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Authors

Fuhr, Addis S
Sautet, Philippe
Alexandrova, Anastassia N

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Heterogeneity in Local Chemical Bonding Explains Spectral Broadening in Quantum Dots with Cu Impurities

Addis S. Fuhr,^{†,‡} Philippe Sautet,^{‡,§,#} Anastassia N. Alexandrova,^{§,#*}

[†] Chemistry Division, Los Alamos National Laboratory, Los Alamos, New Mexico 87545, United States

[‡] Department of Chemical and Biomolecular Engineering, University of California, Los Angeles, Los Angeles, California 90095, USA

[§]Department of Chemistry and Biochemistry, University of California, Los Angeles, Los Angeles, California 90095, USA

[#]California NanoSystems Institute, University of California, Los Angeles, Los Angeles, California 90095, USA

* Address correspondence to ana@chem.ucla.edu

ABSTRACT

Quantum dots (QDs) with optically active Cu impurities have been proposed as heavy-metal free alternatives to Cd and Pb chalcogenides. However, the origin of their unusual optical properties is not well understood. In particular, spectral broadening is an issue for their use in high color purity light-emitting diodes, and reabsorption-free solar windows. Here, we show with density functional theory calculations that chemical bonding variations have a major effect on the optical properties of Cu doped ZnSe QDs. The Cu-Se coordination sphere is highly covalent, and therefore sensitive to local variations in electrostatics and bond geometry. Correspondingly, changes in the Cu impurity environment lead to large shifts in their ground state energy, which causes spectral broadening when multiple Cu impurity bonding environments coexist as subensembles with distinct absorption and emission energies. We conclude that while electron-phonon coupling is stronger for these systems than for typical II-VI QDs, spectral broadening predominantly occurs due to the inhomogeneous spatial distribution of Cu impurities. This is in agreement with studies that have shown narrow (~ 60 meV) single-particle emission linewidths in related $\text{Cu}_x\text{In}_{2-x}\text{Se}_y\text{S}_{2-y}$, or “CIS” QDs, which also emit through Cu impurities. Hence, we predict that narrow ensemble emission in photonic devices can be achieved if heterogeneity is controlled.

INTRODUCTION

The size-tunable band gap, solution processability, and multiexcitonic effects of II-VI and IV-VI quantum dots (QDs) make these materials attractive for a broad range of electro-optical applications.¹ Unfortunately, the use of toxic heavy metals (*e.g.* Cd or Pb) have limited their commercial viability.²⁻³ While environmental concerns have spurred research interest in heavy-metal-free multinary and transition metal doped structures, their optical transitions are not well understood, and significantly differ from Cd and Pb chalcogenides.⁴⁻¹³ For example, QDs with Cu, or Mn cations have large Stokes shifts (Δ_S , defined as the energy difference between absorption and emission energies), broad ensemble spectral linewidths, long radiative lifetimes, and tunable magnetic exchange interactions.^{6, 14} One possible reason for these peculiar properties is the smaller ionic radii of 3d transition metals, which have greater polarizing power than Cd or Pb, and should form more covalent bonds with early chalcogens. This, in addition to their complex multinary structure make it easier for *extrinsic* (dopant), or *intrinsic* (native defect) impurities to localize photo- or electro-excited carriers to small regions of the crystal lattice where local structural distortions will more strongly affect carrier interactions than delocalized band-edge states.

Of these transition metal based structures, QDs with Cu impurities are particularly interesting. Radiative recombination occurs through a hole localized at a Cu impurity and a delocalized conduction band electron.^{4, 7-12, 15} This is distinct from Mn doped QDs where Mn transitions localize *both* carriers.¹⁶⁻¹⁸ Consequently, Mn emission can only shift within a small range of the visible spectral window due to changes in local strain environment altering the crystal field splitting energy.¹⁸ Cu impurities, on the other hand, have emission energies that are far more tunable, and extend across the visible and infrared regime making them appealing for a

broader range of applications.^{4, 7-12, 15, 19} However, for each of these applications, improvements in device performance will require a better understanding on how modified environment can affect the optical transitions. We propose here that chemical bonding plays a key role. Specifically, Δ_S can vary by > 500 meV for Cu impurities in QDs with the same basic structure (*e.g.* CIS QDs),^{9, 20} and even more (>1 eV) when comparing different structures (*e.g.* Cu doped CdS and CdTe QDs).¹² Further, single particle spectroscopy studies have shown that the intrinsic photoluminescence (PL) linewidth for CIS QDs is over 80% narrower (60 vs. 352 meV) than the ensemble; and, there are large dot-to-dot variations in PL linewidth (~ 150 meV), emission energy (~ 300 meV), and radiative lifetimes (~ 250 ns) within the *same* ensemble.¹⁰ Controlling these properties will be essential to achieving narrow emission for high color purity LEDs, reduce spectral overlap for reabsorption-free solar windows, and tune emission energy for infrared photodetectors.^{3, 10, 21-25}

In this work, we use density functional theory (DFT) calculations to systematically investigate the effects of the local environment and chemical bonding on the Cu impurity energy levels in Cu-doped ZnSe QDs. We predict the effects of structural heterogeneity on electronic states by altering the bonding environment of Cu impurities, and compare the electronic structure, charge distribution, and absorption spectra for several kinetically trapped local minima. The Stokes shift and spectral linewidth for QDs with Cu impurities is highly sensitive to the impurity position (*e.g.* surface vs. subsurface), coordination environment (*e.g.* tetrahedral vs. distorted trigonal planar), and concentration (Figure 1). We further note that while there are significant variations in the experimental properties of Cu impurities in QDs, large Stokes shifts, broad linewidths, and long radiative lifetimes are consistently observed across all structures, and

suggest that our predictions should be applicable to similar materials such as Cu-doped InP or CIS QDs.^{8,19}

COMPUTATIONAL METHODS

Plane-wave PAW DFT in VASP²⁶⁻²⁹ was used for all geometry optimizations and electronic structure calculations. For geometry optimizations, we used the PBE³⁰ functional. While, HSE06³¹ was used for all electronic structure and charge distribution calculations. The energy cut-off (320 eV) was the same for all calculations, and all structures were relaxed until forces were smaller than 0.05 eV/Å per atom. The screening parameter for all HSE06 calculations was $\omega = 0.13$, as described in previous reports.³²⁻³³ The experimental properties of bulk ZnSe were reproduced by sampling the Brillouin zone of a ZnSe unit cell with a (6x6x6) Monkhorst-Pack k-point grid. Bulk Cu¹⁺ and Cu²⁺-doped ZnSe calculations utilized a 2x2x2 supercell where the Brillouin zone was sampled using a Gamma-centered (2x2x2) k-point grid. Spherical QDs were constructed based on the (111) and (200) surface facets with a vacuum spacing of ~ 15 Å to isolate each QD, and avoid QD-QD interactions. The geometry for the entire QD (including pseudo-hydrogens) was optimized. For QDs, the Brillouin zone was sampled at the Gamma point only. Cu²⁺ impurities in both bulk and QD calculations were modeled by replacing a Zn²⁺ atom with Cu, and using the MAGMOM tag to capture magnetic interactions. Cu¹⁺ calculations used the same procedure, but without the MAGMOM tag and with an electron added to the cell. Atomic charges were calculated using the Bader charge algorithm with PW-DFT.³⁴

RESULTS AND DISCUSSION

Properties of Cu Impurities in ZnSe QDs. We systematically explored the effect of Cu impurity position, coordination environment, and concentration on the optical properties of ZnSe QDs (Figure 1). Chalcogen-rich (Zn:Se ratio $\sim 1:1.25$), spherical ZnSe QDs based on the zinc

blende crystal phase were constructed exposing (111) and (200) surface facets, and terminated by pseudo-hydrogens to maintain charge balance. This eliminates most of the dangling bond surface states by using ^xH where x is the fractional charge used to achieve local charge neutrality (here, $x = 0.25$),³⁵⁻³⁸ and mimics the surface passivation of long-chain organic ligands typically used in experiment to disperse QDs in organic solvents.^{4, 7-8, 11} This approach is effective at reducing the surface state contribution to the density of states (DOS) and predicting optical absorption and emission energies. However, considering the extreme sensitivity of the absolute QD band positions to ligand selection,³⁹⁻⁴⁰ this approach would not be accurate for determining QD band positions *vs.* vacuum. We determined the local minima structures using the Perdew-Burke-Ernzerhof (PBE) functional because of its ability to provide good geometries and low computational expense.³⁰ However, the Heyd-Scuseria-Ernzerhof (HSE06) functional was used for all other calculations due to its ability to accurately predict semiconductor band gaps.⁴¹ We tested this procedure on bulk ZnSe (Figure S1), and found excellent agreement with experiment.⁴²

Figure 1. Calculated local minima for 1.5 nm ZnSe QDs doped with Cu^{1+} atoms. “Sub” refers to subsurface impurities, “Surf4” and “Surf3” refer to surface impurities with a coordination number of 4 or 3, “Sub/Surf3” refers to QDs with 2 Cu impurities in the “Sub” and “Surf3” positions, and “Cu₄” refers to QDs with 4 Cu atoms doped as a cluster. For Sub and Surf3, additional calculations with Cu^{2+} dopants are also described. Zn atoms are depicted in green, Se in blue, Cu in red, and pseudo-hydrogens in grey.

For direct comparison with QDs, we calculated the electronic structure of bulk ZnSe doped with either Cu^{1+} or Cu^{2+} impurities (Figure S2). Considering that the expected oxidation state of Zn in ZnSe is 2+, Cu impurities that replace Zn as anti-site Cu_{Zn} defects are expected to

be Cu^{2+} . Indeed, the spin-polarized density of states (DOS) show a Cu state with an unpaired electron above the Fermi level (unoccupied), which is the expected behavior of a paramagnetic d^9 impurity. The properties of Cu^{1+} impurities, on the other hand, are calculated as an anti-site defect with an additional electron (Cu_{Zn}^-). In this case, the Cu state is below the Fermi level (occupied) as expected of a d^{10} cation. While we will eventually show that traditional description of Cu oxidation states is complicated due to covalent bonding, this result suggests that describing their photophysics in the context of d^{10} (occupied) or d^9 (unoccupied) cations is still informative. Figure 2a shows the calculated DOS for a QD doped with Cu^{1+} at a subsurface lattice site, which exemplifies the basic optical properties (*e.g.* large Stokes shift) predicted for all of the Cu doped QD systems studied here. The band-edge (BE) states are marked by solid black lines and labeled as “VB” for valence band or “CB” for the conduction band. BE and impurity states were determined by analyzing the charge density distribution for each DOS (Figure 2b-d). CB (Figure 2b) refers to the lowest unoccupied delocalized state, and VB (Figure 2d) is the highest occupied delocalized state. The electronic wave function squared for the Cu impurity (labeled “IG” for intragap state) is localized to the Cu-Se tetrahedra (Figure 2c), and marked by a dashed line in the DOS. We note here that our description of “delocalized” states, while reflecting a significant symmetry-allowed mixing of molecular orbitals (MOs), does not necessarily indicate a highly shared charge distribution over the entire QD. Considering that QDs are smaller than the exciton Bohr radius (distance between the electron-hole pair), excitons formed *via* BE states are localized by the confinement potential. Hence, BE excitons will be delocalized across the entire QD regardless of whether the chemical bonds forming the VB and CB states are truly delocalized.

Figure 2. (a) DOS for subsurface Cu^{1+} doped ZnSe QDs. Band-edges (BE) are marked by solid black lines and the intragap “IG” Cu^{1+} impurity state is marked by a dashed line (here, at the Fermi level). Possible optical absorption transitions are marked by colored arrows and the theoretical Stokes shift, or Δ_S (energy off-set between IG and VB) is also labeled. The CB was determined to be the lowest unoccupied delocalized state (b), IG to be the Cu-Se occupied localized state (c), and VB to be the highest occupied delocalized state (d) based on the charge density distributions, which are shown in purple for occupied, and yellow for unoccupied energy levels. All unlabeled states between VB and IG are surface “trap-like” states. (e) The molecular orbital (MO) diagram for the QD, which includes the local tetrahedral coordination environment predicting the orbital hybridization for Cu-Se σ bonds. The BE states for Zn are also shown, and their full description is presented in Figure S3 using bulk ZnSe. The panel on the right of (e) depicts possible optical absorption (grey arrows) and emission (red arrow) transitions corresponding with the MO diagram.

The VB has almost 90% Se (p) orbital character, while the CB has a nearly equal contribution of Se (~60%) and Zn (~40%) (s) electrons. Further comparison with bulk ZnSe shows similar trends, but with less Se character for both bands (~81% in the VB and ~45% in the CB). This small deviation is expected due to the higher concentration of Se atoms in the QD.

Indeed, the orbital DOS for the QD CB in Figure S4 shows that the (s) electron ratio for Se and Zn is roughly the same as the bulk calculation (Zn:Se $\approx$ 1.10:1 for the QD, and 1.17:1 for bulk), but there is a larger Se (p) contribution in the CB that is roughly equivalent to the excess Se ($\sim$ 22.9%). Nonetheless, the orbital contribution of ZnSe in both the QD and bulk calculations can be explained using simple crystal field theory considerations (summarized in Figure 2e and shown in more detail in Figure S3). Three of the metal (d) orbitals (specifically, d_{xy} , d_{xz} , d_{yz}) exhibit the same t_2 symmetry as the metal (p) orbitals in tetrahedrally coordinated transition metal complexes. These MOs overlap to form σ bonds with the (p) orbitals of the ligand (here, Se), which also exhibit t_2 symmetry. For Zn^{2+} , which has an [Ar]3d¹⁰ electron configuration, the σ bonding orbitals would form occupied $1t_2$ and $2t_2$ states. The latter of which would act as the QD HOMO. The anti-bonding $3t_2$ states, however, would be higher in energy than the anti-bonding σ^* states formed between the metal and ligand (s) orbitals, which have the a_1 symmetry and act as the LUMO (Figure 2e and Figure S3). This description of the band structure using crystal field theory will be important in our later description of Cu bonding and shifts in ground state energy levels. However, we note here that the other two (d) orbitals in Cu and Zn (d_z^2 , $d_{x^2-y^2}$) would have the e symmetry and should form an additional nonbonding energy level (Figure S3). In both cases, the e state would be below $2t_2$. This is insignificant for predicting optical trends for Zn as the $2t_2$ state would still be the highest occupied delocalized state (VB). On the other hand, for Cu, this may lead to additional absorptive/emissive sub-band gap infrared transitions not discussed here (*e.g.* $2t_2 \rightarrow 2e$) if the Cu $2e$ state is higher in energy than the VB.⁴³

The QDs studied here are far smaller than the exciton Bohr radius for ZnSe (1.5 nm *vs* 4.5 nm).⁴⁴ Consequently, they are in the strong confinement regime and have a significantly larger band gap than in the bulk calculation. The confinement energy (defined as the energy

difference between the bulk band gap and the gap of the quantum confined structure) is ~ 0.9 eV, which is close to what is predicted by the effective mass model.⁴⁵ IG, in the case of Cu^{1+} is at the Fermi level, and is therefore occupied. Hence, a maroon arrow marking a possible optical absorption transition (labeled IG_{abs}) is shown in addition to the expected BE absorption transition (BE_{abs}) in the DOS (Figure 2a), and a scheme is included in Figure 2e next to the MO diagram for the expected absorption/emission transitions. Additional unlabeled states between the VB (~ -1 eV) and Cu (~ 0 eV) are of surface origin (Figure S5) and typically form traps. The projected density of states (PDOS) indicate that IG has a large ($\sim 42\%$) contribution from Se (p) atomic orbitals, and the projected charge density is localized across the entire Cu-Se tetrahedra. Similar to our ZnSe bulk calculations, we plot the PDOS (Figure S4) for each MO of the QD, and also find that the Cu IG level is predominantly composed of the d_{xy} , d_{xz} , d_{yz} orbitals with a small contribution from the Cu (p) orbitals. This suggests that, much like in ZnSe, the t_2 symmetry allows Cu to form σ bonds with the (p) orbitals of Se, and IG is the Cu-Se $2t_2$ state.

Chemical Bonding Effects on Cu Impurity Energy Levels. Figure 3a shows the DOS for Cu^{1+} impurities in 3 different configurations: subsurface (Sub), surface with tetrahedral geometry (Surf4), and surface with distorted trigonal planar geometry (Surf3). These configurations represent three of the four possible impurity environments for ZnSe. The fourth, Surf2, is unlikely to form due to the high diffusivity of Cu in QDs.^{7, 11} We calculated the formation energies for the different impurity configurations using eq 1.

$$\Delta E_{\text{Cu-conf.}} = E_{\text{Cu:QD}} - E_{\text{QD}} + \sum_{\alpha} n_{\alpha} (E_{\alpha}^{\text{solid}} + \mu_{\alpha}) \quad (1)$$

where $E_{\text{Cu:QD}} - E_{\text{QD}}$ represents the energy difference between the “pure” QD and QD with Cu impurities, $E_{\alpha}^{\text{solid}}$ is the energy per atom of elemental solid α (Cu or Zn), n_{α} is the number of atoms added ($n_{\alpha} = -1$) or removed ($n_{\alpha} = +1$), and μ_{α} is the chemical potential of α , which

can range from $\Delta H_f^{\text{bulk}}_{\alpha X_n} \leq \mu_\alpha \leq \mu_\alpha^{\text{bulk}}$. The lower bound corresponds with the α poor condition and the upper bound corresponds with the α rich condition.⁴⁶⁻⁴⁷ For simplicity, we assumed $\Delta\mu_\alpha = 0$ for both Cu and Zn, which corresponds with Cu-rich and Zn-rich synthesis conditions. The formation energy for each structure is negative ($\Delta E_{\text{Sub}} = -0.382 \text{ eV}$, $\Delta E_{\text{Surf4}} = -1.758 \text{ eV}$, and $\Delta E_{\text{Surf3}} = -0.214$), thus suggesting that Se has a higher affinity towards Cu than Zn, and that Cu-Se chemical bonds should correspondingly be stronger than Zn-Se. However, we note here that our calculated Cu impurity formation energies are not precise, as the reaction conditions for synthesizing Cu-doped ZnSe QDs are generally Cu-poor and Zn-rich.^{4,7} This would lead to a negative $\Delta\mu_{\text{Cu}}$, result in positive formation energies, and prevent the formation of a competing Cu_{2-x}Se phase.⁴⁶ In addition, while Surf4 has the lowest formation energy of the series, binding with surface ligands and leaching of Cu into the solution are commonly observed in experiment.^{7, 11} A full understanding of the most stable impurity environments would require studies comparing the impurity formation energy at different surface facets to their binding energy with organic ligands. Issues with determining the absolute formation energy of Cu impurities aside, the *comparative* formation energies between the different bonding environments should not be significantly affected by $\Delta\mu_{\text{Cu}}$. Surf4 is the thermodynamically most stable impurity ($\sim -1.376 \text{ eV}$ vs. ΔE_{Sub}), and Surf3 is the least stable ($\sim +0.168 \text{ eV}$ vs. ΔE_{Sub}). The large difference in formation energies indicate that the different configurations are not thermodynamically competitive, and we postulate that they are kinetically trapped during crystal growth as described with Mn impurities.⁴⁸⁻⁴⁹

Figure 3. (a) Effect of impurity position, coordination environment, and concentration on the DOS. The charge density distribution for each labeled IG state (marked by dashed lines) is depicted in (b-g) along with its orbital contribution to the corresponding DOS. A higher concentration of Cu (1.85%, 3.77%, and 7.84%, respectively) leads to additional absorptive/emissive states. For moderately doped QDs (e-f) the charge density of each labeled state is separately localized on its respective impurity (Δ_{S1} on the 3-coordinated surface Cu, and Δ_{S2} on the subsurface Cu). At higher impurity concentrations (g) the charge density is localized on all 4 Cu dopants regardless of the IG state energy.

In each of these cases, the impurity concentration is the same ($\sim 1.85\%$ based on the Cu/Zn ratio). Hence, two additional calculations (also shown in Figure 3a) were performed in which the concentration was increased to 3.77% (Sub/Surf3) and 7.84% (Cu₄). For the case where the impurity concentration is 3.77%, one Cu atom is in the Sub configuration and the other is in the Surf3 configuration. The QD with the highest concentration of Cu impurities (7.84%) is labeled Cu₄ to indicate that it includes 4 Cu impurities, similar to what is expected for Cu doped QDs synthesized by the cluster-seeded method.⁴⁸ Three of the Cu impurities are in the subsurface while one is on the surface, and all are tetrahedrally coordinated. For all impurity bonding environments and concentrations, Δ_S is defined as the energy difference between the VB and the Cu state in accordance with the optical absorption and emission mechanisms described in Figure 2e. Clearly, there is considerable variation in the ground state energy and orbital hybridization

for Cu impurities as their position, bonding environment, and concentration change. For example, the DOS for the Sub IG state has a considerably larger orbital contribution from Cu than the IG state in Surf3, but a smaller Cu contribution than the IG state in Surf4. Correspondingly, its theoretical Δ_S is intermediate between the two. If the impurity concentration increases to 3.77% (as in Sub/Surf3), we observe two distinct IG states related to the two different Cu impurities. The distorted trigonal planar Cu impurity on the surface (same environment as Surf3) has a smaller Stokes shift (Δ_{S1}), and a larger Se contribution than the impurity located in the subsurface (Δ_{S2}). Interestingly, the DOS for the Cu₄ composition similarly shows multiple Cu states, but the charge density distribution appears to be delocalized over all four Cu tetrahedra. This complicates a further discussion of the individual Cu impurities in Cu₄ (Figure 3g). In Figure S6 we project the DOS the states on each Cu tetrahedral, and show that they all contribute significantly to all IG states, though dominant ones are still present in each state. Moreover, Surf4 is still the Cu impurity with the largest Stokes shift (Δ_{S4}), and has the largest Cu contribution.

We summarize these results in Figure 4, and come back to our earlier strategy of describing Cu energy levels with crystal field theory. As shown in Figure 4a-c, tetrahedral Cu impurities clearly have a larger Δ_S , and orbital contribution from Cu, than in the distorted trigonal planar geometry. This suggests that the smaller Δ_S for Surf3 is due to breaking of tetrahedral symmetry, which increases the orbital overlap between Cu (d) and Se (p) in the distorted trigonal planar geometry, and results in higher Se character in the DOS. This relationship between coordination number and Se contribution can be explained by VESPR. As the coordination number reduces from 4 to 3, the average bond angle increases from 108.5° to 119.2° (ideal 109.5° for tetrahedral and 120° for trigonal planar, respectively) in order to reduce

repulsion between Se (p) electrons. The reduced Se-Se repulsion allows for the average Cu-Se bond length contraction from ~ 2.48 to 2.39 Å. The bonds become stronger and more covalent. The covalency is additionally afforded by the AO-hybridization on Cu, which becomes more pronounced the context of the reduced symmetry of Cu coordination (Figure S7). As a result of stronger and more covalent bonding, the IG state is lower in energy.

Figure 4. Summary of the effects of chemical bonding on the theoretical Stokes shift. The clearest trends emerge in (a-c), which show that the ground state energy of Cu impurities is predominantly determined by coordination geometry and orbital contribution from Cu. IG states with less Cu character and in the distorted trigonal planar geometry tend to have smaller Stokes shifts. All bond distances and angles are presented as the average between each Cu-Se bond in the coordination sphere, and error bars represent the standard deviation from the average bond angle or distance. (d) There does not appear to be a trend in changes of the ground state energy for surface vs. subsurface Cu impurities.

Considering that the distorted trigonal planar geometry is unlikely to occur for subsurface impurities, this implies that Δ_s should be consistently smaller for surface Cu. However, if we plot Δ_s for surface vs. subsurface Cu in Figure 4d, we clearly observe that there is no correlation

between Δ_S and proximity to the surface. Surface impurities with tetrahedral coordination (Surf4) have a *larger* Δ_S than at the subsurface location. We explore reasons for this observation in Figure 5 by analyzing the charge density difference plots and Bader charges (Table S1). The charge distribution confirms that the surface and subsurface Zn-Se bonds are more ionic, whereas the Cu-Se bonds are more covalent. However, both become more polar at the surface: the average charge of the Se surface atoms (-1.18 e) is significantly more negative than Se in the subsurface (-0.83 e), whereas the average Bader charge on Cu and Zn is relatively unchanged (at $q(\text{Cu}) \approx +0.37$ e and $q(\text{Zn}) \approx +0.80$ e). This effect might be impacted by the model nature of the passivation with pseudo-hydrogen atoms. Specifically, the “mimicking” of ligand passivation with pseudo-hydrogens should be similar to experiments utilizing chalcogen-rich QDs and/or thiol surface passivation,⁷ but may not be applicable to experiments using metal-rich QDs and/or different ligands (*e.g.* oleic acid).⁴ On the other hand, the basic optical properties of Cu impurities (*e.g.* Δ_S and linewidth) are not significantly affected by ligand exchange, which generally only has a notable impact on quantum yield due to a shift in the Fermi level that alters the carrier trapping mechanism.^{7, 9} We therefore expect that differences between charge-distribution at the surface *vs.* the subsurface should also occur for other surface treatments as well, but the exact effects on chemical bonding may somewhat vary based on the specific surface and/or passivating ligand. The higher bond polarity is destabilizing for covalent Cu-Se bonds, and leads to increased repulsion between Se atoms, and stretches the Cu-Se bonds (average around ~ 0.05 Å, or an increase from ~ 2.47 to ~ 2.52 Å). The overlap between Cu (d) and Se (p) orbitals reduces, increasing the energy of the Cu-Se states relative to the VB. However, the destabilizing effects of increased bond polarity at the surface are mostly overcome by the switch from T_d to D_{3h} symmetry, which allows for a bond contraction as described earlier. Accordingly,

this indicates that the energy of Δ_S is a consequence of covalent overlap, which is affected by geometry and reflects itself in the charge distribution.

As expected, Cu^{2+} is less covalent than Cu^{1+} both in Sub, and Surf3. However, it is still more covalent than Zn-Se, which can be explained by Fajan's rules for polarizing power. Cu^{2+} should have a greater polarizing power than Zn^{2+} due to its unfilled (d) shell, which reduces shielding and makes charge transfer from Se (p) more favorable. The changes in charge and bond length after an electron is added are largely asymmetric, and suggestive of Jahn-Teller effects. Indeed, these Jahn-Teller effects are expected, as indicated in computational chemistry studies on homogeneous broadening mechanisms (electron-phonon coupling) in Cu-doped QDs.⁵¹

Figure 5. Charge density difference plots and Bader charges for each of the Cu impurity centers. QDs with a single Cu^{1+} impurity are shown in (a-c), which represent the Sub, Surf4, and Surf3 systems, respectively. Calculations for Surf3 (d) and Surf4 (Figure S8) were repeated using single Cu^{2+} impurities. QDs with multiple Cu^{1+} impurities are shown in (e-f) where (e) represents the Sub/Surf3 system and (f) represents the Cu_4 system.

In order to determine if our observations were an artifact of the jellium positive background induced to compensate the electron injected in the QD to create Cu^{1+} , we repeated our calculations for Sub and Surf3 without the addition of an electron. In this case, calculations were spin-polarized due to the magnetic exchange interactions observed experimentally in QDs with Cu^{2+} (d^9) impurities.^{6, 8} Figure 5c,d shows a comparison of Surf3 with (Cu^{1+}) and without (Cu^{2+}) an extra electron, while Figure S8 shows the same comparison for the Sub QD. In both

cases, Bader charges are far from what is expected by the typical description of Cu oxidation states in QDs. In the Cu_{Zn} , or “ Cu^{2+} ” scenario, the Bader charge on Cu is only +0.46 e for both Surf3 (Figure 5d) and Sub (Figure S8). After an electron is added, the charge on Cu in Surf3 and Sub changes by -0.08 e and -0.1 e, respectively. The more negative charge on Cu is accompanied by a small bond contraction (average ~ 0.01 Å for Sub, and ~ 0.03 Å for Surf3). However, the overall qualitative picture holds true without the background charge.

Effects of Variations in Chemical Bonding on Optical Spectra. We calculate the absorption spectrum for ZnSe QDs as a function of Cu^{1+} impurity concentration using linear response theory (independent orbital approximation/single particle level, see Figure 6). The absorption coefficient (α) of the materials was calculated from the frequency-dependent dielectric constant with eq. 2 and eq. 3.

$$\kappa(\omega) = \sqrt{\frac{\varepsilon_1(\omega)^2 + \varepsilon_2(\omega)^2 - \varepsilon_1(\omega)}{2}}$$

(2)

$$\alpha(\omega) = \frac{4\pi}{\lambda} \kappa(\omega)$$

(3)

where $\kappa(\omega)$ is the extinction coefficient, and $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$ are the real and imaginary terms of the dielectric constant, respectively. The transitions near 2.7 eV in the absorption spectra represent the direct excitation of an electron from the Cu^{1+} impurity to the CB, transitions ~ 3.4 eV represent VB $\rightarrow$ CB or BE absorption, and higher energy transitions reflect absorption from either the VB or Cu^{1+} to higher energy unoccupied states. As expected, the BE transition is relatively constant (~ 3.4 eV) regardless of the Cu impurity concentration, and reflects the confinement energy expected from the DOS. IG and higher energy transitions, on the other hand, are strongly dependent on the concentration of Cu^{1+} . The BE peak becomes less clear as it is

“smeared” by the additional low energy “tail,” and high energy transitions from Cu^{1+} to the CB and higher energy states. These results indicate that broadening of experimental absorption spectra is predominantly a reflection of the concentration of Cu^{1+} impurities. This also suggests that, if hole localization from the VB is fast enough, at high concentrations of Cu^{1+} impurities the bleach in transient absorption spectroscopy measurements could become dominated by low energy impurity transitions instead of BE absorption as proposed in a recent study on related CIS QDs.⁵²

Figure 6. Computed absorption spectra for Cu doped ZnSe QDs with different impurity concentrations (left panel). A high Cu content leads to additional absorptive states, and inhomogeneous broadening. Considering that these impurities are also emissive, the same effects should also lead to broadening of emission spectra (right panel). For the scheme, BE absorption is marked by the grey arrow, Cu absorption by black arrows, and Cu emission by red arrows.

In addition to the absorption transitions, the scheme in Figure 6 also shows expected emission transitions. While these are not directly calculated, extensive experimental work has shown that emission in QDs with Cu impurities arise from a CB electron recombining with a hole localized at Cu.^{4, 7-8, 11, 19} Therefore, variations in the ground state energy of Cu^{1+} due to heterogeneity should also be reflected in the emission spectra. We note, however, that broadening of the absorption spectra by Cu impurities can *only* occur due to variations in the

ground state energy of Cu^{1+} . PL broadening, on the other hand, will also reflect changes in the ground state energy of Cu^{2+} impurities, Franck-Condon shifts, electron-phonon coupling, and other *excited* state interactions.^{10, 49} These limitations aside, recent single particle spectroscopy measurements on CIS QDs, which also emit *via* Cu impurities has shown that variations in emission energy are far larger than expected based on polydispersity of QD size.¹⁰ In addition, these measurements revealed that the PL linewidth can be as narrow as 60 meV, and vary by ~ 150 meV in the same ensemble. This suggests that inhomogeneous broadening (*e.g.* variations in QD structure) more significantly impacts the ensemble linewidth than electron-phonon coupling, which would be an intrinsic optical process and reflected in all room temperature spectra. It was therefore hypothesized that the emission energy of Cu impurities is highly sensitive to their location in the QD. Our calculations confirm this interpretation. Hence, we predict that Cu impurities in other QD systems such as ZnSe should also show narrow emission spectra if the Cu impurity concentration is low, and photon anti-bunching experiments indicate that emission is from a single-particle. Moreover, our calculations predict that if heterogeneity is better controlled, ensemble spectra can also be narrow and Cu impurities can be utilized in environmentally benign high color purity LEDs.

An additional phenomenon that our calculations may help explain is the mysteriously large variation of radiative lifetimes and spectral linewidths for Cu impurities at the single particle level, which also cannot be accounted for fully in other models. For example, electron-phonon coupling mechanisms expect larger singlet-triplet splitting energies for Cu impurities located closer to the QD core.⁴⁹ This would suggest a systemic relation between Stokes shift and linewidth for individual particles. In a separate study, it was hypothesized that excited-state holes localized at Cu impurities near the QD surface would exhibit stronger wave function overlap

with the delocalized CB electron than impurities located below the surface.⁴⁹ This would result in smaller Stokes shifts and shorter radiative lifetimes for surface Cu impurities. However, while the radiative lifetimes and spectral linewidths for CIS QDs at the single particle level can vary by as much as 250 ns and 150 meV, there is no systematic relation between the Stokes shift and the PL linewidths or radiative lifetimes. Instead, experimental measurements of PL linewidths and radiative lifetimes have a “random” distribution when plotted *vs.* single-particle emission energy.¹⁰ Inability to reconcile either of these models with experimental variations in radiative lifetimes and PL linewidths indicates that an *additional* factor must contribute to large variations in the emission energy. According to our DFT calculations, heterogeneity also alters the *ground* state energy of the impurity, which should not have any notable effect on the radiative lifetime. The Stokes shift for individual particles is therefore most likely a convolution of heterogeneity in the *ground* state energy due to chemical bonding effects, additional shifts in the *excited* state due to changes in the wave function overlap between a localized hole and delocalized CB electron,¹⁰ and homogeneous broadening due to electron-phonon coupling.⁴⁹ Considering that only excited state interactions should have an impact on the radiative lifetime, and both effects should alter the Stokes shift, the net result would be a random distribution of experimental radiative lifetimes as a function of emission energy. In addition, variations in the concentration of Cu impurities across experimental ensembles would also broaden individual spectra, and it would be difficult to deconvolute the effects of electron-phonon coupling as a function of emission energy in experimental ensembles where the concentration of impurities per QD is not uniform, thereby, also leading to a “random” distribution of PL linewidths as a function of Stokes shift in single-particle experiments. An interesting, but unexplored consequence of the “random” distribution of PL linewidths and radiative lifetimes might be significant variation in the rates of nonradiative

decay. While this is beyond the scope of our study, nonadiabatic molecular dynamics may prove to be a useful tool for resolving this mystery.⁵³⁻⁵⁵

CONCLUSIONS

In this study, we used DFT calculations to show the influence of chemical bonding on the properties of Cu impurities in ZnSe QDs. We find that Cu-Se bonds are covalent, and therefore highly sensitive to their proximity to the QD surface, and coordination number. If Cu-Se retains its tetrahedral coordination at the QD surface, the increased polarity from excess electrons on Se will destabilize the coordination sphere due to increased Se-Se repulsion. Correspondingly, the Cu-Se bonds will stretch, the overlap between Cu (d) and Se (p) electrons will be reduced, and the energy of the intragap (IG) state will increase relative to the band-edges (BEs). This would lead to an increased Stokes shift at the single particle level. However, if the tetrahedral coordination is lost and Cu-Se becomes distorted trigonal planar at the surface, Se-Se repulsion will be reduced due to an increase in bond angles, the Cu-Se bonds will contract, and increased overlap between Cu (d) and Se (p) electrons would decrease the Stokes shift. If the concentration of impurities is high, this would lead to multiple IG states, several absorption/emission transitions, and single particle spectra will broaden. Accordingly, broad ensemble spectra can be explained by a combination of electron-phonon coupling and the coexistence of several kinetically trapped local Cu-Se minima where large variations in absorption/emission energy lead to spectral broadening after ensemble averaging.

A clear experimental implication from our study is that spectral broadening for QDs with Cu impurities is predominantly due to inhomogeneity, and can be controlled if the per QD concentration of impurities, and their spatial distribution across the ensemble are uniform. Moreover, our calculations show that modeling efforts to study doped or defective QDs where

impurities are optically active should emphasize structural/spectral variations in the ensemble, which form subensembles with distinct optical properties. Correspondingly, prediction of their optical properties should be based on several local minima instead of a global minimum.

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at <http://pubs.acs.org>. These include bulk ZnSe calculations, orbital PDOS for different QDs, charge-density distribution for QD surface states, and Bader charge calculations for Cu²⁺ doped QDs.

AUTHOR INFORMATION

Corresponding Author

*E-mail: ana@chem.ucla.edu

ORCID

Addis S. Fuhr: 0000-0002-8819-8255

Philippe Sautet: 0000-0002-8444-3348

Anastassia N. Alexandrova: 0000-0002-3003-1911

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