Quantum Zeno Effect Rationalizes the Phonon Bottleneck in Semiconductor Quantum Dots

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Quantum confinement can dramatically slow down electron-phonon relaxation in nanoclusters. Known as the phonon bottleneck, the effect remains elusive. Using a state-of-the-art time-domain ab initio approach, we model the observed bottleneck in CdSe quantum dots and show that it occurs under quantum Zeno conditions. Decoherence in the electronic subsystem, induced by elastic electron-phonon scattering, should be significantly faster than inelastic scattering. Achieved with multiphonon relaxation, the phonon bottleneck is broken by Auger processes and structural defects, rationalizing experimental difficulties.

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Energy deposited during photoexcitation in traditional semiconductor materials is rapidly lost to lattice phonons. The ability to slow down phonon-assisted energy relaxation plays a key role in many applications ranging from optoelectronics and photovoltaics, to biology and medicine [1,2]. Colloidal semiconductor quantum dots (QDs) are promising materials for the development of low cost, high efficiency devices, including lasers [3–5] fluorescent biotags [6,7], quantum computers [8], light-emitting diodes [9], and solar cells [2,5]. The discrete electronic transitions seen in the QD optical spectra [10] suggest a mismatch between the electronic and vibrational energy quanta, allowing for a dramatic decrease in the electron-phonon relaxation, known as the phonon bottleneck [2,11]. Despite theoretical predictions [2], the majority of time-resolved experiments have shown picosecond relaxation, similar to that observed in bulk materials [12–14]. Moreover, the relaxation rates increase with decreasing QD size, despite the increasing electronic energy spacing [13–15]. The phonon-bottleneck has been observed only under very special conditions [16].

Several origins of the unexpectedly fast energy relaxation in QDs have been proposed. Auger-type processes break the bottleneck by allowing energy exchange between the excited electrons and holes, thereby opening up additional relaxation channels [17,18]. Typically, holes form denser state manifolds and relax more quickly than electrons, and an Auger transfer of energy from the electron to the hole speeds up the relaxation. Further, QDs are not ideal structures. The underlying atomic structure, surface reconstruction and thermal fluctuations break electronic state degeneracies, creating complicated distributions of electronic states [19]. New non-radiative relaxation pathways result from surface impurities, defects, and passivating ligands, creating intermediate states with strong electron-vibrational couplings [12,13,20,21].

Experimental realization of the phonon bottleneck is extremely difficult. As suggested by Kambhampati [13,22], the bottleneck can be achieved by attenuation of the alternative relaxation channels. This idea was verified by Pandey and Guyot-Sionnest [16], who observed nanosecond relaxation of electrons from the $1P_e$ to $1S_e$ state, by synthesizing CdSe QDs with multiple layers of shells and ligands and separating electrons from holes [16]. Thick shells composed of multiple ZnS and ZnSe layers were needed to protect the QD core from a surface environment, to localize the electronic wave function inside the CdSe core, and to suppress the ligand-mediated relaxation channel [23,24]. The authors also suggested that the shells trapped holes, decoupling them from core-bound electrons and suppressing Auger relaxation [25]. The slowed relaxation allowed for hot electron extraction [23,26] that constitutes an important mechanism for enhancing solar cell efficiencies [2,27]. The difficulties in achieving the phonon bottleneck in semiconductor QDs highlight the need for rigorous theoretical modeling of these systems.

The current Letter reports time-domain density functional theory (TDDFT) calculations of the electron-phonon relaxation in CdSe QDs. In contrast to the traditional TDDFT calculations, which treat phonons classically, the present approach describes phonons semiclassically. The semiclassical description explicitly incorporates quantum decoherence effects within the electronic subsystem and shows, for the first time, that the phonon bottleneck is directly related to the quantum Zeno effect. To achieve the bottleneck, elastic electron-phonon scattering inducing decoherence must be faster than the coherent electronic transition. The calculated electron-phonon relaxation time shows excellent agreement with the experimental data. The strong dependence of the relaxation time on the decoherence rate obtained by the ab initio time-domain simulation is rationalized analytically by a Fermi golden rule analysis. The suppression of the Auger processes is characterized by
calculations on CdSe/ZnS core-shell QDs with and without defects. The atomistic study shows that the electron excited in the CdSe/ZnS system is contained within the core, while the hole is localized in the shell. This separation decouples the electron from the hole, preventing Auger recombination [17,28]. Defects in the shell can destroy the electron-hole decoupling, allowing for fast relaxation. The established relationship between the phonon bottleneck and the quantum Zeno effect, together with the atomistic details provided by the simulation, generate an understanding of the conditions necessary to achieve and control the phonon bottleneck experimentally.

The vast majority of current theoretical and computational studies of semiconductor QDs focus on QD structure [29–32] and spectra [33–37]. Despite the availability of extensive experimental data on time-resolved excited state dynamics, [12–14,38] time-domain simulations directly mimicking such experiments are rare [19,39], largely due to the state-of-the-art methodologies needed for such simulations as well as the computational expense involved. Nonadiabatic molecular dynamics (NAMD) combined with TDDFT [19,40] allows for ab initio modeling of nonequilibrium electron-phonon processes in nanoscale materials. The semiclassical treatment [41] of quantum decoherence effects is essential for accurate description of electronic transitions. Decoherence can be understood as a measurement of the state of the electronic subsystem performed by the phonon environment. Also known as pure dephasing, decoherence is caused by elastic electron-phonon scattering, which determines, for instance, luminescence linewidths of individual nanoparticles [42–44]. Fast decoherence, corresponding to frequent measurements of the quantum-mechanical state, inhibits transitions, leading to the quantum Zeno effect [45–50]. The reported simulations show explicitly that the phonon bottleneck is a manifestation of this phenomenon.

The optimized geometries of the Cd$_{33}$Se$_{33}$ and Cd$_{33}$Se$_{33}$/Zn$_{78}$S$_{78}$ core-shell QDs are shown in Fig. 1. The black circles mark sulfur atoms removed from the ZnS shell to study the effect of shell defects on the electronic structure of the core-shell QDs. Each cluster was constructed using bulk wurzite lattice and relaxed to its lowest energy configuration at 0 K. The geometry was optimized using DFT with a plane wave basis, as incorporated in the Vienna ab initio simulation package (VASP) [51]. The Perdew and Wang (PW91) functional [52], paired with the Vanderbilt pseudopotentials [53], were used to account for electron exchange and correlation interactions. The simulations were performed in a periodically replicated cubic cell with at least 8 A of vacuum between QD replicas. The electronic structure of the QDs in the optimal geometries was characterized further with the hybrid B3LYP functional and the LANL2dz basis set incorporated into GAUSSIAN 03 [54] as described in the previous work [21,55]. The CdSe QD was brought up to 300 K by repeated velocity rescaling in VASP, and a 3 ps microcanonical MD trajectory was generated. 500 initial conditions were sampled from this trajectory to perform the NAMD-TDDFT simulations, as described in detail in Refs. [40,56]. The vibrational and electronic degrees of freedom were evolved using 1 fs and 1 as time steps, respectively.

The decoherence time was obtained with the optical response formalism [57], which allows one to use classical MD simulation. Decoherence of a quantum-mechanical superposition of two electronic states with the energy gap $E$ is associated with fluctuations in the energy levels due to coupling to phonons. The pure-dephasing function is defined as

$$D(t) = \exp(i\omega t) \left( \exp \left( -\frac{i}{\hbar} \int_0^t \Delta E(\tau) d\tau \right) \right),$$

(1)

where the angular bracket denotes canonical averaging, $\Delta E = E - \langle E \rangle$ is the deviation of the energy gap from its average value, and $\omega = \Delta E/\hbar$. The above expression can be approximated using the 2nd order cumulant expansion,

$$D(t) = e^{-g(t)},$$

$$g(t) = \frac{1}{\hbar^2} \int_0^t \int_0^t d\tau_1 \int_0^{\tau_1} d\tau_2 \langle \Delta E(\tau) \Delta E(0) \rangle.$$  

Equation (2) shows better numerical convergence than the direct expression (1), which involves averaging of an oscillating function. Both direct and cumulant methods have shown excellent agreement with experiment for several systems [42–44].

Following the experiment [16], we model the relaxation of the photoexcited electron from the $1P_e$ to $1S_e$ state of the CdSe QD. These states correspond to the 2nd and 1st
and cumulant dephasing functions, shown in Fig. 1(a), will fluctuate less in phase due to disorder and involvement in nanoscale systems [42–44]. The sub-100 fs decay of the correlation function, $C(t)$, is typical of condensed phase systems [42–44,48]. One can expect similar decay times in larger QDs, since on the one hand, the electron-phonon coupling decreases with system size leading to longer-lasting correlations, while on the other hand, LUMO and LUMO + 1 will fluctuate less in phase due to disorder and involvement of more phonon modes in larger systems. The direct and cumulant dephasing functions, shown in Fig. 1(a), agree with each other and can be well fitted with a Gaussian function with the characteristic pure-dephasing (decoherence) time of 36 fs. This time is typical of other nanoscale systems [42–44].

Figure 2(b) shows the time-dependent population of the $1P_e$ state of the electron (LUMO + 1) obtained using TDDFT-NAMD [40] with the semiclassical decoherence correction [41]. The population decay is due to the nonadiabatic, electron-phonon transition into the $1S_e$ state (LUMO). In addition to the calculated 36 fs pure-dephasing time, $54 = 1.5 \times 36$ and $90 = 2.5 \times 36$ times are considered. Decreasing the coherence interval from 90 to 36 fs increases the decay time. This phenomenon is indicative of the quantum Zeno effect [45–50]. In the limit of infinitely short coherence, the quantum transition stops. The calculated 670 ps lifetime of the $1P_e$ state is in good agreement with the measured 1 ns lifetime [16]. The electron-phonon interaction and phonon-induced pure dephasing can be modified through introduction of defects and ligands [21,41], providing quantum control of the phonon bottleneck.

Further understanding of the relationship between the phonon-bottleneck and the quantum Zeno effect is provided by the following analytic analysis based on the Fermi golden rule, describing the rate of transition between states 1 and 2:

$$k_{12} = \frac{2\pi}{\hbar} |V_{12}|^2 \sum_{\{f\}} |\langle i|f\rangle|^2 \delta(E_{1i} - E_{2f}).$$

Here, $V_{12}$ is the nonadiabatic, phonon-induced coupling between electronic states 1 and 2. The Franck-Condon factor is determined by the overlap of the vibrational wave functions, $\langle i|f\rangle$, associated with the initial and final electronic states. It is computed by summing over the set of final vibrational states, $\{f\}$, subject to equality of the initial, $E_{1i}$, and final, $E_{2f}$, electron-vibrational (vibronic) energy. Note that the Franck-Condon factor is closely related to the Huang-Rhys factor, e.g., see Eq. (19) of Ref. [58] and Eq. (V.9) of Ref. [59]. Represented in the energy domain in terms of vibronic eigenstates, Eq. (3) can be recast in the time domain, e.g., see Eq. (42) of Ref. [60]

$$k_{12} = \frac{1}{\hbar} |V_{12}|^2 \int \exp(i\Delta E_{12}t/\hbar)D(t)dt/\hbar.$$  

The time-domain representation of the Franck-Condon factor can be interpreted as a Fourier transform of the overlap of the vibrational wave packets evolving in the two electronic states. The overlap gives the decoherence function [60]. The Fourier transform is evaluated at the electronic energy gap. Assuming that the decoherence function is Gaussian, $D(t) = \exp(-t^2/2\tau_D^2)$, Fig. 2(a), one easily obtains an analytic expression for the transition rate, $k_{12}$, which depends on three parameters: the nonadiabatic coupling, $V_{12}$, the electronic energy gap, $E_{12}$, and the decoherence time, $\tau_D$. Using order-of-magnitude values, $V_{12} = 10 \text{meV}$ [61], $E_{12} = 0.1 \text{eV}$, and $\tau_D = 30 \text{fs}$, Fig. 2, one obtains the transition time, $1/k_{12} \sim 1 \text{ns}$. The transition time shows Gaussian dependence on the electronic energy gap. Decreasing the gap to $E_{12} = 0.1 \text{eV}$, the calculated 670 ps lifetime of the $1P_e$ state is in good agreement with the measured 1 ns lifetime [16].
$E_{12} = 0.01 \text{ eV}$ characteristic of the quasicontinua of QD states at high excitation energies [19], shortens the transition time to $1/k_{12} \sim 50 \text{ fs}$. This simple analytic model supports the 	extit{ab initio} calculations and indicates that in order to achieve the phonon bottleneck, one requires pure-dephasing times in the $10 \text{ fs}$ range and electronic energy gaps on the order of $0.1 \text{ eV}$. Since the phonon frequencies of semiconductor QDs composed of heavy chemical elements are on the order $100 \text{ cm}^{-1} \sim 0.01 \text{ eV}$, nonradiative electronic transitions across $0.1 \text{ eV}$ energy gaps require multiphonon processes, as suggested earlier [14,38].

Elucidating the role of the shell in decoupling the electron from the hole and eliminating the Auger relaxation channel, Fig. 3 shows the density of states (DOS) in the Cd$_{33}$Se$_{33}$ and Cd$_{33}$Se$_{33}$/Zn$_{78}$S$_{78}$ core-shell QDs. Recall that the shell was essential in the experimental observation of the phonon bottleneck [16]. The DOS is higher for the valence band (VB) than the conduction band (CB), and the lowest energy hole states are closely spaced, in contrast to the electron states. Therefore, the Auger pathway indeed should accelerate the relaxation, breaking the phonon bottleneck. The ZnS shell creates additional VB states near the band gap, but it does not affect the structure of the CB edge. The lowest energy states of the hole reside in the ZnS shell, while the electron remains inside the CdSe core, supporting the electron-hole separation concept. Removal of S atoms from the shell, representing shell defects, creates trap states close to the edge of the VB, Fig. 4(a). The defects do not change the properties of the 1$S_x$ state of the electron (LUMO), top row in Fig. 4(b), but they do alter the localization of the lowest state of the hole (HOMO). In two of the three cases considered, S1 and S2, the HOMO is located the Zn dangling bond left by the missing S atom. These defect states are notably delocalized into the CdSe core: compare the HOMO of the perfect core-shell system in Fig. 3(b) with the HOMO of the S1 and S2 systems in Fig. 4(b). The electron and hole are less isolated from each other in the presence of shell defects, opening up the Auger relaxation pathway [17] and rationalizing why imperfect shells lead to fast electron relaxation in the experiments [16].

In conclusion, the present work clearly shows that the phonon bottleneck to the electron-phonon relaxation in semiconductor QDs is a special case of the quantum Zeno effect. Therefore, the conditions necessary for the quantum Zeno effect are also required for the phonon bottleneck. In particular, the decoherence (pure-dephasing) time determined by elastic electron-phonon scattering...
should be significantly faster than the time-scale of the coherent electronic transition. The connection was illustrated by both explicit time-domain \textit{ab initio} simulation and a Fermi golden rule analysis. The \textit{ab initio} simulations showed good agreement with the experimental data. The simulations also indicated that the core-shell CdSe/ZnS structure used in the experiment indeed provides spatial separation of the electron and hole, which is essential for eliminating the Auger relaxation channel involving electron-hole energy exchange. Defects in the shell diminish the electron-hole separation, opening up the Auger channel. Introduction of shells, dopants, defects, and ligands can be used to alter the pure-dephasing rate, thereby providing quantum control over the conditions required for the quantum Zeno effect and the phonon bottleneck.

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