

Computational Studies of the Optical Emission of Silicon Nanocrystals

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Abstract: We have computed absorption and emission energies of silicon nanocrystals as a function of size and of surface passivants, using both density functional theory and quantum Monte Carlo calculations. We have found that the ionic rearrangements and electronic relaxations occurring upon absorption and emission are extremely sensitive to surface chemistry. In particular, nanoclusters with similar sizes and similar absorption gaps can exhibit strikingly different emission energies. Our results provide a unifying interpretation of several recent measurements, which have observed significantly different emission energies from clusters with similar sizes. Our calculations also show that a combination of absorption and emission measurements can provide a powerful tool for identifying both the size and the surface passivants of semiconductor nanocrystals.

Introduction

The combination of novel physical properties and promising technological applications has led to an enormous growth in the study of semiconductor nanoclusters over the past decade.¹ In the nanometer size range, quantum confinement effects significantly alter the optoelectronic properties of semiconductors. As the size of a semiconductor cluster is decreased, its optical gap and dipole oscillator strength increase with respect to the bulk value. Recently, many of the size-dependent optical properties of various semiconductor nanoclusters have been measured and characterized using a variety of experimental methods.^{2–8} In addition, theoretical calculations have complemented and helped interpret these experiments by, for example, predicting ideal absorption gaps^{9–11} and spectra.^{12,13}

Most of the theoretical effort has been devoted to calculations of the absorption gap of semiconductor nanocrystals; this is often referred to as the optical gap or band gap. However, the emission energy is actually most often measured and is usually more relevant for technological applications. In general, the absorption gap is larger than the emission gap; that is, light absorbed by

semiconductor clusters is red-shifted to longer wavelengths on emission. This red shift is referred to as the Stokes shift, and its origin, magnitude, and size dependence have been a notable source of controversy in the recent literature, especially for silicon nanoclusters.^{5,7,14–26} Some measurements have found size-dependent Stokes shifts that decrease starting from ~ 1.0 eV in small Si clusters.^{16,19} Other measurements have found small, or negligible, Stokes shifts in Si clusters with diameters from 2 to 5 nm.^{5,7} Still other measurements have reported an almost constant Stokes shift of ~ 1.2 eV for clusters ranging in size from 0 to 4 nm.^{25,26} Understanding the effect of cluster size, surface structure, and surface chemistry on measured Stokes shifts is of the utmost importance if semiconductor nanostructures are to be utilized in optoelectronic devices.

In this article, we present ab initio calculations of both the absorption and the emission energies of a range of prototype silicon nanoclusters up to 2.0 nm in size, as a function of size, surface structure, and surface passivants. We used density functional theory (DFT) to determine atomic geometries and

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single-particle gaps, and quantum Monte Carlo (QMC) to compute optical gaps. We studied nanocrystalline silicon particles with ideal, hydrogen terminated surfaces, as well as nanoparticles with reconstructed surfaces, and with surfaces partially passivated with oxygen in two different bonding geometries. Experimentally, hydrogen termination of Si nanocrystals can be achieved by hydrogen fluoride etching, while the presence of oxygen passivation is typically detected in samples exposed to air before the surface is completely passivated.

Our calculations show that ionic rearrangements and electronic relaxations occurring upon absorption and emission and the resulting Stokes shift are extremely sensitive to the presence of surface passivants such as oxygen *and* to their bonding configuration. In particular, we found that nanoclusters with oxygen double bonded to the surface display the *largest* Stokes shifts. In contrast, a cluster with bridged oxygen on the surface, or with reconstructed hydrogenated surfaces, exhibits the *smallest* Stokes shifts. In addition, our results show that two nanoclusters exhibiting similar absorption gaps may have significantly different Stokes shifts and, hence, different emission energies. Our calculations help explain existing differences among measured values of the absorption, emission, and Stokes shift energies.

Computational Methods

The relaxed ground-state structure of each nanocrystal was obtained by minimizing the calculated total energy within the local density approximation (LDA) to DFT, using a pseudopotential, plane wave approach.²⁷ All clusters were placed in a supercell with a sufficient surrounding vacuum region to remove interactions among periodic images. We used norm conserving, nonlocal Hamann pseudopotentials²⁸ for silicon and oxygen and a Giannozzi pseudopotential²⁹ for hydrogen. The Kohn–Sham orbitals were expanded in a plane wave basis with an energy cutoff of 35 Ry for clusters without oxygen, and 62 Ry for those including oxygen. The exchange–correlation energy and potential are of the Ceperley–Alder form.³⁰

The core of Si nanoclusters was assumed to be crystalline, with bond lengths equal to those of bulk silicon, prior to geometry optimization. Surface dangling bonds were passivated with hydrogen atoms initially placed along the appropriate tetrahedral direction at the experimental Si–H distance in SiH₄. To model clusters with reconstructed surfaces, dimers were formed on the surface by removing a hydrogen atom from neighboring surface Si atoms and then forming an additional bond between the Si atoms, similar to a (2 × 1) reconstruction on a Si (100) surface. For clusters with oxygen passivants, we considered two distinct geometries. In the case of nanocrystals with {100}-type facets, the alignment of the SiH₂ dihydrides on the surface allows oxygen to bond to neighboring Si atoms in an energetically favorable Si–O–Si configuration. For clusters such as Si₃₅H₃₆ where no such adjacent dihydrides exist, the most energetically favorable location for an oxygen atom is to be double bonded to a Si atom stripped of the two hydrogen atoms initially passivating the ideal surface.³¹ For all structures, the initial atomic positions described above were relaxed within DFT until the residual forces were less than 1 × 10^{−4} eV/Å.

While LDA is expected to accurately determine the atomic geometries of semiconductor clusters, this approximation substantially underestimates optical gaps. To overcome the LDA shortcomings and compute optical gaps comparable with experiment, we used QMC

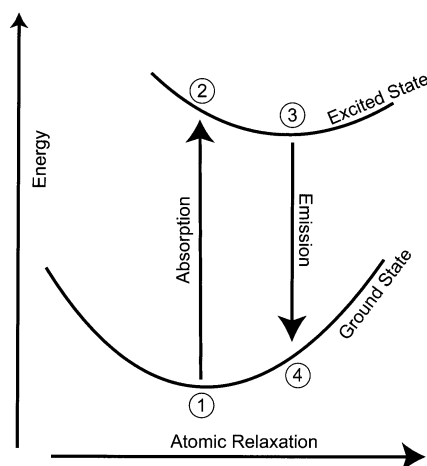


Figure 1. Schematic representation of a Stokes shift relaxation. In position 1, the cluster is in its electronic ground state, and the atomic geometry is relaxed to its lowest energy configuration. On absorption of a photon, the cluster undergoes a vertical electronic excitation from (1) to (2). Once in the excited electronic state, the atomic geometry of the cluster relaxes to a lower energy configuration (from point 2 to 3). Finally, the excited electron and hole recombine via another vertical transition, (3) to (4).

techniques.³² By stochastically sampling the Schrödinger equation, QMC includes many-body effects in the wave function and has been demonstrated to be a highly accurate theoretical tool for calculating total energies, ionization potentials, and optical gaps of both solids³³ and clusters.^{11,34,35} By utilizing a localized basis of Wannier functions, the QMC calculations scaled nearly linearly with system size.³⁶ This favorable scaling has allowed one to tackle systems much larger than previously possible with ordinary algorithms scaling as the third power of the number of electrons; in particular, in our study it enabled the calculations of optical gaps of clusters as large as 1.8 nm in size. Within QMC, the optical absorption gap, E^{opt} , can be determined as the difference in the total energies of the cluster in the ground state (E^0) and the first electronically excited state (E^*) as $E^{\text{opt}} = E^* - E^0$.

The calculations of Stokes shifts are more elaborate and complex than the calculations of absorption gaps, which already represent a challenging task within QMC. In the absence of surface traps, Stokes shifts are determined by Franck–Condon-like relaxations, shown in Figure 1. In our investigation, we computed Stokes shifts as

$$E^{\text{Stokes}} = E^{\text{absorption}} - E^{\text{emission}} = (E_2 - E_1) - (E_3 - E_4)$$

where $E^{\text{absorption}}$ is the difference in the energy required to excite the cluster from its ground state to the first excited state (i.e., the energy difference between (1) and (2) in Figure 1), and E^{emission} is the energy released during electronic relaxation from points 3 to 4. The calculation of forces within QMC for clusters with many degrees of freedom is still prohibitively expensive. Therefore, we first used LDA to determine the ground-state atomic geometry at points 1 and 2 and the excited-state geometry at points 3 and 4. We then employed both LDA and QMC to determine the total energy at each of these four points. The total energy of the two ground-state points (E_1 and E_4) was determined from closed shell electronic configurations. After the vertical excitation from (1) to (2), the singlet state is the correct spin state of the excited-state configuration. However, previous calculations have demonstrated

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Table 1. Calculated Absorption Gaps, Stokes Shifts, and Stokes Shift Displacements in Different Silicon Nanocrystals^a

cluster	structure	diameter (nm)	optical gap (eV)		Stokes shift (eV)		rms displacement (Å)
			LDA	QMC	LDA	QMC	
Si ₂₉ H ₃₆	hydrogenated	0.9	3.6	5.3(1)	0.69	1.0(1)	0.31
Si ₃₅ H ₃₆	hydrogenated	1.1	3.4	5.0(1)	0.57	0.8(1)	0.25
Si ₆₆ H ₆₄	hydrogenated	1.3	2.8	4.7(1)	0.50		0.19
Si ₈₇ H ₇₆	hydrogenated	1.5	2.5	4.2(2)	0.22		0.14
Si ₁₄₈ H ₁₂₀	hydrogenated	1.8	2.1	3.9(3)	0.13		0.11
Si ₂₁₁ H ₁₄₀	hydrogenated	2.0	2.0		0.06		0.05
Si ₂₉ H ₂₄	reconstructed	0.8	2.6	3.6(1)	0.34	0.4(1)	0.13
Si ₆₆ H ₄₀	reconstructed	1.3	1.9	3.3(1)	0.16		0.11
Si ₂₉ H ₃₄ O	Si–O–Si	0.9	3.1	4.7(1)	0.27	0.5(1)	0.08
Si ₃₅ H ₃₄ O	Si=O	1.1	2.2	2.5(1)	1.16	1.3(1)	0.30
Si ₆₆ H ₆₂ O	Si=O	1.3	2.2		1.22		0.33
Si ₈₇ H ₇₄ O	Si=O	1.8	2.0		1.13		0.31

^a LDA and QMC calculated absorption gaps and Stokes shifts are quoted in eV. QMC statistical error bars are shown in parentheses. The rms displacements are in Å. Structures with bridged oxygen are labeled Si–O–Si, and double bonded oxygen is labeled Si=O.

that the splitting between the singlet and triplet excited states of nanometer silicon clusters is only a few millielectronvolts.^{21,22} Therefore, to improve the convergence of our LDA calculations, the total energy of geometries 2 and 3 was calculated assuming a triplet spin configuration. The calculation of the geometry in the triplet state allows standard energy minimization procedures to be adopted, and they are used here to calculate the excited-state geometry. In the QMC calculations of the energy of points 2 and 3, the correct singlet configuration was adopted, although the structure was taken from the LDA triplet calculation.

Results

Table 1 reports our calculated values of the LDA single-particle gap, the QMC optical gap, and the LDA and QMC values of the Stokes shift for a range of silicon nanoclusters with different sizes and different surface structure and passivants. For comparison, the single-particle gap was also calculated using a gradient-corrected functional and found to be very similar to the LDA values. Before describing in detail our results for the Stokes shift, it is worth summarizing the results on optical gaps. The gaps of nanoclusters with hydrogen terminated, unreconstructed surfaces are the largest and, in agreement with previous investigations,¹¹ are found to increase as the size of the cluster is reduced due to quantum confinement effects. The difference between the LDA gaps and the QMC gaps is roughly constant over this limited size regime, but it will decrease as the bulk limit is approached.¹¹ The gap of nanoclusters with surfaces partially passivated with double bonded oxygen atoms is smaller than that of fully hydrogenated clusters. Nanoclusters with double bonded oxygen at the surface have been previously shown to exhibit significantly smaller optical gaps than hydrogen terminated clusters for diameters smaller than ~ 2 nm.^{37,38} These findings are confirmed by the results found here for Si₃₅H₃₄O, Si₆₆H₆₂O, and Si₈₇H₇₄O clusters. The values of the gap are different if the oxygen at the surface is in a bridged or a double bonded configuration. Nanoclusters with oxygen partially passivating the surface in a bridged Si–O–Si configuration experience minimal surface distortion due to the passivant and have an optical gap smaller than that of hydrogen terminated

clusters, but significantly larger than that of nanoclusters with double bonded oxygen passivation. Similarly, clusters with reconstructed surfaces have smaller gaps than those of ideal hydrogenated structures due to geometrical distortions at the surface, yet the gap is larger than that of a cluster of the same size with double bonded oxygen passivation.

The LDA and QMC values of the Stokes shift reported in Table 1 show that, similar to computed optical gaps, LDA predicts qualitatively correct *trends* as a function of size and surface character, but it consistently underestimates the value of the Stokes shift by 0.2–0.3 eV. Motivated by the experimental measurements, we grouped the clusters into three classes: (i) clusters exhibiting a small Stokes shift between 0 and 0.3 eV, (ii) clusters with size-dependent Stokes shifts up to 0.8 eV, and (iii) clusters with Stokes shifts larger than 0.8 eV that are independent of size. Our calculations show that clusters with reconstructed surfaces and surfaces with bridged oxygen consistently exhibit the smallest Stokes shifts, ranging from 0.1 to 0.3 eV as a function of size, and thus fall into the first category [(i)]. Clusters with ideal, hydrogenated surfaces produce instead intermediate values of the Stokes shift that range from 0.3 to 0.8 eV as a function of size. These clusters belong to the second category [(ii)]. Finally, clusters with oxygen double bonded (Si=O) to the surface exhibit Stokes shifts of ~ 1.2 eV, relatively independent of size, and fall into the third category [(iii)].

To gain insight into the physical reasons responsible for the large differences in the above Stokes shifts, we examined the nature of the electronic states responsible for absorption and emission, that is, the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). The change in the charge density introduced by the excitation of an electron from the HOMO to the LUMO induces forces on each atom due to the changes in the corresponding orbital densities.

The HOMO and LUMO orbitals of four clusters, all approximately 1 nm in size, are shown in Figure 2. Figure 2a shows that in a nanocluster with hydrogen passivated, unreconstructed surfaces (e.g., Si₃₅H₃₆), both the HOMO and the LUMO are delocalized throughout the core of the nanocluster. In contrast, the HOMO and LUMO are localized at the surface of the cluster when the surface is reconstructed (e.g., Si₂₉H₂₄) as shown in Figure 2b. In the presence of a single oxygen atom placed in a Si–O–Si bridged position on an otherwise unreconstructed surface [(e.g., Si₂₉H₃₄O), Figure 2c], the HOMO and LUMO charge densities are partially drawn toward the surface with most charge still existing in the core of the cluster. Finally, Figure 2d shows that the placement of a single oxygen atom in an Si=O double bonded position on the surface of an otherwise unreconstructed cluster (e.g., Si₃₅H₃₄O) induces an almost complete localization of both the HOMO and the LUMO on the Si=O double bond.

The structural changes resulting from the creation of an exciton in the various nanoclusters studied here were represented by the rms displacement of all of the cluster atoms and are summarized in Table 1. These displacements are shown in the right-hand column of Figure 2 by arrows proportional to the vector displacement of the atoms from positions 2 to 3 (Figure 1). The rms displacement of atoms in the completely hydrogenated structures, for example, Si₃₅H₃₆, is ~ 0.3 Å for 1 nm

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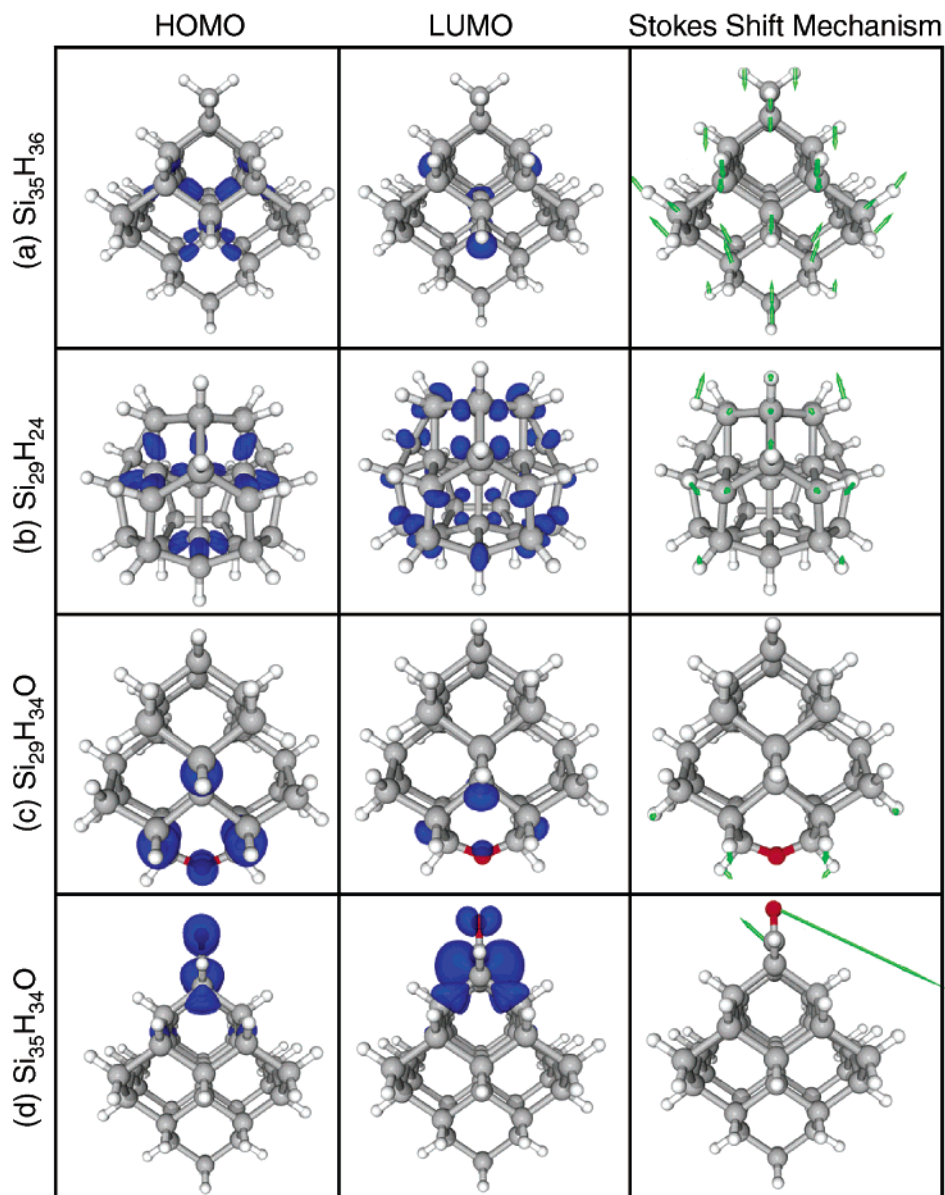


Figure 2. The two left columns show charge density isosurfaces of the HOMO and LUMO orbitals of 1 nm clusters with different surface structures and different passivants. The silicon atoms are gray, the hydrogen atoms are white, and the oxygen atoms are red. The isosurfaces are chosen at 50% of the maximum amplitude. The right column shows vectors proportional to the displacement of each atom during the Stokes shift (see text). The displacements have been magnified by 10 for clarity.

structures and rapidly decreases to less than 0.1 \AA as the cluster size increases to $\sim 2 \text{ nm}$. In these clusters, Figure 2a shows that the change in charge density resulting from the HOMO to LUMO excitation is distributed relatively evenly throughout the cluster and hence all atoms experience forces of approximately equal magnitude. This equality of forces is confirmed by the similar magnitude of the vector displacements plotted in the right column of Figure 2a. These displacements show that the shape of hydrogenated clusters changes from spherical to elliptical upon excitation of one electron. As the size of the hydrogenated clusters increases, the relative change in charge density around each atom due to the excitation of a single electron decreases inversely proportionally to the number of atoms, and hence the rms displacements also decrease (see the first five rows of Table 1).

The clusters with reconstructed surfaces, for example, $\text{Si}_{29}\text{H}_{24}$ (Figure 2b), and those with Si–O–Si bridged oxygen on the

surface, for example, $\text{Si}_{29}\text{H}_{34}\text{O}$ (Figure 2c), show smaller rms displacements than do the completely hydrogenated clusters. In these reconstructed clusters, the charge density change associated with the HOMO–LUMO excitation is localized at the surface, and therefore the surface atoms experience the greatest force. Similar to hydrogenated clusters, as the size of the reconstructed clusters increases, the change in charge density due to the excitation of a single electron from the HOMO to LUMO is distributed over a larger area, and hence the force on each individual surface atom again decreases with size; this is confirmed by the decreasing rms displacements of the larger reconstructed clusters.

In the clusters with oxygen double bonded to the surface, for example, $\text{Si}_{35}\text{H}_{35}\text{O}$ (Figure 2d), the rms displacement is slightly larger. However, in this case, considering the rms displacement is somewhat misleading as almost all of the atomic relaxation is concentrated on the double bonded oxygen atom.

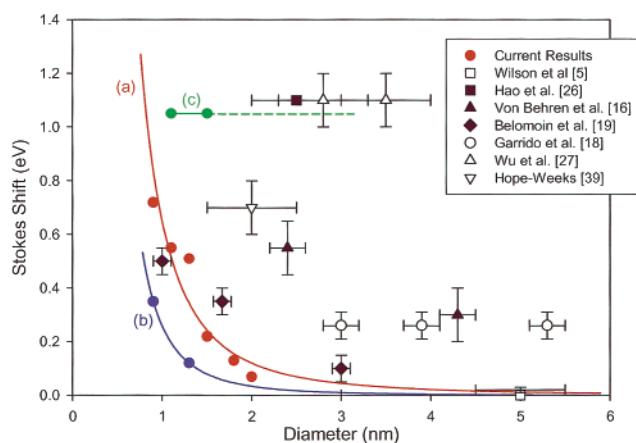


Figure 3. A comparison of measured values of the size dependence of the Stokes shift in silicon nanoparticles with theoretically predicted LDA values (see text). The green curve shows the calculated Stokes shift with double bonded oxygen at the surface. The red curve shows the calculated Stokes shift with idealized hydrogen passivation. The blue curve shows the calculated Stokes shift with bridged oxygen or reconstructed surfaces.

The displacement vectors plotted in Figure 2d show that the double bonded oxygen atom rotates by over 42° when excited into the triplet state. This localization of the Stokes shift relaxation on the double bonded oxygen atom results from the localization of the HOMO and LUMO orbitals on the double bond as shown in Figure 2d. In these clusters, the Stokes shift is relatively independent of the size of the cluster as the relaxation mechanism depends only on specific bonds *at the surface*.

Comparison with Experiment

A wealth of experimental measurements of the optical absorption and emission wavelengths of silicon nanostructures has been published in recent years.^{5,7,14–19,25,26} Unfortunately, there appears to be little consensus among experimental results appearing in the recent literature. Interpreting and classifying the large number of gaps and Stokes shifts is difficult due to long-standing problems synthesizing monodisperse samples with well-characterized surfaces. However, on the basis of the results described in the previous section, we propose that many apparently conflicting measurements can be explained by considering differences in the size and surface properties of the samples.

Figure 3 combines the results of a number of published values for the experimentally measured Stokes shift of silicon nanocrystals. The Stokes shift is plotted as a function of the size of the nanocluster. The horizontal error bars are largely due to difficulties determining the exact size of a given sample, while the vertical error bars are determined mostly by the size dispersion and small structural variations of the samples. For comparison, we include in Figure 3 the results of our LDA calculations from Table 1. The LDA rather than the more accurate QMC results were plotted as they are available for larger size clusters. The QMC values can then be used to quantitatively correct the LDA values, which, however, give the correct qualitative trend as a function of size. QMC values rigidly shift LDA results by ~ 0.2 – 0.3 eV. As a guide to the eye and as a means of extrapolating our results to sizes of nanoclusters beyond those currently accessible with *ab initio* techniques, we fit our LDA data results to the curves shown by

three different colors in Figure 3. The three curves correspond to the three classes of Stokes shifts discussed in the previous section. The bulk derived, hydrogenated nanoclusters are represented by the red curve (a), which shows Stokes shifts that rapidly decrease from over 2 eV for 0.5 nm clusters to 0.1 eV for 2 nm clusters. The hydrogenated nanoclusters with reconstructed surfaces and bridged Si–O–Si oxygen are represented by the blue curve (b), which shows Stokes shifts that are smaller than curve (a) and are decreasing to less than 0.1 eV in 2 nm clusters. The size dependence of the Stokes shift in curves (a) and (b) was fit to $E^{\text{Stokes}} \propto D^{-n}$, where D is the cluster diameter, and both curves show a size dependence of $n \approx 2.5$. The nanoclusters with oxygen double bonded to the surface are represented by the green curve (c), which shows Stokes shifts of ~ 1.2 eV, roughly independent of size.

While many of the error bars are fairly large in Figure 3, the experimental values for the Stokes shift can be broadly divided into three classes, which approximately correspond to the three classes of Stokes shifts identified by our calculations. The most striking agreement is between the results of Wu et al.²⁶ and Hao et al.²⁵ and the results we found for the Stokes shift of clusters with oxygen double bonded to the surface. Wu et al. find values of the Stokes shift of ~ 1.2 eV, which are almost independent of the size of the nanocluster. These measurements agree with our model for the Stokes shift of clusters where the structural relaxation is localized almost entirely on the silicon/oxygen double bond, due to the localization of the HOMO and LUMO charge densities on this bond.

The Stokes shifts measured by von Behren et al.¹⁶ and Hope-Weeks³⁹ display the same size dependence as absorption gaps, with the Stokes shift decreasing as the size of the cluster increases. We interpret these results as suggesting that the nanoclusters synthesized in these experiments correspond to hydrogenated clusters with unreconstructed surfaces (similar to $\text{Si}_{35}\text{H}_{36}$). Those clusters with the smaller Stokes shifts in this class, for example, those characterized and observed by Belomoin et al.,¹⁹ may exhibit partially reconstructed surfaces which, as we have shown, suppress the magnitude of the Stokes shift (see, e.g., $\text{Si}_{29}\text{H}_{24}$).

Finally, the Stokes shifts measured by Garrido et al.¹⁸ are very small over a range of sizes/gaps. These clusters are surrounded by an SiO_2 matrix and may well contain the bridged Si–O–Si bonds at the surface, which we have shown to be responsible for a significant suppression of the Stokes shift. This explanation based on the surface structure of the clusters resolves the contradiction noted by von Behren et al.¹⁶ that their measured values of the Stokes shift (0.3–0.6 eV) were not in agreement with the negligible value measured by Wilson et al.⁵ for similar size clusters.

As mentioned earlier, our LDA predicted values of Stokes shift for hydrogenated clusters are lower than those measured. For clusters with diameters of ~ 1 nm, the agreement with experiment is significantly improved by including QMC corrections which increase the predicted Stokes shift by ~ 0.2 – 0.3 eV. We note that to further improve the comparison between our calculations and experiment, additional phenomena should be taken into account. In addition to the structural relaxation calculated here, a red shift can be introduced by (i) absorption into a state higher than the emitting state. Such a situation may

(39) Hope-Weeks, L., private communication.

arise either by a singlet–triplet splitting of the band edge levels due to the electronic exchange interaction or by the smallest possible transition being optically forbidden. In either case, light is absorbed into the higher energy exciton level and emitted from the lower energy, optically forbidden, “dark exciton” level. We expect the singlet–triplet splitting to be negligible in nanoclusters with diameters larger than 1 nm,²¹ and thus it was not included here. For the clusters studied here, the lowest singlet–singlet transition is only optically forbidden in clusters with one oxygen double bonded to the surface (e.g., Si₃₅H₃₄O).^{31,40} In this idealized case, the Stokes shift would actually increase by an approximate 0.2 eV in the smallest clusters due to the excitations into the next highest state. (ii) The existence of “surface traps” with energies in the middle of the optical gap of idealized hydrogenated clusters can contribute to the Stokes shift. An exciton is initially formed in the core of the cluster, and then either the electron or the hole migrates to a lower energy surface localized trap state before recombination and the emission of a photon. In this work, we choose to study representative prototype clusters, and therefore surface trap states were not present. Adding such an effect would increase the predicted value of the Stokes shift, but the magnitude is extremely sensitive to the nature of the trap. (iii) A broad size distribution itself can contribute to the Stokes shift. Light is absorbed by clusters with a range of sizes, and the absorption peak is close to that of the mean size cluster. The excitons then lower their energy by transferring to neighboring larger clusters, before recombination and emission. In this manner, the average measured emission would tend to be from the larger clusters of a given size distribution, which in turn leads to larger measured Stokes shifts.⁴¹

In addition to comparing with measured values, it is interesting to compare our results with previous calculations appearing in the literature. To date, we are aware of five calculations,^{20–24} the majority based on a variety of empirical models for

determining the structural relaxation of a cluster in an excited electronic state.^{21,22} There are two cases where the smallest of the nanoclusters included in this work have been previously studied. A previous calculation of the Stokes shift of a 14-atom silicon nanocluster, passivated with hydrogen, was predicted to be 0.7 eV.²⁴ This is in agreement with our LDA calculation, but our more accurate QMC calculations predict a larger value of 1.1 eV. Another previous LDA calculation of the Si₂₉H₃₆ cluster predicted the single-particle gap and Stokes shift to be 3.3 and 0.22 eV, respectively.²⁰ In this case, we predict significantly larger LDA values of 3.6 and 0.7 eV and QMC values of 5.3 and 0.9 eV, respectively. We attribute the previously calculated smaller LDA values to be due to the use of too small of a basis (6 Ry as compared with 35 Ry in our calculation).

Conclusion

In conclusion, using state-of-the-art electronic structure calculations, we have determined that in silicon nanoclusters the value of Stokes shifts is extremely sensitive to the size, surface structure, and chemistry of the nanocrystal. For ~1 nm sized clusters, the Stokes shift ranges from less than 0.1 eV to greater than 1.0 eV depending on the detailed surface structure and the presence of oxygen in either bridged or double bonded configurations. Our results enabled us to provide explanations for the seemingly contradictory results of a number of experiments. These results demonstrate that combining measurements of the absorption and emission energies provides a powerful tool for optically characterizing both the size and the surface structure of semiconductor nanoclusters.

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