Coherent two-dimensional terahertz-terahertz-Raman spectroscopy of liquids

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We demonstrate 2D-THz-THz-Raman spectroscopy to investigate the dynamics of liquids. By varying the timing between two intense terahertz pulses, we control the orientation of molecules in the liquid and excite nonlinear vibrational coherences. We have sufficient sensitivity to observe non-rephasing and rephasing nonlinear signals.

Detailed molecular pictures of the structure and dynamics of liquids drive our understanding of chemistry and biology. Nonlinear two dimensional (2D)-infrared and -nuclear magnetic resonance spectroscopies have revealed many specifics of liquid behavior [1, 2]. However, the motions that directly participate in solvation and chemical reactivity are manifest in the terahertz (THz) region of the spectrum, making 2D-THz studies especially valuable. Here, we demonstrate 2D-THz-THz-Raman (2D TTR) spectroscopy to study the low-energy motions of liquids and other isotropic materials. By varying the timing between two intense THz pulses, we control the orientational alignment of molecules in a liquid, and nonlinearly excite vibrational coherences. We describe the instrument in detail and present a comparison of experimental and simulated 2D TTR spectra of bromoform, carbon tetrachloride, and dibromodichloromethane, which show previously unobserved anharmonic coupling between thermally populated vibrational modes. The sensitivity of the instrument allows for the measurement of both non-rephasing and rephasing contributions of the nonlinear signal.

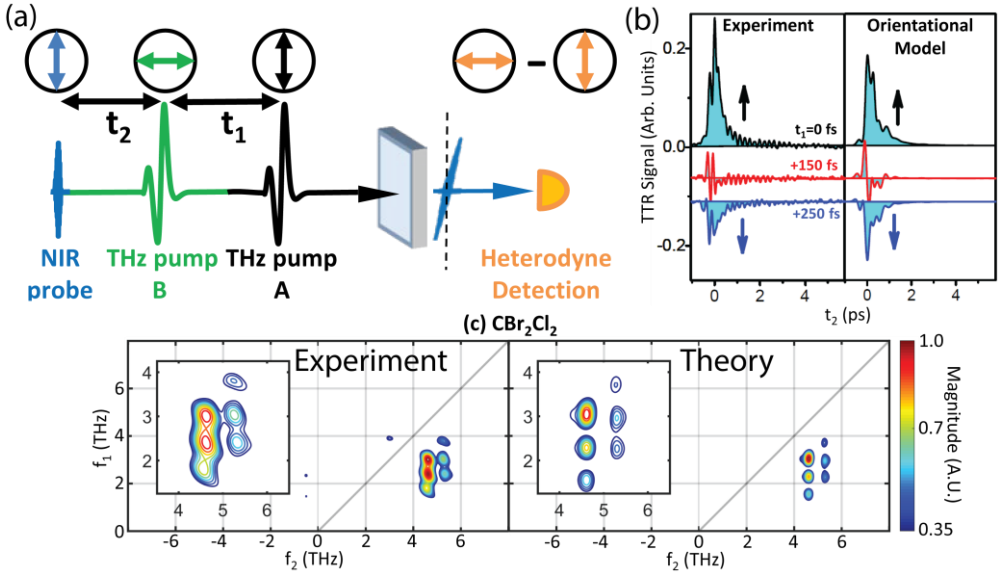

Figure 1. (a) Diagram of Pulse sequence and polarization. (b) 1D-TTR traces demonstrating that changing time between THz pulses changes molecular orientation. (c) 2D TTR plots (experimental and calculated) showing the anharmonic coupling in CBr_2Cl_2.

[1] Ramasesha, K., et al. Nat. Chem. **5**, 935-940 (2013).
[2] Macura, S. & Ernst, R., Mol. Phys. **41**, 95-117 (1980).