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Time-Resolved Spectroscopy of Energy Transfers in Optoelectronic Media

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A Calculations of energy exchange between Si NCs and Er³⁺ ions

Confined electrons and holes energy levels as well as their wave functions calculated in multiband effective mass approximation [76] are used in this consideration. Luttinger Hamiltonian in the spherical approximation has been used for holes and the strong anisotropy of the electron effective mass in silicon has been taken into account. The wave function and flux continuities were the boundary conditions used. When calculating wave functions outside the NC, isotropic effective masses being equal to m_0 and $5m_0$ were used for electron and hole states correspondingly. Spin-orbit splitting was neglected in both Si and SiO₂.

The conduction band of Si has six equivalent minima in the first Brillouin zone, situated in the neighborhoods of the six X -points. The wave function of electron can be presented in the form:

$$\psi_\nu^e = \xi^e(\mathbf{r})u_{c\nu} \exp(i\mathbf{k}_{0\nu}\mathbf{r}), \quad (\text{A.1})$$

where $u_{c\nu}$ and $\mathbf{k}_{0\nu} = 0.85 \times (2\pi/a_{\text{lat}})$ are the Bloch amplitude and wave vector corresponding to the bottom of valley ν ($a_{\text{lat}} = 0.54$ nm is the lattice constant of silicon). Envelope functions $\xi^e(\mathbf{r})$ are found as a result of a numerical solution to the Schrödinger equation after separating the angular part $\exp(im\phi)$ as there is a strong anisotropy of the electron effective mass: $m_{\parallel} = 0.916m_0$, $m_{\perp} = 0.19m_0$. There are series of electron states for each value of $M = |m|$ (m can be any integer number): 6 times degenerate in energy for $M = 0$, and 12 times degenerate for $M \geq 1$. (This degeneracy is given without taking an addition spin degeneracy into account.) So the states are marked with the letter e with an index, indicating the value of M , and the number in a series in front of it. For example, the ground state is marked as $1e_0$, which means that this is the first state with $M = 0$.

There are three types of hole states in spherical quantum dots: i) mixed states (hm) formed by the combination of heavy and light ones, ii) heavy hole

(*hh*) states, and iii) light hole (*hl*) states. Each state is also characterized by the full angular momentum F (0 for the light hole states and positive integer for the other ones) and it is $2F + 1$ times degenerate as the projection M of momentum F onto the quantization axis (arbitrary selected) can be any integer number having absolute value not larger than F . The space quantization forms a series of each type of the states with fixed F . So they are marked with the letters showing the type of the states with index indicating the value of F , and the number in a series in front of it all. For example, the hole state with the lowest energy is of mixed type— $1hm_1$.

The calculated lower energy levels of electrons and holes confined in Si NC of diameter in the range 2.9 nm ÷ 3.3 nm are shown in Fig. 2.12. The energy range is limited to the one of optical pumping used in experiments (2.85 eV). Due to the large energy difference between neighboring space quantization levels energy relaxation of “hot” confined carriers is suppressed. Thus, an Auger excitation of erbium ions in silicon dioxide is possible, similar to the impact ionization by hot carriers in bulk silicon, where it plays a significant role in electroluminescence, but just negligibly affects the excitation of the erbium photoluminescence due to the fast energy relaxation of hot carriers in the bulk material.

A.1 Excitation due to intra-band transition

When dealing with the Coulomb interaction between an f -electron of an Er³⁺ ion situated in SiO₂ and a carrier confined in Si NC, one should take into account the difference in dielectric constant values of Si ($\varepsilon_1 = 12$) and SiO₂ ($\varepsilon_2 = 2$). Note that the Auger process is determined by the high frequency dielectric constant, as the transition energy $\Delta_{ff'}$ is much larger than the lattice vibration energy [78].

The potential created by a point charge q at the distance \mathbf{a} from the center of the sphere of radius R ($R < a$) with dielectric constant ε_1 in the media with dielectric constant ε_2 is obtained as a solution to the Poisson equation and is given by the equations:

$$\Phi_1(\mathbf{r}, \mathbf{a}) = \frac{q}{\varepsilon_2 a} \left[1 + \sum_{l=1}^{\infty} \left(\frac{r}{a}\right)^l \frac{(2l+1)\varepsilon_2}{l\varepsilon_1 + (l+1)\varepsilon_2} P_l(\cos\vartheta) \right], \quad (\text{A.2})$$

inside the sphere ($r < R$), and

$$\Phi_2(\mathbf{r}, \mathbf{a}) = \frac{q}{\varepsilon_2 |\mathbf{r} - \mathbf{a}|} - \frac{q(\varepsilon_1 - \varepsilon_2)}{\varepsilon_2 r} \sum_{l=1}^{\infty} \left(\frac{R}{a}\right)^{l+1} \frac{l}{l\varepsilon_1 + (l+1)\varepsilon_2} \left(\frac{R}{r}\right)^l P_l(\cos\vartheta), \quad (\text{A.3})$$

outside the sphere ($r > R$), where ϑ is the angle between \mathbf{r} and \mathbf{a} : $\cos(\vartheta) = (\mathbf{r}, \mathbf{a})/ra$. Note that the Coulomb potential in the case of interaction of two charges is given by $\frac{1}{2} [\Phi(\mathbf{r}, \mathbf{a}) + \Phi(\mathbf{a}, \mathbf{r})]$, but it is easy to show that in our case $\Phi(\mathbf{r}, \mathbf{a}) = \Phi(\mathbf{a}, \mathbf{r})$.

The probability of Auger excitation of an erbium ion situated in SiO_2 at the distance a from the center of a Si NC as the result of the transition of a ‘‘hot’’ confined carrier from the state i into the state i' is given by the Fermi golden rule:

$$W_{i'i} = \frac{2\pi}{\hbar} \frac{1}{N_f} \sum_{ff'} |\langle f', i' | e\Phi | f, i \rangle|^2 J_T(N) \delta(E_i - E_{i'} - \Delta_{ff'} - N\hbar\omega_{\text{ph}}), \quad (\text{A.4})$$

where Φ is the potential created by the f -electron of the Er^{3+} ion; f, f' enumerate the states of f -electrons of the ion; and N_f is the degeneracy degree of the f state. The integration in the matrix elements of Eq. (A.4) is to be produced over the carriers confinement space and the f -electron coordinate. Due to the energy conservation law, confined carrier transition is accompanied by the emission of N phonons with energy $\hbar\omega_{\text{ph}}$.

In the Huang-Rhys model (the model of two displaced oscillators with the same frequency), the phonon factor $J_T(N)$ is given by [123]:

$$J_T(N) = \exp \left[-2S \left(N_T + \frac{1}{2} \right) \right] \exp \left[\frac{N}{2} \frac{\hbar\omega_{\text{ph}}}{kT} \right] I_N \left[2S \sqrt{N_T (N_T + 1)} \right] \quad (\text{A.5})$$

where S is the Huang-Rhys factor which in the one mode approximation is given by

$$S = \frac{\varepsilon_{\text{opt}} - \varepsilon_{\text{th}}}{\hbar\omega_{\text{ph}}} \quad (\text{A.6})$$

with ε_{opt} and ε_{th} corresponding to the optical and thermal ionization energy, respectively; N_T is the Bose-Einstein factor:

$$N_T = \frac{1}{\exp \left(\frac{\hbar\omega_{\text{ph}}}{kT} \right) - 1}, \quad (\text{A.7})$$

and $I_N(x)$ is the modified Bessel function of order N .

As the energy levels are highly degenerate, one should produce averaging over all the initial states with the energy E_i and sum over all the final states corresponding to the energy $E_{i'}$ in Eq. (A.4). All these states are actually split due to nonsphericity of NCs and other factors. This fact is taken into account by assuming the broadening of levels and adding the value δE to the argument of δ -function in Eq. (A.4) and averaging over this value in the energy range

$\Delta_E = 60$ meV, which is equal to the energy of optical phonon in bulk Si. Eq. (A.4) transforms into

$$W_{i'i} = \frac{2\pi}{\hbar} \frac{1}{\Delta_E} \frac{1}{N_i} \sum_{M, M'} \frac{1}{N_f} \sum_{ff'} |\langle f'; i', M' | e\Phi | f; i, M \rangle|^2 J_T(N) \quad (\text{A.8})$$

where N_i is the degeneracy degree of the initial state i . M and M' enumerate the degenerate states of levels i and i' , and final and initial energies are related through

$$E'_i \simeq E_i - \Delta_{f, f'} - N\hbar\omega_{\text{ph}} \quad (\text{A.9})$$

Let us consider the potential Φ in Eqs. (A.4, A.8). Introducing the coordinate \mathbf{r}' related to the center of the ion ($r' \lesssim r_f$, where r_f is the size of the f -shell) and using the fact that $r_f \ll a$, the potential can be expanded into a series by \mathbf{r}' taking into account the linear term only:

$$\Phi(\mathbf{r}, \mathbf{a} + \mathbf{r}') \approx \Phi(\mathbf{r}, \mathbf{a}) + \frac{\partial\Phi(\mathbf{r}, \mathbf{a})}{\partial\mathbf{a}} \mathbf{r}'. \quad (\text{A.10})$$

In order to use formulae (A.2) and (A.3) the integration in matrix elements in Eq. (A.8) should be produced over \mathbf{r}' for $0 < r' < r_f$. Relatively high energy barriers at the boundary of NC (3.2 and 4.3 eV for electrons and holes, respectively) allow only a small portion of the confined carriers charge density to penetrate outside. The charge density of confined carriers occurring in SiO₂ due to tunnelling accounts just a few percents [76]. Therefore the largest contribution is given by the Coulomb interaction induced by the carrier density inside the NC. To that end, it is enough to use potential Φ_1 (see Eq. A.2) only. We can write for it

$$\frac{\partial\Phi_1(\mathbf{r}, \mathbf{a})}{\partial\mathbf{a}} = \frac{q}{a^2\varepsilon_2} \mathbf{J}, \quad (\text{A.11})$$

where

$$\mathbf{J} = -\frac{\mathbf{a}}{a} J_1 + \frac{\mathbf{r}}{r} J_2, \quad (\text{A.12})$$

and

$$J_1 = 1 + \sum_{l=1}^{\infty} \frac{(2l+1)\varepsilon_2}{l\varepsilon_1 + (l+1)\varepsilon_2} \left(\frac{r}{a}\right)^l \left[(l+1)P_l(\cos\vartheta) + \cos\vartheta \frac{\partial P_l(\cos\vartheta)}{\partial \cos\vartheta} \right], \quad (\text{A.13})$$

$$J_2 = \sum_{l=1}^{\infty} \frac{(2l+1)\varepsilon_2}{l\varepsilon_1 + (l+1)\varepsilon_2} \left(\frac{r}{a}\right)^l \frac{\partial P_l(\cos\vartheta)}{\partial \cos\vartheta}. \quad (\text{A.14})$$

So, Eq. (A.8) transforms into

$$W_{i'i} = \frac{2\pi e^2}{\hbar\Delta_E \varepsilon_2^2 a^4} \frac{1}{N_i} \sum_{M, M'} \frac{1}{N_f} \sum_{ff'} |\mathbf{d}_{ff'} \langle i', M' | \mathbf{J} | i, M \rangle|^2 J_T(N), \quad (\text{A.15})$$

where the ion dipole momentum is given by

$$\mathbf{d}_{ff'} = \int \psi_{f'}^*(\mathbf{r}) \mathbf{r} \psi_f(\mathbf{r}) d^3\mathbf{r}. \quad (\text{A.16})$$

Averaging Eq. (A.15) over the directions of $\mathbf{d}_{ff'}$ one gets

$$W_{i'i} = \frac{2\pi e^2}{3\varepsilon_2^2 \hbar\Delta_E R^4} \frac{1}{N_f} \sum_{ff'} |\mathbf{d}_{ff'}|^2 I_{i'i}(a) J_T(N), \quad (\text{A.17})$$

where the dimensionless factor $I_{i'i}(a)$ is defined by

$$I_{i'i}(a) = \frac{1}{N_i} \left(\frac{R}{a}\right)^4 \sum_{M, M'} |\langle i', M' | \mathbf{J} | i, M \rangle|^2, \quad (\text{A.18})$$

where the square of the matrix element absolute value is assumed to be averaged over the directions of vector a .

Introducing the radiative lifetime τ_{rad} of the erbium ion in the first excited state (${}^4I_{13/2}$) [124]

$$\frac{1}{\tau_{\text{rad}}} = \frac{1}{N_{f'}} \sum_{ff'} \frac{4}{3} e^2 d_{ff'}^2 \frac{\sqrt{\varepsilon_2} (\Delta_{ff'})^3}{\hbar^4 c^3}, \quad (\text{A.19})$$

one gets finally

$$W_{i'i} = \frac{\pi}{2\sqrt{\varepsilon_2}} \frac{1}{\tau_{\text{rad}}} \frac{1}{R^4} \left(\frac{\hbar c}{\Delta_{ff'}}\right)^3 \frac{e^2}{\varepsilon_2^2 \Delta_E} I_{i'i}(a) J_T(N). \quad (\text{A.20})$$

Evaluation of Eq. (A.20) using values $\tau_{\text{rad}} = 2$ ms, and $R_{\text{NC}} = 1.55$ nm leads to

$$W_{i'i} = 8.3 \times 10^9 \left(\frac{1.55 \text{ nm}}{R}\right)^4 I_{i'i}(a) J_T(N) \text{ s}^{-1}. \quad (\text{A.21})$$

The results of calculations of the factors $I_{i'i}(a)$ for electrons are shown in Fig. 2.12. Corresponding plots for holes can be found in [77]. It has been shown that $I_{i'i}$ are actually the functions of the relation a/R only, at least for NC sizes in the range 2.4–3.3 nm.

For completeness, we consider the contribution of carrier density outside the dot to the probability of Er³⁺ excitation. The potential Φ_2 given by Eq. (A.3) should be used outside the NC. We get

$$\frac{\partial \Phi_2(\mathbf{r}, \mathbf{a})}{\partial \mathbf{a}} = \frac{q}{R^2 \varepsilon_2} \mathbf{J}', \quad (\text{A.22})$$

where

$$\mathbf{J}' = \frac{\mathbf{a}R}{a^2} J'_1 - \frac{\mathbf{r}R}{ar} J'_2 + \frac{(\mathbf{r} - \mathbf{a})R^2}{|\mathbf{r} - \mathbf{a}|^3}, \quad (\text{A.23})$$

$$J'_1 = \sum_{l=1}^{\infty} \frac{\varepsilon_1 - \varepsilon_2}{l\varepsilon_1 + (l+1)\varepsilon_2} \left(\frac{R}{a}\right)^{(l+1)} \left(\frac{R}{r}\right)^{(l+1)} \left[(l+1)P_l(\cos \vartheta) + \cos \vartheta \frac{\partial P_l(\cos \vartheta)}{\partial \cos \vartheta} \right], \quad (\text{A.24})$$

$$J'_2 = \sum_{l=1}^{\infty} \frac{\varepsilon_1 - \varepsilon_2}{l\varepsilon_1 + (l+1)\varepsilon_2} \left(\frac{r}{a}\right)^l \frac{\partial P_l(\cos \vartheta)}{\partial \cos \vartheta}. \quad (\text{A.25})$$

Producing the calculations analogous to the ones described above for the carriers being inside the NC, one can find that the contribution of the confined carriers tunnelling to the excitation probability is given by an expression similar to Eq. (A.20). Our calculations have shown that the input is negligible.

The parameters of the multiphonon transition accompanying the Auger processes are not well defined. There is no data on the electron-phonon interaction for Er³⁺ ions in the state ⁴I_{13/2} in SiO₂ either. Thus the interaction of confined carriers with optical phonons should be considered. The dispersion of optical phonons in bulk silicon can be neglected and the multimode model of phonon transition becomes equivalent to the one-mode Huang-Rhys model [78]. Phonon factor $J_T(N)$ is presented in Table A.1 (and 2.2) calculated with a reasonable value of Huang-Rhys parameter $S = 0.1$ at room temperature. The interaction with optical phonons is forbidden for electrons in silicon, so one can suppose that the interaction of confined carriers with oxygen vibration is also responsible for multiphonon assisted Auger processes in the system under consideration. The values of phonon factor $J_T(N)$ at $\hbar\omega_{\text{ph}} = 140$ meV corresponding to the oxygen vibrations are shown in Table A.1 as well.

N	-2	-1	0	+1	+2	+3
$\hbar\omega_{\text{ph}} = \mathbf{60 \text{ meV}}$	5.2×10^{-5}	0.0096	0.87	0.098	0.0054	0.2×10^{-3}
$\hbar\omega_{\text{ph}} = \mathbf{140 \text{ meV}}$	9.0×10^{-8}	0.0004	0.9	0.091	0.0046	0.15×10^{-3}

Table A.1: Phonon factor $J_T(N)$ calculated with $S = 0.1$ for two different phonon energies $\hbar\omega_{\text{ph}}$ and temperature $T = 300$ K.

A.2 Erbium excitation by the recombination of confined carriers

Let us consider the excitation of Er^{3+} ions by recombination of confined electron and hole. For the NCs under consideration ($d \sim 3.1$ nm) the recombination energy is larger than 1.5 eV. Therefore the energy transfer to the Er^{3+} ion by an Auger recombination of such an exciton can be effective only if it causes the direct transition of the ion into the third excited state ${}^4\text{I}_{9/2}$ (energy of transition from the ground state ${}^4\text{I}_{15/2}$ is $\Delta_{03} = 1.55$ eV), the fourth ${}^4\text{F}_{9/2}$ (transition energy $\Delta_{04} = 1.9$ eV) or higher excited states. One should notice that the Er^{3+} ion can not be excited directly into the state ${}^4\text{I}_{13/2}$ via such a process. In order to calculate the transition probability we can use formula (A.8), just assuming that initial and final states of confined carriers now belong to different bands and dividing the probability by the degeneracy of the final state as far as only one final state is empty if there is one electron-hole pair in the NC. One should also choose appropriate parameters of the phonon system.

Crucial for the matrix element evaluation is keeping in mind that the value $\hbar\Delta k$ of momentum transmitted during recombination process is large. The minima of the conduction band in k -space is shifted from the Γ point by the wave vector $k_0 = 0.85k_X$ (k_X is the Brillouin zone edge). And it was shown in Ref. [125] that the momentum to transmit is even larger than $\hbar k_0$: $\hbar\Delta k = 1.15\hbar k_X$. Such a great momentum can only be transferred to the f -shell of the erbium ion by the Coulomb interaction at a distance less than the lattice constant of silicon. So the interaction has a contact character and is determined by the electron and hole wave function values at the position \mathbf{a} of the erbium.

Once carriers are strongly confined in the NC, and the tunnelling is weak, the interaction is possible either inside the NC or in its vicinity. When dealing with the Coulomb interaction at distances smaller than the lattice constant, no screening should be taken into account any more, and the effective dielectric constant value can be assumed to be $\varepsilon_{\text{eff}} = 1$. In this case the absolute value square of the matrix element in Eq. (A.8) averaged over the degenerate electron and hole states can be calculated in analogy to bulk Auger processes [126, 127] as

$$\overline{|\langle f', i' | e\Phi | f, i \rangle|^2} = \frac{(2\pi)^2 e^4}{\varepsilon_{\text{eff}}^2} |\langle f | z^2 | f' \rangle|^2 |\langle u_0 | u_{cz} \rangle|^2 |\xi^{e,i}(\mathbf{a})|^2 \frac{1}{N_{i'}} \sum_{M'} |\xi_{M'0}^{h,i'}(\mathbf{a})|^2, \quad (\text{A.26})$$

where $\xi^{e,i}(\mathbf{r})$ is the electron envelope function in the initial state and for shortness of notations the total hole wave function in the final state is written as

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$\psi_{FM}^{h,i'}(\mathbf{r}) = \sum_m \xi_{Mm}^{h,i'}(\mathbf{r})u_m$ with u_m ($m = -1, 0, +1$) being the hole Bloch functions; $N_{i'} = 2F' + 1$ is the degeneracy of the hole state; $|\langle u_0 | u_{cz} \rangle| \approx 0.25$ is the overlap integral between the bottom of the valence band $\Gamma_{25'}^l$ and the second conduction band Δ_2^c , with k at the position in the first Brillouin zone where the first conduction band has its minimum [128]. Using expression (A.26) for the right hand side of Eq. (A.8) divided by $N_{i'}$ we get the expression for the transfer probability for given position of Er³⁺ and radius of the NC

$$W_{\text{tr}}(\mathbf{a}; R) = \frac{3\pi}{2} \frac{1}{\hbar^2 \omega_{\text{ph}}} \left(\frac{e^2}{\varepsilon_{\text{eff}} R} \right)^2 Q(\mathbf{a}; R) |\langle u_0 | u_{cz} \rangle|^2 \frac{\gamma_f r_f^4}{R^4} J_T(N). \quad (\text{A.27})$$

Here the factor $\gamma_f r_f^4$ comes from the summation over f and averaging over f' of the absolute value square of the matrix element $\langle f | z^2 | f' \rangle$, where $r_f \approx 0.43 \text{ \AA}$ is the radius of the $4f$ -shell of the Er³⁺ ion and the unknown factor γ_f is of the order of 1. We have introduced a dimensionless factor $Q(\mathbf{a}; R)$ defined by

$$Q(\mathbf{a}; R) = \left(\frac{4\pi}{3} R^3 \right)^2 |\xi^{e,i}(\mathbf{a})|^2 \frac{3}{N_{i'}} \sum_{M'} |\xi_{M'0}^{h,i'}(\mathbf{a})|^2. \quad (\text{A.28})$$

If we assume the homogeneous probability distribution for the Er³⁺ ion inside the NC then the probability of excitation transfer averaged over the position of the Er³⁺ ion inside the NC is given by Eq. (A.27) where in place of $Q(\mathbf{a}; R)$ we have

$$Q_{\text{in}}(R) = \frac{1}{\frac{4\pi}{3} R^3} \int_{a < R} d^3 \mathbf{a} Q(\mathbf{a}; R). \quad (\text{A.29})$$

In order to calculate the average transfer probability at some distance D from the NC boundary we introduce

$$Q_{\text{surf}}(R) = \frac{1}{4\pi} \int d\Omega Q(\mathbf{R}; R), \quad (\text{A.30})$$

where the integral is taken over the full solid angle Ω . Then the above-mentioned probability is given by Eq. (A.27) where in place of $Q(\mathbf{a}; R)$ we have

$$Q_{\text{surf}}(R) \exp[-2(\tilde{\kappa}_e + \tilde{\kappa}_h)D/R]. \quad (\text{A.31})$$

Here the dimensionless factors

$$\tilde{\kappa}_{e(h)} = \sqrt{\frac{2m_{e(h)}^0 [U_{e(h)} - E_{e(h)}] R^2}{\hbar^2}} \quad (\text{A.32})$$

determine the decay of the electron and hole wave functions outside the NC, E_e and E_h are the electron and hole quantization energies, m_e^o and m_h^o are the electron and hole masses outside the NC and $U_e = 3.2$ eV and $U_h = 4.3$ eV are the corresponding energy barriers at the NC boundary. For the considered NCs $2(\tilde{\kappa}_e + \tilde{\kappa}_h)$ is on the order of 10^2 (see Table A.2). Therefore the probability of the excitation transfer by the electron-hole recombination decays rapidly with increase of the distance between the erbium and NC. It becomes negligible at the distance of only several angstroms.

For local vibrations of erbium ions in fluorozirconate glass by optical transitions from the higher excited states into the ground state the values around $\hbar\omega_{\text{ph}} = 60$ meV and $S = 0.1$ were reported in Ref. [129]. Notice that bulk optical phonons in Si also have approximately the same energy. These values we have used for the calculation of the phonon factor $J_T(N)$ in the transfer probability (see Table A.1). For the estimation of the transfer probability we have also used $\gamma_f = 1$. Then Eq. (A.27) can be written as

$$W_{\text{tr}} = 0.8 \times 10^{11} Q J_T(N) \text{ s}^{-1}. \quad (\text{A.33})$$

We have analyzed transitions induced by electron and holes being in one of the two lowest states. The numerical factors Q_{in} and Q_{surf} are given in Table A.2 for $R = 1.55$ nm together with the corresponding energies which should be compensated by phonons and the decay factor $2(\tilde{\kappa}_e + \tilde{\kappa}_h)$.

Transition	$E_{i_i} - \Delta_{03}$	$E_{i_i} - \Delta_{04}$	Q_{in}	Q_{surf}	$2(\tilde{\kappa}_e + \tilde{\kappa}_h)$
$1e_0 \rightarrow 1hm_1$	-41 meV	-391 meV	1.34	0.043	98.9
$2e_0 \rightarrow 1hm_1$	186 meV	-164 meV	1.24	0.98	98.0
$1e_0 \rightarrow 1hh_1$	128 meV	-222 meV	1.06	0.19	97.7
$2e_0 \rightarrow 1hh_1$	327 meV	-23 meV	0.77	0.20	96.8

Table A.2: *Calculated parameters of several interband transitions for NC diameter of 3.1 nm.*

A.3 Dipole-dipole contribution

The probability of the excitation governed by the dipole-dipole interaction can be presented as

$$W_{\text{dd}} = \frac{8\pi}{3} \frac{1}{\hbar^2 \omega_{\text{ph}} \varepsilon_{\text{eff}}^2 a^6} \frac{e^4}{d_{\text{ex}}^2} \sum_{j \geq 3} d_{0j}^2 J_T(N_j), \quad (\text{A.34})$$

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where $J_T(N_j)$ is the phonon factor and d_{ex} is the dipole momentum of the confined exciton, which can be estimated by using the its relation to the confined exciton radiative lifetime

$$\frac{1}{\tau_{\text{ex}}^{\text{rad}}} = \frac{4e^2 E_{\text{ex}}^3 d_{\text{ex}}^2 n_{\text{eff}}}{3\hbar^4 c^3}. \quad (\text{A.35})$$

Here E_{ex} is the exciton energy and the effective refraction index n_{eff} is determined by the formula [130]

$$n_{\text{eff}} = \left(\frac{\varepsilon_{\text{m}}}{\varepsilon_{\text{eff}}} \right)^2 \varepsilon_{\text{m}}^{1/2}, \quad (\text{A.36})$$

where ε_{Si} and ε_{m} are the dielectric constants of silicon and medium, respectively, and $\varepsilon_{\text{eff}} = (\varepsilon_{\text{Si}} + 2\varepsilon_{\text{m}})/3$.

Matrix elements d_{0j} in (A.34) correspond to the transitions in the f -shell of Er³⁺, and can be expressed via the corresponding oscillator strengths P_{0j} :

$$d_{0j}^2 = \frac{3\hbar^2}{2m_0 \Delta_{0j} n_{\text{m}}} P_{0j}, \quad (\text{A.37})$$

where, in the simplest approximation, n_{m} is the refraction index of the medium [131]. To our knowledge, there are no data in the literature concerning the oscillator strengths of transitions between the levels of the Er³⁺ ion in the considered inhomogeneous media. However, we can estimate them via the oscillator strengths found for several glasses and solutions [131,132]: $P_{03} = 1 - 3 \times 10^{-7}$ for transition ${}^4\text{I}_{9/2} \rightarrow {}^4\text{I}_{15/2}$, $P_{04} \approx 2 \times 10^{-6}$ for transition ${}^4\text{I}_{9/2} \rightarrow {}^4\text{I}_{15/2}$. Based on these data we estimate $d_{03}^2 = 1 \times 10^{-22} \text{ cm}^2$, $d_{04}^2 = 7 \times 10^{-22} \text{ cm}^2$.

The calculation leads to the estimation

$$W_{\text{dd}} \lesssim 10^{-1} \left(\frac{R}{a} \right)^6 \frac{1}{\tau_{\text{ex}}^{\text{rad}}}. \quad (\text{A.38})$$

Thus, one can see that the Förster mechanism does not work effectively for the considered system, especially at some distance from the NC, because the radiative recombination of confined carriers is a quicker process. Again the excitation of the first excited state of the Er³⁺ is additionally delayed by the multiphonon relaxation from the higher excited states.