Supporting Information

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$\chi^{(4)}$ Raman Spectroscopy for Buried Water Interfaces

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1. Sample

Rhodamine 800 (R800) was purchased from Exciton as LD 800 (perchlorate) and dissolved in HPLC-grade distilled water (Wako) without further purification. The bulk concentration of R800 was saturated ($8.3 \times 10^{-5} \text{ mol dm}^{-3}$). The surface excess of R800 at the air/water interface was determined to be $0.03 \text{ molecules nm}^{-2}$ by a surface tension measurement based on the ring method.^[1, 2] All the experiments were performed at room temperature.

2. Electronic Sum Frequency Generation (ESFG)

The multiplex ESFG spectroscopic setup is shown in Figure S1. Briefly, the ω_1 pulse was obtained from a part of the output of a Ti:sapphire regenerative amplifier (Spitfire, Spectra Physics). The bandwidth of the ω_1 pulse at 795 nm was narrowed by a near IR interference filter (F1.5-794.7-4-1.00, CVI) down to 20 cm^{-1} . Another part of the regenerative amplifier output was focused into water to generate a white light continuum that was used as the ω_2 pulse. The spectrum of the ω_2 pulse extended from 540 nm to $1.2 \text{ }\mu\text{m}$. The actual ω_1 pulse energy is described in the caption of Figure 1. The typical pulse energy of the ω_2 pulse was $10 \text{ }\mu\text{J}$. The ω_1 and ω_2 pulses were noncollinearly focused onto the same spot (ϕ 0.1 mm) at the interface of a sample solution at an incident angle about 45° from the interface normal. The linear polarization of the ω_1 and ω_2 beams was in the plane of reflection (i.e. p-polarization). When the ω_1 and ω_2 pulses were temporally overlapped, sum frequency (SF, $\omega_1 + \omega_2$) was generated at the interface. The SF light was collected and focused onto the entrance slit of a single polychromator (HR-320, Jobin Yvon). The spectrally dispersed SF light was detected by a liquid nitrogen cooled CCD (Spec-10:2KBUV, Roper Scientific). Unwanted second harmonic generation (SHG) contribution (i.e. $2\omega_1$

and $2\omega_2$) was rejected by a spatial filter and by a background subtraction on a computer. A cylindrical quartz cell was used to contain the sample solution that was stirred by a 2 mm magnetic stirring flea.

3. Polarization SHG

To investigate the orientation of R800 at the interfaces, polarization SHG measurements were performed. Figure S2 shows the polarization SHG setup. The fundamental input at 795 nm (ω) from the regenerative amplifier was focused onto the interface, and SHG at 397.5 nm (2ω) from the interface was collected in the reflection configuration. In the case of the air/water interface, the angle between the input beam and the interface normal (i.e. incident angle) was 45° , and that between the output SHG beam and the interface normal was also 45° . The fused silica/water interface was irradiated by the fundamental input from the fused silica side. Because of the refraction, the angle between the input beam and the silica/water interface normal was 29.1° , and that between the output SHG beam and the interface normal was 28.8° . The SHG signal was detected by a photomultiplier tube (R2295, Hamamatsu) after passing through a set of interference and glass filters (for rejection of background fluorescence and fundamental input), an analyzer, and a depolarizer. The linear polarization of the fundamental input was controlled by a computer-driven half-wave plate. The polarization of the SHG signal was controlled by the analyzer to choose the s- or p-polarization.

Figure S3 (a) and (b) show the input polarization dependence of the p- and s-polarized SHG intensity of R800 at the air/water interface, respectively. Figure S3 (c) and (d) show the input polarization dependence of the p- and s-polarized SHG intensity of R800 at the fused silica/water interface, respectively. From these data, we can determine the relative values of the three independent $\chi^{(2)}$ tensor elements ($\chi^{(2)}_{ZZZ}$, $\chi^{(2)}_{XXZ}$, $\chi^{(2)}_{ZXX}$; X and Z are laboratory axes and Z denotes the interface normal) of SHG.^[3-5] Theoretically, the p- and s-polarized SHG intensity (I_p , I_s) depends on the input polarization in the following way.^[3-5]

$$I_p = \left| \left(c_2 \chi^{(2)}_{XXZ} + c_3 \chi^{(2)}_{ZXX} + c_4 \chi^{(2)}_{ZZZ} \right) \cos^2 \gamma + c_5 \chi^{(2)}_{ZXX} \sin^2 \gamma \right|^2, \quad (S1)$$

$$I_s = \left| c_1 \chi_{xxz}^{(2)} \sin \gamma \cos \gamma \right|^2, \quad (\text{S2})$$

where γ stands for the angle between the linear polarization direction of the input beam and the incident plane ($\gamma = 0^\circ$ for the p-polarization), $c_1 \sim c_5$ are constants determined by the incident angle and the dielectric constants of the media sandwiching the interface. As shown in Figure S3, the polarization SHG data are well reproduced by the fitting curves based on eqs (S1) and (S2). Table S1 shows the relative values of the $\chi^{(2)}$ tensor elements determined by the fitting analyses. For dye molecules such as R800, it is already known that β_{zxx} and β_{xxz} are predominant in the molecular hyperpolarizability tensor elements and the other elements are negligible.^[5, 6] (The molecular axes (x, z) are defined as Figure S4 shows.) Then, assuming a very narrow (δ -function) distribution of the orientational angle of R800 at the interface, one can obtain the following relation between $\chi^{(2)}$ and the orientational angle:^[4, 5]

$$\cos^2 \xi = \frac{\chi_{zzz}^{(2)}}{3\chi_{zzz}^{(2)} + 2\chi_{zxx}^{(2)} + 4\chi_{xxz}^{(2)}}, \quad (\text{S3})$$

where ξ is the angle between the molecular long axis (x) of R800 and the interface normal, which is schematically shown in Figure S5. Table S2 shows the orientational angle ξ determined from the values in Table S1 and eq (S3).

We thank one of the reviewers for suggesting surface characterization.

4. Conventional Raman Spectroscopy

The spontaneous Raman spectrum of R800 powder was measured by using a commercial Raman microscope (LABRAM, Jobin Yvon). The excitation wavelength was 514.5 nm, and the excitation power was less than 0.2 mW. The observed bandwidth (FWHM) of the Rayleigh scattering was 22 cm^{-1} , which can be regarded as the spectral resolution of the measurements. The FT-Raman spectrum of R800 in ethanol was measured by using a commercial spectrometer (System 2000R, Perkin Elmer). The excitation

wavelength was 1064 nm, and the excitation power was 200 mW. The spectral resolution was 16 cm^{-1} . The inverse Raman spectrum of R800 in water was measured by using a laboratory-made pump-probe femtosecond time-resolved absorption setup. The pump wavelength was 795 nm, and the pump pulse energy was $4.8\text{ }\mu\text{J}$. The probe pulse was a white light continuum covering from 450 nm to 780 nm. The observed bandwidth (FWHM) of the Rayleigh scattering of the pump pulse was 27 cm^{-1} , which can be regarded as the spectral resolution of the measurements.

We thank Prof. Akira Sakamoto (Saitama University) for the FT-Raman measurement.

5. DFT Calculations

DFT calculations were performed at B3LYP/6-31+G* using Gaussian03, to obtain the optimized structures and vibrational frequencies of R800 and the R800-(H₂O)_n clusters. We used the 6-31+G* basis set for the atoms that are important for the C≡N stretching frequency (i.e., 1 O and 13 C atoms in the central xanthene ring of R800, 2 H atoms directly bonded to the xanthene ring, C and N atoms in the C≡N group, all the atoms of water), and adopted the 6-31G basis set for the others, because of the limitation of the computing time.

We thank the RIKEN Super Combined Cluster (RSCC) for the computational resources.

6. Heterodyne Nature of $\chi^{(4)}$ Signals

When the optical signal is directly detected, the signal intensity is proportional to the square modulus of the electric field of the signal,

$$I \propto |E_s|^2.$$

This way of detection is called homodyne detection. A nonlinear optical signal is intrinsically very weak, because it originates from second- or higher-order terms of perturbation. Therefore, to practically increase the signal intensity, the heterodyne detection is often carried out, in which the signal light is mixed with other strong light (a local oscillator) and the sum of them is measured. Then, the intensity of the signal becomes,

$$I \propto |E_{\text{LO}} + E_{\text{S}}|^2 = |E_{\text{LO}}|^2 + 2\text{Re}(E_{\text{LO}}^* \cdot E_{\text{S}}) + |E_{\text{S}}|^2 \approx |E_{\text{LO}}|^2 + 2\text{Re}(E_{\text{LO}}^* \cdot E_{\text{S}}).$$

Here, the cross term of the weak and strong electric fields is much larger than the absolute square of the electric field of the weak signal itself, which makes the detection of the nonlinear signal easier and brings about improvement in the data quality. In addition, the signal intensity is linearized to the electronic field (and hence relevant susceptibility) of the nonlinear signal of interest. An important requisite for the heterodyne technique is that the weak and strong electric fields must have the same frequency and the same propagation direction, otherwise they are not mixed with each other. In the present $\chi^{(4)}$ Raman spectroscopy, the $\chi^{(2)}$ ESFG signal has the same photon energy and the same propagation direction as the $\chi^{(4)}$ Raman signal, and naturally, the electric field of $\chi^{(2)}$ ESFG signal is much stronger than that of the $\chi^{(4)}$ Raman signal. Therefore, the $\chi^{(2)}$ ESFG signal acts as a local oscillator and the $\chi^{(4)}$ Raman signal is heterodyned.

7. Background Subtraction for $\chi^{(4)}$ Raman Spectra

In Figure 2b and 2c, the vibrational bands appear on structureless backgrounds. These backgrounds are not due to the $\chi^{(4)}$ Raman process, but are attributable to other nonlinear processes that are not resonant with vibrational transitions of the molecules. Because of its structureless nature, these background can be reasonably subtracted in a relatively narrow wavenumber range by simply assuming a straight-line background. Figure S6 shows the C $\equiv$ N bands in five different environments, where the $\chi^{(4)}$ Raman spectra with and without background subtraction are compared. The C $\equiv$ N peak positions of the $\chi^{(4)}$ Raman spectra do not change upon the background subtraction practically.

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Table S1. Relative values of the $\chi^{(2)}$ tensor elements of R800 at the air/water and fused silica/water interfaces.

	$\chi^{(2)}_{xxz}/\chi^{(2)}_{zzz}$	$\chi^{(2)}_{zxx}/\chi^{(2)}_{zzz}$
Air/Water	-0.29 ± 0.03	1.3 ± 0.07
Fused Silica/Water	-0.48 ± 0.3	2.1 ± 0.5

Table S2. Orientational angle (ξ) of R800 at the air/water and fused silica/water interfaces.

	ξ
Air/Water	$61^\circ \pm 2^\circ$
Fused Silica/Water	$64^\circ \pm 10^\circ$

Figure S1. Schematic of the ESFG experimental setup.

Figure S2. Schematic of the polarization SHG experimental setup.

Figure S3. Input polarization dependence of SHG of R800 at the air/water ((a), (b)) and fused silica/water ((c), (d)) interfaces. The polarization of SHG is p-polarization for (a) and (c), and s-polarization for (b) and (d). The open circles are experimental data, and the solid lines are fitting curves.

Figure S4. Definition of the molecular axes.

Figure S5. Definition of the orientational angle ξ .

Figure S6. C≡N Raman bands in different environments. (a) Background subtraction was not performed for the $\chi^{(4)}$ Raman spectra. (b) Straight-line background subtraction was performed for the $\chi^{(4)}$ Raman spectra. The C≡N peak positions of the $\chi^{(4)}$ Raman spectra do not change upon the background subtraction.