Ultrafast Manipulation of Electro-Absorption in Colloidal Quantum Dots by MV/cm-THz Fields from DAST driven by mid-IR Pulses

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Abstract: We present a comparative study on efficient THz generation by optical rectification of 3.9 µm and 1.95 µm pulses in DAST, achieving up to 40 MV/cm field amplitudes. The ultrafast free-space THz signal is encoded onto an optical signal probing the absorption of CdSe/CdS core/shell quantum dots.

Recently, a considerable progress has been demonstrated in THz generation by optical rectification (OR) in organic crystals, conventionally driven by near-IR fs-pulses centered at the telecommunication wavelength of 1.5 µm. Although high optical- to THz conversion efficiencies of 1-3% with pulse energies of up to 0.9 mJ [1] were reported, further scaling of the performance is deteriorated by multiphoton absorption and is fundamentally limited by the optical damage threshold of the crystal. This restricts the applicable pump fluence to nothing more than 20 mJ/cm².

In this work, we report on efficient THz generation in DAST (4-N, N dimethylamino-4’-N’ methylstilbazolium tosylate) when the crystal is pumped with mid-IR sub 100-fs pulses centered at (i) 3.9 µm and (ii) its second harmonic at 1.95 µm [2]. Suppression of multi-photon absorption shifts the onset of saturation of the THz conversion efficiency to pump energy densities, which are almost an order of magnitude higher as compared to the conventional pump schemes at 1.5 µm. The observed high sensitivity of the THz generation to the parameters of the mid-IR driving pulses motivates an in-depth study of the underlying interplay of nonlinear wavelength- and intensity-dependent effects. The resulting strong THz field is capable of driving electro-absorption modulation in CdSe/CdS quantum dots (QDs), inducing astonishing 15% change in transmission of a visible probe pulse with an extinction ratio exceeding 6 dB. The results lay the groundwork for high-speed optical communication systems with data rates in the Tbit/s range.

Fig. 1. Optical- to THz conversion efficiency (red) and THz energy (black) with respect to the pump fluence and input energy for (a) 3.9 µm and (b) 1.95 µm driving pulses. (c) Transmission of DAST with respect to the pump fluence at 1.95 µm (red), showing no signature of multi-photon absorption. And transmission spectrum (black), indicating a comparable transmission at 1.5 µm and 1.95 µm. (d) Spectrum of the 1.95 µm pump pulse (red) and spectral transformations of the pump pulse after propagation in DAST (blue).

We first investigate THz generation by pumping at 3.9 µm, where the transmission of DAST drops to ~10% [2]. Despite strong linear absorption at 3.9 µm, DAST exhibits a high optical-to-THz conversion efficiency (see Fig. 1(a)), which we attribute to advantageous matching between the THz phase velocity and group velocity of the driving pulse and to a resonantly-enhanced nonlinearity. Moreover, no saturation of the conversion efficiency can be
distinctively identified even for a high pump fluence of more than 100 mJ/cm². The peak THz electric field strengths of 40 MV/cm is obtained by measuring the THz pulse energy, spot size and temporal field evolution with electro optical sampling (EOS). At 1.95 µm we find that low linear and multi-photon absorption (Fig. 1(c)) leads to record optical- to THz conversion efficiencies approaching 6% (Fig. 1 (b)). To further investigate the mechanism of this efficient THz generation, we monitor spectral transformations of the pump pulse after propagation in DAST. Increasing spectral broadening and significant redshift with a rising pump fluence until the onset of saturation (Fig.1 (d)) can be observed. This observation strongly indicates cascaded OR, wherein a pump photon, which emits a THz photon, experiences a small red shift and can then contribute again to THz generation by OR. Although this process initially results in higher optical to THz conversion efficiencies, eventually it limits THz generation because the phase mismatch due to the material dispersion with the newly generated photons is enhanced and ultimately inhibits efficient THz generation.

A change in absorption in the QD film of a 622 nm, sub 50-fs probe pulse with respect to the time delay of the THz pulse is measured in a balanced detection scheme. When an external electric field is applied to such a 0D quantum structure, it bends valence and conduction energy bands and shifts the absorption edge to smaller energies. In addition, the overlap between the electron and hole wave functions decreases, which diminishes the amount of absorption, as described by the quantum confined stark effect (QCSE) [4]. Previous works [5,6] report on a THz induced QCSE where the required electric field strength in the MV/cm range was achieved with field enhancing microstructures. In contrast, in this work the manipulation of the optical absorption in the sub-picosecond time scale is achieved in QDs deposited onto a glass substrate by a simple drop-casting method (see a QD sample in Fig. 2 (b)). We show that, when a broad bandwidth THz pulse with an electric field of more than 10 MV/cm (Fig.2 (c)) is applied, the relative change in absorption (red line in Fig.2. (d)) of a probe pulse with a photon energy just above the absorption edge of the QDs evidently follows the THz field variation (blue area). For an applied field of 13.3 MV/cm, an extreme change in transmission of more than 15% is measured when the probe pulse temporally overlaps with the maximum of the THz electric field, which is, to the best of our knowledge, the highest value ever reported for solution processed electro-absorption materials at room temperature. However, the poor modulation contrast between the ON/OFF signals (when the ultrafast THz field crosses zero) is fundamentally limited by the time bandwidth product of the probe pulse and short THz period. Thus, we insert a long pass filter with a cut off frequency at 2 THz to elongate the THz period (Fig.2 (e)). The resulting THz induced absorption modulation (blue line in Fig.2 (f)) exhibits an extinction ratio of more than 6 dB, which is comparable with quantum well electro-absorption modulators operating in the GHz range.

![Fig2. (a) Transmission electron microscopy (TEM) image of colloidal QDs. (b) QD films deposited on a glass substrate with drop casting. (c) Unmodified THz-field transient and spectral intensity (inset) measured with EOS. (d) Normalized change in optical density (red line) and THz intensity (blue area) of the field transient shown in (c). (e) THz field when a long pass filter with a cut off frequency of 2 THz is inserted. (e) Corresponding THz intensity (grey area) and change in optical density (blue line).](image)

A possibility to access the QCSE directly without any field enhancing structures, potentially allows us to study a large variety of samples and excludes possible artefacts from the enhancement structures. The obtained results demonstrate a feasibility to manipulate the electronic structure of QDs by direct THz excitation and paves the way for further fundamental studies of THz driven QCSE as well as for future developments in the areas of THz opto-electronics, wireless communications with data rates of Tbit/s and THz driven non-linear optics.