

Electronic Supplementary Information

Nature of Electronic Excitations in Small Non-stoichiometric Quantum Dots

Manav Bhati,^{a,b,c} Sergei A. Ivanov,^{d,e} Thomas P. Senftle,^c Sergei Tretiak,^{a,b,e,*}

Dibyajyoti Ghosh ^{a,b,e,f*}

^a *Theoretical Division, Los Alamos National Laboratory, Los Alamos, NM, 87545, USA*

^b *Center for Nonlinear Studies, Los Alamos National Laboratory, Los Alamos, NM, 87545, USA*

^c *Department of Chemical and Biomolecular Engineering, Rice University, 6100 Main Street, Houston, TX 77005-1892, USA*

^d *Materials Physics and Applications Division, Los Alamos National Laboratory, Los Alamos, New Mexico, 87545 USA*

^e *Center for Integrated Nanotechnologies, Los Alamos National Laboratory, Los Alamos, NM, 87545, USA*

^f *Department of Materials Science and Engineering and Department of Chemistry, Indian Institute of Technology, Delhi, Hauz Khas, New Delhi 110016, India*

* Corresponding authors; E-mails: serg@lanl.gov, dibyajyoti@iitd.ac.in

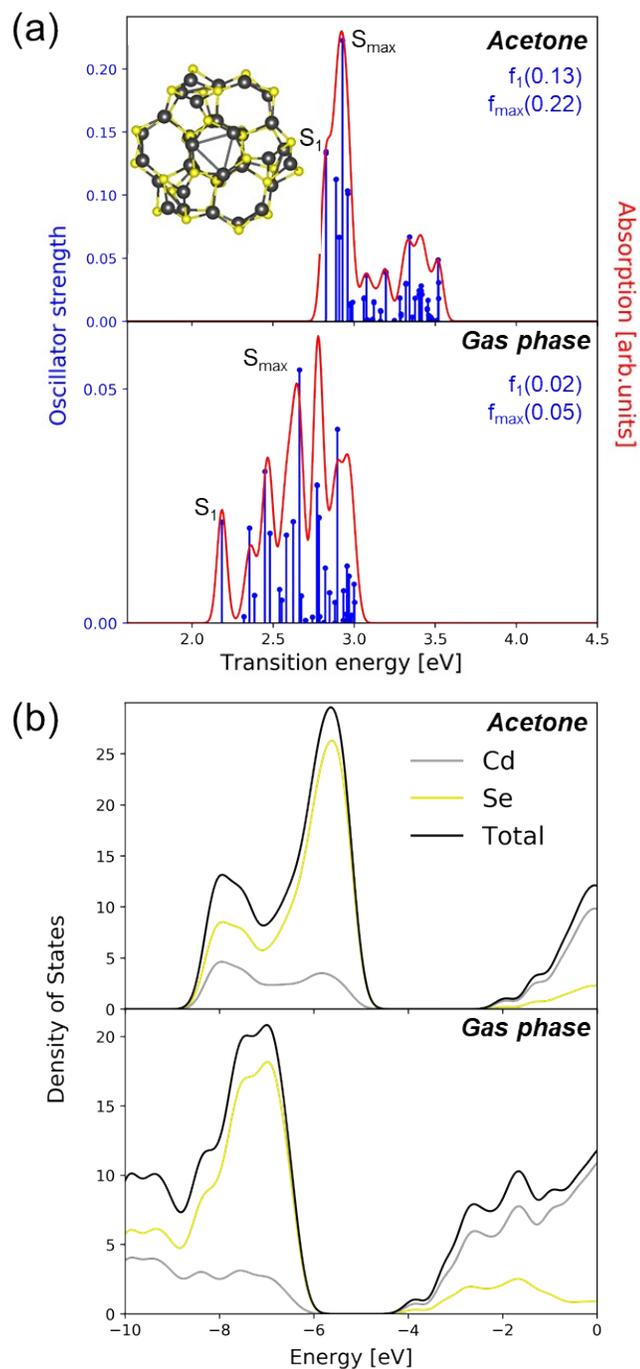


Figure S1. (a) Calculated absorption spectra of the stoichiometric $Cd_{33}Se_{33}$ quantum dot in acetone (top row) and the gas phase (bottom row). The absorption spectra (shown in red) are obtained from the Gaussian convolution of the line-stick spectra (shown in blue) with a 0.035 eV line-broadening parameter (see Methods in the main text). The inset shows the atomic structure of the quantum dot. Atoms in yellow: Se, grey: Cd. The first electronic transition state is marked as S_1 and the state with maximum oscillator strength is marked as S_{max} . The oscillator strengths of these two states are written in blue in the top right corner of the plots as f_1 and f_{max} , respectively. (b) Partial

density of states (PDOS) plots of the stoichiometric $\text{Cd}_{33}\text{Se}_{33}$ QD in acetone (top row) and gas phase (bottom row) delineating contributions of Cd, and Se atomic orbitals.

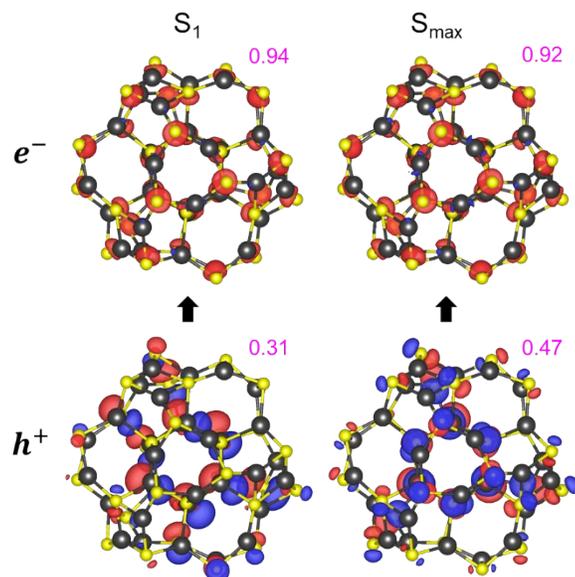


Figure S2. The natural transition orbitals (NTO) of electron (top row) and hole densities (bottom row) of S_1 and S_{\max} of the stoichiometric $\text{Cd}_{33}\text{Se}_{33}$ QD in acetone. The isosurface values of $0.016 e\text{\AA}^{-3}$ and $0.020 e\text{\AA}^{-3}$ were used to generate the isosurfaces for the electron and hole density plots, respectively. The inverse participation ratio (IPR) value for each NTO is shown in pink.

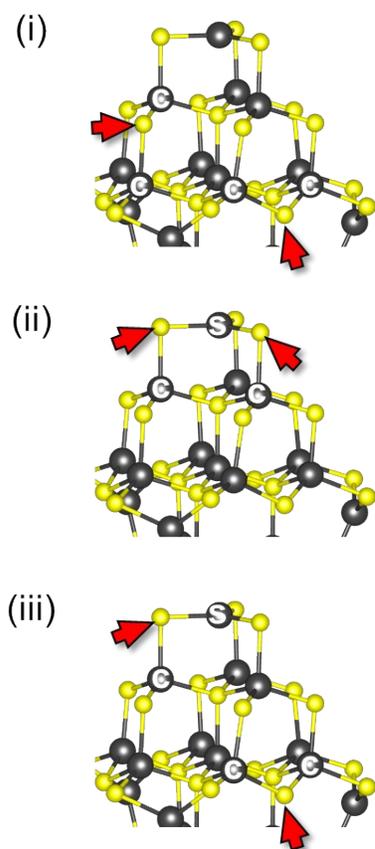


Figure S3. The three categories of chemically viable QD configurations, created by selecting two non-ligated bare surface atoms. An example of a Se-rich QD is shown here with red arrows pointing at the two Se atoms that are to be kept bare (all other Se atoms would be bonded to H atoms). Each selected surface Se atom is bonded to two Cd atoms, which can either be a core atom or a surface atom represented as ‘c’ and ‘s’, respectively. The core Cd atoms are 4-coordinated, and the surface Cd atoms are 3-coordinated. The three categories are as follows: (i) each bare atom is bonded to just core atoms, (ii) each bare atom is bonded to both core and surface atoms, (iii) one bare atom is bonded to just core atoms, and another to surface and core atoms.

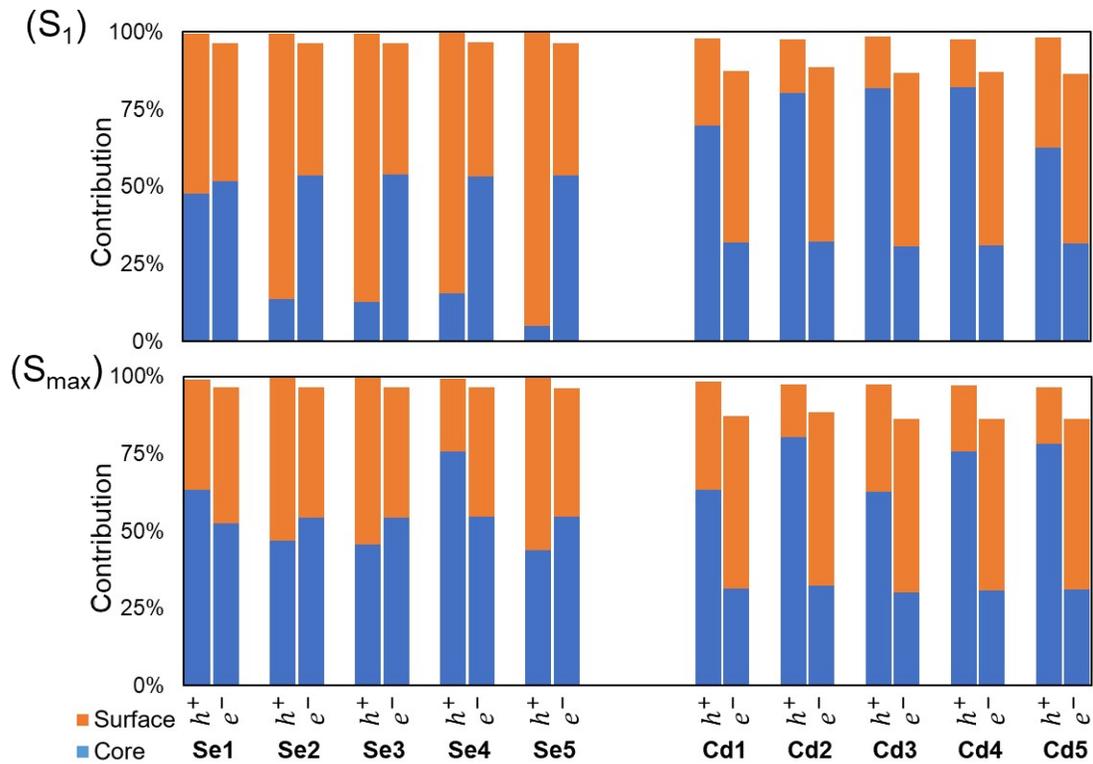


Figure S4. The relative contributions of surface (orange) and core (blue) atoms into electron and hole transition orbitals for S_1 and S_{max} transitions in non-stoichiometric Se-rich (Se1-5), and Cd-rich (Cd1-5) QDs shown in Figure 4.