Supporting information for

Effect of Pressure on Interband and Intraband Transition of Mercury Chalcogenides Quantum Dots

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1. HgTe CQD synthesis

Figure S1a and b are respectively TEM image and zero pressure infrared spectrum from HgTe CQD with a band edge energy at 6000 cm$^{-1}$. c and d are respectively TEM image and zero pressure infrared spectrum from HgTe CQD with a band edge energy at 4000 cm$^{-1}$. e and f are respectively TEM image and zero pressure infrared spectrum from HgTe CQD with a band edge energy at 2000 cm$^{-1}$. 
2. HgSe CQD synthesis

Figure S2a and b are respectively TEM image and zero pressure infrared spectrum from HgSe CQD with an intraband peak energy at 3000 cm$^{-1}$. c and d respectively TEM image and zero pressure infrared spectrum from HgSe CQD with an intraband peak energy at 2500 cm$^{-1}$. e and f respectively TEM image and zero pressure infrared spectrum from HgSe CQD with an intraband peak energy at 1000 cm$^{-1}$.
3. Material characterization

Under high pressure, the zinc blende phase of the HgTe nanocrystal switches toward a cinnabar phase, which refined diffractogram is provided in Figure S 3a. A scheme of the cinnabar HgTe unit cell is given in Figure S 3b. We found the structural parameter of the hexagonal phase of HgTe to be $a=b=0.447$ nm and $c=0.943$ nm under 5.5 GPa of pressure.

Figure S 3 a. Experimental and refined X-ray diffractogram from HgTe nanocrystal under a 5.5 GPa pressure. b. Scheme of the HgTe cinnabar unit cell.
4. IR spectroscopy under pressure

4.1. Signal filtering
The infrared data obtained from the setup described in figure 2 of the main text present oscillations, see Figure S 4. They result from interference with the diamond cell. The high frequency oscillations are then removed using an FFT filtering procedure, see Figure S 4.

Figure S 4 a raw and filtered infrared spectrum obtained from HgSe CQD with intraband peak energy at 2500 cm\textsuperscript{-1}. b is a zoom on the same spectrum in the range of energy between 4000 and 5000 cm\textsuperscript{-1}.

4.2. IR spectroscopy under high pressure (P > 3 GPa)

Figure S 5 a. Infrared spectra for HgTe CQD, with a 6000 cm\textsuperscript{-1} band edge at zero pressure, in the 3 to 10 GPa range of pressure. b Infrared spectra for HgSe CQD, with a 1000 cm\textsuperscript{-1} intraband peak at zero pressure, in the 3 to 10 GPa range of pressure.
5. \( \mathbf{k} \cdot \mathbf{p} \) simulation

The energy dispersion \( E(k) \) with wavevector \( k \) in the Brillouin zone is calculated using a Pidgeon-Brown 8 band \( \mathbf{k} \cdot \mathbf{p} \) formalism as shown in Figure S 6a.\(^1 \) The bulk states at the \( \mathbf{k} \) vector are developed on a limited set consisting in 8 zone center Bloch states of \( \Gamma _6, \Gamma _7 \) and \( \Gamma _8 \) symmetry. Through adjustable parameters the 8x8 matrix accounts for the \( \mathbf{k} \cdot \mathbf{p} \) interaction between these states but also for the perturbative influence of the zone center states outside of the basis set. These \( \mathbf{k} \cdot \mathbf{p} \) parameters are chosen to reproduce as closely as possible the band structure given in the figure 3(c) from Ref.\(^2 \) obtained through the h-QSGW scheme of Svane et al. Note that on purpose we do not introduce the linear term in the \( \mathbf{k} \cdot \mathbf{p} \) matrix that leads to the splitting of the heavy \( \Gamma _8 \) band along \( \Gamma - L \) obtained by Svane et al since this splitting plays a negligible contribution to the interband energy. The obtained \( \mathbf{k} \cdot \mathbf{p} \) dispersions \( E(k) \) of the 8 bands are given Figure S 6a. It is plotted using the same scale as Ref\(^2 \) in order to be readily compared.

The dispersion of the two \( \Gamma _6 \) bands can be approximated near the Brillouin zone center through the Dresselhaus-Kip-Kittel formula\(^3 \)

\[
E(k) = E(k = 0) + Ak^2 \pm \sqrt{B^2 k^4 + C^2 \left(k_x^2 k_y^2 + k_y^2 k_z^2 + k_z^2 k_x^2\right)},
\]

with \( A = 37.8 \, \hbar^2 / 2m_0 \), \( B = 20.39 \, \hbar^2 / 2m_0 \), \( C = -107.8 \, \hbar^2 / 2m_0 \) obtained from the \( \mathbf{k} \cdot \mathbf{p} \) hamiltonian. \( \hbar = h / 2 \pi \) is the reduced Plank constant and \( m_0 \) is the electron mass. This formula amounts to a parabolic dispersion along each direction of the Brillouin zone. We use this parabolic dispersion to evidence the strong non parabolicity of \( E(k) \) a few percent away from the Brillouin zone in the comparison of Figure 5a.

In semiconductors exhibiting a cubic structure, a hydrostatic pressure \( P \) produces a scalar deformation tensor \( \epsilon \) so that for the diagonal elements \( \epsilon_{xx} = \epsilon_{yy} = \epsilon_{zz} = P / 3B \) where \( B \) is the bulk modulus and \( \epsilon_{xy} = \epsilon_{yz} = \epsilon_{zx} = 0 \) for the shear strain component.\(^4 \) Since the contraction of the lattice parameter produces an expansion of the Brillouin zone and simultaneously an expansion of the wavevectors \( k \) involved in the confined states, we neglect these two roughly self-cancelling effects in the strained electronic structure calculations. The effect on strain on the energy dispersion is accounted for through the change in the energy difference between \( \Gamma _6 \) and \( \Gamma _8 \) state energies at the zone center with a deformation potential of \( d(E_{\Gamma _6} - E_{\Gamma _8}) / d\epsilon \approx -2.4 \, \text{eV} \). As depicted in Figure S 6b and 5a, the pressure first results in a decrease of the conduction band effective mass \( m^*_e(k=0,P) \), until \( \epsilon = -2.2\% \) where the band gap opens and the effective mass increases again. The equivalent mass \( m^*_e(k,P) \) calculated at \( k = 10\% \ 2\pi / a \) along the \( \Gamma - L \) direction follows the same trend but with much less amplitude variation.

**Figure S 6** Simulated band structure of HgTe at zero strain from \( \mathbf{k} \cdot \mathbf{p} \) simulation. Parameters are obtained by fitting the predicted band structure by Svane et al.\(^2 \). b. Equivalent mass of the conduction band as a function of strain \( \epsilon \), at the zone center and at 10% of the Brillouin zone along \( \Gamma - L \). The equivalent mass is the mass \( m^* \) that gives the energy \( E \) of the conduction band at \( k \) point through the formula \( E = E(k = 0) + \frac{\hbar^2 k^2}{2m^*} \).
6. References


