Symmetric Band Structures and Asymmetric Ultrafast Electron and Hole Relaxations in Silicon and Germanium Quantum Dots: Time-Domain Ab Initio Simulation

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Abstract

State-of-the-art time domain density functional theory and non-adiabatic (NA) molecular dynamics simulations are used to study phonon-induced relaxation of photoexcited electrons and holes in Ge and Si quantum dots (QDs). The relaxation competes with productive processes and causes energy and voltage losses in QD solar cells. The *ab initio* calculations show that quantum confinement makes the electron and hole density of states (DOS) more symmetric in Si and Ge QDs compared to bulk. Surprisingly, in spite of the symmetric DOS, the electron and hole relaxations are quite asymmetric: the electrons decay faster than the holes. The asymmetry arises due to stronger NA coupling in the conduction band (CB) than in the valence band (VB). The stronger NA coupling of the electrons compared to the holes is rationalized by the larger contribution of the high-frequency Ge-H and Si-H surface passivating bonds to the CB relative to the VB. Linear relationships between the electron and hole relaxation rates and the CB and VB DOS are found, in agreement with Fermi's golden rule. The faster relaxation of the electrons compared to the holes in the Ge and Si QDs is unexpected and is in contrast with the corresponding dynamics in the majority of binary QDs, such as CdSe. It suggests that Auger processes will transfer energy from holes to electrons rather than in the opposite direction as in CdSe, and that a larger fraction of the photoexcitation energy will be transfered to phonons coupled with electrons rather than holes. The difference in the phonon-induced electron and hole decay rates is larger in Ge than Si, indicating that the Auger processes should be particularly important in Ge QDs. The simulations provide direct evidence that the high-frequency ligand modes on the QD surface play a pivotal role in the electron-phonon relaxation dynamics of semiconductor QDs.

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I. INTRODUCTION

Confinement of charge carriers in quantum dots (QDs) of sizes smaller than the Bohr exciton radius of the corresponding bulk material determines the QD electronic properties and leads to a variety of applications. High cross-sections for light absorption make QDs excellent materials for photovoltaic devices [1, 2]. Further advantages of QDs in solar energy conversion include the possibility of generating multiple electron-hole pairs upon absorption of a single photon [3–5] as well as decreased electron-phonon relaxation rates [6]. These features create a great potential for increasing solar energy conversion efficiencies relative to those seen in bulk and molecular systems, by providing new mechanisms for utilization of the excess photon energy and avoiding the energy loss to heat [1, 2]. Other applications of semiconducting [7, 8] and metallic [9, 10] QDs include light-emitting diodes [11], field-effect transistors [12], lasers [13], quantum emitter antennas [14], fluorescent biological imaging probes [15], quantum information processing [16, 17], spintronics [18], thermopower devices [19] and so on.

Understanding the dynamics of the electronic excitations in QDs is very important from both fundamental and practical points of view. Similarly to molecular systems, spatial confinement of electronic states creates relatively strong electron-phonon coupling in QDs [20, 21]. As a result, the electron-phonon interactions play important roles in most of the applications listed above. Efficiencies of the QD photovoltaic devices [1], and lasers [22] depend on the electron-phonon relaxation rates. Their use in quantum information processing is limited by the phonon-induced dephasing of spin [23] and electron [24] states. The electron-phonon interactions define the linewidths in the QD optical spectra [24–26]. Inelastic electron-phonon scattering affects electron tunneling through QDs and is responsible for the transport blockade and energy loss [27].

The phonon-mediated relaxation of electrons and holes in QDs is the focus of many experimental [1, 6, 28–31] and theoretical [2, 32–35] efforts. Various time-resolved experimental techniques are used to probe the intricate features of the electron-phonon dynamics [6, 23, 26, 28–31]. At the same time, most of the theoretical approaches focus on the QD structure and spectra [2, 36–44]. Few theoretical studies are performed in the time-domain [2, 32, 33], directly mimicking the experiments. Quantization of the electronic energy levels induced in QDs by spatial confinement [36, 37] results in a mismatch between

the electronic gaps and phonon frequencies. The mismatch leads to the expectation of a dramatic slowing down of the electron-phonon relaxation, known as the phonon-bottleneck [1]. The spacing between the electronic levels is clearly seen in the optical spectra [26]. Unexpectedly, the majority of the recent time-resolved experiments show picosecond relaxation, similar to that observed in bulk semiconductors [28–31]. Moreover, the relaxation rates increased with decreasing QD size, even though the electronic energy spacing became larger. Recently, the phonon-bottleneck has been observed but only under very special conditions in carefully designed QDs [6]. By slowing down the decay of the electronic energy, the phonon-bottleneck can minimize losses during solar energy harvesting and allow generation of additional charge carriers [1, 3–5].

Charge-phonon dynamics are closely tied with the Auger channel of energy relaxation [45]. Auger processes provide an additional mechanism for conversion of the photon energy to heat and, therefore, decrease of the solar energy conversion efficiency. Coulomb interaction between electrons and holes that are confined within the small volume of a QD allows rapid exchange of energy between the two charge carriers. If the electron and hole densities of states (DOS) are asymmetric, as in the majority of the QD materials, the Coulomb interaction will funnel the photon energy to the charge carrier that relaxes faster due to its higher DOS. For instance, in CdSe the hole DOS is significantly higher than the electron DOS, and the Auger process is considered to be the main relaxation channel [30, 31, 45]. As a result, the phonon-bottleneck could be seen in CdSe only when the electrons were prevented from exchanging energy with the holes by hole trapping and charge injection [6]. Almost symmetric DOS render the Auger channel inefficient. This is the case with PbSe, in which both electrons and holes relax by direct coupling to phonons although the latter relaxes slightly faster than the former due to slightly denser DOS for holes. [28, 29].

Surface states are believed to play a particularly important role in the charge-phonon relaxation dynamics in QDs, since they can create traps for the charge carriers and involve high-frequency vibrational modes associated with surface ligands [46, 47].

The present study reports the first time-domain ab initio simulations of the charge-phonon relaxation dynamics in small Si and Ge QDs. The properties of these materials are particularly important for the solar cell industry, since the vast majority of currently produced solar cells are Si based [21, 35, 48–50]. Also, Si and Ge are less toxic than the binary materials such as CdSe, PbSe and GaAs. In contrast to the binary QDs, Si and

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Ge are indirect gap semiconductors and therefore, show weak absorption at the fundamental band-gap energy. Studies indicate that relatively small Si and Ge QDs with quantum confinement energies greater than 1 eV exhibit pseudo-direct band-gap behavior with increasing absorption cross-sections at the gap energy [51]. Ge possesses a narrower band-gap and higher absorptions cross-sections than Si. The energy difference between the indirect and first direct band-gaps in Ge is small, making the confinement-induced transformation to the pseudo-direct regime easier than in Si.

Our *ab initio* calculations show quantum confinement makes the electron and hole DOS more symmetric in Si and Ge QDs compared to bulk. However, despite the symmetric DOS, the phonon-induced relaxation times of the photoexcited electrons and holes differ substantially, with the electrons decaying faster than the holes. The analysis presented below shows that the asymmetric relaxation can be rationalized by a stronger electron-phonon coupling associated with the conduction band (CB) states occupied by the photoexcited electrons relative to the valence band (VB) states supporting the holes. The stronger electron-phonon coupling of the electrons arises due to a larger contribution of the high-frequency vibrational modes associated with the Ge-H and Si-H bonds passivating the QD surfaces. The CB states are delocalized onto the surface bonds more significantly than the VB states. The faster relaxation of the electrons than the holes in the small Si and Ge QDs is quite surprising, since it is in stark contrast with the relaxation processes seen in the binary QDs: the holes in CdSe, PbSe and GaAs decay faster than the electrons. As a result of the faster electron relaxation, the Auger processes in Si and Ge QDs should proceed in the opposite direction, transferring energy from the holes to the electrons rather than from the electrons to the holes. Since the phonon-induced electron and hole decay times differ more in the Ge than Si QDs, the Auger processes should be more important in the former material. For the first time, the time-domain simulations described in the following sections provide direct evidence that the high-frequency ligand modes localized on the QD surface play an important role in the electron-phonon relaxation dynamics of semiconductor QDs. The results suggest that understanding the surface properties of the QDs is particularly important for the application of QDs to solar energy conversion. The present simulations imply that the solar energy losses that occur due to the charge-phonon interactions are quite different in Si and Ge QDs compared to their binary counterparts.

II. THEORY: TIME-DEPENDENT DENSITY FUNCTIONAL THEORY AND FEWEST SWITCHING SURFACE HOPPING

In a mixed quantum/classical framework, the quantum character of a few selected degrees of freedom is included explicitly while the remainder of the system is treated classically. Separation of the total system into a classical part and a quantum mechanical part is not trivial due to the fundamental problems encountered in coupling classical and quantum dynamics [52–54]. The degrees of freedom that are treated quantum mechanically must evolve correctly under influence of the classical degrees of freedom, while the motion of the classical degrees of freedom in turn must be determined correctly by the force generated by the quantum degrees of freedom. Often, such a realistic force cannot be obtained by the mean field theory (MFT) [55], where a force is averaged over population of each state. In a fully quantum description of a coupling region, the wave function splits into branches which overlap and interfere. While this branching phenomenon is not accounted for by the MFT, the surface hopping method can incorporate the branching. Tully supplemented the original surface hopping idea [56] with the so-called fewest switches surface hopping (FSSH) method [57–61] which minimizes the number of hops between the surfaces. FSSH uses a stochastic algorithm that generates trajectory branching and satisfies detailed balance. Detailed balance ensures that transitions up in energy are less likely than transitions down in energy by the Boltzmann factor. It is essential for studying charge-phonon relaxation and achieving thermodynamic equilibrium in the long time limit.

The electronic structure and adiabatic molecular dynamics (MD) are computed with the Vienna Ab initio Simulation Package (VASP) code [62], using converged plane-wave basis density functional theory (DFT) in cubic simulation cells periodically replicated in three dimensions. The Perdew-Wang-91 generalized-gradient density functional and the projector-augmented-wave pseudopotentials were used.

The present atomistic calculations were performed with $Ge_{29}H_{24}$ and $Si_{29}H_{24}$. The initial QD geometries were generated from bulk, fully optimized at zero temperature, and heated up to ambient temperatures by MD with repeated nuclear kinetic energy rescaling. In order to prevent spurious interactions between periodic images of the QDs, the cells were constructed to have at least 8 Å of vacuum between the QD replicas. Microcanonical trajectories of 5 ps duration were produced for the ambient temperature QDs using the Verlet algorithm with

a 1 fs time-step and Hellman-Feynman forces in the ground electronic state. The electronic time step was set as 10^{-3} fs. The nuclear trajectories from this microcanonical MD were then used to sample 1000 initial conditions to create ensemble averages for the NA dynamics. Finally, we performed the FSSH method described below.

A. Time-Domain Density Functional Theory

The time-domain DFT simulation of the electron-phonon relaxation dynamics is based on the implementation [63] of the FSSH method [57–61] within the time-domain Kohn-Sham (TDKS) theory [64]. The electron density is written in the KS representation as

$$\rho(\mathbf{r}, t) = \sum_{p=1}^{N_e} |\phi_p(\mathbf{r}, t)|^2, \tag{1}$$

where N_e is the number of electrons and $\phi_p(\mathbf{r}, t)$ are the single-electron KS orbitals. The evolution of $\phi_p(\mathbf{r}, t)$ is determined by application of the time-dependent variational principle to the expectation value of the KS density functional and leads to the system of coupled equations of motion for the single-particle KS orbitals

$$i\hbar \frac{\partial \phi_p(\mathbf{r}, t)}{\partial t} = H(\phi(\mathbf{r}, t))\phi_p(\mathbf{r}, t), p = 1, \ldots, N_e. \tag{2}$$

The equations are coupled, since the Hamiltonian H depends on the density, Eq. 1, obtained by summing over all KS orbitals occupied by the N_e electrons. Expanding the time-dependent KS orbitals $\phi_p(\mathbf{r}, t)$ in the adiabatic KS orbital basis $\tilde{\phi}_k(\mathbf{r}; \mathbf{R})$,

$$\phi_p(\mathbf{r}, t) = \sum_{k=1}^{N_e} c_{pk}(t)|\tilde{\phi}_k(\mathbf{r}; \mathbf{R})\rangle, \tag{3}$$

transforms the TDKS Eq. 2 into the equation of motion for the expansion coefficients

$$i\hbar \frac{\partial c_{pk}(t)}{\partial t} = \sum_{m=1}^{N_e} c_{pm}(t)(\epsilon_m \delta_{km} - i\hbar \mathbf{d}_{km} \cdot \dot{\mathbf{R}}). \tag{4}$$

Here, each adiabatic KS orbital $\tilde{\phi}_k(\mathbf{r}; \mathbf{R})$ was calculated with DFT using the plane-wave basis for the current atomic positions from the MD trajectory. The non-adiabatic(NA) coupling,

$$\mathbf{d}_{km} \cdot \dot{\mathbf{R}} = \langle \tilde{\phi}_k(\mathbf{r}; \mathbf{R})|\nabla_{\mathbf{R}}|\tilde{\phi}_m(\mathbf{r}; \mathbf{R})\rangle \cdot \dot{\mathbf{R}} \tag{5}$$

$$= \langle \tilde{\phi}_k(\mathbf{r}; \mathbf{R})|\frac{\partial}{\partial t}|\tilde{\phi}_m(\mathbf{r}; \mathbf{R})\rangle, \tag{6}$$

arises from the dependence of the adiabatic KS orbitals on the phonon dynamics $\mathbf{R}(t)$, and was computed numerically using the right-hand-side of Eq. 6.

B. Fewest Switches Surface Hopping

The FSSH simulation is performed separately for an electron and a hole in the basis of the single-particle adiabatic KS orbitals. FSSH prescribes a probability for hopping between quantum states. FSSH can be viewed as a quantum master equation, in which the state-to-state quantum transition rates depend on time through coupling to phonon dynamics. Specifically, the probability of a hop from a given state k to another state m within the time interval dt is given by

$$dP_{km} = \frac{b_{km}}{a_{kk}} dt, \tag{7}$$

where

$$b_{km} = -2\mathrm{Re}(a_{mk}\mathbf{d}_{mk} \cdot \dot{\mathbf{R}}); a_{mk} = c_m^* c_k. \tag{8}$$

Here, c_k and c_m are the coefficients evolving according to Eq. 4. The velocity rescaling and hop rejection rules in FSSH give detailed balance between the upward and downward transitions [59]. The current, simplified FSSH makes the assumption that the energy exchanged between the electronic and nuclear degrees of freedom during the hop is rapidly redistributed among all nuclear modes. With this assumption, the distribution of energy in the nuclear modes is Boltzmann at all times, and the velocity rescaling/hop rejection step can be replaced by multiplying the probability, Eq. 7, for transitions upward in energy by the Boltzmann factor. This simplification of the original FSSH technique gives great computational savings, allowing us to determine the time-dependent potential that drives the dynamics of the electronic subsystem using the ground-state trajectory.

III. RESULTS AND DISCUSSION

The $Ge_{29}H_{24}$ and $Si_{29}H_{24}$ QDs used in the present study are shown in Fig. 1. Each initial QD had bulk structure and was passivated by hydrogen atoms, see the upper panels of Fig. 1. Bare Ge and Si QDs without the hydrogen atoms are 5 Å in diameter. The geometries of the QDs optimized at 0 K are displayed in the middle panels of Fig. 1. A typical geometry of the QDs heated up to ambient temperatures is shown in the lower panels of Fig. 1. The QD images indicate that the QDs preserved the bulk topology during the simulations, and that the dynamics involved neither bond breaking nor other major changes in the QD atomic

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or electronic structure. The atomically and electronically stable QD structure ensured that the 5 ps trajectories provided converged results.

A. Absorption Spectra and Density of States

Figure 2 shows the linear absorption spectra of $Ge_{29}H_{24}$ and $Si_{29}H_{24}$. The integrated spectra were obtained by summing over individual transitions, defined by transition energies and oscillator strengths, obtained for the QD geometries at 0 K and broadened by 0.1 eV in order to account for thermal atomic motions. The bars shown in Fig. 2 were obtained by adding the intensities of individual transitions over one fiftieth of the total energy range. It is likely that the absolute excitation energies are underestimated by the current calculations, since pure DFT functionals are known for this systematic error. The spectra show distinct peaks, whose intensities grow with energy as expected. The intensity decay at higher energies is a calculation artifact that is due to the finite number of electron and hole states taken into consideration. The calculated spectra are in harmony with Weissker's results [49] in terms of their peak energies and peak shapes for the calculated energy window.

The DOS of $Ge_{29}H_{24}$ and $Si_{29}H_{24}$ are shown in Fig. 3. The QDs geometries optimized at 0 K were used in the DOS calculation. The calculated zero temperature energy gaps are 2.06 eV for $Ge_{29}H_{24}$, and 2.51 eV for $Si_{29}H_{24}$. These values are likely underestimated due to the known systematic error of DFT. The underlying atomic structure, thermal fluctuations, as well as the spin-orbit and Coulomb interactions break the electronic degeneracy, creating complicated multilevel band structures. In order to account for thermal atomic motions, the DOS shown in Fig. 3 were generated by broadening the band energy levels by 0.1 eV as before for the spectra, Fig. 2. At ambient temperatures, the energy levels inside the CB and VB significantly fluctuate and approach each other. The gaps between the levels nearly disappear at certain instances of time and the states mix. This fluctuating and smoothed DOS gives rise to the ultrafast relaxation dynamics of the photoexcited electrons and holes.

The results shown in Fig. 3 demonstrate that the quantum confinement effect can make the electron and hole DOS quite symmetric. The VASP calculation on bulk Si gives the expected bulk result; the electron DOS is twice denser than the hole DOS in bulk Si [65]. In the language of the effective-mass theory [1], quantum confinement changed the ratio of the effective masses for the holes and electrons to about 1 in both Si and Ge QDs. In contrast,

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the electron effective mass is twice and 1.5 times heavier than the hole effective mass for bulk Si and Ge, respectively. Such a quantum confinement effect has never been found in other semiconductor QDs such as PbSe and CdSe, in which the QD DOS is similar to the bulk DOS [32, 33, 44]. Symmetric DOS were seen in cubic Ge and Si QDs [35]; however, the currently studied QDs are spherical, but generally, a cubic QD geometry results in bigger differences between bulk and QD DOS than a spherical QD geometry. The symmetric DOS in the Si and Ge QDs imply that the threshold photon energy for multiexciton generation in these QDs should be closer to three times the band gap energy ($3E_g$) rather than $2E_g$ [4, 42, 43, 48, 66]. The reported $2.5E_g$ threshold photon energy implies some symmetry breaking and may be attributed to the colloidal effect in the experimental sample [35, 48].

B. Charge-Carrier Dynamics

The electron and hole dynamics in $Ge_{29}H_{24}$ and $Si_{29}H_{24}$ QDs were calculated by the FSSH method. In the FSSH simulations, an electron and a hole are initially excited to various states with different energies. Figures 4(a) and 5(a) show the half life-time of the initially excited state the of electron and hole, half time initial (HTI), for the Ge and Si QDs, respectively. The data points correspond to the number of initially excited states. This life-time measure includes all decay channels of the initially excited state, including both the nearest energy states and states far in energy. The HTI almost linearly depends on the energy gap between the excited state and the nearest lower energy state. The HTI shows little correlation with the energy difference between the initially excited and band-gap states as well as with the absolute excitation energy. The linear correlation shown in Figs. 4(a) and 5(a) indicates that most of the excited state energy flows into the nearest lower energy state. Considering only three nearest lower energy states already shows no meaningful correlation with the HTI. The linear correlation makes it possible to predict the local DOS at the excited state energy from the HTI, and vice versa.

Figures 4(b) and 5(b) show the half life-times of the total excited energy of the electron and hole, half time total (HTT), for the Ge and Si QDs, respectively. The HTT is defined as the time when the energy difference between the excited electron and LUMO, or between the excited hole and HOMO, becomes a half of the initial value. The HTT exhibits a nearly perfect linear correlation with the energy difference between the initially excited CB orbital

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and LUMO for the electrons (or the initially excited VB orbital and HOMO for the holes) normalized by the total number of states in this energy range. The initial-final state energy difference divided by the number of states is the inverse of the average DOS over the energy range sampled by the relaxing particle. Since the inverse of the life-time is proportional to the relaxation rate, the linear relationships shown in Figs. 4(b) and 5(b) are the inverses of the corresponding linear relationships between the relaxation rate and the average DOS. The HTT shows no correlation with the energy gap between the excited state and the nearest lower energy state, used to correlate HTI in Figs. 4(a) and 5(a). The HTT is also independent of the absolute excitation energy. For example, it is sometimes possible that the HTT from a lower energy excited state is longer than the HTT from a higher energy band; in this case, the higher energy state relaxes with a faster rate owing to the larger average DOS.

In the above linear relationships, the slopes for the electron relaxation are smaller than those for the hole relaxation. Even though the symmetric DOS of the electrons and holes in both Si and Ge QDs, Fig. 3, imply that the relaxation of the opposite charges should also be symmetric, the simulated charge-phonon decay dynamics are quite asymmetric. Analysis shows that the asymmetry arises due to the stronger charge-phonon NA couplings for the CB states than the VB states. Table I shows the average absolute values of the NA couplings together with the corresponding root-mean-square values. The NA couplings for the electrons are generally larger than for the holes. Owing to these larger NA couplings in the CB, the photoexcited electrons relaxed faster than the photoexcited holes in both Si and Ge QDs. Since the difference between the NA coupling strengths of the CB and VB is smaller in $Si_{29}H_{24}$ than in $Ge_{29}H_{24}$, the difference between the electron and hole slopes in Figs. 4 and 5 is smaller in the Si QD than the Ge QD. The root-mean-squares of the NA couplings shown in Table I are significantly greater than the absolute values, indicating that the NA coupling notably fluctuates with time, and that there exist particular instances when NA transitions are most likely to occur. The results demonstrate that the NA coupling strength is very important for the electron and hole relaxation dynamics. With the nearly symmetric DOS, the NA coupling entirely determines the relative values of the decay rates.

C. Analysis of the Electron and Hole Relaxation Rates

The linear relationships found in Figs. 4(b) and 5(b) can be described by Fermi's golden rule:

$$k_F = \frac{2\pi}{\hbar}|V|^2\rho(E_{\text{band}}),$$ (9)

where k_F is the relaxation rate, V is the coupling, and ρ is the DOS. In present, the relaxation rate k_F is the inverse of the HTT, V is the charge-phonon NA coupling, and $\rho(E_{\text{band}})$ is the DOS averaged over the energy band between the initially photoexcited electron or hole state and the corresponding band-gap state, i.e. LUMO or HOMO, respectively. Using the total average absolute values of the NA coupling from Table I, Eq. 9 fits the electron data of Figs. 4(b) and 5(b) without any prefactor. Fermi's golden rule also almost holds for the holes except for a constant prefactor 1.87 and a non-zero x-intercept. The ratio of the slopes of the hole data in Figs. 4(b) and 5(b) is 1.260. Following Fermi's golden rule, this ratio nearly perfectly relates to the ratio of the squares of the absolute NA coupling values for the holes in the Ge and Si QDs from Table I. This ratio equals 1.260. The NA coupling was first directly connected to the coupling V in Fermi's golden rule. Fermi's golden rule was also used with the electronic chromophore-semiconductor coupling in the studies of electron transfer at a molecule-semiconductor interface where the adiabatic ET dominates the overall dynamics [67]. The current result allows us to estimate relaxation rates of electrons and holes in QDs by knowing the average NA coupling strength and local DOS within the relavant energy range. It should be noted that the electron and hole relaxation dynamics produced by the current time-domain atomistic simulation is significantly more complex than the simple exponential decay implied by Fermi's golden rule. The relaxation includes both exponential and Gaussian parts [32, 33], both of which cannot be simultaneously described by a simple perturbation theory. However, in the time region of HTT, there could be simple relaxation processes, resulting in the agreement of the slopes of the data with Fermi's golden rule. In contrast to HTT, Fermi's golden rule cannot be used to describe the linear relationships for HTI, Figs. 4(a) and 5(a). This is because most of the photoexcitation energy flows from the initially excited state to the nearest lower energy state. The fact that the final state for HTI is a single state and not a continuum of states conflicts with the assumptions used to derive Fermi's golden rule [68].

D. Active Phonon Modes

In order to rationalize the differences between the NA coupling strengths for the electrons and holes in the Si and Ge QDs, Table I, we investigated the phonon modes that couple to the photoexcited charges. Figures 6 and 7 show the spectral densities (SD) of the phonon modes that couple to the CB and VB states of $Ge_{29}H_{24}$ and $Si_{29}H_{24}$. The SDs were computed by taking Fourier transforms of the trajectories of the CB and VB energy levels, which fluctuate in time by interacting with the vibrating atoms. All panels in both figures use arbitrary units with the same scaling for the y-axis. Figure 6 shows the low-frequency component of the SDs. Low-frequency motions correspond to the vibration modes of the Ge-Ge and Si-Si bonds. The SD of $Si_{29}H_{24}$ shows higher frequencies than the SD of $Ge_{29}H_{24}$, as expected. The larger SD intensity for both CB and VB of $Ge_{29}H_{24}$ relative to $Si_{29}H_{24}$ indicates stronger electron-phonon NA coupling, see Table I, and properly correlates with the smaller Ge slopes in Figs. 4 and 5. Comparing the SD intensities for CB and VB in each QD, one observes little differences. Although some differences appear around 400 cm^{-1} and 600 cm^{-1} in $Si_{29}H_{24}$, they are seen only with a few states and do not involve the whole set of states participating in the electron and hole relaxation in the Si QDs. Essentially no differences are seen with the Ge QD either. Thus, the lower-frequency parts of the SDs shown in Fig. 6 can explain neither the asymmetry in the NA couplings in the CB and VB of each QD, nor the notably faster relaxation of the electrons relative to the holes despite the symmetric DOS, Fig. 3. The asymmetry in the NA coupling for the CB and VB of each dot, as well as the faster electron relaxation can be rationalized by considering the higher-frequency component of the SDs shown in Fig. 7. The upper and lower panels in Fig. 7 show clear differences. The SDs of the CB states are significantly more intense than the SDs of the VB states in both $Ge_{29}H_{24}$ and $Si_{29}H_{24}$. The differences are seen with almost all states. This result indicates that the stronger NA couplings in the CBs are due to the stronger interaction between the CB states and the higher-frequency phonon modes. The higher frequencies correspond to vibrations of the Ge-H and Si-H bonds. Hence, it is the passivation of the QD surface with ligands, hydrogen atoms in the present case, that produces the asymmetric NA couplings in the CB and VB. It should be noted, since the absolute intensities of the SD are smaller for the high frequencies than the low frequencies in both QDs, compare Figs. 6 and 7, the contribution of the low-frequency modes to the overall electron and hole relaxation dynamics is larger

than that of the high-frequency modes. Nevertheless, since the NA coupling is proportional to the nuclear velocity, Eq. 5, higher-frequency modes with faster velocities can strongly influence the charge relaxation process [69].

Figure 8 shows that the surface Ge-H and Si-H bonds play an important role in the electronic structure of the $Ge_{29}H_{24}$ and $Si_{29}H_{24}$ QDs. The LUMOs of both Ge and Si QDs, shown in the upper panel of Fig. 8 have more electron density around the Ge-H and Si-H bonds than the HOMOs shown in the lower panel. Thus, the electrons in Si and Ge are more strongly coupled to the surface passivating bonds than the holes. This is in sharp contrast with such materials as CdSe, in which VB states are notably delocalized onto surface bonds and holes are easily trapped by ligands. [6] The stronger coupling of the CB states to the surface bonds in the Si and Ge QDs rationalizes the more significant participation of the high-frequency hydrogen atom modes in the dynamics of electron relaxation compared to the holes, Fig. 7. For the first time, the time-domain simulations gave direct evidence that the high-frequency ligand modes localized on QD surfaces play a key role during the charge-phonon relaxation dynamics in semiconductor QDs.

IV. SUMMARY

We applied the state-of-the-art time-domain DFT and NA MD approaches to study the phonon-induced relaxation dynamics of the photoexcited charge carriers in Ge and Si QDs. The relaxation competes with productive processes and causes energy losses in photovoltaic devices utilizing semiconductor QDs. The calculations showed that the electron and hole DOS of the Ge and Si QDs were distinct from the bulk DOS. The quantum confinement effect made the electron and hole DOS significantly more symmetric in the spherical nanocrystals. Unexpectedly, in spite of the DOS symmetry, the electron and hole relaxation times differed substantially from each other, with the electrons decaying much faster than the holes. The difference between the electron and hole energy decays was more significant in the Ge QD than in the Si QD. The simulations revealed linear relationships for the electron and hole relaxation dynamics. The life-time of the photoexcited state increased linearly with the energy gap between the photoexcited state and its nearest lower energy state. The decay rate of the initial excitation energy linearly correlated with the average DOS within this energy range. The latter linear correlation was well described by Fermi's golden rule. The

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surprising observation that the electron and hole decays were very asymmetrical despite the symmetric DOS was rationalized by the stronger electron-phonon NA coupling within the CB states versus the VB states. The investigation of the phonon modes that determined the NA coupling showed that the coupling disparity for the CB and VB states arose due to the high-frequency phonons. While the low-frequency vibrations gave similar contributions to the NA coupling, the high-frequency modes played an important role for the NA transitions within the CBs of both Si and Ge QDs, and were a factor of 4 less important for the NA transitions within the VBs. These high-frequency modes involved motions of the surface Ge-H and Si-H bonds. The analysis of the orbital densities proved that indeed the LUMO supporting the electrons had a significantly higher density around the Ge-H and Si-H bonds than the HOMO, demonstrating that the electrons and not the holes can be strongly coupled to the passivating bond modes. The study provided the first direct evidence that the high-frequency modes on passivated QD surfaces play a vital function in the phonon-induced relaxation of the photoexcited charge carriers in small semiconductor QDs. The faster relaxation of the electrons relative to the holes in the Si and Ge QDs was in striking contrast to the relaxation processes observed in the binary QDs, such as CdSe, PbSe and GaAs. The holes in these materials decay faster than the electrons. Since the electron and hole relaxation trends are opposite in the QDs composed of the pure group IV elements and those made of the II-VI, IV-VI and III-V binary semiconductors, the Auger processes in small QDs composed of these two types of materials should proceed in the opposite direction as well. The reported simulations suggest that the Auger energy transfer in the Si and Ge QDs should occur from electron to holes. The difference between the electron and hole decays was greater in Ge than Si QDs, hence, the Auger processes should be more significant in Ge. The results reported here provided valuable insights into the electronic band structure and excited state dynamics in the semiconductor QDs. The simulations contributed to the understanding of the roles of quantum confinement, surface passivation and electron-phonon coupling in determining the efficiency of solar energy conversion. The study indicated that the solar energy losses that occur due to the charge-phonon interactions are quite different in Si and Ge QDs compared to their binary counterparts. The QD surface properties played a particularly important role in the observed phenomena. Therefore, carefully controlled synthetic inorganic chemistry involving reactions between the inorganic semiconductors and molecular ligands is a very valuable tool needed for advancing the experimental aspects of the QD research aimed at

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the efficient harvesting and conversion of solar energy.

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TABLE I: Averaged absolute values of the NA couplings. The units are meV. The root-mean-squares of the NA couplings given in parentheses are significantly larger than the averages, indicating that the NA couplings significantly fluctuate. The NA couplings for the electrons are generally larger than those for the holes, rationalizing why the former relax faster than the latter, Figs. 4 and 5.

$Ge_{29}H_{24}$	Electron	Hole	Ratio
Total	8.99(25.3)	5.10(18.9)	1.76(1.34)
Nearest Neighbor	37.4(81.1)	25.7(61.2)	1.46(1.33)

$Si_{29}H_{24}$	Electron	Hole	Ratio
Total	6.77(22.3)	4.54(18.0)	1.49(1.24)
Nearest Neighbor	34.3(76.5)	26.6(62.7)	1.29(1.22)

Figure Caption

FIG. 1: Structures of the $Ge_{29}H_{24}$ and $Si_{29}H_{24}$ QDs. Each QD was initially cut from bulk structure and passivated by white-colored hydrogen atoms (upper panel). Then, the bulk-like QDs were fully optimized at 0 K (middle panel), and brought up to ambient temperatures (lower panel).

FIG. 2: Calculated linear absorption spectra of the $Ge_{29}H_{24}$ and $Si_{29}H_{24}$ QDs. The lines show the integrated spectra, and the bars correspond to individual excitations grouped by energy. The spectra decay at high energies due to a finite number of states considered in the calculations. The lower energy part of the spectra show distinct peaks in agreement with the previous results [49].

FIG. 3: Density of electron and hole states in the $Ge_{29}H_{24}$ and $Si_{29}H_{24}$ QDs. The Fermi energies are set to zero, as indicated by the blue lines. The electron and hole DOS are quite symmetric – more symmetric than the corresponding bulk DOS due to quantum confinement. This is in contrast with the majority of other semiconductor QDs, such as CdSe.

FIG. 4: Linear relationships found in the ultrafast electron and hole relaxations in $Ge_{29}H_{24}$; (a) half-time initial (HTI) defined as half of the life-time of the initially excited state due to its decay to all other states, and (b) half-time total (HTT) defined as half of the decay time from the initially excited state to the lowest excited state. HTI scales linearly with the gap between the initially excited state and the next lower energy state. HTT scales linearly with the average gap between the initially excited state and the lowest excited state. The HTI slopes are 377.976 and 718.907 for electrons and holes, respectively. The corresponding HTT slopes are 899.42 and 5225.6. The electrons decay significantly faster than the holes. The inverse of the life-time is proportional to the relaxation rate, while the inverse of the gap gives the average DOS. The rates scale linearly with the DOS, leading to Fermi's golden rule. The smaller slopes for electron excitation than those for hole excitation indicate faster relaxation of an electron in CB than a hole relaxation in VB.

FIG. 5: The same as Fig. 4 but for $Si_{29}H_{24}$. The HTI slopes are 732.917 for electrons and 846.549 for holes. The corresponding HTT slopes are 1584.12 and 6586.2. The difference between the electron and hole slopes is smaller for $Si_{29}H_{24}$ than $Ge_{29}H_{24}$, see Fig. 4.

FIG. 6: Low-frequency phonon spectral densities (SD) for the CB (upper panel) and VB (lower panel) states of the $Ge_{29}H_{24}$ and $Si_{29}H_{24}$ QDs. The y-axis units are arbitrary and the same in all panels. The SD of $Si_{29}H_{24}$ shows peaks at higher frequencies than $Ge_{29}H_{24}$, as expected. The larger SD intensity in $Ge_{29}H_{24}$ explains the smaller life-time slopes for both CB and VB in Fig. 4 compared with the life-time slopes for $Si_{29}H_{24}$ in Fig. 5. The intensities of the SDs for the CB and VB in each QD are very similar.

FIG. 7: The same as Fig. 6, but in the high frequencies. The SDs of CB are clearly larger than the SDs of VB in both $Ge_{29}H_{24}$ and $Si_{29}H_{24}$.

FIG. 8: HOMO and LUMO electron densities in the $Ge_{29}H_{24}$ and $Si_{29}H_{24}$ QDs. LUMO has higher electron density around the passivating surface bonds than HOMO in both QDs.