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Quantitative Analysis of Electronic Spectral Broadening of a Solvatochromic Dye at the Air/Water Interface and Inhomogeneity of Solvation Sites

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The unique property of molecules adsorbed at the interface is the nonzero value of even-order nonliner susceptibility ($\chi^{(2n)}$), which makes second harmonic generation (SHG) and sum frequency generation (SFG) spectroscopy interface specific.[1] Recently, our group developed heterodyne-detected electronic SFG (HD-ESFG) spectroscopy by which we can obtain a very high quality electronic $\chi^{(2)}$ spectrum of molecules adsorbed at the interface.[2] In the present work, we applied HD-ESFG to coumarin 110 (C110) at the air/water interface. The signal to noise ratio of the data is as good as a spectrum of molecules in the bulk solvent. We quantitatively analyzed the spectral shape of the interfacial electronic spectrum of C110 to gain a precise knowledge about the inhomogeneity and fluctuation of the solvent environment surrounding the probe dye molecule at the air/water interface.

Figure 1 shows the complex electronic $\chi^{(2)}$ spectrum of C110 at the air/water interface. The real and imaginary parts of the $\chi^{(2)}$ spectrum show dispersive and symmetric line shape, respectively. The peak position of the imaginary $\chi^{(2)}$ (Im[$\chi^{(2)}$]) spectrum is in very good agreement with the $|\chi^{(2)}|^2$ spectrum of the same sample which we reported recently.[3] The imaginary $\chi^{(1)}$ (Im[$\chi^{(1)}$]) spectra (obtained from UV-visible absorption spectra) of C110 in water and cyclohexane are also shown in Figure 1 for comparison. The Im[$\chi^{(2)}$] spectrum of C110 at the interface is located in between the Im[$\chi^{(1)}$] spectra in bulk water and cyclohexane, which indicates that the effective polarity sensed by C110 at the air/water interface is in between the polarity of polar bulk water and that of nonpolar bulk cyclohexane. The bandwidth of the Im[$\chi^{(2)}$] spectrum seems slightly narrower than that of the Im[$\chi^{(1)}$] spectrum in water but broader than in cyclohexane, which suggests that the air/water interface provides less inhomogeneous microenvironment than bulk water but more than bulk cyclohexane.

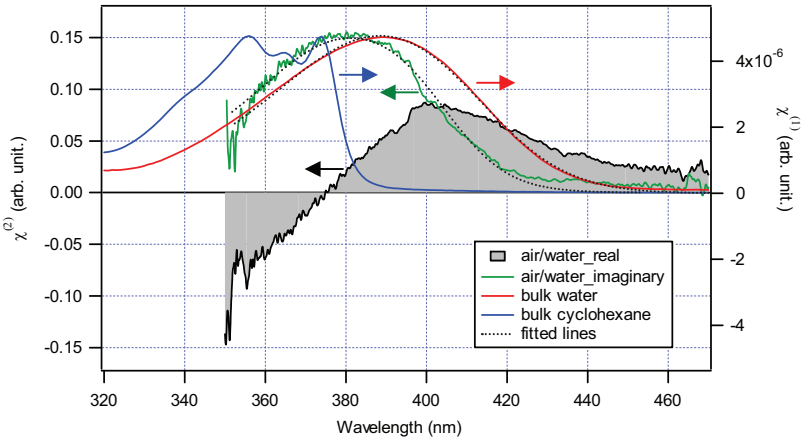

Figure 1: Complex $\chi^{(2)}$ spectrum (measured in SPS polarization configuration) of C110 at the air/water interface. The green line represents Im[$\chi^{(2)}$], and the black line shaded with gray stands for Re[$\chi^{(2)}$]. Red and blue lines represent Im[$\chi^{(1)}$] spectra (obtained from UV-visible absorption spectra) of C110 in bulk water and bulk cyclohexane, respectively. Black dotted curves are fitted lines to the corresponding spectra.

To quantitatively analyze the spectra in Figure 1 for deeper understanding of the effective polarity and inhomogeneity at the interface, we adopted a spectral analysis method proposed by Fee and Maroncelli.[4] In this analysis an electronic spectrum in a polar environment is assumed to be reproduced by superposition of an electronic spectrum in a nonpolar solvent with horizontal (i.e. frequency or photon energy) shifts (δ) and vertical (i.e. intensity scale) weights, which is mathematically expressed in the following way:

Table 1: Fitting parameters of C110 spectra

System	δ_0 (cm^{-1})	σ (cm^{-1})
C110-bulkwater	-2.4×10^3	0.9×10^3
C110-air/water	-1.8×10^3	0.7×10^3

$$\mathrm{Im}[\chi^{(2)}(\nu)] \propto \int \mathrm{Im}[\chi^{(1)}_{\mathrm{np}}(\nu-\delta)]p(\delta)d\delta = \int \nu^{-1}A_{\mathrm{np}}(\nu-\delta)p(\delta)d\delta \qquad (1)$$

where ν is the frequency, A_{np} represents the absorption spectrum of C110 in cyclohexane, and $\mathrm{Im}[\chi^{(1)}_{\mathrm{np}}(\nu)]$ is the imaginary part of the linear susceptibility of C110 in cyclohexane directly given by A_{np}. $p(\delta)$ is a Gaussian distribution function describing the horizontal shifts and the vertical weights:

$$p(\delta) = \frac{1}{\sqrt{2\pi}\sigma}\exp\left[\frac{-(\delta-\delta_0)^2}{2\sigma^2}\right] \qquad (2)$$

where δ_0 is the centre frequency of the shift induced by the polar environment and σ is the distribution width. By using Equations (1) and (2), fitting analyses were performed for the imaginary $\chi^{(2)}$ spectrum at the air/water interface and the absorption spectrum in bulk water. ($\mathrm{Im}[\chi^{(2)}(\nu)]$ was replaced with $\mathrm{Im}[\chi^{(1)}_{\mathrm{p}}(\nu)] = \nu^{-1}A_{\mathrm{p}}(\nu)$ in Equation (1) for the analysis of the absorption spectrum ($A_{\mathrm{p}}(\nu)$) in bulk water.) The best fits are shown as dotted curves in Figure 1, which indicates that the experimental data were very well reproduced by the present analysis. Table 1 shows the values of δ_0 and σ for the air/water interface and bulk water determined in the fitting analyses. Simply speaking, δ_0 and σ quantitatively reflect the effective polarity and inhomogeneity, respectively. The ratio of δ_0 for the air/water interface to that for bulk water is 0.75 that effectively corresponds to the normalized $E_{\mathrm{T}}(30)$ polarity scale sensed by C110 at the interface. This value is in good agreement with our recent paper.[3] The ratio of the σ for the air/water interface to that for bulk water is also 0.75, which gives the quantitative estimation of the inhomogeneity of the interface for the first time. It is concluded that the air/water interface provides not only less polar environment but also less inhomogeneous environment for C110 than bulk water.

References

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