Heterodyning of Interface-Selective Nonlinear Spectroscopy

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One of the most important targets of recent molecular science is soft interfaces such as liquid interfaces. We recently developed new interface-selective electronic and vibration nonlinear spectroscopies to study soft interfaces [1-6]. Among them, multiplex electronic sum-frequency generation (ESFG) spectroscopy and femtosecond time-resolved ESFG (TR-ESFG) spectroscopy enabled us to obtain steady-state and time-resolved electronic spectra at liquid interfaces with unprecedented high quality. These new interface-selective electronic spectroscopies attract much attention as new powerful tools for study of soft interfaces [7]. ESFG spectroscopy, however, does not provide information of $\chi^{(2)}$ itself but gives data about its square modulus, i.e., $|\chi^{(2)}|^2$, because the intensity of the nonlinear optical signal is directly detected (homodyne detection).

This drawback of the homodyne ESFG spectroscopy can be overcome by heterodyne detection in which the signal light is mixed with local oscillator with a controlled phase relation. We extended the original ESFG spectroscopy to heterodyne measurements by utilizing a tandem configuration, as shown in Fig. 1. In this configuration, a liquid sample to be studied is set at one sample point, and GaAs, which generates LO, is placed at the other. The interference of the SFG signals from the sample and GaAs is detected with a spectrograph and a CCD. We successfully achieved heterodyne detection of ESFG for the first time (HD-ESFG) [8]. On the basis of this HD-ESFG scheme, we also carried out heterodyning of vibrational sum-frequency generation (VSFG). We obtained the imaginary part and real part of

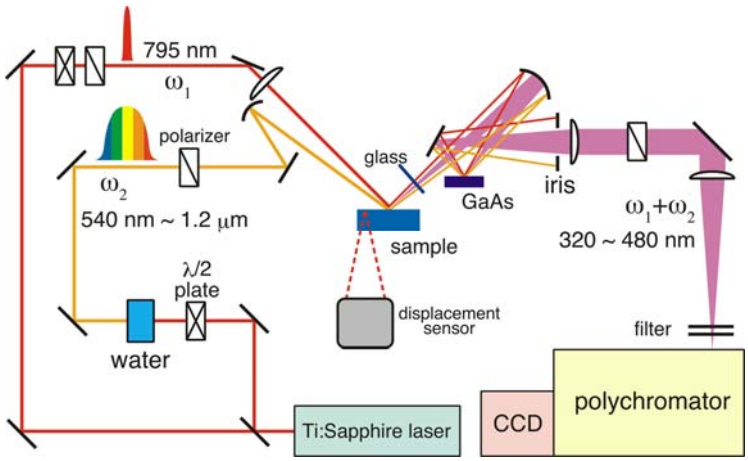

Fig. 1 Setup of heterodyne detected electronic sum-frequency generation (HD-ESFG) spectroscopy

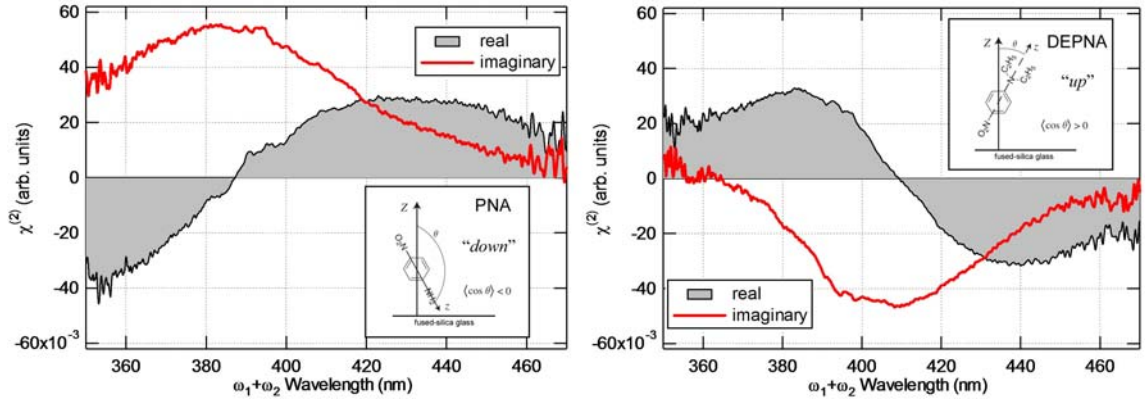

Fig. 2 HD-ESFG spectra of p-nitroaniline (PNA: left) and N,N'-diethyl-p-nitoroaniline (DEPNA: right). at the air/fused-silica interface (red: imaginary part; black: real part). The opposite sign of the spectra manifest the opposite orientation of PNA and DEPNA at the interface.

vibrationally resonant $\chi^{(2)}$ spectra in multiplex VSFG measurements for the first time [9].

With the heterodyning of ESFG and VSFG, we are now able to directly obtain experimental data that are linearized to electronically resonant or vibrationally resonant $\chi^{(2)}$. One of the unique information obtainable with the heterodyned second-order nonlinear spectroscopy is the absolute orientation of interfacial molecules. Actually, we observed flip-flop of p-nitroaniline derivatives at the air/glass interface with HD-ESFG (Fig. 2) [8] and revealed flip-flop of water molecules at the air/water interface with HD-VSFG [9].

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