Supporting Information

Interfacial molecular organization at aqueous solution surfaces of atmospherically relevant dimethylsulfoxide and methane sulfonic acid using sum frequency spectroscopy and molecular dynamics simulation

Xiangke Chen[1], Babak Minofar[2], Pavel Jungwirth[3], and Heather C. Allen[1*]

Polarization null angle method

As mentioned in the paper the average molecular orientation can be retrieved from the measured ratio of VSFG intensities in different polarization combinations. However, sometimes the VSFG intensity of a specific polarization combination could be very low (for example, the ppp spectrum of DMSO CH_3 is more than 10 fold lower than the ssp spectrum), which as a result leads to large experimental errors in orientation analysis from a quantitative aspect.

Polarization null angle method, as shown in the literature,[1, 2] can improve the accuracy of the measured ratio of macroscopic second-order susceptibilities $\chi^{(2)}$. In VSFG experiment the polarization of the output sum frequency beam is determined by the polarization of incident visible and IR beams and the macroscopic second-order susceptibilities $\chi^{(2)}$. If we incorporate the polarization angle of each beam, the total effective second-order susceptibilities $\chi^{(2)}$ can be written as:[1]

$$\chi^{(2)}_{eff,total} = \chi^{(2)}_{eff,ssp} + \chi^{(2)}_{eff,sps} + \chi^{(2)}_{eff,pss} + \chi^{(2)}_{eff,ppp}$$

$$\begin{aligned}
\chi^{(2)}_{eff,total} &= \sin\Omega_{SF}\sin\Omega_{vis}\cos\Omega_{IR}L_{yy}(\omega_{SF})L_{yy}(\omega_{vis})L_{zz}(\omega_{IR})\sin\theta_{IR}\chi_{yyz} \\
&+ \sin\Omega_{SF}\cos\Omega_{vis}\sin\Omega_{IR}L_{yy}(\omega_{SF})L_{zz}(\omega_{vis})L_{yy}(\omega_{IR})\sin\theta_{vis}\chi_{yzy} \\
&+ \cos\Omega_{SF}\sin\Omega_{vis}\sin\Omega_{IR}L_{zz}(\omega_{SF})L_{yy}(\omega_{vis})L_{yy}(\omega_{IR})\sin\theta_{SF}\chi_{zyy} \qquad (1) \\
&- \cos\Omega_{SF}\cos\Omega_{vis}\cos\Omega_{IR}L_{xx}(\omega_{SF})L_{xx}(\omega_{vis})L_{zz}(\omega_{IR})\cos\theta_{SF}\cos\theta_{vis}\sin\theta_{IR}\chi_{xxz} \\
&- \cos\Omega_{SF}\cos\Omega_{vis}\cos\Omega_{IR}L_{xx}(\omega_{SF})L_{zz}(\omega_{vis})L_{xx}(\omega_{IR})\cos\theta_{SF}\sin\theta_{vis}\cos\theta_{IR}\chi_{xzx} \\
&+ \cos\Omega_{SF}\cos\Omega_{vis}\cos\Omega_{IR}L_{zz}(\omega_{SF})L_{xx}(\omega_{vis})L_{xx}(\omega_{IR})\sin\theta_{SF}\cos\theta_{vis}\cos\theta_{IR}\chi_{zxx} \\
&+ \cos\Omega_{SF}\cos\Omega_{vis}\cos\Omega_{IR}L_{zz}(\omega_{SF})L_{zz}(\omega_{vis})L_{zz}(\omega_{IR})\sin\theta_{SF}\sin\theta_{vis}\sin\theta_{IR}\chi_{zzz}
\end{aligned}$$

where Ω_{SF}, Ω_{vis} and Ω_{IR} are the detection polarization angles of the sum frequency beam, of the visible beam, and the IR beam, respectively. Here Ω = 0° for p-polarization and Ω = 90° for s-polarization. If the incident visible beam is s-polarized and IR is p-polarized then the effective susceptibility $\chi_{eff,total}^{(2)}$ is reduced to $\chi_{eff,ssp}^{(2)}$.

Typically, a p-polarized (0°) IR pulse and a - 45° linear polarized (half s and half p polarized) visible pulse are used for in polarization null angle method. In this case, Equation (1) is reduced as:

$$\chi^{(2)}_{eff,total} = \frac{\sqrt{2}}{2}(\chi^{(2)}_{eff,ppp}\cos\Omega_{SF} - \chi^{(2)}_{eff,ssp}\sin\Omega_{SF}) \qquad (2)$$

Therefore a null angle in detection polarization is inferred from Equation (2) at which the VSFG intensity will vanish, with:

$$\begin{aligned} &\chi^{(2)}_{eff,total} = 0 \\ &\tan\Omega_{null,SF} = \chi^{(2)}_{eff,ppp} / \chi^{(2)}_{eff,ssp} \end{aligned} \qquad (3)$$

Because the VSFG intensity is proportional to the absolute square of $\chi_{eff,total}^{(2)}$, the null angle can be retrieved through fitting of the measured VSFG intensity at a range of detection polarization angles as shown in Equation (4):

$$I_{SF} = \left|\chi^{(2)}_{eff,total}\right|^2 = A\left|\sin(\Omega_{SF} - \Omega_{null,SF})\right|^2 \qquad (4)$$

The macroscopic second-order susceptibility ratio obtained from the polarization null angle method is similar to the VSFG intensity ratio of different polarizations, which can then be used for orientation analysis.

Fresnel Factors

VSFG experiments can be conducted with a variety of polarization combinations of incident visible and IR pulses such as ssp, sps, pss and ppp, where the three polarizations refer to the polarization of sum frequency light, visible light, and IR light in that order. For instance, ssp means s-polarized output sum frequency signal with s-polarized incident visible and p-polarized incident IR pulses. The s-polarized light has its electric field vector perpendicular to the plane of incidence, while the p-polarized light has its electric field vector parallel to the plane of incidence. The Fresnel factors serve as the local-field correction factors of each electric field at the interface. For reflection VSFG geometry, Fresnel factors are functions of the refractive indices of the beam in different media, the incident (reflection) angle and the refractive angle:[3]

$$L_{xx}(\omega_i) = \frac{2n_1(\omega_i)\cos\gamma_i}{n_1(\omega_i)\cos\gamma_i + n_2(\omega_i)\cos\theta_i}$$

$$L_{yy}(\omega_i) = \frac{2n_1(\omega_i)\cos\theta_i}{n_1(\omega_i)\cos\theta_i + n_2(\omega_i)\cos\omega_i} \quad (5)$$

$$L_{zz}(\omega_i) = \frac{2n_2(\omega_i)\cos\theta_i}{n_1(\omega_i)\cos\gamma_i + n_2(\omega_i)\cos\theta_i}\left(\frac{n_1(\omega_i)}{n'(\omega_i)}\right)^2$$

in which $n_m(\omega_i)$ is the refractive index of medium m (m = 1, 2, ') at frequency ω_i (i = SF, vis, IR), θ_i is the incident (reflection for SF) angle to the surface normal in medium 1 and γ_i is the refractive angle into medium 2 defined by Snell's $n_1(\omega_i)\sin\theta_i = n_2(\omega_i)\sin\gamma_i$. In Fresnel factors, all variables are known values except for the refractive index of the interface $n'(\omega_i)$. The value of $n'(\omega_i)$ can be estimated from an empirical model with $n_1(\omega_i) = 1$:[3]

$$\left(\frac{1}{n'(\omega_i)}\right)^2 = \frac{4n_2^2(\omega_i)+2}{n_2^2(\omega_i)(n_2^2(\omega_i)+5)} \quad (6)$$

In this work, the refractive index of air/aqueous solution interface is chosen to be 1.18.[3] The refractive indices of bulk 0.2 *x* DMSO and 0.1 *x* MSA are 1.40 and 1.37 for visible; 1.41 and 1.42 for IR, respectively as shown in Table 1.[4, 5] It should be pointed out that the refractive indices for IR have little effect on the retrieved orientation angles under the current experiment setup. The incident angles of visible and IR are 53° and 68°, respectively.

Refractive indices used for orientation calculations

Table S1. Refractive index for DMSO and MSA used in orientation calculations.

	0.2 *x* DMSO		0.1 *x* MSA	
	vis	IR	*vis*	IR
n_1	1	1	1	1
n_2	1.40	1.41	1.37	1.42
interface n'	1.18	1.18	1.18	1.18

Raman depolarization ratio data

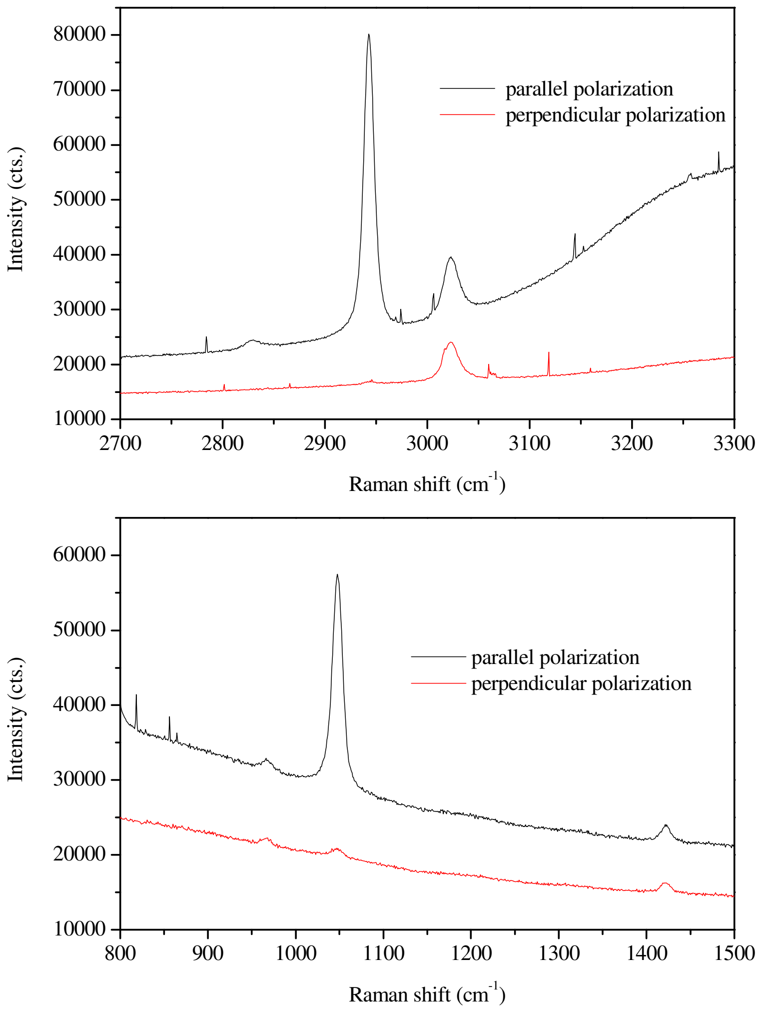

Figure S1. Polarized Raman spectra of MSA CH_3 and SO_3^- groups.

References

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