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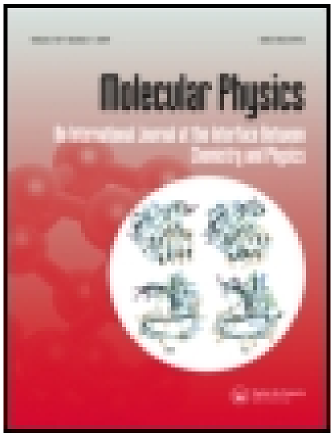

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Multiphonon relaxation of excited rare-earth ions in ionic matrices

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Multiphonon relaxation of excited rare-earth ions in ionic matrices

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A theory of multiphonon relaxation for rare-earth ions in ionic crystals and glasses is presented. The theory is based on the static coupling scheme. The electron–vibration coupling is assumed to be linear with respect to the relative ligand rare-earth displacements. The multiphonon transitions are induced by higher-order lattice anharmonicity of the ionic motions. The probability of multiphonon transitions could be related to the IR multiphonon spectrum. A simplified form of the general expression is proposed. The electronic part of the expression obtained has exactly the same form as the corresponding expression in the well-known Judd–Ofelt theory for optical transitions between multiplets of rare-earth ions in solids.

1. Introduction

The majority of excited states of rare-earth (RE) ions in solids and liquids loses its energy by non-radiative processes. Therefore, the interest in explaining these processes has a long tradition. From a physical point of view it has been clear that the energy has to be transferred from the ions to the lattice vibrations by Coulomb interactions. A theory for energy transfer between electronic donors and acceptors by electric multipole interactions has been developed by Förster [1] and Dexter [2]. So, it was a challenge to apply this theory to non-radiative transitions by considering the RE ions as donors and the lattice vibrations as acceptors. The first attempt for such an explanation was done for the non-radiative transition $^5D_1 \rightarrow {}^5D_0$ in $Eu(C_2H_5SO_4)_3{\cdot}9H_2O$ [3]. It was assumed that the electronic energy is transferred by an inductive resonance process to the nine water molecules surrounding the Eu^{3+} ion. The electric dipole–quadrupole interaction between the dipole moment of the water vibrations and the crystal-field induced quadrupole moment of the Eu^{3+} $^5D_1 \rightarrow {}^5D_0$ transition was taken as the mechanism. Using only spectroscopic data excellent agreement between theory (15 μs) and experiment (20 μs) was found for the lifetime of the $^5D_1$ state. Furthermore, it could be shown experimentally for a number of hydrated salts of Eu^{3+} and Tb^{3+} that the non-radiative transition probabilities from the levels $^5D_0$ (Eu^{3+}) and $^5D_4$ (Tb^{3+}) can be split up into a factor depending only on the RE ion and a factor depending only on the lattice.

The idea to use the Förster–Dexter theory to explain non-radiative transitions was extended to multiphonon transitions on the basis of electric dipole–dipole interactions between the ions and overtones of the anharmonic lattice vibrations [4–9]. In this model the non-radiative transition probability separates into an ion and lattice factor. From the fact that the lattice factor depends on the overtone dipole moments, it follows that the non-radiative transition probability and the absorption coefficient of the lattice are proportional one to another as a function of energy [6, 9]. The absorption coefficient of the overtones decreases exponentially with energy [10, 11]. On this basis the model can furthermore explain the well-known exponential energy-gap law for multiphonon transitions [6, 9]. This law has been nicely demonstrated experimentally in a number of papers [12–16]. Although the model has a phenomenological character, it can explain a number of aspects of non-radiative transitions quite well, qualitatively as well as quantitatively.

More fundamental microscopic theories of multiphonon relaxation, used first in harmonic approximation, were extended to anharmonic vibrations [17–19]. It was demonstrated that the anharmonicity of the

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vibrations plays a crucial role in these theories too. However, numerical results can only be given under the quite simplifying assumption that the electronic excitation energy is only transferred to the vibration of one chemical bond.

Here we extend the microscopic theory of multiphonon transitions worked out in [20–22] to anharmonic vibrations. We will show that the multiphonon relaxation rate $W(\Omega)$ and the infrared absorption coefficient $k(\Omega)$ are proportional to each other as in the above mentioned Förster–Dexter dipole–dipole energy-transfer model. The paper is organized as follows. In section 2 we give general expressions for the non-radiative transition rates in the case of linear electron–vibration coupling. In section 3 we will show that $W(\Omega)$ is proportional to $k(\Omega)$ and give the expression for the coefficient of proportionality. Section 4 is dedicated to the discussion of our results in comparison with previous theories.

2. General expressions for non-radiative transition rate

In this section we will give general expressions for non-radiative transition rates in the case of linear electron–vibration coupling. The theory is based on the static coupling scheme [23–27], zero electron–phonon Huang–Rhys parameter and the crystal-field approximation for the Stark splitting of the free-ion states.

In order to proceed with the calculation of the multiphonon relaxation rate we will use the 'exchange-charge' model [28] of the crystal field. In this model the crystal field is considered as

$$H = H_{\mathrm{M}} + H_{\mathrm{E}}, \tag{1}$$

where H_{M} is the Coulomb interaction of the 4f electrons with the field of the point charges (H^{PC}) and that of the dipole moments (H^{d}) of the ligands. The non-Coulomb Hamiltonian is given by

$$H_{\mathrm{E}} = \sum_{s}\sum_{k} B_k(r_S) \sum_{m} Y^{*}_{km}(\mathbf{r}_S) \sum_{a} Y_{km}(\xi_a) \quad (k = 2, 4, 6). \tag{2}$$

Here ξ_a is the instantaneous radius vector of the ath 4f electron relative to the nucleus of the rare-earth ion; $\mathbf{r}_S = \mathbf{R}_S + \mathbf{u}_S$ is the instantaneous radius vector of the Sth ligand relative to the nucleus of the rare-earth ion and $\mathbf{R}_S$ is the equilibrium radius vector. The non-Coulomb Hamiltonian deals with interactions which are mainly due to the overlap of the 4f electron wave functions with the ligand wave functions and includes the corrections to the Coulomb interaction resulting from the spatial distribution of the ligand electronic charge and the exchange interaction. The contributions from the charge transfer states are also included in H_{E}. In equation (2)

$$\begin{aligned} B_k(r) &= \sum_{\nu} b_{k\nu}(r) \\ &= 8\pi e^2\left(G_s|S_s|^2 + G_\sigma|S_\sigma|^2 + \gamma_k G_\pi |S_\pi|^2\right)/7r. \end{aligned} \tag{3}$$

Here e is the electron charge, G_ν are the crystal-field fitting parameters in the frame of the 'exchange-charge' model, and $\gamma_k = 2 - k(k+1)/12$. $S_\nu = S^0_\nu \exp(-\alpha_\nu r)$ are the overlap integrals of the 4f electron wave functions with the wave functions of the external electronic shells of the ligands. For important practical cases (oxygen and fluorine ions surrounding the RE^{3+} ions) these are the $p\sigma$, $p\pi$ and s orbitals of the ligands.

We have already used this model and the correlation function method to calculate the multiphonon transition rates in the harmonic approximation [20–22, 29–31].

In first-order perturbation theory the probability for a non-radiative transition from an initial state $|i)$ with energy E_i to a final state $|f)$ with energy E_f ($E_i > E_f$) can be written as

$$W_{if} = \frac{1}{\hbar^2}\int_{-\infty}^{\infty} \exp(\mathrm{i}\Omega_{if}t)\langle H'_{if}(t)H'_{fi}\rangle\,\mathrm{d}t. \tag{4}$$

Here $\Omega_{if} = (E_i - E_f)/\hbar$, the symbol $\langle\ldots\rangle$ denotes the average over the initial lattice vibrations, $H' = H - \langle H\rangle$, $H'_{if} = (i|H'|f)$, and

$$H'_{if}(t) = \exp(\mathrm{i}H_{\mathrm{L}}t/\hbar)H'_{if}\exp(-\mathrm{i}H_{\mathrm{L}}t/\hbar), \tag{5}$$

where H_{L} is the vibration Hamiltonian of the matrix.

For the even harmonics of the crystal field the Hamiltonian H' and probability W_{if} can be written as

$$H' = \sum_{S}\sum_{km} B^{(S)}_{km} \sum_{a} Y_{km}(\xi_a) \quad (k = 2, 4, 6), \tag{6}$$

$$\begin{aligned} W_{if} = \frac{1}{\hbar^2}\sum_{km}\sum_{k'm'} &\left(i\left|\sum_{a} Y_{km}(\xi_a)\right|f\right)\left(i\left|\sum_{a} Y_{k'm'}(\xi_a)\right|f\right)^{*} \\ &\times \int_{-\infty}^{\infty} \exp(\mathrm{i}\Omega_{if}t)\sum_{SS'}\left\langle B^{(S)}_{km}(t)B^{(S')*}_{k'm'}\right\rangle \mathrm{d}t \end{aligned} \tag{7}$$

Following the Judd–Ofelt procedure [32, 33] we obtain the following expression for the mean value of W_{if} averaged over all Stark states of initial J and final J' multiplets

$$\begin{aligned} \overline{W_{if}} = \sum_{\text{even } k} \mu_{lk} \sum_{m}\sum_{SS'} \int_{-\infty}^{\infty} \\ \exp(\mathrm{i}\Omega_{if}t)\sum_{SS'}\left\langle B^{(S)}_{km}(t)B^{(S')*}_{km}\right\rangle \mathrm{d}t/4\pi\hbar^2, \end{aligned} \tag{8}$$

where

$$\begin{aligned}\mu_{lk} &= 4\pi(l\|Y_k\|l)^2\left(J\middle\|U^{(k)}\middle\|J'\right)^2/[k][J][J'] \\ &= [l]^2\begin{pmatrix} l & k & l \\ 0 & 0 & 0\end{pmatrix}^2\left(J\middle\|U^{(k)}\middle\|J'\right)^2/[J][J'] \qquad (9)\end{aligned}$$

and $(J\|U^{(k)}\|J')$ is the reduced matrix element of the unit tensor operator $U^{(k)}$ of rank k, $[x] = 2x + 1$ and $l = 3$ for 4f-electrons.

For the odd harmonics $Y_{1m}(\xi)$ of the point-charge field the Hamiltonian H' and probability W_{if} can be written as

$$H' = \sum_S \sum_m A^S_{1m} \sum_a \xi_a Y_{1m}(\xi_a), \tag{10}$$

$$\begin{aligned}W_{if} &= \frac{1}{\hbar^2}\sum_{mm'}\left(i\middle|\sum_a \xi_a Y_{1m}(\xi_a)\middle|f\right)\left(i\middle|\sum_a \xi_a Y_{1m'}(\xi_a)\middle|f\right)^* \\ &\quad\times\int_{-\infty}^{\infty}\exp(\mathrm{i}\Omega_{if}t)\sum_{SS'}\left\langle A^{(S)}_{1m}(t)A^{(S')*}_{1m'}\right\rangle \mathrm{d}t, \qquad (11)\end{aligned}$$

where

$$A_{1m} = (4\pi/3)e\sum_S q_S Y^*_{1m}(\mathbf{r}_S)/r^2_S. \tag{12}$$

In equation (12) q_S is the effective charge of Sth ligand.

In the following, the electron–vibration coupling H' is assumed to be linear with respect to the relative ligand rare-earth displacements. This means that the multiphonon relaxation is due to the anharmonicity of the lattice vibrations. (In the Appendix we discuss equation (11) also for nonlinear interaction). Averaged over all orientations of the vectors $\mathbf{R}_S$ the correlator $\langle A^{(S)}_{1m}(t)A^{(S')*}_{1m'}\rangle$ is equal to

$$\overline{\left\langle A^{(S)}_{1m}(t)A^{(S')*}_{1m'}\right\rangle} = 8\pi e^2 q_S q_{S'} K_{SS'}(t)\delta_{SS'}\delta_{mm'}/3R^2_S R^2_{S'} \tag{13}$$

with the correlation function of the displacements

$$K_{SS'}(t) = \langle \mathbf{u}_S(t)\mathbf{u}_{S'}\rangle/3R_S R_{S'}. \tag{14}$$

Substituting $\overline{\langle A^{(S)}_{1m}(t)A^{(S')*}_{1m'}\rangle}$ for $\langle A^{(S)}_{1m}(t)A^{(S')*}_{1m'}\rangle$ in equation (11) and averaging over the Stark splittings leads to

$$W^{\mathrm{PC}}_1 = \overline{\overline{W_{if}}} = 2\sum_s (eq_S/\hbar R_S)^2(S_{JJ'}/R^2_S)J^{(1)}_{SS}(\Omega_{if})/[J][J'] \tag{15}$$

with the spectral density of the displacements

$$J^{(1)}_{SS}(\Omega) = \int_{-\infty}^{\infty}\exp(\mathrm{i}\Omega t)K_{SS}(t)\,\mathrm{d}t \tag{16}$$

and the optical line strength $S_{JJ'}$, which can be written, following Judd and Ofelt [32, 33], as

$$S_{JJ'} = \sum_k \Omega_k\left(J\middle\|U^{(k)}\middle\|J'\right)^2. \tag{17}$$

With $R_S = R$ and $q_S = q$ equation (15) can be rewritten as

$$W^{\mathrm{PC}}_1(\Omega_{if}) = 2Z(eq/\hbar R)^2(S_{JJ'}/R^2)J^{(1)}(\Omega_{if})/[J][J']. \tag{18}$$

Here R is the radius of the first coordination shell of the RE ion and Z is the coordination number.

Under the same assumptions the contribution from the even harmonics of the point-charge field is [20, 21]

$$W^{\mathrm{PC}}_{\mathrm{even}} = \overline{\overline{W_{if}}} = \sum_{\text{even }k} W^{\mathrm{PC}}_k, \tag{19}$$

with

$$W^{\mathrm{PC}}_k = Z(k+1)(eq/\hbar R)^2\mu_{lk}\left(\overline{\xi^k}/R^k\right)^2 J^{(1)}(\Omega_{if}) \quad (k=2,4,6). \tag{20}$$

For the 'exchange-charge' model we have

$$W^{\mathrm{E}}_{\mathrm{even}} = \overline{\overline{W_{if}}} = \sum_{\text{even }k} W^{\mathrm{E}}_k \tag{21}$$

with

$$\begin{aligned}W^{\mathrm{E}}_k &= (Z/4\pi\hbar^2)\mu_{lk}\left[2k^2(k+1)\left(\sum_\nu b^0_{k\nu}\right)^2\right. \\ &\quad\left.+(2k+1)\left(\sum_\nu b^0_{k\nu}(1+\tau_\nu)\right)^2\right]J^{(1)}(\Omega_{if}). \qquad (22)\end{aligned}$$

Here $b^0_{k\nu} = b_{k\nu}(r_S)$ are the parameters of the 'exchange-charge' field taken at the equilibrium distance $r_S = R_S = R$ and $\tau_\nu = 2\alpha_\nu R$.

It should be noted that for all considered cases the multiphonon transition rate W could be written as

$$W = \omega^2_1 J^{(1)}(\Omega_{if}), \tag{23}$$

where

$$\omega^2_1 = \sum_k \omega^2_{1k}\left(J\middle\|U^{(k)}\middle\|J'\right)^2 \tag{24}$$

is the 'electronic part' and $J^{(1)}(\Omega_{if})$ is the 'lattice part'.

As can be seen from equations (23) and (24), the 'electronic part' of all the expressions for the multiphonon rates has the same form as the well-known Judd–Ofelt [32, 33] expression for radiative $4f \rightarrow 4f$ transitions.

In the harmonic approximation of the lattice vibrations, the spectral density $J^{(1)}(\Omega_{if})$ will become zero if Ω_{if} exceeds the maximum frequency $\omega_{\max}$ of the matrix vibrations. The same is true for the IR absorption coefficient $k(\Omega)$ of ionic matrices.

In the next section we will show that the spectral density $J^{(1)}(\Omega)$ and the IR absorption coefficient are proportional to each other.

3. Relationship between the spectral density of the displacements and the IR absorption coefficient

The IR absorption coefficient $k(\Omega)$ of ionic matrices can be written as

$$k(\Omega) = \frac{2\pi\Omega\chi}{3\hbar cVn}\int_{-\infty}^{\infty} \exp(\mathrm{i}\Omega t)\langle \mathbf{d}(t)\mathbf{d}\rangle \,\mathrm{d}t, \tag{25}$$

where Ω is the frequency of the absorbed radiation, c is the light velocity, V and n are volume and index of refraction of the matrix, respectively, $\chi = [(n^2+2)/3]^2$ and $\mathbf{d}(t)$ is the Heisenberg representation of the dipole moment $\mathbf{d}$:

$$\begin{aligned} d_\mu &= \sum_{l\kappa} A_{\mu,\alpha}(l\kappa)u_\alpha(l,\kappa) \\ &\quad + \sum_{l\kappa}\sum_{l'\kappa'} B_{\mu,\alpha\beta}(l\kappa;l'\kappa')u_\alpha(l\kappa)u_\beta(l'\kappa') + \dots . \end{aligned} \tag{26}$$

In equation (26) $\mathbf{u}(l\kappa)$ is the displacement of the κth nucleus in the lth unit cell from its equilibrium position. (We omitted a factor $1-\exp(-\hbar\Omega/kT)$ on the right side of equation (25), since $\hbar\Omega \gg kT$ for multiphonon transitions.)

We will not calculate the absorption coefficient $k(\Omega)$. Our objective is to connect the spectral density $\int_{-\infty}^{\infty}\exp(\mathrm{i}\Omega t)\langle\mathbf{d}(t)\mathbf{d}\rangle\,\mathrm{d}t$ with the spectral density $J^{(1)}(\Omega_{if})$ involved in equation (23) for the multiphonon relaxation rate W.

We will neglect higher-order moments in equation (26). As noted in [11], the effect of higher-order moments is expected to be less important for highly ionic compounds since the constituent ions are generally less polarizable. For simplicity we assume that $A_{\mu\alpha}(l\kappa) = q(\kappa)\delta_{\mu\alpha}$, where $q(\kappa)$ is the effective charge of the κth ion in the unit cell. Under this assumptions,

$$\begin{aligned} k(\Omega) &= \frac{2\pi\Omega\chi}{3\hbar cnV}\int_{-\infty}^{\infty} \exp(\mathrm{i}\Omega t)\sum_{l\kappa}\sum_{l'\kappa'} q(\kappa)q(\kappa') \\ &\quad \times \langle \mathbf{u}(l\kappa;t)\mathbf{u}(l'\kappa')\rangle\,\mathrm{d}t. \end{aligned} \tag{27}$$

For reasons of mathematical convenience, we will choose the simplest lattice model, a diatomic ionic crystal of the NaCl structure. In this case equation (27) can be rewritten as

$$k(\Omega) = \frac{2\pi\Omega\chi e^2}{3\hbar cVn}\sum_{l=1}^{l=N/2}\sum_{l'=1}^{l'=N/2} j(ll';\Omega). \tag{28}$$

N is the number of ions in the crystal and

$$j(ll';\Omega) = \int_{-\infty}^{\infty} \exp(\mathrm{i}\Omega t)K(ll';t)\,\mathrm{d}t \tag{29}$$

with

$$K(ll';t) = \langle [\mathbf{u}(l+;t)-\mathbf{u}(l-;t)][\mathbf{u}(l'+)-\mathbf{u}(l'-)]\rangle. \tag{30}$$

The sign denotes the charge of the corresponding ion.

In the following we assume that

$$j(ll';\Omega) = j(ll;\Omega) \quad \text{if} \quad |\mathbf{x}(l)-\mathbf{x}(l')| \le R_\mathrm{c} \tag{31}$$

and

$$j(ll';\Omega) = 0 \quad \text{if} \quad |\mathbf{x}(l)-\mathbf{x}(l')| > R_\mathrm{c}. \tag{32}$$

In equations (31) and (32) $\mathbf{x}(l)$ is the position vector of the lth unit cell and R_c designates a coherence length. R_c is taken to be sufficiently short. (See section 4 for a more detailed discussion.) These assumptions give rise to higher-order harmonics at frequencies Ω, which exceed significantly the maximum fundamental frequency ω_max of the matrix vibration. With these assumptions equation (28) can be written in the form

$$k(\Omega) = \frac{\pi\Omega\chi e^2 NN_\mathrm{c}R^2}{2\hbar cnV}\overline{J(\Omega)}, \tag{33}$$

where N_c is the number of ions in the volume $V_\mathrm{c} = 4\pi R_\mathrm{c}^3/3$ and

$$\overline{J(\Omega)} = \sum_{l=1}^{l=N/2} j(ll;\Omega)/[3R^2(N/2)]. \tag{34}$$

In crystals $\overline{J(\Omega)} = j(11;\Omega)/3R^2$, since the spectral density $j(ll;\Omega)$ is independent of l (cf. with equation (10) of [9]). In ionic glasses the sum $\sum_{l=1}^{l=N/2} j(ll;\Omega)/(N/2)$ is the mean value of the spectral density $j(ll;\Omega)$. Taking into account that R is the distance between nearest ions and that the lattice constant a is equal to $2R$, we have

$$\overline{J(\Omega)} = \gamma k(\Omega) = \frac{8Rn}{\pi\Omega\chi\alpha N_\mathrm{c}}k(\Omega), \tag{35}$$

where $\alpha = e^2/\hbar c$ is the fine structure constant.

Now let us compare the expressions for $\overline{J(\Omega)}$ and $J^{(1)}(\Omega_{if})$. According to equations (29), (30) and (34) we have

$$\begin{aligned} \overline{J(\Omega)} &= \int_{-\infty}^{\infty} \exp(\mathrm{i}\Omega t)\sum_{l'=1}^{l=N/2}\langle[\mathbf{u}(l+;t)-\mathbf{u}(l-;t)] \\ &\quad \times [\mathbf{u}(l+)-\mathbf{u}(l-)]\rangle\,\mathrm{d}t/[3R^2N/2]. \end{aligned} \tag{36}$$

On the other hand, according to equations (14) and (16) we have

$$J^{(1)}(\Omega) = \int_{-\infty}^{\infty} \exp(\mathrm{i}\Omega t)K(t)\,\mathrm{d}t \tag{37}$$

with

$$K(t) = \langle [\mathbf{u}(\mathrm{RE}; t) - \mathbf{u}(\mathrm{L}; t)][\mathbf{u}(\mathrm{RE}) - \mathbf{u}(\mathrm{L})] \rangle / 3R^2, \tag{38}$$

where $\mathbf{u}(\mathrm{RE})$ and $\mathbf{u}(\mathrm{L})$ are the displacements of the RE and ligand ions, respectively. Note, that the RE ion charge is opposite in sign to the ligand one. Comparing the last three equations, one can expect that

$$J^{(1)}(\Omega) \approx \overline{J(\Omega)} \tag{39}$$

and as a result

$$W \approx \omega_1^2 \overline{J(\Omega_{if})} = \omega_1^2 \gamma k(\Omega) \tag{40}$$

with

$$\gamma = 8nR/\pi\alpha\chi\Omega N_c \tag{41}$$

4. Discussion

The total rate k_{nr} of the multiphonon transition $J \rightarrow J'$ is

$$k_{\mathrm{nr}} = \sum_{if} \rho_i W(\Omega_{if}), \tag{42}$$

where ρ_i is the population of the ith substate of the J multiplet. Substitution of expression (11) into equation (42) and using equation (40) leads to the expression

$$k_{\mathrm{nr}} = \frac{8Zcn^2}{\pi^3 V_R N_c \chi^2} \int \sigma_{\mathrm{em}}(\lambda) k(\lambda)\, \mathrm{d}\lambda, \tag{43}$$

where $V_R = 4\pi R^3/3$ and $\sigma_{\mathrm{em}}(\lambda)$ is the emission cross-section of the $J \rightarrow J'$ transition. Payne and Bibeau (see equation (21) of [9]) derived a similar expression starting from the Förster–Dexter dipole–dipole energy-transfer model:

$$W_{\mathrm{PB}} = \frac{(2/3)c}{(\pi n)^2 V_{\min}} \int \sigma_{\mathrm{em}}(\lambda) k(\lambda)\, \mathrm{d}\lambda. \tag{44}$$

From equations (43) and (44) we obtain

$$k_{\mathrm{nr}} = \frac{12Z}{\pi N_c} \left(\frac{R_{\min}}{R} \right)^3 \left(\frac{n^2}{\chi} \right)^2 W_{\mathrm{PB}}. \tag{45}$$

As seen from equation (45), the two different approaches give similar results. The factor $(n^2/\chi)^2$ in equation (45) arises because the Förster–Dexter theory supposes that the distance between the interacting dipoles is larger than the size of the dipoles. For this reason, in the Förster–Dexter theory the square of the matrix element of the dipole–dipole interaction is corrected by the factor $(\chi/n^2)^2$ due to polarization of the medium [9, 10]. In our approach we do not need to introduce this factor, because there are no other ions between the RE ion and ligand. The authors of paper [9] suppose that $R_{\min}$ is roughly equal to the RE ion radius. Since $Z^{3/2} R_{\min} \approx R$, the main difference between equation (43) and equation (44) is the factor $1/N_c$ in equation (43). Therefore the results obtained by the two methods are in close agreement if $N_c \sim 1$. (In our model $N_c \sim 1$ corresponds to a total breakdown of the correlation between the ion motions in different unit cells. Indeed, the approximation of completely uncorrelated motion was used in [12] to explain the exponential dependence of the IR absorption coefficient on the light frequency. The authors used a gas of diatomic ions as model of an anharmonic crystal.)

Although equations (43) and (44) are identical for $N_c \sim 1$, one has to point out the completely different physical approach. In our model we do not have any energy transfer to more distant cells. The RE ion interacts only with its nearest ligands and does not transfer energy to distant neighbours. The similarity with the IR spectrum results from the fact that the charge of the RE ions is positive and that of the ligands negative. This way the RE–ligand cell has a dipole moment close to that of undoped cells (in the sense of the vibrational motion, correlation function and spectral density). Formally this is demonstrated by equation (39).

However, the multiphonon relaxation process may be interpreted in terms of the Förster–Dexter theory, if the crystal contains high-frequency quasi-molecular atomic groups, such as PO_4, OH, H_2O, etc., with strongly anharmonic vibrations.

Finally, we would like to point out that from equations (15) and (20) one can easily estimate the relative contributions of the crystal-field harmonics of second and first order, $Y_{2m}(\xi)$ and $Y_{1m}(\xi)$, to the relaxation process, i.e. the relative contributions of the 'quadrupole–dipole' and 'dipole–dipole' parts of the relaxation:

$$\frac{W_2^{\mathrm{PC}}}{W_1^{\mathrm{PC}}} = \frac{14}{5} \left(\frac{\overline{\xi^2}}{R^2} \right)^2 \frac{R^2}{S_{JJ'}} \left(J \middle\| U^{(2)} \middle\| J' \right)^2 \tag{46}$$

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Appendix

The contribution of the odd harmonics $Y_{1m}(\xi)$ of the point-charge field in the harmonic approximation is given by

$$W_1^{\mathrm{PC}}(n) = \overline{\overline{W_{if}}} = Z \left(\frac{eq_S}{\hbar R} \right)^2 \frac{(2n+2)! S_{JJ'}}{3!\, n!\, 2^n R^2 [J][J']} J^{(n)}(\Omega_{if}), \tag{A 1}$$

where

$$J_{SS}^{(n)}(\Omega) = \int_{-\infty}^{\infty} \exp(\mathrm{i}\Omega t) K_{SS}^n(t)\, \mathrm{d}t. \tag{A 2}$$

If a single frequency (ω_0) model of the lattice vibrations is employed, the probability of a n-phonon transition between two multiplets $J \rightarrow J'$ can be expressed as

$$W_1^{\mathrm{PC}}(n) = \omega_0 Z \left(\frac{eq_S}{\hbar\omega_0 R}\right)^2 \frac{(2n+2)!S_{JJ'}}{n!R^2[J][J']} \eta^n. \qquad \text{(A 3)}$$

The quantity $\eta = \langle u^2 \rangle / R^2$ in equation (A 3) is a parameter characterizing the dynamical properties of the lattice [20, 21, 29–31]. The term $\langle u^2 \rangle$ can roughly be estimated as $\hbar/4M\omega_0$, where M is the reduced mass of the ions involved, mainly the ligands. Hence, values of η are expected in the region of 10^{-3}–10^{-4}.

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