Strong Coupling of Light with Collective Terahertz Vibrations in Organic Materials

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Abstract: We demonstrate for the first time strong coupling between a terahertz cavity and collective, intermolecular vibrations in organic crystals. Beyond observing the Rabi splitting, we directly measure the vacuum Rabi oscillations using time-domain THz spectroscopy. © 2019 The Author(s)

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Since the first observation of the strong coupling between an optical microcavity and Frenkel excitons in organic semiconductors, strong coupling of light and molecules has been increasingly drawing interest, driven by the opportunities for novel optoelectronic devices [1]. Moreover, several years ago it was demonstrated that the creation of hybrid polaritonic wavefunctions under strong coupling can be exploited for tailoring the material properties of molecules [2,3], which led to the emergence of a new field known as "polaritonic chemistry". Recently, strong coupling of intra-molecular vibrations in mid-infrared resonators was introduced as a new paradigm [4], in which the creation of vibro-polaritons allows the manipulation of molecular processes occurring at the electronic ground-state, by targeting a specific bond inside the molecules. Here, we take vibrational strong coupling into a new regime: we demonstrate, for the first time, strong coupling of collective vibrations in organic molecule crystallites, occurring at THz frequencies. Unlike previously studies of vibrational strong coupling, here the cavity mode is coupled to inter-molecular vibrations, i.e. an oscillatory motion of the molecules with respect to one another.

In our experiments, an open-cavity geometry [see Fig. 1(a)] is utilized, in which the cavity is formed by two thin Au mirrors (~6nm) deposited on quartz substrates. The α-lactose pellet is mounted on a fixed Au mirror, while the position of the second mirror is adjusted using a translation stage. (b) THz absorption spectrum of crystalline α-lactose pellet, showing a sharp absorption peak at 0.53 THz, which corresponds to a collective vibration of the molecular crystal. The inset shows the chemical structure of a single α-lactose molecule.

In our experiments, an open-cavity geometry [see Fig. 1(a)] is utilized, in which the cavity is formed by two thin gold mirrors deposited on quartz substrates, with one of the mirrors mounted on a translation stage, such that the length of the cavity can be continuously varied. As the active material, we use α-lactose crystallites, which exhibit a sharp absorption peak at 0.53 THz, with a linewidth of 21 GHz, as shown in Fig. 1(b). This absorption line corresponds to a collective, intermolecular vibration in the molecular crystal, in which the molecules move with respect to each other as a rigid body [5]. We prepare a 250 µm-thick pellet of α-lactose and attach it to the fixed mirror of the cavity. To study the dynamics of the coupled system we use time-domain THz spectroscopy [6], which allows us to record the THz field including its oscillating phase. We generate a single-cycle THz pulse, as shown in Fig. 2(a), and launch it into the cavity. The power spectrum of the incoming pulse [Fig. 2(b)] is centered around 0.6 THz, with a usable spectrum covering the 0.1-1.2 THz range. We first characterize the empty cavity, i.e. with only air between the mirrors, with the distance between them set to 640 µm. As shown in Fig. 2(c), when the single-cycle THz pulse passes through the cavity, it is stretched to an exponentially-decaying oscillatory signal, as expected for a resonant cavity with a finite lifetime. By Fourier-transforming the signal and calculating the ratio between its power
spectrum and the input pulse power spectrum [Fig. 2(b)], we obtain the empty cavity transmission spectrum [Fig. 2(d)]. As seen, the resonant Fabry-Perot cavity modes are clearly visible, with a linewidth of 14 GHz.

Next, we repeat these measurements for the cavity with the α-lactose pellet, adjusting the cavity length such that its second-order mode is tuned to the vibrational absorption peak at 0.53 THz. As seen in Fig. 2(e), we observe a similar exponentially-decaying oscillation as for the empty cavity, but here the signal is modulated by a periodic envelope. In the spectral domain [Fig. 2(f)], we observe a clear Rabi-splitting around the α-lactose vibrational frequency, signifying the strong coupling between the collective vibrations in the α-lactose crystallites and the cavity and the formation of two THz vibro-polariton states. Furthermore, when we numerically remove the peaks corresponding to the first and third-order modes of the cavity (at 0.25 and 0.83 THz) and reconstruct the time-domain signal by inverse Fourier transform [Fig. 2(g)], the periodic modulation observed in Fig. 2(e) becomes much clearer. This modulation, with a period of ~15psec, corresponds to the coherent vacuum Rabi-oscillations, directly observed in the time domain.

Finally, we vary the cavity length to scan its resonance across the vibrational absorption line of the α-lactose, repeat the measurements and extract the location of the two vibro-polariton peaks. In Fig. 2(h) we plot the polariton frequencies (marked by circles) as a function of the resonance frequency of the cavity mode. By fitting the results to dispersion curves obtained from a coupled-oscillator model (solid black lines), we extract a coupling strength of 68 GHz, which is larger than the linewidths of both the cavity and the collective molecular vibration. This confirms that our system is indeed within the strong coupling regime. This first observation of strong coupling with THz molecular vibrations take strong light-matter coupling into a new class of material, including polymers, proteins and other organic materials, in which collective, spatially extended degrees of freedom participate in the dynamics.

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