Absolute Orientation of Molecules at Interfaces

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A method to determine the absolute orientation of molecules at liquid interfaces by sum frequency generation (SFG) is reported. It is based on measurements of the orientations of two nonparallel vibrationally active chromophores in the molecule of interest combined with a rotation matrix formulation to obtain the absolute molecular orientation. We chose *m*-tolunitrile, a planar molecule adsorbed to the air/water interface, as a proof-of-method experiment. Quantitative analysis of different polarization sum frequency intensities facilitate unique peak assignments of the methyl and nitrile groups of *m*-tolunitrile. The SFG analysis of the measurement yields a nitrile group tilting at 53° to the surface normal, and the C_3 axis of the methyl group is almost upright at 23° with respect to the surface normal. Using a rotation matrix formulation, we found that the angle between the surface plane and the *m*-tolunitrile molecular plane is 70°.

1. Introduction

Knowledge of molecular orientation at surfaces and interfaces is of widespread interest to scientists because of its relevance to chemical reactions, long- and short-range molecular interactions, phase transitions, and the electronic and vibrational states of interfacial molecules.[1−3] Because the molecular interface is only a few molecules thick, interfacial populations are very small. As a consequence, a useful optical technique must be interface specific and sensitive to composition, orientation, and structure at the interface. Second harmonic generation (SHG) and sum frequency generation (SFG), as second-order interactions, can be employed to specifically investigate interfaces that are accessible to light, including buried interfaces.[2,3] SHG depends primarily on the electronic properties of the interfacial molecules, whereas SFG is sensitive to molecular vibrations when one of the incident beams is in the infrared. Traditionally, SFG has been performed by scanning the incident IR light point by point and mixing it with visible light of picosecond or nanosecond duration. A new approach to the measurement of vibrational spectra using SFG (broadband SFG) has been developed and has proven to be successful.[4] It entails combining a spectrally broad IR pulse, which is characteristic of femtosecond IR pulses, with a spectrally narrow visible pulse.[4] In the frequency-resolved SFG experiment, the bandwidth of the incident IR pulse is much larger than that of the vibrational resonance. The frequency-resolved sum frequency signals cover several hundred wavenumbers, which makes it possible to more rapidly obtain vibrational spectra of interest. The spectral resolution results from the spectrally narrow (10 cm^{-1}) picosecond visible laser pulse.

With the recent developments in laser technology, SFG is widely used not only in fundamental studies of interfaces, but also in technological studies of catalysis, chemical vapor deposition, electrochemistry, polymers, and environmental interfaces.[2,3,5−8] Orientation measurements of chemical groups at interfaces and surfaces were realized soon after the SFG technique was applied to the study of interfaces and surfaces.[9] Recently, the orientational angle with respect to the surface normal and the twist angle relative to the plane comprising the surface normal and the symmetry axis of the isopropyl head-group of a leucine molecule at the air/water interface was measured.[10] However, a complete determination of the absolute orientation of this entire molecule or other molecules has not been reported.

The basic idea of the method reported here is to measure the orientations of two SFG active chromophores with respect to the surface normal to obtain the absolute orientation defined by both symmetry axes and the molecular plane with respect to the surface normal. Combining these measured values with the known orientations of the chromophores with respect to each other in the molecule together with a rotation matrix operation formulation, we obtain the absolute orientation of the interfacial molecule. Generally, the alignment of the molecule at the interface, that is, which part of the molecule projects toward which bulk phase, is known. If not, phase measurements will provide the up versus down alignment. We chose *m*-tolunitrile, which is a planar molecule having two distinct vibrational chromophores, as a proof-of-method example to demonstrate how to obtain the absolute orientation of the molecule at the interface.

2. Theoretical Considerations

Here we shall briefly outline the fundamental theory of SFG as it applies to surfaces and interfaces to facilitate the discussion that follows. We consider the case of two incident lasers, one infrared and one visible, neither of which is one- or two-photon resonant with excited electronic states.

The sum frequency intensity is proportional to the square of the sum over all macroscopic sum frequency susceptibility terms separated into a nonresonant part, $\chi^{(2),NR}$, and a resonant part, $\chi^{(2),R}(\omega)$.

$$I^{SF}(\omega) \propto |\chi^{(2),NR} + \sum_{q}^{n} \chi^{(2),R}(\omega, q)|^2$$

$$\chi^{(2),R}(\omega, q) \propto \frac{A_q}{\omega_{ir} - \omega_q + i\Gamma_q} \tag{1}$$

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where A_q contains the product of the Raman and IR matrix elements of the qth normal mode, ω_q denotes the resonant frequency of the qth vibrational normal mode, ω_{ir} is the frequency of the IR light, and Γ_q is the spectral width of the vibrational state. In the case of dielectric interfaces, the contribution from the nonresonant parts is small compared to the resonant terms of interest.

Here we define the *XY* plane in the laboratory coordinate system (*X*, *Y*, *Z*) as the plane of the interface, the *Z* axis as the surface normal, and *YZ* as the plane of incidence. Among the total 27 macroscopic susceptibility tensors $\chi^{(2)}_{IJK}$ (*I*, *J*, and *K* being the three laboratory coordinates), there are 7 nonzero terms for a rotationally isotropic interface ($C_{\infty v}$ symmetry), namely, $\chi^{(2)}_{XXZ} = \chi^{(2)}_{YYZ}$; $\chi^{(2)}_{XZX} = \chi^{(2)}_{YZY}$; $\chi^{(2)}_{ZXX} = \chi^{(2)}_{ZYY}$; and $\chi^{(2)}_{ZZZ}$. In our experiments the *YZ* plane was the plane of incidence for both the visible and IR beams. The two polarization combinations measured in each experiment were *SSP* and *PPP*, where the first letter denotes the polarization of the sum frequency, the second one denotes the polarization of the visible light, and the last one denotes the polarization of the IR light. These polarizations are connected with the laboratory coordinates by nonlinear Fresnel coefficients and appropriate projections.[11−13] The seven nonzero macroscopic susceptibilities in the laboratory coordinates are obtained from the four polarization combinations.

We approximate the macroscopic sum frequency susceptibility tensors $\chi^{(2),R}_{IJK}(\omega)$ in the laboratory coordinates (*X*, *Y*, *Z*) (*I*, *J*, and *K* being the three coordinates) with the microscopic hyperpolarizability tensor elements $\beta^{(2)}_{ijk}$ in the molecular coordinates (*x*, *y*, *z*) (*i*, *j*, and *k* being the three coordinates) yielding

$$\chi^{(2)}_{IJK} = N_s \langle (\hat{I}\cdot\hat{i})(\hat{J}\cdot\hat{j})(\hat{K}\cdot\hat{k}) \rangle \beta^{(2)}_{ijk} = N_s \langle \hat{R}_{I\cdot i}\hat{R}_{J\cdot j}\hat{R}_{K\cdot k} \rangle \beta^{(2)}_{ijk} \quad (2)$$

where N_s is the number density of the interface moiety under investigation, $\hat{R}$ is the element of the rotation transformation matrix from the molecular frame to the laboratory frame, and $\langle\,\rangle$ denotes the ensemble average over the orientation of the interfacial molecules of interest.

In the theory of vibrational SFG with a single resonance at the IR frequency, the tensor elements of the hyperpolarizability are related to the IR and Raman properties of the vibrational mode, and are given by the partial derivative of the Raman polarizability tensor and the IR transition dipole moment of the qth mode with respect to the normal coordinate of the same mode.[14] It is given by the following equation:

$$\beta^{(2)}_{ijk,q} = \frac{1}{2\epsilon_0 \omega_q} \frac{\dfrac{\partial\alpha_{ij}}{\partial Q_q}\dfrac{\partial\mu_k}{\partial Q_q}}{\omega_{ir} - \omega_q + i\Gamma_q} \quad (3)$$

where $\partial\alpha_{ij}/\partial Q_q$ is the derivative of the Raman polarizability element, and $\partial\mu_k/\partial Q_q$ is the derivative of the transition dipole moment for the qth normal mode.

To determine orientational structure, we chose to use the null angle method in our data analysis rather than the intensity ratio method. A comparison of the two methods applied to both SHG and SFG orientational analysis was carried out.[12,15] It was found that the primary disadvantage for the intensity ratio method is that *PPP* or *SSP* SFG intensity is often small, which, as a consequence, makes it difficult to obtain an accurate intensity ratio from direct SFG intensity measurements. Nonetheless, it is to be noted that there are vibrations for which the intensity ratio method is satisfactory. In the experiments reported here, the null angle method is used to obtain five nonvanishing
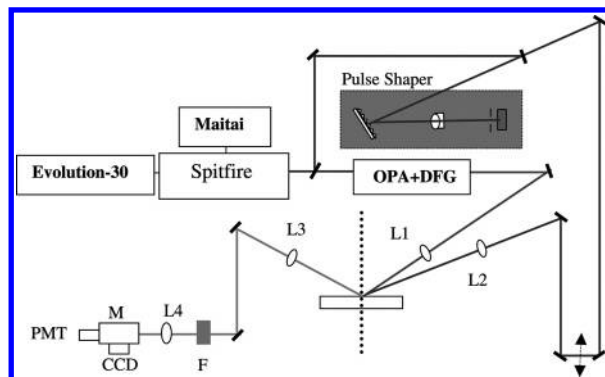

Figure 1. The layout of the broadband SFG system. L1: 10 cm FL CaF2 lens; L2: 20 cm FL silica lens; L3: 20 cm FL BK7 lens; L4: 15 cm FL BK7 lens. The pulse shaper consists of grating, a 15 cm FL cylindrical lens, and a high-reflectivity dielectric mirror. F: dichroic mirrors; M: monochromator; PMT: photomultiplier tube; CCD: charge-coupling device.

elements by analyzing the SFG intensities at different detection polarization angles.

3. Experimental Section

3.1 Laser. An 800 nm regeneratively amplified Ti:sapphire system (Spitfire, Spectra Physics) seeded with a MaiTai 80 MHz, 80 fs oscillator, at a 1 kHz repetition frequency was employed in the present experiments. A reflected 20% output from the regenerative amplifier was used to produce a picosecond 800 nm pulse. A signal generated by the input of the 800 nm femtosecond pulse into an optical parametric amplification (OPA) was in the range of 1.1−1.6 μm, and the idler was in the range of 1.6−2.8 μm. By difference frequency generation in a 1 mm AgGaS2 crystal, tunable IR light between 3 μm and 8.5 μm with a bandwidth of about 150 cm^{-1} (fwhm) was generated.

Figure 1 is a schematic experimental setup of the system. The reflected femtosecond beam from the regenerative amplifier was spectrally narrowed using a home-built pulse shaper to provide an 800 nm pump pulse with a bandwidth of 10 cm^{-1} and a time duration of 2.5 ps, which was determined from temporal cross-correlation measurements with the femtosecond 800 nm laser. The output power after pulse shaping was typically 17 μJ per pulse. The IR beam is focused onto the sample by a BaF2 lens with a 100 mm focal length (FL) at an angle of 67° relative to the surface normal and a spot size of around 120 μm. The visible light field is focused to 210 μm spot size by a BK glass lens with a 250 mm FL at an angle of 76° from the surface normal.

A 0.5 m spectrograph with one entry and two exits (Acton Research, three gratings, including 1200 grooves/mm with 450 nm blazed, 1200 grooves/mm with 500 nm blazed, and 600 grooves/mm with 4 μm blazed) was used. The 500 nm blazed grating was chosen to measure sum frequency signals from the methyl and the nitrile groups, and the 4 μm blazed grating was used for an IR intensity measurement. One exit was configured for detecting the dispersed signal with a liquid-nitrogen-cooled, back-thinned charge-coupled device (CCD) camera (Roper Scientific, 1340 × 400 pixels) operating at −120 °C.

3.2 Sample Preparation. The purity of *m*-tolunitrile was checked by gas chromography and NMR and used without further purification. Its chemical structure is shown in the inset of Figure 2. The samples used in this work were at 6 mM. From the surface tension measurements in Figure 2, the surface area occupied per molecule of *m*-tolunitrile at 6 mM was found to
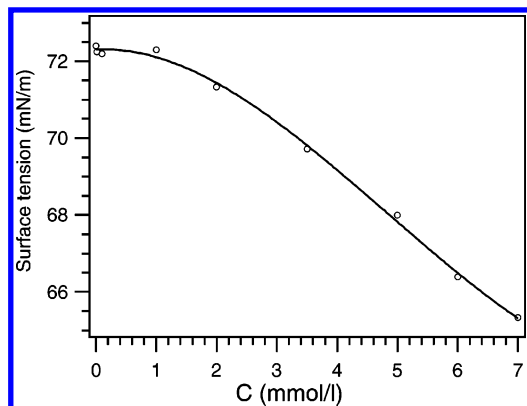
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Figure 2. The surface tension of *m*-tolunitrile aqueous solutions at different *m*-tolunitrile concentrations.

be 56 Å^2. To avoid thermal effects, the sample holder was placed on a rotating stage at 4 rpm in all experiments. The experiments were performed at 21 °C.

4. Results and Discussion

When thinking about the orientation of *m*-tolunitrile at the air/aqueous solution, it is reasonable to assume that the hydrophilic nitrile group preferentially projects into the bulk water, as was found in SFG studies of various hydrocarbon nitriles at the air/aqueous nitrile solution, whereas the hydrophobic methyl group is out of the water. In this discussion, we have defined the so-called "left-handed screw" to define the Euler transformation between the laboratory coordinates (*X*, *Y*, *Z*) and the molecular coordinates (*x*, *y*, *z*).[16] We adopted the center of the ring as the origin (*O*) of all coordinates. The direction from the nitrogen toward the carbon is designated as positive *z*, the *x* axis is perpendicular to the molecular plane, and the *y* axis is in the molecular plane. We define the direction of the unit vector from the origin *O* toward the carbon of the C−CH$_3$ to be along the *Oz'* axis. The orientational angle of the nitrile group and the methyl group with respect to the surface normal are designated as θ_1 and θ_2, respectively. We shall assume δ-function distributions for orientational angles. From the orientational angles of the two groups with respect to the surface normal, together with a rotation matrix formalism to obtain the angle between the normal to the phenyl plane and the normal to the interface, we obtained the absolute orientation of *m*-tolunitrile.

4.1 Nitrile Group of *m*-Tolunitrile at the Air/Aqueous Interface. Figure 3 shows the SFG spectra of a 6 mM *m*-tolunitrile aqueous solution taken at two different polarization combinations, *SSP* and *PPP*, with the visible beam at 800 nm and the IR centered at 4.7 μm with a bandwidth of 140 cm^{-1}. From fits of the SFG spectrum using two Lorentzian functions, the peak at 2234 cm^{-1} in the *SSP* polarization spectrum was assigned to the symmetric stretching mode of −CN, with a shoulder at 2270 cm^{-1}, which becomes more prominent in the *PPP* spectrum. We considered three possibilities in the assignment of the shoulder at 2270 cm^{-1}. One possibility is that the molecules form aggregates at the interface. To check this, we diluted the *m*-tolunitrile bulk concentration by a factor of 2 and found no change in the spectrum. The SFG intensity decreased by a factor of 4, which is expected for bulk concentrations that are in the linear part of the *m*-tolunitrile adsorption isotherm. We conclude that aggregation is not responsible for the 2270 cm^{-1} shoulder. Another possibility is that the nitrile group of *m*-tolunitrile is hydrogen bonded with water.[17,18] We performed
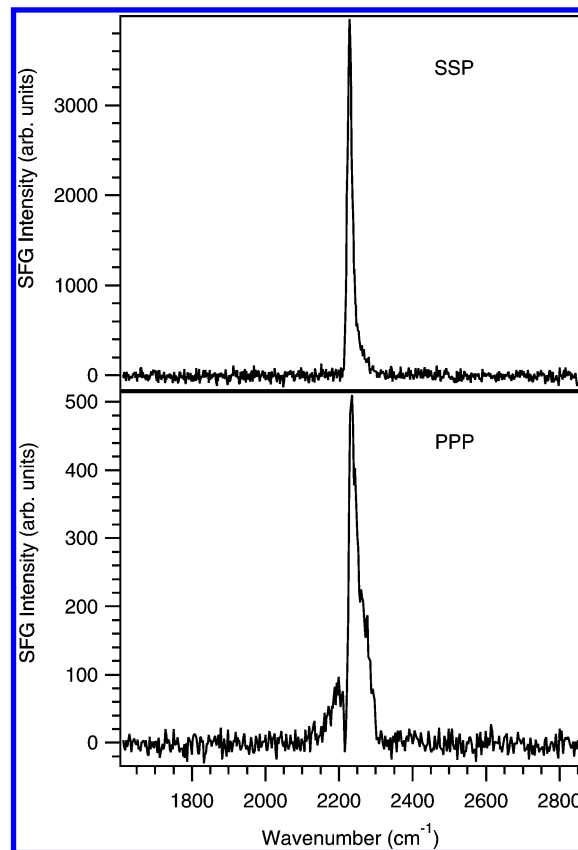

Figure 3. The nitrile (−CN) *SSP* and *PPP* sum frequency spectra of 6 mM *m*-tolunitrile with visible light at 800 nm and the IR centered at 4.7 μm.

Raman experiments with 6 mM *m*-tolunitrile aqueous solution and neat *m*-tolunitrile and found that the two Raman spectra are the same with only one peak at 2224 cm^{-1} (the data are not shown here); noting, however, that hydrogen bonding of the −CN with water can differ at the interface compared with that in the bulk aqueous nitrile solution. The third possibility is that the 2270 cm^{-1} shoulder is a combination band of some modes in the 1000−1200 cm^{-1} energy range.[18,19] In the *PPP* spectrum, we observed the peak at 2234 cm^{-1}, the shoulder at 2270 cm^{-1}, and a weak peak at 2205 cm^{-1}. The weak peak at 2205 cm^{-1} is attributed to the overtone of the C−H in-plane bending mode of the phenyl ring of *m*-tolunitrile at 1100 cm^{-1}.[20] We have found that there is a strong Raman peak at 1100 cm^{-1} in both neat *m*-tolunitrile and 6 mM *m*-tolunitrile aqueous solution. The *SPS* and *PSS* spectra for the −CN stretching mode were not detected under our experimental setup, which is consistent with our simulated results described later.

There are three nonvanishing elements for the $C_{\infty v}$ symmetry of −CN, namely, $\beta_{xxz} = \beta_{yyz} = r\beta_{zzz}$, where *r* is β_{xxz}/β_{zzz}. From eq 3 we see that $r = \alpha_{xx}^{Raman}/\alpha_{zz}^{Raman}$, that is, the ratio of the Raman perpendicular polarizability element to the Raman parallel polarizability element of the −CN bond. From Raman polarization measurements, two possible ratios are obtained; which one is correct cannot be determined from the Raman measurements alone. However, as has been shown in previous work, a determination of the relative sign of $\chi_{xxz}^{(2)}$ and $\chi_{xzx}^{(2)}$ from SFG measurements can be used to identify the correct value of the polarizability ratio *r*, which is 0.26.[17,21] To obtain the orientation of the −CN chromophore, null angle measurements of the nitrile stretch mode were performed. The measured intensity plotted against the polarization angle of the analyzer is shown in Figure 4. The null angle Ω_{CN} can be fitted from
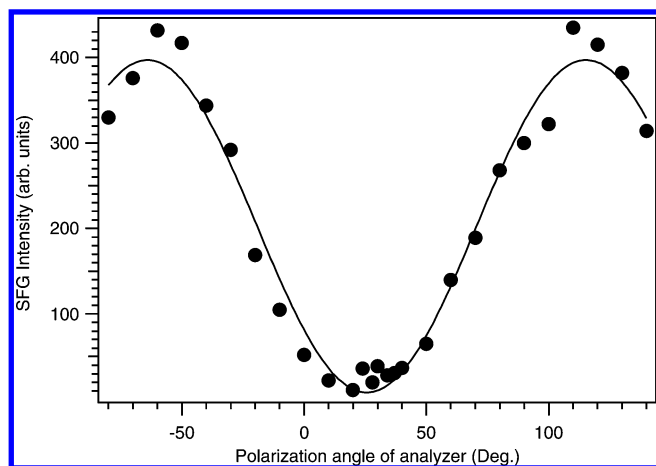
Figure 4. SFG intensity of the nitrile ($-CN$) 2234 cm^{-1} peak plotted against the polarization angle of the analyzer. The solid line is the calculated fit.
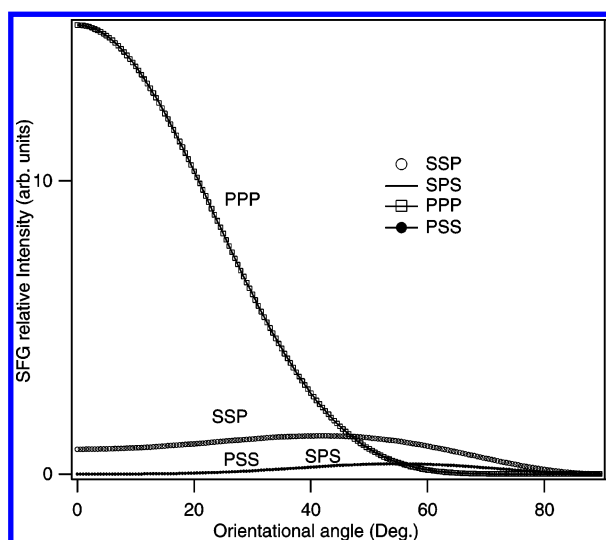

Figure 5. The numerically calculated SFG relative intensities of the nitrile group under four different polarization combinations (*SSP*, *PPP*, *SPS*, and *PSS*) vs the orientation of the nitrile group ($-CN$) with respect to the interface normal. The refractive index of the *m*-tolunitrile aqueous solution and monolayer are set to be 1.40 and 1.20, respectively, at all wavelengths.

Figure 4,[15,22,23] from which we found that the orientational angle θ_1 of the nitrile group is 53.0 ± 1.3° with respect to the surface normal.

We also calculated the orientational angle using the intensity ratio method with the intensity of *PPP* and *SSP* polarization. The orientational angle was found to be 51.0 ± 2.1°, which is in good agreement with the orientational angle obtained with the null angle method. To assist us in the interpretation of our results, we performed numerical calculations to obtain the relative intensities of the four polarization combinations using a specific calculation procedure.[24] Briefly, we considered the macroscopic susceptibilities and their connections with the microscopic hyperpolarizabilities under different polarization combinations. Calculations of the relative intensities of the generally used polarization combinations *SSP*, *PPP*, *SPS*, and *PSS* show the relative intensities as a function of the orientational angle in Figure 5. For the *SPS* and *PSS* polarizations, the relative intensities are less than that in the case of *PPP* polarization, which brings them below our detection limit. This is consistent with our experimental findings that we did not observe SFG signals for the *SPS* and *PSS* polarization combinations.
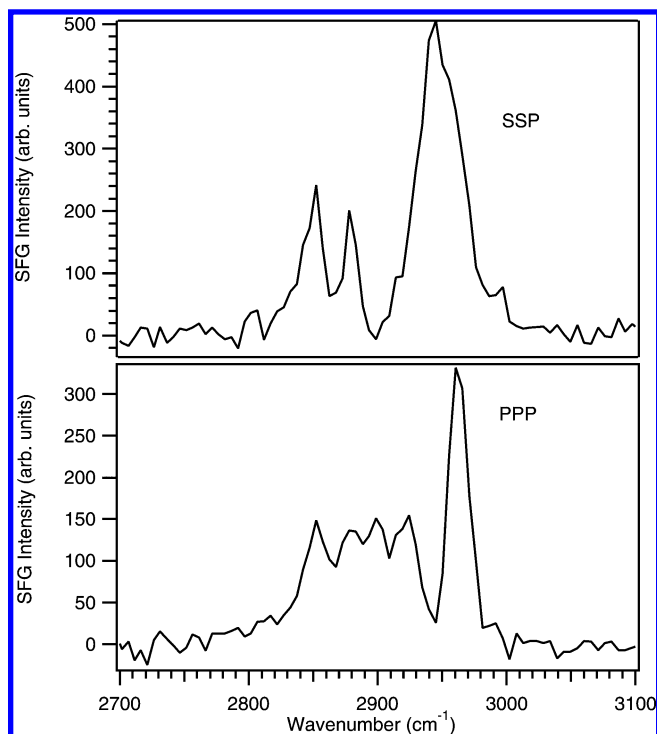

Figure 6. The methyl group ($-CH_3$) *SSP* and *PPP* sum frequency spectra of a 6 mM *m*-tolunitrile aqueous solution with the visible light at 800 nm and the IR centered at 3.4 μm.

4.2 Methyl Group Vibration of *m*-Tolunitrile at the Air/Aqueous Interface. Figure 6 shows the SFG spectra of *m*-tolunitrile at the air/aqueous interface taken at two different polarization combinations, *SSP* and *PPP*, with the visible wavelength at 800 nm and the IR wavelength centered at 3.4 μm with a bandwidth of 150 cm^{-1}. The *PPP* polarization combination spectrum shows a strong peak centered at 2961 cm^{-1}. On the red side of the peak, there are three weak peaks at 2853, 2878, and 2898 cm^{-1}. In the case of the *SSP* polarization spectrum, there is a strong peak centered at 2945 cm^{-1} and two weaker features at 2853 and 2878 cm^{-1}. The strong peak at 2945 cm^{-1} in the *SSP* SFG spectrum is assigned to the symmetric stretch of the methyl group,[25,26] and the 2961 cm^{-1} peak of the *PPP* spectrum was assigned to the antisymmetric stretch mode.[25,26] For the aromatic methyl group of a di-substituted benzene, the two peaks at 2853 and 2878 cm^{-1} are assigned to overtones of CH$_3$ antisymmetric bending vibrations or to the mixing of C$-$C stretching and C$-$H bending modes of the phenyl ring.[20,27] The small feature at 2898 cm^{-1} can result from the Fermi resonance of the methyl symmetric stretch mode with the overtone of the CH$_3$ antisymmetric bending mode.

A plot of the sum frequency intensity versus the polarization angle of the analyzer at 2945 cm^{-1} is shown in Figure 7. For the symmetric stretch mode, two nonvanishing elements of the hyperpolarizabilities exist, namely, $\beta_{xxz} = \beta_{yyz} = r\beta_{zzz}$, where the ratio r value of 2.3 was used by combining the Raman depolarization of the methyl group in acetonitrile with the SFG measurements of the relative sign of the $\chi^{(2)}_{XXZ}$ and $\chi^{(2)}_{XZX}$ susceptibility elements.[17] Using the null angle method, the calculated orientational angle of the C_3 axis of the methyl group is 23.0 ± 1.6°. The refractive index of the *m*-tolunitrile aqueous solution and monolayer are set to be 1.40 and 1.20, respectively, at all wavelengths. We also employed the intensity ratio of the *SSP* and *PPP* spectrum at the 2945 cm^{-1} peak to calculate the orientational angle of the methyl group and found the value to

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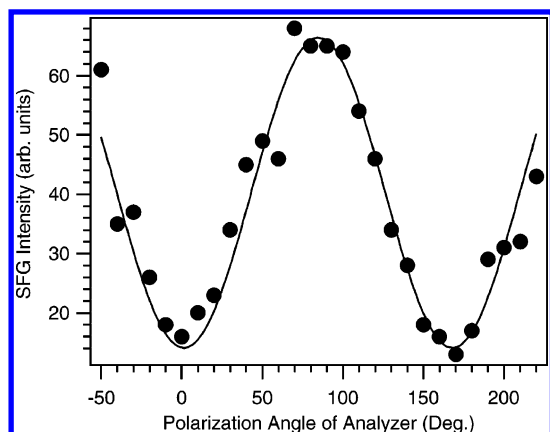
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Figure 7. SFG intensity of the methyl group ($-CH_3$) 2945 cm^{-1} peak plotted against the polarization angle of the analyzer. The solid line is the calculated fit.

be $28° \pm 1.2°$, which is close to the results from the null angle measurements.

4.3 The Absolute Orientation of *m*-Tolunitrile at the Air/ Aqueous Solution. Now that we have obtained the orientational angle θ_1 of the nitrile group and the orientational angle θ_2 of the methyl group, we can determine the absolute orientation of

the *m*-tolunitrile molecule at the air/aqueous interface.[16] To extract the remaining angle needed to determine the absolute orientation of *m*-tolunitrile, we performed two rotation operations. The remaining angle to be determined involves the orientation of the phenyl group, which we define as the angle between the normal to the phenyl plane and the interface normal. The two rotation operations relate the laboratory axes (X, Y, Z) and the molecular axes (x, y, z). Initially, we set the molecular plane in the ZY plane of the laboratory coordinates, the symmetry axis of the $-CN$ is along both the z molecular axis and the Z laboratory axis (negative), and, finally, the X and x axes are perpendicular to the molecular plane, as shown in Figure 8A. Thus, in the laboratory coordinates, the initial coordinates of the methyl group C_3 axis expressed in terms of the direction cosines with the laboratory axes ($l^0_{CH_3,X}$, $l^0_{CH_3,Y}$, $l^0_{CH_3,Z}$) is (0, cos 30°, cos 60°).

As the first step, the molecular coordinates are rotated by an angle of $\theta_1 = 53°$ around the X axis such that the orientational angle of the nitrile group with respect to the surface normal is 53° as obtained from null angle measurements (Figure 8B). This rotation operation $R_X(\theta_1)$ changes the spatial coordinates of the methyl group C_3 axis from its initial orientation (0, cos 30°, cos 60°) to the orientation ($l^1_{CH_3,X}$, $l^1_{CH_3,Y}$, $l^1_{CH_3,Z}$) of the methyl group after the first rotation operation $R_X(\theta_1)$, where $\theta_1 = 53°$.

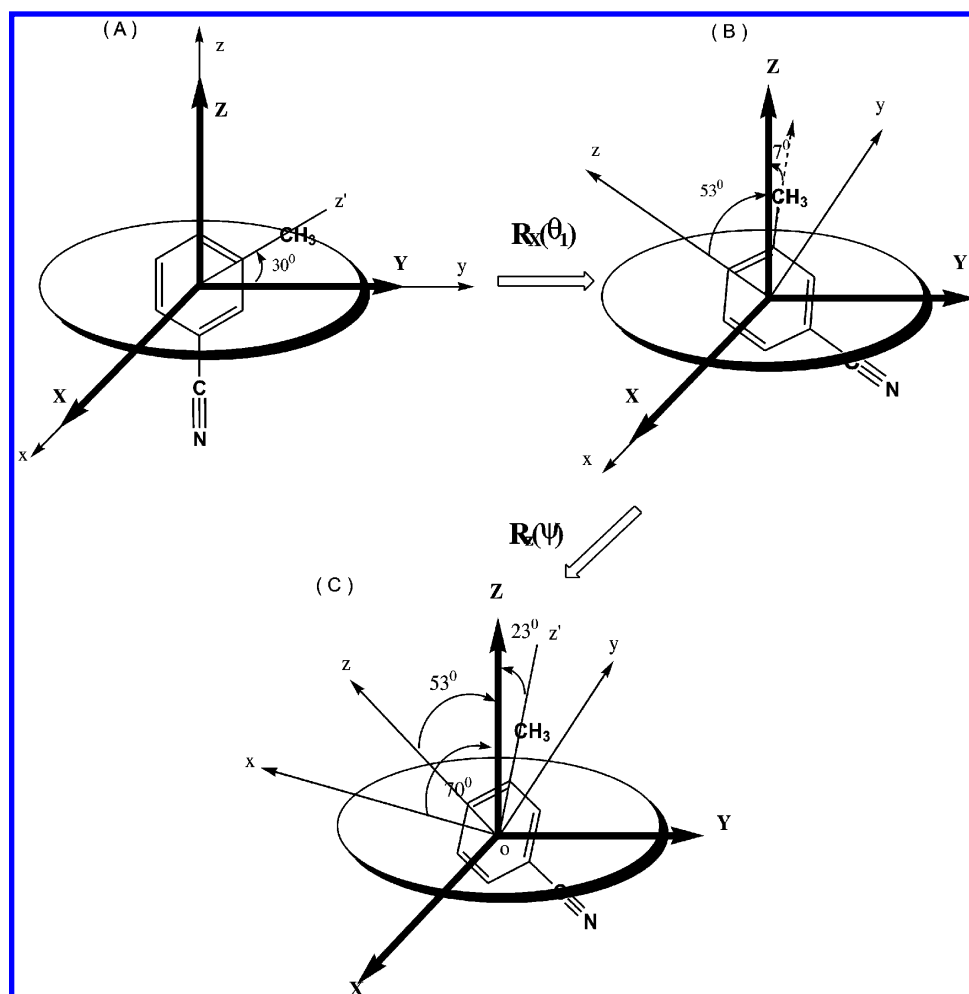**Figure 8.** The rotation operations used to obtain the orientation of the molecular plane from the measured orientations of the $-CN$ and $-CH_3$ groups. (A) The initial configuration of the *m*-tolunitrile in the laboratory coordinates with the Z axis along the $-CN$ symmetry axis and the X axis perpendicular to the molecular plane. (B) The molecular configuration after the first rotation operation of 53° (measured orientation of $-CN$ with respect to the interface normal Z) around the laboratory X axis. (C) The final molecular configuration after the second rotation around the molecular z axis, bringing the C_3 axis of the CH_3 group to its measured orientation of 23° with respect to the interface normal Z. The normal to the molecular plane, given by the molecular coordinate x, is found to be 70° with respect to the surface normal.

This rotation operation can be written as

$$
\begin{pmatrix} l^1_{CH_3,X} \\ l^1_{CH_3,Y} \\ l^1_{CH_3,Z} \end{pmatrix} = R_X(\theta_1) \cdot \begin{pmatrix} l^0_{CH_3,X} \\ l^0_{CH_3,Y} \\ l^0_{CH_3,Z} \end{pmatrix} =
$$

$$
\begin{pmatrix} 1 & 0 & 0 \\ 0 & \cos\theta_1 & -\sin\theta_1 \\ 0 & \sin\theta_1 & \cos\theta_1 \end{pmatrix} \cdot \begin{pmatrix} 0 \\ \cos 30° \\ \cos 60° \end{pmatrix} = \begin{pmatrix} 0 \\ \cos 83° \\ \cos 7° \end{pmatrix} \quad (4)
$$

The methyl group C_3 axis initially at 30° with respect to the Y axis is now at an angle of 83° with respect to the Y axis and 7° with respect to the Z axis after a rotation of 53° about the X axis. For the nitrile group, the rotation is simple and will be shown later.

To bring the angle of the methyl group C_3 axis with respect to the surface normal Z to its measured value of 23°, a rotation of ψ degrees about the molecular z axis ($-$CN) is performed (Figure 8C). The mathematical representation of the rotation of the methyl about the molecular z axis can be expressed as a product of rotations about the laboratory X and Z axes.[16] This leads to a final expression

$$
R_z(\psi) \cdot R_X(\theta_1) \cdot \begin{pmatrix} 0 \\ \cos 30° \\ \cos 60° \end{pmatrix} = \begin{pmatrix} l^{final}_{CH_3,X} \\ l^{final}_{CH_3,Y} \\ l^{final}_{CH_3,Z} \end{pmatrix} = \begin{pmatrix} \cos 112° \\ \cos 86° \\ \cos 23° \end{pmatrix} \quad (5)
$$

Since the $-$CN bond remains in the YZ plane in the laboratory coordinates under this rotation, the orientation of the $-$CN axis in the laboratory coordinates $\hat{e}_{CN}$ is (0, $\cos 37°$, $-\cos 53°$). Note that the carbon is closer to the origin than the nitrogen, and the $-$CN bond is located at a negative z coordinate.

By taking the cross product of the unit vector $\hat{e}_{CH_3}$ corresponding to the methyl orientation ($l^{final}_{CH_3,X}$, $l^{final}_{CH_3,Y}$, $l^{final}_{CH_3,Z}$), with the unit vector $\hat{e}_{CN}$ corresponding to the $-$CN orientation ($l^{final}_{CN,X}$, $l^{final}_{CN,Y}$, $l^{final}_{CN,Z}$), we obtain a vector $\hat{e}_x$, which is normal to the molecular plane, and $\hat{e}_x = \hat{e}_{CH_3} \times \hat{e}_{CN}$ is expressed as direction cosines ($\cos 39°$, $\cos 77°$, $\cos 73°$). We can now calculate the molecular orientation, assuming that the molecules are isotropically distributed in the surface XY plane. By projecting the unit vector $\hat{e}_x$ onto the laboratory Z axis, we can calculate the angle φ of the normal to the molecular plane $\hat{e}_x$ and the surface normal $\hat{Z}$, which is also the angle between the molecular plane and the surface plane.

$$
\varphi = \cos^{-1}(\hat{e}_x \cdot \hat{Z}) = 70° \quad (6)
$$

Combining the orientation of the $-$CN, the methyl C_3 axis and the molecular plane, we can depict the m-tolunitrile at the air/aqueous interface, as shown in Figure 8C.

5. Conclusions

In this paper, we have performed a proof-of-concept experiment demonstrating that measurements of the orientation of two nonparallel chromophores in the molecule of interest when combined with a rotation matrix formulation yield the absolute molecular orientation at the interface. The orientations of the nitrile group ($-$CN) and the methyl ($-$CH$_3$) C_3 axis of m-tolunitrile at the air/water interface were obtained with SFG measurements of these IR and Raman active vibrational chromophores. The SFG measurements showed that, with respect to the surface normal, the nitrile group tilts at 53°, the C_3 axis of the methyl group tilts at 23°, and, combining these results with a two-rotation operation procedure, we find that the angle between the molecular and surface planes is 70°.

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