Resolving multi-exciton generation by attosecond spectroscopy

A. J. Neukirch,¹ D. M. Neumark,^{2,3} M. F. Kling,⁴ and O. V. Prezhdo^{5,*}

 ¹Department of Physics and Astronomy, University of Rochester, Rochester, NY 14627 USA
 ²Department of Chemistry, University of California, Berkeley, CA 94720 USA
 ³Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA 94720 USA

⁴Department für Physik, Ludwig-Maximilians-Universität, Am Coulombwall 1, 85748 Garching, Germany

⁵ Department of Chemistry, University of Southern California, Los Angeles, CA 90089 USA *prezhdo@usc.edu

Abstract: We propose an experimentally viable attosecond transient absorption spectroscopy scheme to resolve controversies regarding multiexciton (ME) generation in nanoscale systems. Absence of oscillations indicates that light excites single excitons, and MEs are created by incoherent impact ionization. An oscillation indicates the coherent mechanism, involving excitation of superpositions of single and MEs. The oscillation decay, ranging from 5 fs at ambient temperature to 20 fs at 100 K, gives the elastic exciton-phonon scattering time. The signal is best observed with multiple-cycle pump pulses.

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OCIS codes: (030.1640) Coherence; (160.4236) Nanomaterials; (300.6530) Ultrafast spectroscopy.

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1. Introduction

Semiconductor quantum dots are good candidates for the development of low cost, high efficiency devices including lasers [1], flourescent biotags [2, 3], and solar cells [4, 5]. One of the most promising properties that occurs in a variety of nanoscale materials is multi-exciton (ME) generation (MEG) which is important for both fundamental and practical reasons. It can lead to increased solar cell efficiency [5–11], but impedes optical gain in lasers [12]. There exist a number of unresolved issues regarding the MEG mechanisms, and their competition with other ultrafast processes [13–16]. Impact ionization known in bulk semiconductors gives incoherent MEG [17]. Enhanced by confinement, electron-hole interactions allow excitation of coherent superpositions of single excitons (SE) and MEs, followed by dephasing to form pure ME or SE states [18–23]. This photoexcitation mechanism operates within femtoseconds, out-competing energy losses to heat. Time resolved *ab initio* studies have suggested that different mechanisms may take place, and that the dominant mechanism depends on the material, temperature, as well as the defects and ligands incorporated into the system [21, 24]. A comprehensive MEG description would facilitate MEG optimization and requires an account of the ultrafast decoherence between SEs and MEs that takes place on the femtosecond time scale [25–27].

Attosecond spectroscopy offers the possibility of investigating ultrafast non-adiabatic quantum dynamics on time scales that are commensurate with electron motion [28, 29]. Attosecond sources promise to shine new light on delayed photoemission from atoms [30, 31] and surfaces [32], ultrafast Auger decay [33], non-Born-Oppenheimer reaction dynamics [34, 35], and quantum path manipulation [36] There is much interest in extending attosecond spectroscopy to nanoscale systems. Theorists study collective electron dynamics in nanostructured surfaces [37–42] and transient opto-electronic properties of dielectrics in strong fields [43], triggering experimental research [44–50]. Recently demonstrated [51], attosecond transient absorption (TA) is a powerful tool for detection of valence electron motion and wavepacket interference in atoms and ions [51–55], investigation of ultrafast semi-metalization of dielectrics [49, 50], and quantum phase control of Fano-resonances [56]. So far, the opportunities arising from the use of attosecond light pulses have not been considered for low-dimensional nanomaterials, including zero-dimensional quantum dots (QD).

In this letter, we show how attosecond spectroscopy can be used to detect the subfemtosecond formation of MEG, establish the mechanism of MEG, and resolve the controversies regarding MEs in nanoscale materials. In the investigated approach a pump pulse excites electrons from the valence band to the conduction band. The ensuing dynamics are investigated by measuring the absorption of a probe pulse that excites core electrons into the holes existing in the valence band. The proposed experiments will show whether the ME state is photoexcited in a superposition with SE states, or if MEs are created in a separate step, subsequent to SE excitation. An oscillation in the attosecond absorption signal will indicate the formation of superpositions of SEs and MEs, while absence of oscillation will indicate the sequential mechanism. Interactions with the environment will cause a superposition to dephase into either a pure ME or pure SE state. The decay of the signal oscillations will determine the time scale of the elastic exciton-phonon scattering, responsible for decoherence of the superposition of SEs and MEs. The calculations predict that the coherence persists for 5 fs at ambient temperature and 20 fs at 100 K. The coherence oscillations are longer lived when the superposition is created by a smaller spectral bandwidth, 6-cycle pump pulse, compared to a wide bandwidth, 2-cycle pulse. By applying the proposed attosecond technique to QDs made from various semiconductors and having different size, shape, surface ligands and core/shell architecture, one can study systematically, for the first time, the sub-10 fs processes underlying exciton dynamics in nanoscale materials. The proposed technique can be easily extended from quasi-zero dimensional QDs, to one-dimensional carbon nanotubes, to two-dimensional graphene, MoS₂, and to other nanoscale materials.

The ultra-violet (UV) or vacuum-ultraviolet (VUV) pump pulse serves to excite electrons from the valence band (VB) to the conduction band (CB) in a QD. Experimental parameters may depend on the particular system, motivating us to study two types of QDs, PbSe and Si. We chose these particular systems since theoretical models have indicated that MEG in PbSe [21] and Si [24] QDs are fundamentally different. For PbSe QDs, calculations suggest a sharp transition from single to double excitons between 2.5 and 3 times the band gap [21], while in Si QDs there is an energy range where the excited state is a combination of SEs and MEs [24]. Once electrons are excited from the VB to the CB, the transient absorption of an attosecond extreme ultraviolet (EUV) probe pulse is used to interrogate the exciton dynamics. As schematically shown in Fig. 1, the probe energy necessary to promote a core electron to an ME valence hole is larger than the energy required to promote it to an SE hole.



Fig. 1. Experimental method. A femtosecond or attosecond UV/VUV pump pulse creates a superposition of SE and ME states. Phonon-induced dephasing and relaxation are probed using attosecond transient absorption via promotion of a core electron into the valence band using an EUV probe pulse.

We have modeled PbSe QDs at 0, 128, and 347 K. It has been shown that the MEG rate increases rapidly at energies three times larger than the band gap, and PbSe QDs have band gaps on the order of 1 eV. Pulses at 3.15 eV are obtainable through frequency doubled Ti-

tanium:Sapphire lasers [57], and this is the energy used in the following analysis. There are several trade-offs when choosing the duration of the pulse. The coherence oscillations under investigation exist for about 10 fs, while analysis of the transient absorption in the probe pulse is best done once the pump pulse has vanished. However, a short pulse means a larger bandwidth, which allows for a more complicated range of transitions to be accessed, creating many excited states that interfere with each other. In order to discern the influence of a longer pulse compared to a pulse with a larger bandwidth, both double cycle (2.66 fs) and six cycle (8 fs) transform limited pulses are investigated. Since the Se(3d) electron is bound by 55 eV with respect to ionization, we choose an attosecond probe pulse centered at 47 eV with a duration of 300 as.

 $Si_{29}H_{24}$ is modeled at 0, 80, and 300 K. It has a band gap of about 2.5 eV. For this system, we consider transform limited 2-cycle (1.08 fs) and 6-cycle (3.25 fs) 7.5 eV pulses, which can be experimentally produced [58, 59]. Adapted to the Si(2p) absorption, we choose a probe pulse centered at 90 eV with 300 as duration. An experiment of this kind could be performed with solid nanoparticles tethered to a metal foil substrate [60]. Unless otherwise stated, the pulse shapes are taken to be Sech².

At three times the band bap, PbSe QDs have a size independent absorption coefficient $\mu = 2.062 \times 10^5 \text{ cm}^{-1}$ [61]. For 1 nm QDs, this corresponds to a per particle absorption cross section of $1 \times 10^{-16} \text{ cm}^2$. If the pump laser has a $10 \,\mu\text{m}$ diameter and the substrate has $10 \,\%$ coverage, then a pulse as weak as 5 nJ will cause every QD on the substrate to absorb an average of 1 photon per pump pulse. Even for QD systems that have a smaller cross section, obtaining a pump pulse with sufficient energy to excite most of the QDs in the sample should be experimentally attainable. Estimating the probe absorption rate is more difficult, as the cross section for core electrons into the VB have yet to be studied experimentally or theoretically. When assuming a very conservative cross section of $1 \times 10^{-18} \text{ cm}^2$, an observable TA signal of 1 mOD would require an EUV flux of 10^7 photons per pulse. Such high-flux sources have been demonstrated [62].

Quantum beats may arise from the interference between SE and ME holes. The interference of excitation paths results in coherence, quantified with the reduced density matrix, $\rho_{I,I'}$, as described in Goulielmakis *et al* [51]. Interaction with a probe pulse sends an excited QD from an initial state with energy E_I to a final state with energy E_F [51]. In this case, the EUV absorption cross section at a particular frequency is given by Eq. 1,

$$\sigma(\omega,t) = \frac{4\pi}{c} \Im \sum_{I,I'} \rho_{I,I'}(t) \sum_{F} \frac{\langle I|Z|F \rangle \langle F|Z|I' \rangle}{E_F - \frac{i}{2}\Gamma - E_I - \omega}.$$
(1)

The rate Γ of decay of the final state is taken to be 0.088 eV [51]. *I* and *I'* each represent a set of initial states. Only the absorption cross section at the resonance frequency of the ME state is modeled. Since the detuning from the ME frequency is large, the SE states contribute very little to the absorption and can be neglected. For that reason, *I* is only summed over the ME state, and *I'* is summed over all states. The final state is taken to be a single state, a hole in a Se(3d) or Si(2p) core for the PbSe or Si system, respectively. The dipole transition elements in Eq. (1) are taken to be constant. We assume that the pump pulse leaves the system in a superposition that is 10% a single ME state, and 90% a multitude of SE states [63]. Both PbSe and Si QDs have symmetric CB and VB. As a starting point, the density of states in the valence and conduction bands are taken to be continuous and constant, turning the sum in Eq. 1 into an integral. This assumption is quite reasonable, as atomistic calculations show that the spacings between excited state energies is very small [20]. These simplifications allow for the assumption that all transitions are symmetric about the band gap [25], and that the SE populations are determined by the energy distribution of the pump pulse. For example, if the

pump pulse has an energy of 3.15 ± 0.05 eV, the final distribution of holes (electrons) is a Sech² distribution centered at 1.575 ± 0.025 eV below (above) the Fermi level.

Determining of population distribution allows for the formation of the fully coherent reduced density matrix shown in Eq. (2),

$$\begin{bmatrix} \rho_{ME,ME} & \cdots & \rho_{ME,SE_n} e^{-\frac{i\Delta E_t}{\hbar}} e^{\frac{-t^2}{\tau^2}} \\ \vdots & \ddots & \vdots \\ \rho_{SE_n,ME} e^{\frac{i\Delta E_t}{\hbar}} e^{\frac{-t^2}{\tau^2}} & \cdots & \rho_{SE_n,SE_n} \end{bmatrix}.$$
 (2)

Here, ΔE is the energy difference between the components of the two states being considered. τ is the electron-phonon pure-dephasing time calculated to be 11 fs at 128 K, and 5 fs at 300 K for PbSe [64], and 6 fs at 80 K and 3.25 fs at 300 K for Si [26, 64, 65].



Fig. 2. Absorption of the probe pulse centered at the frequency of the transition from a core electron to the ME hole as a function of the pump-probe delay.

Figure 2 shows the absorption cross section as a function of time for PbSe Fig. 2(a)-2(b) and Si Fig. 2(c)-2(d) when pumped with their respective 2-cycle and 6-cycle pulses. The oscillation in the absorption indicates that ME is in a superposition with SE states. The period of the

oscillation depends on the energy difference between the components of the states that are participating in the superposition. The energy difference between the hole at the center of the SE distribution and the hole of the ME state will differ by a quarter of total excitation energy, and determines the oscillation period. Since the PbSe system is pumped at 3.15 eV, the separation between the ME and SE holes is 0.7875 eV, which corresponds to a 5 fs oscillation period. Since Si is pumped by 7.5 eV photons, the corresponding energy separation is 1.875 eV, resulting in a 2.5 fs oscillation period.

Table 1. Dephasing times for a superposition of many states vs. a superposition of two states.

PbSe	128 K	197 K	347 K
Two-state	11.0 fs	8.3 fs	5.0 fs
Multi-state	8.5 fs	7.0 fs	4.5 fs

The decay of the oscillations is determined by the electron-phonon dephasing times, and the distribution width of the SE states. When the double-cycle pump pulse is used, the resulting superposition is short lived, because the double-cycle pulse necessarily includes a wider range of frequencies. The height of the coherence oscillations is determined by the coupling of the populated states to the probe beam, as well as the amount of quantum coherence in the superposition. With the continuous band model, coherence oscillations exhibit total dampening even at 0 K. By fitting the envelopes of the absorption cross sections obtained using Eq. 1 and shown in Fig. 3 with Gaussians, we observe that the signal dampening occurs much faster than the phonon-induced pure-dephasing time, because of the many states involved.



Fig. 3. (a) Population of the SE electron and hole states forming the wave-packet excited in the $Pb_{68}Se_{68}$ QD by the femtosecond pump. (b) Coherence oscillations in the attosecond probe absorption signal at T=347 K (bold green), 128 K (dashed purple), and 0 K (solid blue).

Table 1 compares the dephasing time between one SE and one ME, and the dephasing time between one ME and many SEs. Extending on the simplified calculations described above, we used the Vienna Ab Initio Simulation package [66] and the Perdew-Burke-Ernzerhof (PBE) density functional [67] to calculate the discrete energy levels in the VB and CB. $Pb_{68}Se_{68}$ was optimized at 0 K and heated to 128 K and 347 K. The Sech² distribution for the femtosecond pump was superimposed on top of these energy levels at 1.575 ± 0.025 eV above and below the Fermi energy, to obtain a discrete model for the SE holes and excited electrons. This process still assumes symmetric excitations, but takes into account the system's actual energy levels, rather than assuming a continuous distribution. The new SE distribution is shown for 347 K in

Fig. 3(a), and the coherence oscillations are shown in Fig. 3(b). The biggest difference in the discrete case is that the coherence oscillations at 0 K no longer completely die out, and exhibit quantum revivals [68].

Figure 4 shows the transient absorption spectra for the PbSe QD at 128 K. The attosecond probe pulse is centered at 47 eV. The absorption peak at 46.6 eV is from the SE states, and the absorption peak at 47.4 eV is from the ME state. The oscillations seen in the first 10 fs are an indication that SEs and MEs are in a coherent superposition when the excitation is created. The heights of the two peaks indicate the SE and ME populations.



Fig. 4. Transient absorption spectrum of a PbSe QD. The pulse is centered at 47 eV, the absorption peak at 46.6 eV is from the SE states, and the absorption peak at 47.4 eV is from the MEs.

2. Conclusion

In conclusion, we show that the presence of ME states can be detected in semiconductor QDs by transient absorption spectroscopy with attosecond laser pulses, and that the proposed experiment can discriminate between the coherent and incoherent mechanisms of MEG. An oscillation in the absorption signal indicates a superposition of states, supporting the coherent mechanism. Absence of the oscillation supports the incoherent mechanism. The dephasing of this signal is affected by temperature, and the number of states involved. The dephasing time characterizes the time scale of the elastic exciton-phonon scattering process. The location of the spectral lines identifies the energies of the electrons and holes involved in the photo-excited SE and ME states. By applying the attosecond technique to QDs of various sizes and shapes, made of different semiconducting materials, as well as to carbon nanotubes, graphene, etc. one can study systematically, for the first time, the sub-10 fs processes underlying exciton dynamics in nanoscale materials.

Acknowledgments

The authors are grateful to Heather M. Jaeger for discussions. A.J.N. and O.V.P. acknowledge support by the US Department of Energy, Grant DE-FG02-05ER15755. M.F.K. is grateful for support by the DFG via the Cluster of Excellence: Munich Center for Advanced Photonics (MAP). D.M.N acknowledges support from the Army Research Office, Award W911NF-12-0577.