Origin of one-photon and two-photon optical transitions in PbSe nanocrystals $A - 2$, \cdots , A *National Renewable Energy Laboratory, Golden, Colorado 80401, USA* $(u \rightarrow v^{IV})$ PbSe nanocrystals represent the paradigm nanoscale system exhibiting carrier multiplication upon light absorption, yet their absorption spectrum is poorly understood. Two very different interpretations of the ab- $\mathbf{y} = \mathbf{y}$ is the second absorption peak and $\mathbf{y} = \mathbf{y}$ **dipole-formation peak a** $\mathbf{y} = \mathbf{y}$ **b** $\mathbf{y} = \mathbf{y}$ or a *dipole-allowed P Pe* transition? A recent two-photon photoluminescence-excitation experiment favored the first interpretation, raising the question of why a dipole-forbidden transition would be strongly absorptive. H ere we report atomistic pseudopotential calculations of the one-photon absorption spectra of two-photon absorption spectra of the one-photon absorption spectra of the one-photon absorption spectra of two-photon ab PbSe nanocrystals, showing unequivocally that, contrary to previous interpretations by other authors, the $s \rightarrow 1 \rightarrow 1$ **one-photon peak originates from dipole-allowed** *P P*_{*e*} **1**

 \mathcal{P}_1 is the same \mathcal{E}_2 and \mathcal{E}_3 and \mathcal{E}_4 and \mathcal{E}_5 $\frac{1}{\sqrt{2}}$ 1 $\frac{1}{\sqrt{2}}$ $\frac{1}{\sqrt{2}}$ 0.444 0 TD 0.333 0 TD

tion peak[.14](#page-3-0) As in previous studies favoring this interpretation, $\frac{1}{2}$ the existence of intravallel splitting intravallel splitting $\frac{1}{2}$ $(P^{\parallel}u \quad P^{\perp})$ **c q** \perp **c e d q** \mathbb{R}^n is a calculation of one-photon and two-photon of one-photon and two-photon $p^{\mathbb{T}} p^{\mathbb{T}}$ and $q^{\mathbb{T}} q^{\mathbb{T}} q^{\mathbb{T}}$ spectra that include the spectra that include the **P** $p^{\mathbb{T}} p^{\mathbb{T}}$ spin $p^{\mathbb{T}}$ \sim \sim 0.1 \sim 0.1 couplings.

 $T = \frac{1}{2}$ and $T = \frac{1}{2}$ and $T = \frac{1}{2}$ and $T = \frac{1}{2}$ duces an electrostatic field inside the NC that can change the oscillator strength of the optical transitions. A similar effect \mathbf{A} be expected if the NC has a ground-state dipole momentum \mathbf{A} $\mathbf{y} \rightarrow \mathbf{y} \rightarrow \mathbf{y}$ is equal to the example of $\mathbf{y} \rightarrow \mathbf{y}$ $\mathbf{v}_1 = \begin{pmatrix} 1 & 1 & 1 \ 1 & 1 & 1 \end{pmatrix}$ $t_1 = t_2$ in the presence of a localized surface charge the oscilla-surface charge the charge the charge the osci \bullet \bullet \bullet \bullet S S _c P P _c \bullet \bullet \bullet $P = \begin{bmatrix} 1 & 1 \\ 1 & 2 \end{bmatrix}$ **formally formally for** sitions and some or strength. Due to the largest strength \mathbb{R} is the largest strength. Due to the largest strength in \mathbb{R} dielectric constant of \mathbb{R}^n and \math field is bound to be highly screened. As a result, t[he](#page-3-7) intensity of \mathbb{R}^n \mathbf{S}