

# 3P135 Interferometric Heterodyne ESFG and Polarization Dependent SHG Study at Liquid Interface: Coumarins at Air-Water Interface

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## Introduction:

The nature of solute-solvent interactions at interfaces has profound influence on the local polarity that is experienced by the interfacial solute molecules. The variation of such interfacial polarities may occur due to molecule's absolute position along the interface normal, orientation, and absolute 'up' or 'down' alignment.<sup>1,2</sup> Thus characterizing the preferential orientations of the interfacial molecules are important to understand solute-solvent interactions at the interface.<sup>1,2</sup>

The long standing challenges in second-order nonlinear interfacial electronic spectroscopy were to measure the precise electronic spectra of interfacial molecules and to separate the real and imaginary parts of the interfacial susceptibility.

It has already been shown by our group that multiplex Electronic Sum-frequency Generation (ESFG) technique is unique to measure the precise electronic  $|\chi^{(2)}|^2$  spectra of interfacial molecules.<sup>3</sup> However, this homodyne ESFG technique can not provide the real and imaginary parts of electronic  $\chi^{(2)}$ -spectrum, separately. As another novel approach, we have recently

developed the multiplex heterodyne ESFG technique based on an interferometric method which unfolds the real and imaginary  $\chi^{(2)}$ -spectra of interfacial molecules.

In the present study, we have employed our interferometric heterodyne ESFG method to obtain the precise real and imaginary parts of  $\chi^{(2)}$ -spectra of structurally different coumarins (C-314, C-338 and C-110) at the air-water interface. Single-wavelength polarization dependent SHG measurements were also carried out to determine coumarins' angles of orientation at the interface.

## Experimental:

Figure 1 shows the experimental setup of our interferometric heterodyne ESFG which uses a narrow band near-IR pulse ( $\omega_1$ ; 795 nm; *p*-pol.) and a broadband white-light continuum ( $\omega_2$ ; *p*-pol.; 540 nm ~ 1.2  $\mu$ m) as inputs. The generated ESFG signal ( $\omega_1 + \omega_2$ ; 320 nm ~ 480 nm) from the interface, together with the residual reflected  $\omega_1$  and  $\omega_2$  pulses, was passed through a fused silica glass-plate (1 mm) and directed onto a Gallium-Arsenide plate (GaAs plate) to observe the interference between the sample-ESFG with GaAs-ESFG (local oscillator). The glass-plate introduces a time delay (~170 fs) between sample-ESFG and GaAs-ESFG. The output sample-

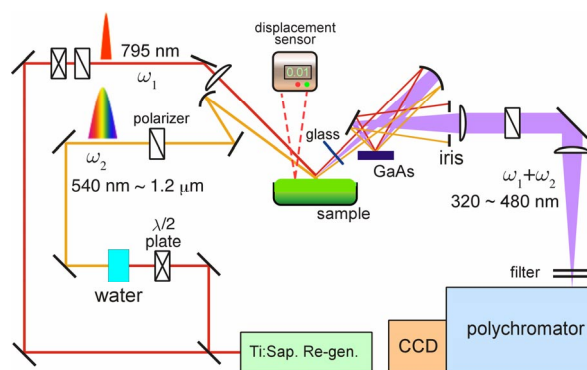


Figure 1: Experimental setup of multiplex interferometric ESFG.

ESFG interferogram (*p*-pol.; 320 nm ~ 480 nm) was recorded on a CCD after passing through a set of filters and a polychromator. The real and imaginary parts were obtained after the Fourier-analysis of frequency-domain interferograms with normalization based on the ESFG from standard quartz. During the measurement the height of the water surface was maintained by a monitoring optical displacement-sensor.

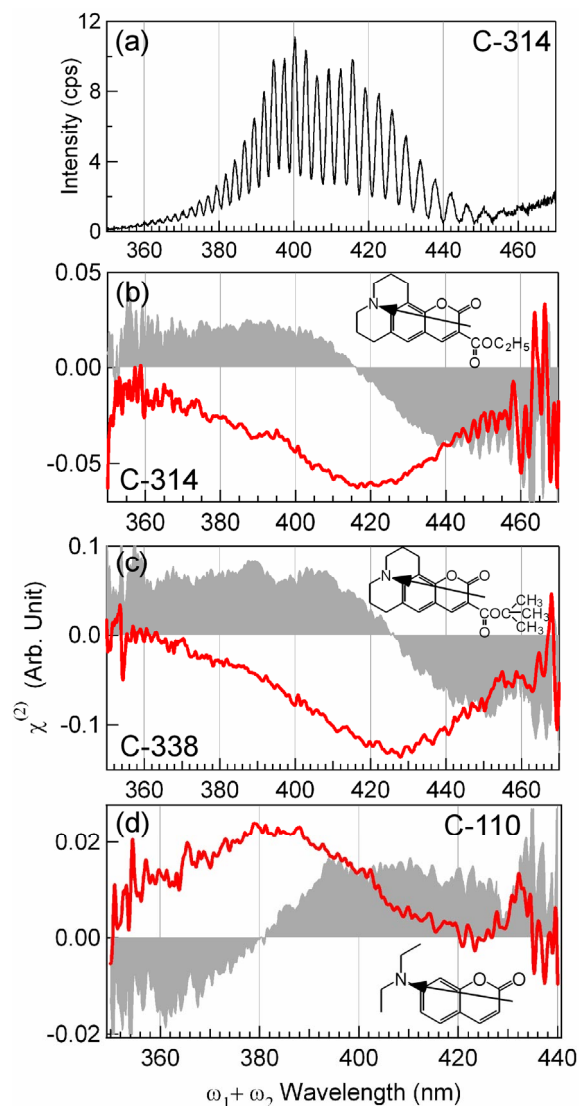
### Results and Discussions:

Figure 2a shows a typical raw data of heterodyne ESFG measurements (C-314) and figures 2b-d show the two-photon single-resonant  $\chi^{(2)}$ -spectra (both real and imaginary parts) of C-314, C-338 and C-110, obtained by the analysis. It is readily seen from fig. 2 that multiplex interferometric heterodyne ESFG method successfully gives precise real and imaginary parts of electronic  $\chi^{(2)}$ -spectra of molecules at liquid interfaces. Some fascinating properties about the coumarin-water interactions at the air-water interface can be found from these  $\chi^{(2)}$ -spectra. First, the sign of the imaginary  $\chi^{(2)}$ -spectra of C-314 and C-338 are negative, whereas it is positive for C-110 at the air-water interface.

Calculating the angle of orientations of coumarins from polarization dependent SHG data and noting the signs of the imaginary  $\chi^{(2)}$ -spectra, we concluded that C314 (134°) and C-338 (131°) take ‘down’ alignment ( $S_1 \leftarrow S_0$  transition dipole pointing down) and C-110 (53°) takes ‘up’ alignment at the air-water interface. Second, by comparing  $\chi^{(2)}$ -spectra of coumarins directly with their linear absorption spectra in bulk liquids, we found different coumarin molecules experience different local polarities and show broad distributions of solvation-sites at the air-water interface.

### References:

- (1) (a) Benjamin, I *Chem. Rev.* **2006**, *106*, 1212. (b) Eisenthal, K. B. *Chem. Rev.* **1996**, *96*, 1343.
- (2) Kemnitz, K. *et al. Chem. Phys. Lett.* **1986**, *131*, 285.
- (3) (a) Yamaguchi, S.; Tahara, T. *J. Phys. Chem. B* **2004**, *108*, 19079. (b) Yamaguchi, S.; Tahara, T. *J. Chem. Phys.* **2006**, *125*, 194711.



**Figure 2:** ESFG frequency-domain interferogram of C-314 (a) and  $\chi^{(2)}$ -spectra of coumarins at air-water interface: C-314 (b), C-338 (c), C-110 (d). Gray-shaded and red curves stand for real and imaginary parts, respectively. Arrows on molecular structures denote the direction of  $S_1 \leftarrow S_0$  transition dipole vector.