

# 3C11 Broadband ESFG Study of Coumarins at Air-water Interface: New Insight into Interfacial Polarity and Molecular Property

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**Introduction:** Polarity expresses the ability of solvents to stabilize a charge or a charge-dipole near its vicinity. The concept of polarity and solvatochromism at interfaces has profound importance in understanding the nature of interfacial solute-solvent interactions. Numerous experimental and theoretical studies have been performed regarding solvent polarity and dynamics at various interfaces.<sup>1,2</sup> These studies showed that the properties of solvents and solute molecules at interfaces are substantially different from that of their bulk counterpart.<sup>1,2</sup> Among the various experiments, surface-specific nonlinear Second Harmonic Generation (SHG) spectroscopy has been employed extensively to study the polarity and solvent response at the interface by measuring resonantly enhanced electronic spectra of interfacial molecules and their time-delay dependence.<sup>1</sup> However, this technique relies on extensive as well as time-consuming procedure of registering output SHG ( $2\omega$ ) intensity by scanning the input fundamental wavelength ( $\omega$ ).<sup>1,2</sup> Thus, the resulting interfacial electronic spectra consist of sparse data points with limited signal-to-noise ratio.<sup>1,2</sup>

A long standing challenge was to obtain precise electronic spectra of interfacial molecules with higher signal-to-noise ratio, which could be compared directly to their linear absorption spectra. Towards this end, the advancements of femtosecond laser technology leads us to design surface-specific multiplex Electronic Sum Frequency Generation (ESFG) technique based on a narrow band near-IR laser pulse and a broadband white light continuum, together with a detection capability of the entire ESFG spectra in a single-shot, using CCD.<sup>3</sup> This technique enables one to register subtle electronic spectra ( $|\chi^{(2)}|^2$ ) of interfacial molecules with ultra-high signal-to-noise ratio and very dense data points. It is worth noting that the precise shape and structure of the electronic spectra obtained with this technique contain wealth of information regarding polarity and solute-solvent interaction at the interface. The uniqueness of this technique has already been explored by our group to unravel the precise electronic spectra of Nile blue.<sup>3</sup>

The purpose of the present study is two fold: (1) to measure the polarity and solute-solvent interaction (spectral shape) sensed by the three structurally different coumarin dyes, Coumarin-314 (C-314), Coumarin-110 (C-110) and Coumarin-6H (C-6H) at the air-water interface and (2) to establish the relationship between the molecular orientation of coumarins and their local polarity.

**Experimental:** The energy diagram and broadband ESFG setup are shown in fig.1.<sup>3</sup> Briefly, a Ti:sapphire regenerative amplifier (Spitfire, Spectra Physics) together with seeds from a mode-locked oscillator (Tsunami, Spectra Physics) was used to generate 1 mJ pulses (1 kHz, 100 fs) at 800 nm. A part of the output was focused into flowing water cell to generate white light continuum ( $\omega_2$ ) (fig. 1B). The other part of the 800 nm was attenuated and used as  $\omega_1$  pulse (bandwidth  $160 \text{ cm}^{-1}$ ). The  $\omega_1$  (16  $\mu\text{J}$ , p-polarized) and  $\omega_2$  (7  $\mu\text{J}$ , p-polarized) pulses were focused onto the same spot at air-water interface of the coumarin solution with incidence angles  $48^\circ$  and  $38^\circ$  respectively (see fig. 1B). The delay between  $\omega_1$  and  $\omega_2$  was controlled by a translation stage. Thus, temporal overlap of  $\omega_1$  and  $\omega_2$  pulses ensures the generation of ESFG signal in reflection mode. The ESFG signal was collected through an iris, a pair of identical lenses and dielectric filters and was focused into a polychromator (HR-320, Jobin Yvon). The entire, spectrally-dispersed ESFG signal (p-polarized) was registered onto a nitrogen-cooled CCD (Spec-10:2KBUV,  $2048 \times 512$  pixels). The resonant  $|\chi^{(2)}|^2$  spectra of coumarins were then obtained by normalizing coumarin's SFG spectra by the standard non-resonant ESFG spectra of a quartz plate, collected at same condition as that of coumarin sample.<sup>3</sup>

The polarization dependent SHG and subsequent angle of orientation of coumarins were measured using conventional SHG setup shown in fig. 1C. In brief, a part (10  $\mu\text{J}$ ) of the amplifier output was used as input fundamental pulse ( $\omega$ ). The  $\omega$ -pulse was tuned near the

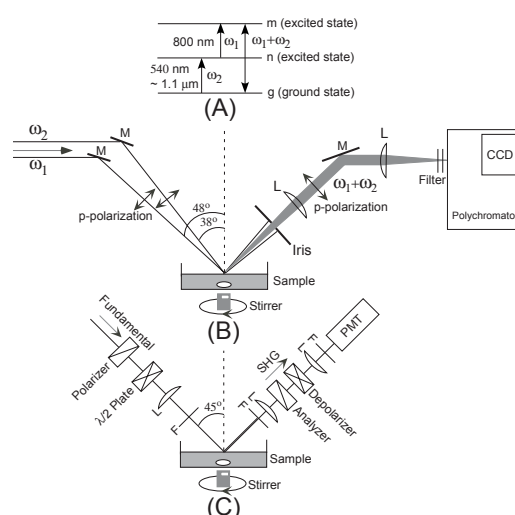


Fig. 1: Energy level diagram (A) and experimental setup (B) of multiplex ESFG. (C) SHG Experimental setup for measuring molecular orientation. L, M and F denote lenses, mirrors and filters respectively.

resonant frequencies of the coumarins and the SHG signal ( $2\omega$ ,  $45^\circ$ -polarized) was collected with a PMT after passing through analyzer and depolarizer, by varying the input polarization of  $\omega$ . This ensures that the angle of orientation, calculated from the polarization dependent SHG signal, is essentially the angle of the  $S_1 \leftarrow S_0$  transition dipole moment of coumarin relative to the surface normal of the air-water interface.

Aqueous solutions of C-314, C-110 and C-6H (all Aldrich) were made by dissolving in HPLC grade water (Wako, Japan). Experiments were done with constantly stirred solutions in a glass petri-dish (see fig. 1).

**Results and Discussions:** The ESFG ( $|\chi^{(2)}|^2$ ) spectra of C-314 and C-110 adsorbed at air-water interface are shown in fig. 2. It is readily seen from fig. 2 that the broadband ESFG technique is unique to obtain precise two-photon single-resonant  $|\chi^{(2)}|^2$  spectra of molecules (coumarin in this case) with ultra-high signal-to-noise ratio. Unlike earlier studies on electronic-SHG of coumarins at air-water interface, the ESFG spectra obtained in the present work show significantly broadened spectral shape.<sup>2a</sup> The spectral shapes of ESFG for all the coumarins are nearly identical to their linear absorption spectra in highly polar solvents. The FWHM (53 nm) of C-314 ESFG spectrum is just a little less than that of its bulk absorption spectrum in water of 55 nm. Similarly, for C-110, FWHM is 54 nm (air-water) compared to 61 nm in bulk water and for C-6H (data not shown), 60 nm (air-water) compared to 75 nm (bulk water). These results clearly show that even at molecularly sharp air-water interface, where molecules experience an anisotropic dielectric environment, there exist a broad distribution of solvation sites for coumarins.

Another interesting finding is the difference in static local solvation of the coumarins. From fig. 2A, it is clearly seen that C-314 experience polarity in between hexane and THF, which is substantially nonpolar (peak at 420 nm) than that of the bulk water (peak at 448 nm). Interestingly however, C-110 (fig. 2B) and C-6H experience a very polar environment similar to ethanol or propanol at the air-water interface. Surprisingly, the ESFG spectrum of C-110 is nearly identical to its linear absorption in ethanol. Thus, the static local solvation of coumarins depends largely on their molecular structure and not the average dielectric environment of the two bulk phases, separated by the interface.

An important property of interfacial molecules, towards their preferential dielectric environment, could come from their angle of orientation at the interface. Owing to the sharpness and roughness of the interface, a small change in molecular orientation could affect their local solvation appreciably. Fig. 3 shows the variation of  $45^\circ$ -polarized output SHG-intensity of interfacial C-314 with input polarization. The polarization dependent SHG intensity can be expressed in terms of macroscopic second-order nonlinear susceptibility tensor elements as:

$$I_t(2\omega) \propto |c_1 \chi_{XXZ} \cos\gamma \sin\gamma \sin\xi + [(c_2 \chi_{XXZ} + c_3 \chi_{ZXX} + c_4 \chi_{ZZZ}) \cos^2\gamma + c_5 \chi_{ZXX} \sin^2\gamma] \cos\xi|^2 \quad (1)$$

where,  $\gamma$  is input polarization angle,  $\xi$  ( $45^\circ$  in the present study) is the analyzer angle for output SHG and  $c_i$ 's are the constants calculated from the relative dielectric constants of the two media and angle of incidence. Note that,  $\gamma = 90^\circ$  corresponds to s-polarized and  $\gamma = 0^\circ$  corresponds to p-polarized fundamental  $\omega$ -pulse. The solid line in fig. 3 shows the fit to data points using eq. (1). Finally, the macroscopic susceptibility tensor elements are related to the molecular hyperpolarizabilities ( $\beta$ ) to calculate the molecular orientation at the interface. Preliminary calculations of molecular orientation show that C-314 orient in a more vertical fashion than that of C-110 and C-6H at the air-water interface. Eventually, a large portion of C-314 molecule dives more into air-like environment than that of C-110 and C-6H. Thus, our results show local polarity of coumarins at air-water interface is sensitive to their molecular structure and, subsequently, the coumarin orientation at the interface.

#### References:

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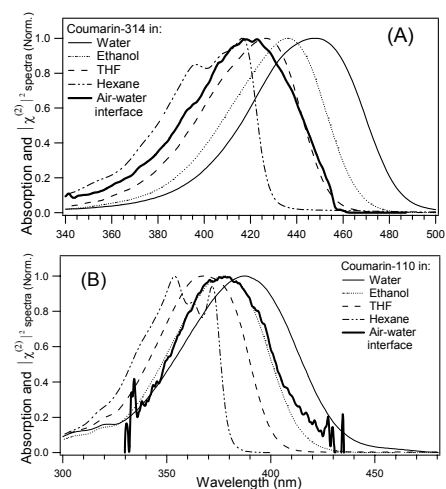


Fig. 2: Bulk absorption and  $|\chi^{(2)}|^2$  spectra of C-314 (A) and C-110 (B) in various environments.

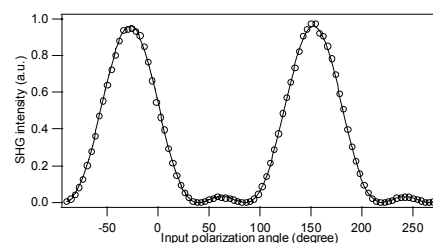


Fig. 3: Polarization dependent SHG of C-314. Output polarization set at  $45^\circ$ .