

Supporting information to the article
**A Vibrational Sum Frequency Spectroscopy Study of the Liquid/Vapor
Interface of Formic Acid/Water Solutions**
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The equations used in the numerical and graphical methods to obtain the molecular orientation are given below:^{1,2}

The SF intensity is described as:

$$I_{SF}(\omega_{SF}) = \frac{8\pi^3 \sec^2 \beta_{SF}}{c^3 n_1(\omega_{SF}) n_1(\omega_{vis}) n_1(\omega_{IR})} \left| \chi_{eff}^{(2)} \right|^2 I_{IR}(\omega_{IR}) I_{vis}(\omega_{vis}) \quad (1)$$

where β_{SF} is the angle of incidence of the SF beam, c the speed of light, n the refractive indices in air, $\chi_{eff}^{(2)}$ the effective susceptibility, I_{IR} and I_{vis} the IR and vis. beam intensities.

The susceptibility contains two contributions, one resonant ($\chi_R^{(2)}$) and one nonresonant ($\chi_{NR}^{(2)}$):

$$\chi^{(2)} = \chi_{NR}^{(2)} + \sum_n \chi_{R,n}^{(2)} \quad (2)$$

where the sum is taken over all surface vibrations contributing to the SF signal. The macroscopic nonlinear susceptibility is related to the microscopic hyperpolarizability, $\beta^{(2)}$, averaged over all molecular orientations, $\langle \beta^{(2)} \rangle$:

$$\chi_{R,n}^{(2)} = \frac{N_s}{\epsilon_0} \langle \beta_n^{(2)} \rangle \quad (3)$$

where N_s is the number of molecules per unit area. The hyperpolarizability can be expressed in terms of the IR transition dipole moment, μ_γ , and the Raman tensor, $\alpha_{\alpha\beta}$, according to

$$\beta_{\alpha\beta\gamma}^{(2)} = \frac{\alpha_{\alpha\beta} \mu_\gamma}{\omega_n - \omega_{IR} - i\Gamma} \quad (4)$$

where ω_n is an IR transition frequency, ω_{IR} the laser frequency, and Γ the damping constant.

The effective susceptibility in equation 1 is expressed as

$$\chi_{eff}^{(2)} = [\hat{e}(\omega_{SF}) \cdot L(\omega_{SF})] \cdot \chi^{(2)} : [L(\omega_{vis}) \cdot \hat{e}(\omega_{vis})] [L(\omega_{IR}) \cdot \hat{e}(\omega_{IR})] \quad (5)$$

where $\hat{e}(\omega_n)$ are the unit polarization vectors and $L(\omega_n)$ the Fresnel factors:

$$L_{xx}(\omega_n) = \frac{2n_1(\omega_n) \cos \gamma_n}{n_1(\omega_n) \cos \gamma_n + n_2(\omega_n) \cos \beta_n} \quad (6a)$$

$$L_{yy}(\omega_n) = \frac{2n_1(\omega_n) \cos \beta_n}{n_1(\omega_n) \cos \beta_n + n_2(\omega_n) \cos \gamma_n} \quad (6b)$$

$$L_{zz}(\omega_n) = \frac{2n_2(\omega_n) \cos \beta_n}{n_1(\omega_n) \cos \gamma_n + n_2(\omega_n) \cos \beta_n} \left(\frac{n_1(\omega_n)}{n'(\omega_n)} \right)^2 \quad (6c)$$

where L_{xx} , L_{yy} , and L_{zz} are the diagonal elements of the Fresnel tensor, β_n and γ_n are the incident and refracted angles for the respective beams, and $n'(\omega_n)$ are the interfacial refractive indices.

For a $C_{\infty v}$ point group at an azimuthally isotropic surface (such as the CH and C=O bonds in formic acid), the following susceptibility elements are nonzero:

$$\chi_{yyz} = \chi_{xxz}, \chi_{zyz} = \chi_{xzx}, \chi_{zyy} = \chi_{zxx}, \text{ and } \chi_{zzz} \quad (7)$$

For the polarization combinations ssp, ppp, and sps, used in this paper, the expressions of the effective susceptibilities take the form:

$$\chi_{eff,ssp}^{(2)} = L_{yy}(\omega_{SF}) L_{yy}(\omega_{vis}) L_{zz}(\omega_{IR}) \sin \beta_{IR} \chi_{yyz} \quad (8a)$$

$$\chi_{eff,sps}^{(2)} = L_{yy}(\omega_{SF}) L_{zz}(\omega_{vis}) L_{yy}(\omega_{IR}) \sin \beta_{vis} \chi_{zyy} \quad (8b)$$

$$\begin{aligned} \chi_{eff,ppp}^{(2)} = & -L_{xx}(\omega_{SF}) L_{xx}(\omega_{vis}) L_{zz}(\omega_{IR}) \cos \beta_{SF} \cos \beta_{vis} \sin \beta_{IR} \chi_{xxz} \\ & - L_{xx}(\omega_{SF}) L_{zz}(\omega_{vis}) L_{xx}(\omega_{IR}) \cos \beta_{SF} \sin \beta_{vis} \cos \beta_{IR} \chi_{xzx} \\ & + L_{zz}(\omega_{SF}) L_{xx}(\omega_{vis}) L_{xx}(\omega_{IR}) \sin \beta_{SF} \cos \beta_{vis} \cos \beta_{IR} \chi_{zxx} \\ & + L_{zz}(\omega_{SF}) L_{zz}(\omega_{vis}) L_{zz}(\omega_{IR}) \sin \beta_{SF} \sin \beta_{vis} \sin \beta_{IR} \chi_{zzz} \end{aligned} \quad (8c)$$

The tensor elements in equation 8 can be expressed as

$$\chi_{xxz,s} = \chi_{yyz,s} = \frac{1}{2} N_s \beta_{ccc} ((1+r) \cos \theta - (1-r) \cos^3 \theta) \quad (9a)$$

$$\chi_{xzx,s} = \chi_{zyy,s} = \chi_{zxx,s} = \chi_{zyy,s} = \frac{1}{2} N_s \beta_{ccc} (1-r)(\cos \theta - \cos^3 \theta) \quad (9b)$$

$$\chi_{zzz,s} = N_s \beta_{ccc} (r \cos \theta + (1-r) \cos^3 \theta) \quad (9c)$$

where the r factor is related to the Raman depolarization ratio ρ according to

$$\rho = \frac{3}{4} \left(1 + \frac{5}{4} \left(\frac{2r+1}{r-1} \right)^2 \right)^{-1} \quad (10)$$

In accordance with equation 2-4, all spectra were fitted by Lorentzian line shapes of the form:

$$\chi_{eff}^2(\omega_{SF}) = A_{NR} + \sum_n \frac{A_n}{\omega_n - \omega_{IR} - i\Gamma} \quad (11)$$

where A_{NR} is the nonresonant amplitude, and A_n the resonant amplitude.

In the numerical method, the experimentally obtained amplitude ratios (A_{ssp}/A_{ppp} , A_{ssp}/A_{sps} , A_{ppp}/A_{sps}) from equation 11 are matched with the ratios of the theoretical equations 8a-c. Subsequently, the nonlinear equation systems are solved in Matlab with the ranges of the amplitude ratios and depolarization ratios restricted as specified in the paper, yielding the interval of the CH and C=O tilt angles.

In the graphical method, the theoretical curves of the effective susceptibility ratios in equation 8a-c are plotted as functions of the tilt angle, which is obtained by inserting the amplitude ratios generated in the fits (equation 11).

The numerical and the graphical methods are based on the same equations and therefore yield the same tilt angles.

References

- (1) Wang, J.; Chen, C; Buck, S.M.; Chen, Z., *J. Phys. Chem. B* **2001**, 105, 12118.
- (2) Tyrode, E.; Johnson, C. M.; Baldelli, S.; Leygraf, C.; Rutland, M. W. *J. Phys. Chem. B* **2005**, 109, 329.