Two-Dimensional Terahertz-Spectroscopy on Aspirin

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Ultrafast phonon dynamics in polycrystalline Aspirin is studied with 2D THz spectroscopy. The hybrid mode of the CH_3-rotations with collective oscillations of the π-electrons shows a nonlinear absorption around 1.4 THz that leads to a coherent emission at 1.9 THz pointing to a dynamic breakup of the strong electron-phonon correlations.

Recent theoretical work [1] on the electronic and phononic structure of crystalline Aspirin (acetylsalicylic acid**,** $C_9H_8O_4$) has shown that its vibrational modes in the THz frequency range [2] exhibit a pronounced coupling to electron density fluctuations in the aromatic rings. Similar to the soft-mode in ferroelectrics [3] the 'free' CH_3-rotation forms a strongly red-shifted hybrid mode with charge oscillations of the π-electrons around 1.7 THz [Fig. 1(d)]. Here, we use ultrafast 2D THz spectroscopy [4] to investigate the nonlinear response of such correlations in the THz frequency range at T = 80 K. We use two THz pulses (center frequency: 2 THz) generated by optical rectification from the output of a femtosecond Ti:sapphire laser system. Their electric fields as functions of real time *t* and of the coherence time τ between the pulses are measured by electro-optic sampling [Fig. 1(a)]. The Fourier transform [Figs. 1(c)] shows strong nonlinear signals at the detection frequency $\nu_t = 1.7$ THz of the hybrid mode. Combining the rephasing with the non-rephasing to a purely absorptive 2D spectrum [Fig. 1(e)] shows that a nonlinear absorption around 1.4 THz leads to a coherent emission at 2 THz pointing to a dynamic breakup of the strong electron-phonon correlations.

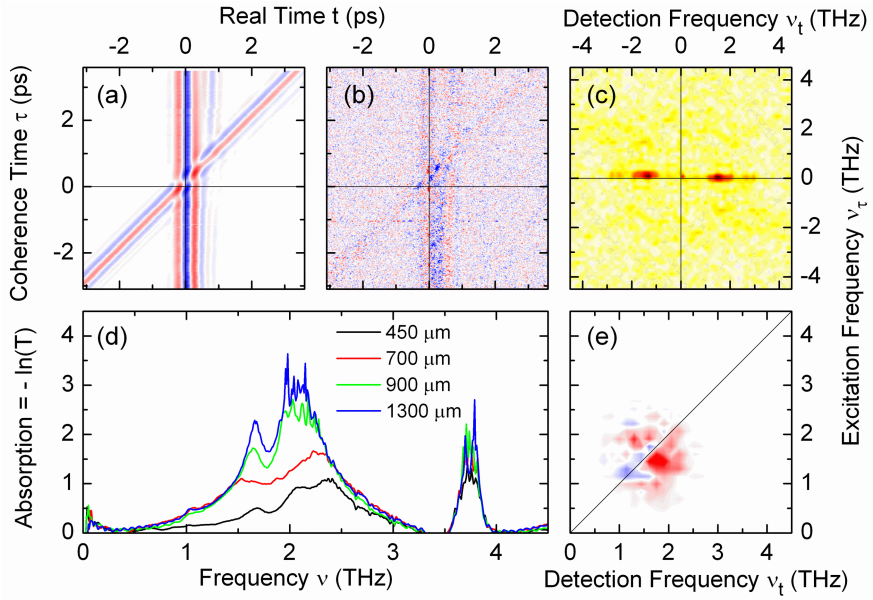

Fig. 1 (a) Electric field transients of two THz pulses A and B as a function of real time *t* and coherence time τ. (b) Corresponding nonlinear signal measured at T = 80 K. (c) Two-dimensional Fourier transforms of the total nonlinear signal. (d) The experimental linear absorption spectra of tablets of polycrystalline Aspirin with different thicknesses. (e) Imaginary part of the purely absorptive 2D spectrum of Aspirin measured at T = 80 K.

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