Background-Free Fourth-Order Optical Spectroscopy of Interfaces

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Recent development of the two-dimensional sum-frequency generation spectroscopy has enabled an insight into the molecular vibrational dynamics at interfaces. Its implementation, however, has so far remained limited to the pump-probe geometry, with its inherent restrictions. Here, we report proof-of-concept background-free measurements of the fourth-order susceptibility using non-collinear optical layout.

Vibrational sum-frequency generation (SFG) spectroscopy is extensively utilized to characterize molecular structure at various interfaces by measuring the second-order optical susceptibility, $\chi^{(2)}$. For the better understanding of the vibrational couplings and dynamics of the interfacial molecules one needs to measure the fourth-order optical susceptibility, $\chi^{(4)}$. This is usually done by using the recently developed two-dimensional SFG (2D SFG) spectroscopy [1]. Due to the phase-matching conditions, in a typical experimental geometry for the 2D-SFG spectroscopy the $\chi^{(4)}$ optical response is emitted along the direction of a much stronger $\chi^{(2)}$ response. Simultaneous detection of both the $\chi^{(4)}$ and $\chi^{(2)}$ responses generates an interference of these signals, which may complicate the interpretation of the measured data.

Because the collinearity of the $\chi^{(4)}$ and $\chi^{(2)}$ signals originates from the collinear geometry for the pump pulses in a typical experimental layout, the background free detection of the $\chi^{(4)}$ response can be achieved by utilizing a non-collinear geometry. Here, we present an experimental implementation of a non-collinear 2D SFG spectroscopy. By using the triangle geometry and the homodyne detection we measure the time- and frequency resolved background-free $|\chi^{(4)}|^2$ response from a model GaAs (110) surface. To add the second frequency dimension we employ the time-domain approach and the heterodyne detection [2], which allows us to perform phase-sensitive measurements [3].

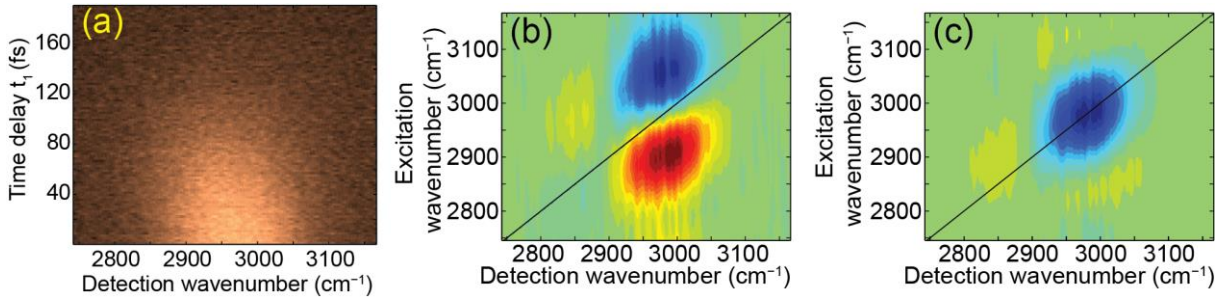

Fig. 1 Background free fourth-order optical response from a GaAs (110) surface: (a) free induction decay of the homodyne-detected $\chi^{(4)}$ signal; (b) real and (c) imaginary parts of the $\chi^{(4)}$ measured by the Fourier transform non-collinear 2D SFG.

[1] J. Bredenbeck *et al.*, JACS **130, 2152** (2008).
[2] W. Xiong *et al.*, PNAS 108, 20902 (2011).
[3] M. Schleeger *et al.*, J. Phys. Chem. Lett. **6**, 2114 (2015)