\xi}$ in Eq. 33 represents projection from molecule coordinates for the OH bond, $\hat{\xi} = (\hat{u}, \hat{v}, \hat{w})$, onto the lab coordinates, $\hat{l} = (\hat{x}, \hat{y}, \hat{z})$. (1) The \hat{z} axis of the lab coordinates points from bulk to vapor along the surface normal, while the xy plane is perpendicular to \hat{z} . The \hat{w} lies along the OH bond with a direction from O to H, while the $\hat{u}\hat{v}$ plane is perpendicular to \hat{w} . θ is the angle between \hat{w} and surface normal, while ϕ is the angle between the projection of \hat{w} onto the xy plane and the

\hat{x} axis. We then have

$$\begin{pmatrix} \hat{u} \\ \hat{v} \\ \hat{w} \end{pmatrix} = \begin{pmatrix} \cos \phi \cos \theta & \sin \phi \cos \theta & -\sin \theta \\ -\sin \phi & \cos \phi & 0 \\ \cos \phi \sin \theta & \sin \phi \sin \theta & \cos \theta \end{pmatrix} \begin{pmatrix} \hat{x} \\ \hat{y} \\ \hat{z} \end{pmatrix} \quad [\text{S1}]$$

Inserting Eq. S1 into Eq. 33, one finds that three items, $a_{q,www}$, $a_{q,uww}$, and $a_{q,vvw}$, survive after summing over all coordinates λ , μ , and ν . We then have

$$\begin{aligned} \chi_{ijk}^{(2)}(\omega) &= -iN_s \int_0^\infty e^{-i\omega t} \langle e^{i \int \omega(Q[t']) dt'} \\ &\times \{ [a_{www}(\hat{w}(0) \cdot \hat{i})(\hat{w}(0) \cdot \hat{j}) + a_{uww}(\hat{u}(0) \cdot \hat{i})(\hat{u}(0) \cdot \hat{j}) \\ &+ a_{vvw}(\hat{v}(0) \cdot \hat{i})(\hat{v}(0) \cdot \hat{j})] [\hat{r}(t) \cdot \hat{k}] \} > dt \end{aligned} \quad [\text{S2}]$$

The right hand side of Eq. S2 can be interpreted as the ensemble average of the projection of the molecule hyperpolarizabilities onto the i , j and k polarization vectors.

For simplicity, we may assume that the hyperpolarizabilities perpendicular to the OH bond are the same. Then Eq. S2 becomes(1)

$$\begin{aligned} \chi_{ijk}^{(2)}(\omega) &= -iN_s \int_0^\infty e^{-i\omega t} \langle e^{i \int_0^t \omega(Q[t']) dt'} \\ &\times \{ [a_{\parallel}(\hat{r}(0) \cdot \hat{i})(\hat{r}(0) \cdot \hat{j}) + a_{\perp}(\hat{i} \cdot \hat{j}) \\ &- a_{\perp}(\hat{r}(0) \cdot \hat{i})(\hat{r}(0) \cdot \hat{j})] [\hat{r}(t) \cdot \hat{k}] \} > dt \end{aligned} \quad [\text{S3}]$$

where $a_{\parallel} = a_{q,www}$ and $a_{\perp} = a_{q,uww} = a_{q,vvw}$. $\hat{r}(t)$ is the OH bond unit vector.

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B. Integrated SSP SFG intensity for Ref. (2). The integrated SSP SFG intensity for dangling OH region in Fig. 1 of Ref. (2) is $1.2 \times 10^{-13} \text{A}^8 \text{e}^2 \text{K}^{-2} \text{cm}^{-1}$. Presuming that A is angstrom, 10^{-10} m, that e is the electronic charge, $1.6 \times 10^{-19} \text{C}$, and that K is the energy unit Kelvin ^{*}, where $1\text{K} = 1.38 \times 10^{-23} \text{J}$ ($8.63 \times 10^{-5} \text{eV}$). So $1.2 \times 10^{-13} \text{A}^8 \text{e}^2 \text{K}^{-2} \text{cm}^{-1} = 1.6 \times 10^{-85} \text{m}^8 \text{V}^{-2} \text{cm}^{-1}$. Then, the value should be divided by the surface area ($18.7 \times 18.7 \text{A}^2$) square, i.e. $1.6 \times 10^{-85} \text{m}^8 \text{V}^{-2} \text{cm}^{-1}$ divide by $(18.7 \times 18.7 \cdot 10^{-20} \text{m}^2)^2 = 1.3 \times 10^{-50} \text{m}^4 \text{V}^{-2} \text{cm}^{-1}$.

1. Wang Y, Hodas NO, Jung Y, Marcus RA (2011) Microscopic structure and dynamics of air/water interface by computer simulations-comparison with sum-frequency generation experiments. *Phys. Chem. Chem. Phys.* 13(12):5388--5393.
2. Perry A, Neipert C, Ridley C, Space B, Moore PB (2005) Identification of a wagging vibrational mode of water molecules at the water/vapor interface. *Phys. Rev. E* 71(5):050601.

^{*}K is normally a unit of absolute temperature but for the units of $|\chi_{\text{eff}}^{(2)}|^2$ in Ref. (2) to translate into the conversional units, we took it to be a unit of energy.