Dependence of a direct THz driven Stark effect on the energy band alignment in heterostructure Quantum Dots

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Abstract: We report on direct ultrafast electro-absorption switching in colloidal CdSe/CdS core/shell quantum dots driven by intense THz pulses without a field enhancing structure, and suggest a route to optimize electro-absorption modulators with respect to the energy band alignment of the heterostructure material. © 2022 The Author(s)

Electro-absorption (EA) modulators based on the quantum confined Stark effect (QCE) play a key role in a continual effort to increase the speed of optical networks. When an external electric field is applied to a quantum-confined structure, it bends the energy bands and shifts the absorption edge to smaller energies. In addition, the overlap between electron and hole wave functions decreases, which diminishes the amount of absorption [1]. Ultrafast interconnect rates of up to Tbits/s should be feasible with THz waveforms applied to such modulators as a driving field. However, in a nanoscale device, the required absorption modulation depth can only be induced if the strength of the externally applied THz field reaches an extremely high MV/cm level. To date, because of the lack of appropriately intense THz emitters, a THz-induced Stark effect could only be demonstrated in elaborate structures that feature a local field enhancement geometry [2,3].

Using a home-built laser-driven THz source [4], we succeed in a direct all-optical encoding of a free-space ultrafast THz signal onto an optical signal that probes the absorption of CdSe/CdS core/shell quantum dots (QDs). The simplified geometry, that strips the system of numerous artefacts found in enhancement geometries, such as electrode-driven charge injection, enables us to solely map the undistorted ultrafast carrier dynamics, allows to adopt a simple intuitive theoretical model which matches the experimental data remarkable well and has a valuable predictive power for the band alignment and modulation depth improvement in next-generation ultrafast optical switches.

![Fig. 1](image-url)

Fig. 1 (a) THz transient measured with EOS and corresponding spectrum (inset). (b) Normalized change in transmission of the QD sample at 622 nm (red line) and THz intensity (blue area), obtained by taking the square of the field transient shown in (a). The right y-axis indicates the modulation depth. (c) and (d) present the same as (a) and (b) for a modulated THz transient.

Characterization of the THz transient in time domain is performed by electro-optical sampling (EOS) with a 50 μm thick GaP crystal. The time evolution of a measured THz pulse is depicted in Fig. 1 (a) with the corresponding power spectrum in the inset. The probe pulse is thereby provided by a wavelength tune-able optical parametric amplifier (OPA). The change in absorption of the probe pulse in a thin QD film is measured in a balanced detection scheme with respect to the time overlap with the THz pulse. The blue area in Fig. 1 (b) represents the THz intensity, given by the square of the THz field amplitude shown in Fig. 1 (a). The relative change in transmission (red line) for a visible probe pulse centred at 622 nm (with a photon energy larger than the band gap of the heterostructure QDs) evidently follows the THz electric field. Measurements with an applied THz field strength of 13.3 MV/cm at the focal position reveal an absolute change in transmission of groundbreaking 15.8%, which is to the best of our knowledge, the highest value of EA modulation ever reported for solution processed materials at room temperature. Nevertheless, the modulation depth of the signal is limited by the pulse duration and spectral width of the probe pulse, as well as the short THz field period. The modulation time can be elongated by inserting a long pass filter with a cut-of frequency.
of 2 THz into the THz beam path, as shown in Fig. 1 (c). The contrast between the THz periods is thereby substantially increased, leading to an extinction ratio of 6.8 dB of the probe signal (see Fig. 1 (d)), which is on a par with conventional quantum-well electro-absorption modulators operating in the GHz range [5], demonstrating the feasibility to manipulate the electronic structure of QDs by direct THz excitation without a need of field enhancement techniques.

In order to investigate the origin of the observed outstanding performance, we conduct Stark spectroscopy measurements by tuning the central wavelength of the probe pulse across the band gap of the QD film, as illustrated in Fig. 2 (a), while keeping the delay between the THz-pump and visible-probe at the position where the induced changes in absorption are the largest. The results of two separate measurements with different field strengths are presented in Fig. 2 (b) by green and red dots. The solid lines show the results of a straightforward theoretical model, strongly supporting our experimental findings. By solving Schrödinger's equation with an envelope based ansatz numerically, we get access to the wave functions and are able to conclude fundamental physical properties from this. Note that the electric field experienced by the excitons of the QDs can be up to an order of magnitude smaller compared to the field amplitude propagating in dry air, due to screening effects of the QD film. With the electric field strength as the final and only fitting parameter, the simulation reproduces the experimental data surprisingly well and justifies further discussion on the energy band alignment of the CdSe/CdS heterostructure QDs.

In general, the energy band alignment of core/shell QDs can be categorized in type-I, quasi-type II, and type-II, depending on the energy band offsets between the core and shell material and probability density of electron and hole wavefunctions. In this work, the energy band structure exhibits a quasi-type II alignment, wherein the holes are located in the core material while the electrons are delocalised across the entire QD. Figure 2 (c) shows the calculated relative change in overlap integral of the electron and hole wavefunction (top) and Stark energy shift (bottom) with respect to an applied electric field strength for three different energy band alignments. As it follows from the simulations, the strongest change of the overlap integral and the largest Stark shift, especially at small and moderate electric field strengths, is expected for type-II and quasi type-II band structures.

![Stark Spectroscopy](image.png)

(a) Optical density (green line) and normalised probe spectra (areas) tuned across the band edge. (b) Measured Stark spectra (dots) for two different field strengths experienced by the excitons of the QDs, and simulated changes in optical density (lines) for 1.1 MV/cm (red) and 1MV/cm (green). (c) Relative change of the squared overlap integral of the electron and hole wavefunction (top) as well as Stark energy shift (bottom) with respect to an applied electric field for three types of energy band alignment (see legend). The electron and hole wavefunctions are denoted as \( \Psi_e \) and \( \Psi_h \), respectively.

We therefor suggest that type-II QDs are promising materials for EA modulators with extremely high modulation signals. The fact that CdSe/CdS QDs can be tuned between the type-I and type-II regime by varying the core radius and shell thickness [6], makes it possible to precisely adjust the energy band structure and optimize the performance as well as tune the operation wavelength for future high-speed optical communication systems.

References