Impact of D$_2$O/H$_2$O Solvent Exchange on the Emission of HgTe and CdTe Quantum Dots: Polaron and Energy Transfer Effects

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SUPPLEMENTARY MATERIAL

1. Effect of "dark" QDs on ensemble photoluminescence quantum yield and lifetimes

Here we analyze the influence of "dark" particles on the effective radiative and non-radiative rates in a QD ensemble.

We shall assume a bimodal distribution of QDs in our ensemble:

(i)   Active (A), normally emitting QDs,

(ii)   Silent (S), poorly emitting QDs.

For the latter, their poor emission is assumed to be caused by their high non-radiative decay rate, i.e.

$$\gamma_{nr}^{S} = \Lambda \gamma_{nr}^{A}; \quad \Lambda > 1 . \tag{S1}$$

For the sake of simplicity, we shall assume that otherwise S and A dots are not different, for instance, their radiative rates are the same, $\gamma_{r}^{S} = \gamma_{r}^{A} = \gamma_{r}$.

Master equations for the populations of excited A and S QDs are:

$$\frac{dn^{A,S}}{dt} = \sigma^{A,S} p^{A,S} N_{QD} I_0 - \frac{n^{A,S}}{\tau^{A,S}} \tag{S2}$$

where $\sigma^{A,S}$ are the excitation cross-sections (we shall assume $\sigma^A = \sigma^S = \sigma$), $p^A = p$ and $p^S = (1 - p)$ are the fractions of A and S QDs, N_{QD} is the total QD concentration, I_0 is the excitation intensity, and

$$\tau^{A,S} = \left(\gamma_{nr}^{A,S} + \gamma_r\right)^{-1} \tag{S3}$$

are the lifetimes of A and S dots.

For <u>steady-state emission</u>, the average quantum yield is determined by stationary solutions of Eqs. (S2):

$$n^{A,S} = \sigma\tau^{A,S} p^{A,S} N_{QD} I_0 \tag{S4}$$

It is given by the ratio of absorbed and emitted intensities,

$$QY = \frac{\gamma_r n^A + \gamma_r n^S}{\sigma N_{QD} I_0} \ . \tag{S5}$$

Substituting (S4) into (S5) and taking into account (S1), we obtain:

$$QY = \frac{p}{1 + q^{-1}} + \frac{1 - p}{1 + \Lambda q^{-1}} \ . \tag{S6}$$

where $q \equiv \gamma_r / \gamma_{nr}^A$. We may rewrite this relation as

$$QY = \left[\frac{1}{1 + \Lambda q^{-1}}\right] + p\left[\frac{(\Lambda - 1)q^{-1}}{\left(1 + q^{-1}\right)\left(1 + \Lambda q^{-1}\right)}\right] , \tag{S6a}$$

to make it evident the linear dependence of the ensemble quantum yield upon the fraction of bright QDs, as it has been observed experimentally [S1].

For <u>emission decay kinetics</u>, we need the time dependent solutions of Eqs. (S2) after a short-pulse excitation, which are:

$$n^{A,S}(t) = \sigma p^{A,S} N_{QD} I_0 \Delta t \exp\left(-t/\tau^{A,S}\right) , \tag{S7}$$

where Δt is the excitation pulse duration ($\Delta t << \tau^{A,S}$). The emission intensity is

$$I(t) = \gamma_r n^A(t) + \gamma_r n^S(t) \tag{S8}$$

and the average photoluminescence (PL) lifetime is given by:

$$\tau_{av} = \frac{1}{I(0)} \int_0^\infty I(t)dt \ . \tag{S9}$$

Substituting (S7) and (S8) into (S9), we obtain:

$$\tau_{av} = \gamma_r^{-1} \left(\frac{p}{1+q^{-1}} + \frac{1-p}{1+\Lambda q^{-1}} \right). \tag{S10}$$

From (S7) and (S10) we have the following <u>exact</u> relation for the radiative decay rate:

$$\gamma_r = \frac{QY}{\tau_{av}} \ . \tag{S11}$$

We could obtain the non-radiative decay rate from the relation

$$\gamma_{nr}^A = q^{-1} \gamma_r$$

if we knew the parameter q. In order to express it through experimentally measurable parameters, we write:

$$
\begin{aligned}
\frac{1-QY}{QY} &= q^{-1} \frac{\dfrac{p}{1+q^{-1}} + \dfrac{\Lambda(1-p)}{1+\Lambda q^{-1}}}{\dfrac{p}{1+q^{-1}} + \dfrac{1-p}{1+\Lambda q^{-1}}} \\
&= q^{-1} \left[1 + \frac{(\Lambda-1)(1-p)(1+q)}{p(\Lambda+q)+(1-p)(1+q)} \right].
\end{aligned}
\tag{S12}
$$

Equation (S12) can be solved in order of q by iterations (assuming that $(1-p)$ is small). It yields:

$$q \approx q_0 \left[1 + \frac{(\Lambda-1)(1-p)(1+q_0)}{p(\Lambda+q_0)+(1-p)(1+q_0)} \right], \tag{S13}$$

where $q_0 = QY/(1-QY)$. Therefore we have

$$\gamma_{nr} = \frac{1-QY}{\tau_{av}} f_{nr}(p,\Lambda,QY), \tag{S14}$$
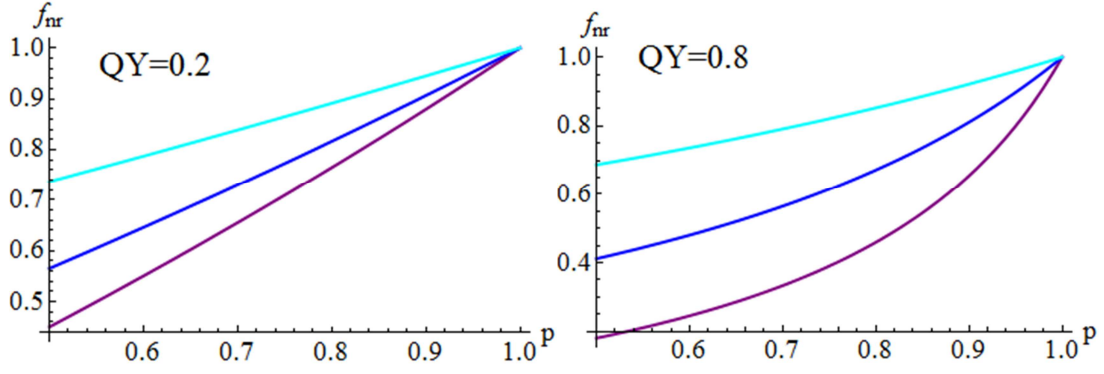
where the correction function is given by

Fig. S1. Correction function for non-radiative lifetime obtained from experimentally measured QY and average PL decay lifetime versus fraction of bright (active) QDs for *QY*=0.2 (left) and 0.8 (right). Different curves correspond to Λ=2 (light blue), 5 (blue) and 100 (purple).

$$f_{nr}(p,\Lambda,QY)=\left[1+\frac{(\Lambda-1)(1-p)}{p(\Lambda(1-QY)+QY)+(1-p)}\right]^{-1}. \qquad (S15)$$

It is plotted in Fig. S1 as a function of the fraction of S dots assuming several values of Λ and QY.
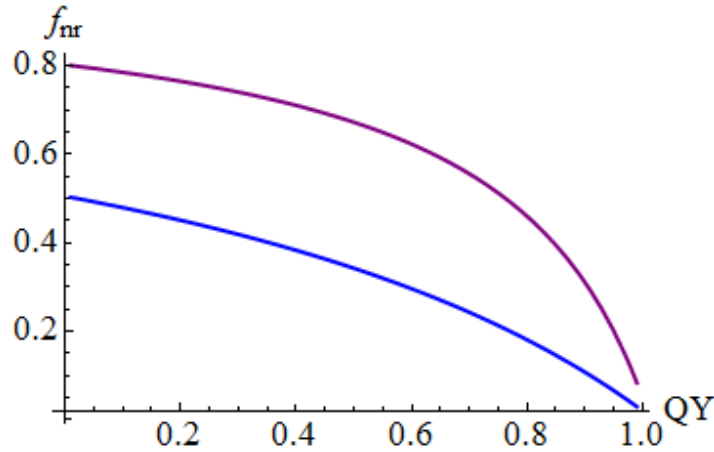

Fig. S2. Correction function (S15) for non-radiative lifetime obtained from experimentally measured QY and average PL decay lifetime versus fraction of bright QDs for Different curves correspond to *p*=0.5 (blue) and *p*=0.8 (purple).

Figure S2 shows how the correction function (S15) varies with QY, for a fixed fraction of bright/dark QDs.

Let us now assume that the time resolution of the experiment is low and the PL kinetics are recorded only after some delay, Δt_1, that may be comparable with τ^S. Then we should write instead of (S9):

$$\tau_{av} = \frac{1}{I(\Delta t_1)} \int_{\Delta t_1}^{\infty} I(t) dt$$

$$= \gamma_r^{-1} \frac{\dfrac{p}{1+q^{-1}} \exp\left(-\dfrac{\Delta t_1}{\tau^A}\right) + \dfrac{1-p}{1+\Lambda q^{-1}} \exp\left(-\dfrac{\Delta t_1}{\tau^S}\right)}{p \exp\left(-\dfrac{\Delta t_1}{\tau^A}\right) + (1-p) \exp\left(-\dfrac{\Delta t_1}{\tau^S}\right)} . \qquad (S16)$$

Considering $\Lambda \gg 1$, we have:

$$\tau_{av} = \gamma_r^{-1} \frac{\dfrac{p}{1+q^{-1}} e^{-\delta} + \dfrac{1-p}{1+\Lambda q^{-1}}}{p e^{-\delta} + (1-p)} , \qquad (S17)$$

where $\delta = \dfrac{\gamma_r \Delta t_1}{1+q^{-1}}$. In steady state, Eq. (S6) holds and we can estimate $q \approx q_0 = QY/(1-QY)$, therefore

$$\delta \approx QY \cdot \gamma_r \Delta t_1 . \qquad (S18)$$

If QY is low, δ is small (unless $\gamma_r \Delta t_1 \gg 1$) and $e^{-\delta} \approx 1$, then we recover Eqs. (S11) and (S14).

<u>In summary</u>, when some silent dots are present in the studied QD ensemble, the simple formula $\gamma_{nr} = (1-QY)\tau_{av}^{-1}$ overestimates the non-radiative recombination rate. The discrepancy [shown by the correction function (S15)] is larger for higher QY. For instance, it can reach ~25 % for $QY = 0.2$ and >50 % for $QY = 0.8$ when some 20% of the dots are completely silent $(\Lambda \gg 1)$. For low QY values, its dependence on the fraction of dark/bright QDs is rather weak.

2. Temperature dependence of the decay rates

Here we provide the expected temperature dependence of the processes of non-radiative recombination and exciton emission within the polaron/trap model. The last step of the e-h recombination process consists in resonant elastic tunneling between an appropriate polaron state and the core valence band state and, according to Eq. (11) of the main text, its probability is proportional to the spectral density of electron-polaron states at the energy of the hole core state.
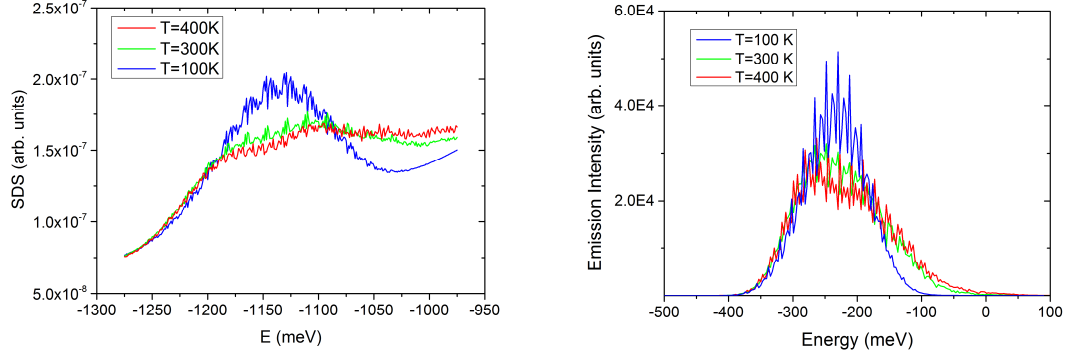
Fig. S3. Temperature dependence of the polaron spectral density of states in the vicinity of the band gap energy (left) and the exciton emission intensity spectrum, also renormalized by the polaron effect (right). Here $\sqrt{S}=0.1$, other parameters are the same as in Fig. 6 of the main text.

The latter is determined by the diagonal elements of the temperature dependent Green's function as given by [S2]:

$$G_{nn}(E) = \frac{1}{Z} \sum_{k,\{m_\nu\}} \left[e^{-\beta E_k} + \exp\left(-\beta \sum_\nu m_\nu \hbar \omega_\nu \right) \right] \frac{\left| C_n^k(\{m_\nu\}) \right|^2}{E - \left(E_k - \sum_\nu m_\nu \hbar \omega_\nu \right) - i0} , \quad (S19)$$

where k numbers different polaron states with energies E_k, $Z = \sum_k e^{-\beta E_k}$, $\beta = 1/k_B T$, k_B is the Boltzmann constant, T is the temperature, ν and n enumerate bare phonon and electronic states, respectively, $m_\nu = 0, 1, \ldots$ are phonon occupation numbers, $\{m_\nu\}$ denotes a certain combination of these numbers, and $C_n^k(\{m_\nu\})$ are coefficients of the expansion of the polaron states in terms of products of bare electronic and phonon states (i.e. eigenvectors of the Hamiltonian of the interacting system, in our case given by Eq. (10) of the main text, written in the basis of the uncoupled states). These coefficients and the polaron energies are obtained by direct numerical diagonalization of the Hamiltonian matrix truncated by considering only a limited number of phonons for each mode ν, as explained in Ref. S2. The exciton emission spectrum (renormalized by the polaron effect) is determined by the imaginary part of the excitonic susceptibility of the QD calculated for "negative frequencies" [see the second line of Eq. (12) of Ref. S2]:

$$\text{Im}\,\chi(E) = \frac{\pi}{VZ'} \left(\frac{e\mathbf{p}}{m_0 E} \right)^2 \sum_{k,\{m_\nu\}} e^{-\beta E_k} \left| C_1^k(\{m_\nu\}) \right|^2 \delta\left(E + E_k - \sum_\nu m_\nu \hbar \omega_\nu \right), \quad (S20)$$

where it has been taken into account that only one e-h transition (namely, that involving core states, denoted by $n = 1$) is allowed, with the momentum matrix element $\mathbf{p}$, and

$$Z' = \sum_{\{m_\nu\}} \exp\!\left(-\beta \sum_\nu m_\nu \hbar \omega_\nu\right).$$

The polaron Green's function (S19) and the susceptibility (S20) are further renormalized by interactions with acoustic phonons whose spectrum is continuous. Basically, each polaron state is dressed by a set of $\{N_\mathbf{q}\}$ acoustic phonons ($\mathbf{q}$ denotes the acoustic phonon wavevector). Interaction with acoustic phonons in the system under consideration here come mostly from the solvent. Since the numbers $N_\mathbf{q}$ fluctuate, each polaron state is broadened in a complex way (and only at high temperatures this broadening becomes looking like a common Lorentzian lineshape). The "dressed" polaron density of states was calculated applying a Monte Carlo (MC) procedure generating a set of $N_\mathbf{q}$ acoustic phonons for each $\mathbf{q}$, with the average number determined by the Bose-Einstein distribution (see Ref. S2 for details). The spectra of Fig. S3 show some "noise" because of the fluctuations in the number of phonons, which mimics the real situation for small systems.

From the calculated results presented in Fig. S3 we conclude that both the SDS (that is, the non-radiative recombination rate) and the exciton emission rate slightly decrease with temperature. However, the latter decreases more substantially than the former, so one may expect that the QD emission quantum yield should diminish as the temperature increases.

3. Solvent effect on the radiative decay rate

In attempt to explain the observed enhancement of the radiative rate when the H_2O solvent is replaced by D_2O, we calculated the absorption and exciton emission spectra (renormalized by the polaron effect) and varied some parameters that might be altered by the solvent replacement. The first such parameter is S, the Huang-Rhys factor that in our model represents the interaction of the trap state with ligand vibration modes. As can be seen from Fig. S4, both absorption and emission spectra show very little changes with respect to the variation of this parameter (in contrast with the polaron SDS far away from the bare electronic state, which is presented in Fig. S3-a).

We also tried to vary parameters of the acoustic phonons included in the model (they mostly smoothen and broaden the polaron spectra). Since we may think that they originate from the solvent, the sound velocity changes substantially between H_2O and D_2O [S3]. However, it results only in very minor changes in the absorption and emission spectra.
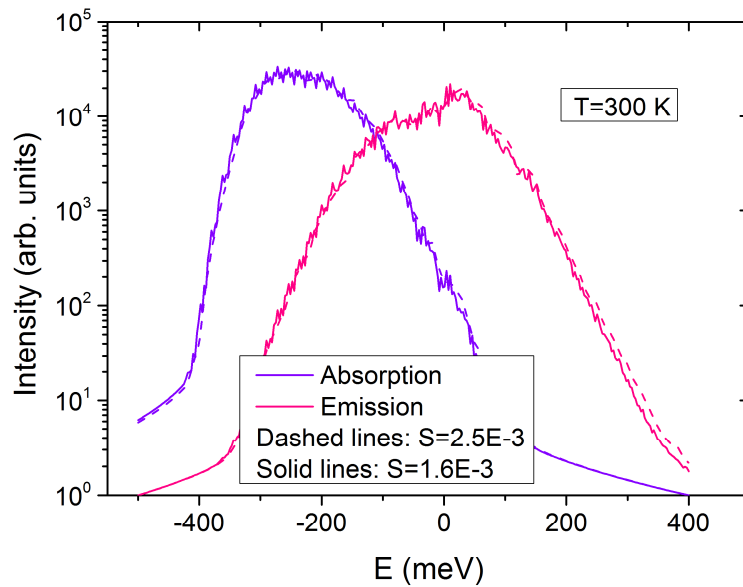
Fig. S4. Calculated fundamental absorption and emission spectra of a HgTe QD for two values of the Huang-Rhys parameter modelling the interaction of the trap state with ligand vibration modes in the cases of H_2O and D_2O solvents. The solid and dashed lines nearly overlap.

We conclude that the proposed model cannot explain the observed changes in the radiative rate under the solvent replacement. One possibility is that the solvent replacement affects those processes that we assumed to be very fast, namely, the hot carrier relaxation into the ground exciton state and/or thermalization of the trapped electron through the polaron spectrum, in reality are not much faster than the emission and the recombination via elastic tunneling, respectively. The rates of these processes (excluded from our model) may depend on the vibrational degrees of freedom of the QD environment and therefore be affected by the solvent replacement.

References

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