Ultrafast vibrational dynamics of CO on Pt(111) studied by time-resolved SFG with phase-sensitive detection

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Time-resolved sum-frequency generation (SFG) has been known as a powerful method to elucidate vibrational dynamics at surfaces. In this paper, we report on our recent achievement to combine a phase-sensitive (heterodyne) detection with the femtosecond IR-visible SFG spectroscopy for carbon monoxide adsorbed on Pt(111) under an UHV condition. We show that the novel technique enables us to obtain separately the real and imaginary parts of the transient changes in $\chi^{(2)}$, and that the Im[$\chi^{(2)}$] of C-O stretching region shows marked transient asymmetry upon excitation with 400 nm, 150 fs pulses, which is ascribed to Fano interference between C-O stretching mode and substrate electronic excitations. We have found that the excitation of frustrated modes enhances the nonadiabatic coupling of the C-O mode with substrate electronic excitation and leads to the spectral asymmetry.

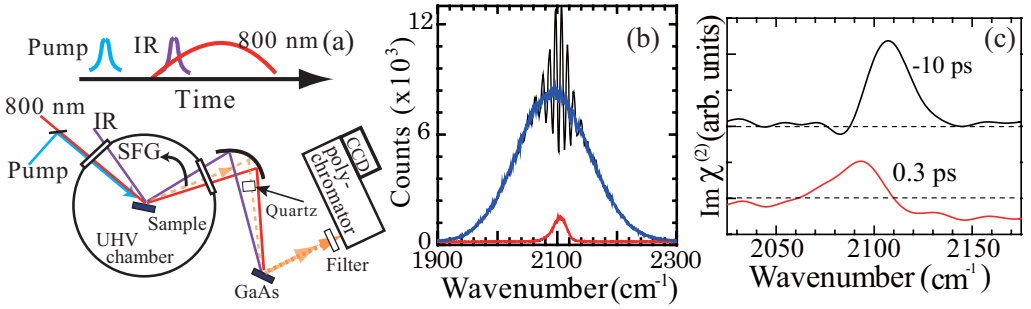

Figure 1: (a) A schematic diagram of setup for time-resolved SFG with heterodyne detection. (b) SFG spectra of on-top CO on Pt(111) observed with heterodyne (black) and homodyne (red) in addition to a spectrum of local oscillator (blue). (c) Time-resolved Im[$\chi^{(2)}$] spectra of C-O stretching band. Pump-IR delay time is indicated in the figure.