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Energy transfer and two-center optical transitions involving rare-earth and OH$^-$ impurities in condensed matter

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We present theoretical calculations for energy transfer and two-center optical processes involving simultaneous rare-earth electronic and OH$^-$ vibrational transitions in condensed matter. [Along the lines sketched at the 1978 Paris Luminescence Conference (J. Luminescence 1979)]. We use an electrostatic coupling model and perturbation theory to develop formal expressions for transition rates. Approximate expressions are derived and numerical results are presented for several specific processes and systems. Comparison with transition rates for rare-earth (RE) ion pairs indicates that the effects discussed can be observed experimentally. The importance of these effects as a local probe of the structure of the RE-ion's environment (not only in solids) as well as means for production of a high population of a specific RE excited state is noted.

I. INTRODUCTION

Much work has been done in the last few decades on energy transfer among atoms, ions, and molecules in gases, liquids, glasses, and solids in organic and inorganic systems. A particularly rich source of phenomena has been in trivalent rare-earth (RE) systems, where, because the inner $4f$ electrons are well shielded, the transition energies in the visible region of the spectra are sharply defined (a few wave numbers) and the densities of states are correspondingly high. In addition to direct energy transfer from one excited ion (the sensitizer or donor) to another (the acceptor or activator) several cooperative effects have been observed and treated theoretically. These include such phenomena as simultaneous energy transfer from two ions to another, absorption of a photon by two ions in cooperation, transfer of part of an ion's excitation energy to another ion with the energy difference being emitted as a photon, and the inverses of these processes, all of which involve either three ions or two ions and a photon. Several reviews which include discussion of the energy transfer and cooperative processes involving RE ions have recently appeared.[1–4]

The interpretation of these effects has almost entirely been based on perturbation theory applied to a tight-binding description of the constituents. The ion's wave functions and energy levels are treated as known and almost independent of the presence of the other ions with which they exchange energy. The probability of direct energy transfer, for example, is calculated by Fermi's golden rule in which the density of states is provided by vibrational motion. This approach was developed by Förster[5] in a classic paper for organic molecules in liquid solution, where the matrix element appearing in the transition probability was that for induced dipole-dipole coupling between the molecules. For many transfer events of interest this is not the dominant mechanism, but rather one expands the electrostatic interaction in a multipole expansion for the classical part and includes exchange where necessary,[6] as in dealing with triplet states in aromatic hydrocarbons, for example.

Among RE ions the interactions are weak, and it appeared to us that ion-pair effects comparable to those observed with RE ion pairs should be observable with RE, OH$^-$ ion pairs. More specifically, we are interested in energy transfer, cooperative absorption, its inverse, simultaneous emission and energy transfer, and its inverse for RE, OH$^-$ pairs. Energy transfer to OH$^-$ could be deduced by the quenching of RE luminescence observed in the absence of OH$^-$. Cooperative absorption could be observed by detecting RE luminescence when exciting at the sum of the RE and OH$^-$ excitation energies. In a simultaneous emission and energy-transfer process, a photon which could be detected would be emitted at the energy of a RE transition less the energy transferred to OH$^-$. Single-photon absorption spectra of molecular systems, both liquids and solids, display cooperative electronic-vibrational[7] and vibrational-vibrational phenomena[8] analogous to the cooperative effects involving RE, OH$^-$ ion pairs of interest to us here. Vibronic side bands and multiphonon decay of RE excited states have also been studied but these phenomena involve delocalized vibrational excitations of the host material while we are interested in a specific intramolecular vibrational excitation of a defect. Riseberg and Weber[2] review the multiphonon relaxation processes.

The substitutional OH^- ion has been extensively studied in alkali-halide crystals so that many of the necessary parameters are known in these hosts. Also, the circumstance that a crystal of the $LaCl_3$ structure can be grown also as $La(OH)_3$ (see Ref. 9) ensures that at least a small amount of substitutional OH^- can be incorporated to replace Cl^- in this material. Of course it is well known that RE impurities can readily be added to replace La. Rather surprisingly we were unable to find spectroscopic results for the OH^- impurity in $LaCl_3$, either in the infrared or in the ultraviolet. Accordingly, in the following we use values appropriate to OH^- in the alkali-halide hosts, realizing that they may not be exact. The most significant properties of the OH^- ion for our purposes are as follows. In the infrared, there is an absorption band at about 3600 $^{-1}$ associated with excitation of the OH^- stretching fundamental mode. The absorption band associated with the OD^- stretching fundamental is at about 2600 cm^{-1} and can aid greatly in the identification of the effects to be discussed.[10] In the ultraviolet, there is a strong absorption band at about 6 eV.[11] The Stokes shifted luminescence to excited vibrational levels of the ground electronic state has also been observed in KBr.[12] The high energy of the OH^- vibration can place it in near resonance with electronic energy separations between RE states which ordinarily luminesce in the absence of OH^-, making energy-transfer processes of interest. It also provides a large separation between the purely electronic and the weaker two-center vibronic bands we predict, thus making feasible the observation of the latter.

The quenching of RE luminescence in environments with high-energy vibrational modes has been known for some time. In hydrated crystals only the RE ions near the center of the series of trivalent lanthanides (i.e., Gd^{3+}) luminesce and even large gap transitions, like $Tb^{3+}(^5D_4 \rightarrow {}^7F_J)$ for example, which normally give rise to luminescence are strongly quenched, presumably through nonradiative coupling in the excitation of H_2O vibrations.[13] The same is true in RE trihydroxide crystals where the coupling seems to be to OH vibrations.[14] Auzel[15] has told us that the presence of OH^- in glasses tends to quench RE luminescence and care must be taken to remove OH^- from samples. Nonradiative quenching of luminescence is also observed in aqueous solutions of RE ions and was of considerable interest in the 60's in connection with the development of liquid lasers.[16]

Heber and Hellwege[13] have considered the quenching of $Tb^{3+}(^5D_4)$ and $Eu^{3+}(^5D_0)$ luminescence in a number of hydrated crystals. They treat the quenching mechanism as a multiphonon-type energy-transfer process in which the excitation energy of the RE ion is transferred to vibrational modes of several water molecules. They treat the quenching of $Eu^{3+}(^5D_1)$ luminescence as energy transfer to an H_2O bending mode which is in near resonance with the $^5D_1 \rightarrow {}^5D_0$ splitting.

A theoretical calculation of the energy-transfer rate from $Eu^{3+}(^5D_0)$ and $Tb^{3+}(^5D_4)$ in aqueous solution to vibrational modes of several water molecules has been made by Terpelevskii.[17] Experimental evidence indicates, however, that in solutions the energy of an excited RE ion is transferred to a highly excited vibrational state of a single OH oscillator; the more recent work of Haas and Stein,[18] and Stein and Würzberg[19] done on RE ions in aqueous solutions contains many references to the study of the quenching of RE luminescence in solutions. Haas and Stein have developed a model to explain the nonradiative quenching processes in aqueous solutions and Stein and Würzberg investigate the fitting of the quenching rates for the series of RE ions to a modified energy-gap law.

For our energy-transfer calculations we wish to avoid the strong quenching processes observed in environments which include many centers with high-energy internal modes, and are interested in a system which would luminesce in the absence of OH^- and which contains a dilute concentration of OH^- as a substitutional impurity. Energy-transfer processes in which a RE transition is in near resonance with the OH^- stretching fundamental or the first overtone are of interest to us. We are not mainly concerned with transitions involving transfer of large amounts of electronic excitation energy, hence energy transfer involving higher OH^- overtone bands than the first. However, if the matrix elements were known for the high-energy transitions of H_2O in aqueous solutions, say, where transfer is to a single OH oscillator, then our methods could be applied to calculate the nonradiative transfer rates for large-gap RE transitions in aqueous solution.

Two-center optical transitions involving a trivalent RE ion and an intramolecular vibrational mode of a defect have not been treated previously to the knowledge of the authors. Here we need not only be interested in a system incorporating the OH^- ion as a dilute impurity. Effects involving large-gap RE transitions for which nonradiative decay processes are sufficiently slow that luminescence is observed even in environments containing many centers with high-energy internal modes could also be studied so that the weak effects we propose could have appreciable quantum yields. For example, in hydrated crystals, trihydroxide crystals, or water one could study two-center vibronic transitions involving isolated OH or OD centers by employing isotopic substitution. That is, RE, OD^- ion pairs could be studied in a trihydroxide crystal made with a dilute concentration of OD^- for example. While this manuscript was being prepared this idea has led to the observation of RE, OD and RE, OH two-center optical transitions in aqueous solutions.[20]

We take advantage of the shielding of the RE-ion's $4f$ wave functions by treating the nonradiative energy-transfer processes and two-center optical transitions along the lines of Förster[5] and Dexter.[6,21] That is, tight-binding wave functions are used to describe RE, OH^- ion pairs and perturbation theory is used to include the effects of electrostatic interactions. The formal aspects of the theory are presented in Sec. II of this paper. In Sec. III we derive approximate expressions for matrix elements appearing in the results of Sec. III and make numerical estimates of transfer rates and transition strengths for several specific processes. Section IV contains concluding remarks.

II. ION-PAIR EFFECTS INVOLVING ELECTRONIC AND VIBRATIONAL TRANSITIONS

A theory of ion-pair effects in which one center makes a vibrational transition and the other makes an electronic transition is developed here. It is the sum of electrostatic interactions between centers which gives rise to these effects, where we include both the electron-electron and electron-nuclear interactions when one of the centers may make vibrational transitions. Making use of Born-Oppenheimer wave functions to describe centers with internal vibrational degrees of freedom, we generalize expressions for the transfer probability in Sec. II A and for the cooperative radiative dipole moment matrix elements in Sec. II B. The formalism could easily be generalized to include vibronic transitions at both centers so that transfer involving purely electronic or purely vibrational transitions of centers A and B could be considered to be special cases. However, such a generalization would lead us away from the central point of this paper.

Throughout this paper we neglect the effects of electronic exchange. Theoretical calculations of Kushida[22] which do not include exchange adequately explain the observed magnitudes of many RE ion-pair phenomena. Miyakawa and Dexter[23] have calculated overlap integrals for the $4f$ wave functions of RE ions and found them to be small. While the situation is somewhat different here, that is smaller separations are possible for RE, OH^- pairs than RE pairs and the electronic wave functions of the OH^- ion are not as well shielded as the $4f$ wave functions of the RE ion so that better overlap may be possible, we expect that where low-order multipole moment matrix elements are not disallowed, the inclusion of exchange effects would not materially change the results.

A. Energy transfer

We may write the probability for the transfer of energy between center A, which makes an electronic transition $a \rightarrow a'$, and center B, which makes an electronic transition $b \rightarrow b'$ as[6]

$$P_{AB} = \frac{2\pi}{\hbar} \left| \langle ab | H_{AB} | a'b' \rangle \right|^2 \times \int f_{aa'}(E) F_{bb'}(E)\, dE \quad . \tag{2.1}$$

Here, the integral is over the normalized line-shape functions for the radiative transitions $a \rightarrow a'$ and $b \rightarrow b'$ of the isolated impurity centers and represents the density of energy-conserving states. (This assumes negligible perturbation of transition energies of one object by the proximity of the other.) The interaction energy,

$$H_{AB} = \sum_{ij} \frac{e^2}{\kappa |\vec{r}_i(A) - \vec{R} - \vec{r}_j(B)|} \quad , \tag{2.2}$$

is customarily expanded in a multipole expansion. Here, $\vec{r}_i(A)$ and $\vec{r}_j(B)$ are the coordinates of the electrons of centers A and B measured from their respective centers of mass, κ is the dielectric constant of the solid, and $\vec{R}$ is the separation of the centers. P_{AB} is to be averaged over the components of the initial-state manifold and summed over the components of the final state manifold.

The transfer probability is revised here to treat the transfer of energy between center A, which makes an electronic transition $a \rightarrow a'$, and center B which makes a vibrational transition $0\mu \rightarrow 0\mu'$. (Center B is assumed to be in its ground electronic state.) If we neglect exchange, we may take the zero-order wave functions for the ion pair to be products of the wave functions of each center as in the theory involving only electronic transitions except that a Born-Oppenheimer wave function is used to describe center B (the OH^- ion). The wave functions are

$$\psi_a(\vec{r}(A))\, \phi_{0,\vec{x}(B)}(\vec{r}(B))\, \chi_{0\mu}(\vec{x}(B))$$

for the initial state and

$$\psi_{a'}(\vec{r}(A))\, \phi_{0,\vec{x}(B)}(\vec{r}(B))\, \chi_{0\mu'}(\vec{x}(B))$$

for the final state. The coordinate system is drawn in Fig. 1. Here, $\vec{r}(A)$ and $\vec{r}(B)$ are a shorthand notation for all electronic coordinates of centers A and B. The $\vec{x}(B)$ represent the nuclear coordinates of center B. The wave function $\psi_a(\vec{r}(A))$ describes the electrons of center A; $\phi_{0,\vec{x}(B)}(\vec{r}(B))$ describes the electrons of center B and depends parametrically on the nuclear coordinates. The vibrational wave function $\chi_{0\mu}(\vec{x}(B))$ represents the product of oscillator wave functions, one for each normal coordinate, which describe the nuclei of center B. The nuclear wave function depends on the electronic state of the center, hence the index 0. The index μ represents the quantum numbers which describe the vibrational state of the center.

For a vibrational transition of center B, its initial- and final-state electronic wave functions are not orthogonal so that the interaction of the electrons of center A with the nuclei of center B must also be included in the interaction energy along with the electronic interactions. This contribution to matrix elements will not vanish as in the case of purely electronic transitions at both centers. With these few changes, the transition probability for an event in which B remains in its ground electronic state is written

$$P_{AB}=\frac{2\pi}{\hbar}\left|\langle a0\mu|H'_{AB}|a'0\mu'\rangle\right|^2 \times\int f_{aa'}(E)F_{0\mu0\mu'}(E)\,dE \quad . \tag{2.3}$$

(For direct transfer to OH^- we would normally be interested in the case $\mu=0$.) Here,

$$H'_{AB}=\sum_{ij}\frac{e^2}{\kappa|\vec{r}_i(A)-\vec{R}-\vec{r}_j(B)|}+\sum_{iL}\frac{ez_L}{\kappa|\vec{r}_i(A)-\vec{R}-\vec{x}_L(B)|} \quad , \tag{2.4}$$

where z_L is the charge of the Lth nucleus.

The transfer of energy can go either way, in reducing the electronic excitation energy in A and increasing the vibrational energy on B or vice versa depending on the energies, linewidths, and lifetimes of the states involved. Because the lifetimes of specific vibrational states in condensed matter are typically much smaller than the radiative lifetimes of RE electronic states, it is expected that this kind of transfer could efficiently quench luminescence that would be observed in the absence of the vibrationally excitable centers. Further, because the vibrational modes of center B may be strongly coupled to the lattice (leading to the short nonradiative lifetime), the phonon-assisted energy-transfer process might allow efficient quenching of luminescence even if there is some energy mismatch.

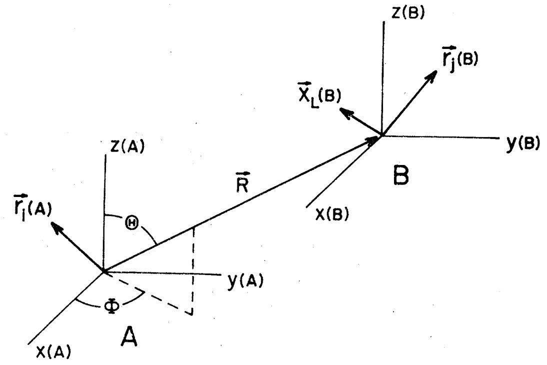

FIG. 1. Two-center coordinate system for a RE (center A), OH^- (center B) ion pair.

B. Cooperative effects

The theory of cooperative optical absorption can be generalized to include the cooperative absorption of a photon by two centers, resulting in the electronic excitation of one and the vibrational excitation of the other. Other ion-pair effects, cooperative luminescence, simultaneous optical absorption and energy transfer, and simultaneous emission and energy transfer are treated similarly. The theory[21(a)] developed to explain the simultaneous excitation of two rare-earth ions, as first observed by Varsanyi and Dieke in $PrCl_3$,[24] is sketched in the next paragraph.

A nonzero transition moment matrix element for cooperative excitation is possible if one uses product wave functions, corrected to first order in perturbation theory to account for electrostatic interactions between electrons of different centers. The wave functions for the ground state and double excitation state can be written

$$\begin{aligned}&\psi_0(\vec{r}(A))\phi_0(\vec{r}(B))-\sum_{a''\neq 0}\sum_{b''\neq 0}\frac{\langle a''b''|H_{AB}|00\rangle}{\delta_{a''}+\epsilon_{b''}}\psi_{a''}(\vec{r}(A))\phi_{b''}(\vec{r}(B)) \quad ,\\ &\psi_{a'}(\vec{r}(A))\phi_{b'}(\vec{r}(B))-\sum_{a''\neq a'}\sum_{b''\neq b'}\frac{\langle a''b''|H_{AB}|a'b'\rangle}{\delta_{a''}-\delta_{a'}+\epsilon_{b''}-\epsilon_{b'}}\psi_{a''}(\vec{r}(A))\phi_{b''}(\vec{r}(B)) \quad .\end{aligned} \tag{2.5}$$

Here 00 denote ground states, $a'b'$ denote final states, and $a''b''$ denote intermediate states for centers A and B, respectively. The radiative dipole moment operator for the ion pair is $\sum_i e\vec{r}_i(A)+\sum_j e\vec{r}_j(B)$ so that the transition moment matrix element with these wave functions is

$$-\Bigg(\sum_{a''\neq 0}\langle a''|\sum_i e\vec{r}_i(A)|a'\rangle\frac{\langle 00|H_{AB}|a''b'\rangle}{\delta_{a''}+\epsilon_{b'}}+\sum_{b''\neq 0}\langle b''|\sum_j e\vec{r}_j(B)|b'\rangle\frac{\langle 00|H_{AB}|a'b''\rangle}{\delta_{a'}+\epsilon_{b''}} + \sum_{a''\neq a'}\langle 0|\sum_i e\vec{r}_i(A)|a''\rangle\frac{\langle a''0|H_{AB}|a'b'\rangle}{\delta_{a''}-\delta_{a'}-\epsilon_{b'}}+\sum_{b''\neq b'}\langle 0|\sum_j e\vec{r}_j(B)|b''\rangle\frac{\langle 0b''|H_{AB}|a'b'\rangle}{\epsilon_{b''}-\delta_{a'}-\epsilon_{b'}}\Bigg) \quad . \tag{2.6}$$

When vibrational transitions of center B are to be considered, the nuclei of center B are to be included in writing the radiative dipole moment operator for the ion-pair system. The perturbing Hamiltonian for the incident radiation is

$$-\sum_i \left(\frac{e}{mc}\right) \vec{\mathfrak{a}}\,(\vec{r}_i(A)) \cdot \vec{p}_i(A) - \sum_j \left(\frac{e}{mc}\right) \vec{\mathfrak{a}}\,(\vec{r}_j(B)) \cdot \vec{p}_j(B) - \sum_L \left(\frac{Z_L}{M_L c}\right) \vec{\mathfrak{a}}\,(\vec{x}_L(B)) \cdot \vec{P}_L(B) \quad . \tag{2.7}$$

Here, $\vec{\mathfrak{a}}$ is the vector potential for the incident radiation, $\vec{p}_i = -i\hbar\vec{\nabla}_{\vec{r}_i}$, and $\vec{P}_L = -i\hbar\vec{\nabla}_{\vec{x}_L}$. The ion-pair system considered here is small compared to the wavelength of light so that the electric dipole approximation may be made for the radiation field

$$\left(\sum_i \frac{e}{m} \vec{p}_i(A) + \sum_j \frac{e}{m} \vec{p}_j(B) + \sum_L \frac{z_L}{M_L} \vec{P}_L(B)\right) \rightarrow i\omega \left(\sum_i e\,\vec{r}_i(A) + \sum_j e\,\vec{r}_j(B) + \sum_L z_L\,\vec{x}_L(B)\right) \quad . \tag{2.8}$$

It will be useful to adopt the following tensor operator notation, viz.,

$$D_q^{(k)}(A) = \sum_i r_i^k(A)\, C_q^{(k)}(\theta_i, \phi_i) \quad ,$$

$$M_q^{(k)}(B) = \sum_j r_j^k(B)\, C_q^{(k)}(\theta_j, \phi_j) + \sum_L \frac{z_L}{e} x_L^k(B)\, C_q^{(k)}(\theta_L, \phi_L) \quad ,$$

and

$$C_q^{(k)}(\theta, \phi) = [4\pi/(2k+1)]^{1/2}\, Y_{kq}(\theta, \phi) \quad . \tag{2.9}$$

Here, $Y_{kq}(\theta, \phi)$ is a spherical harmonic, (r_j, θ_j, ϕ_j) are the spherical polar coordinates of the jth electron, and (x_L, θ_L, ϕ_L) are the spherical polar coordinates of the Lth nucleus. The radiative dipole moment operator is rewritten

$$e\underline{D}^{(1)}(A) + e\underline{M}^{(1)}(B) \quad . \tag{2.10}$$

A Born-Oppenheimer wave function is used to describe center B. As in the theory involving only electronic states, nonzero transition moment matrix elements are not possible between the ground and double excitation state with simple product wave functions because the interaction with the electromagnetic field consists of a sum of one particle interactions. It is the electrons at center A interacting with the electrons and nuclei at center B that give rise to the cooperative effect of interest here. The corrected wave functions for the ground and cooperatively excited states of the ion pair system are

$$\psi_0(\vec{r}(A))\,\phi_{0,\vec{x}(B)}(\vec{r}(B))\,\chi_{00}(\vec{x}(B)) - \sum_{a''\neq 0} \sum_{\substack{b''\mu'' \\ \mu''\neq 0 \text{ when } b''=0}} \frac{\langle a''b''\mu''|H'_{AB}|000\rangle}{\delta_{a''} + \epsilon_{b''\mu''}} \times \psi_{a''}(\vec{r}(A))\,\phi_{b'',\vec{x}(B)}(\vec{r}(B))\,\chi_{b''\mu''}(\vec{x}(B)) \quad ,$$

$$\psi_{a'}(\vec{r}(A))\,\phi_{0,\vec{x}(B)}(\vec{r}(B))\,\chi_{0\mu'}(\vec{x}(B)) - \sum_{a''\neq a'} \sum_{\substack{b''\mu'' \\ \mu''\neq\mu' \text{ when } b''=0}} \frac{\langle a''b''\mu''|H'_{AB}|a'0\mu'\rangle}{\delta_{a''} - \delta_{a'} + \epsilon_{b''\mu''} - \epsilon_{0\mu'}} \times \psi_{a''}(\vec{r}(A))\,\phi_{b'',\vec{x}(B)}(\vec{r}(B))\,\chi_{b''\mu''}(\vec{x}(B)) \quad . \tag{2.11}$$

Here, the quantum numbers 000 denote the ground state, $a'0\mu'$ denote the cooperatively excited state, and $a''b''\mu''$ denote the intermediate states of the ion pair system.

The radiative dipole moment matrix element, with these wave functions, is

$$-\left(\sum_{a''\neq 0} \langle a''|\underline{D}^{(1)}(A)|a'\rangle \frac{\langle 000|H'_{AB}|a''0\mu'\rangle}{\delta_{a''} + \epsilon_{0\mu'}} + \sum_{\substack{b''\mu'' \\ \mu''\neq 0 \text{ when } b''=0}} \langle b''\mu''|\underline{M}^{(1)}(B)|0\mu'\rangle \frac{\langle 000|H'_{AB}|a'b''\mu''\rangle}{\delta_{a'} + \epsilon_{b''\mu''}} + \sum_{a''\neq a'} \langle 0|\underline{D}^{(1)}(A)|a''\rangle \frac{\langle a''00|H'_{AB}|a'0\mu\rangle}{\delta_{a''} - \delta_{a'} - \epsilon_{0\mu'}} + \sum_{\substack{b''\mu'' \\ \mu''\neq\mu' \text{ when } b''=0}} \langle 00|\underline{M}^{(1)}(B)|b''\mu''\rangle \frac{\langle 0b''\mu''|H'_{AB}|a'0\mu'\rangle}{\epsilon_{b''\mu''} - \delta_{a'} - \epsilon_{0\mu'}}\right) \quad . \tag{2.12}$$

The matrix elements involved in cooperative emission, simultaneous absorption and transfer, and the simultaneous emission and transfer effects are similar to the one written for cooperative absorption. These effects all involve two-center optical transitions which have nonzero radiative dipole moment matrix elements when product wave functions describing the initial and final states of the ion-pair system are corrected to first order in perturbation theory to include electrostatic interactions between centers.

We generalize Eq. (2.12) to include transitions from an initial state $|a0\mu\rangle$, which need not be the ground state of the ion pair, to a final state $|a'0\mu'\rangle$, as follows:

$$
\begin{aligned}
-\Bigg(& \sum_{a''\neq a} \langle a''|\underline{D}^{(1)}(A)|a'\rangle \frac{\langle a0\mu|H'_{AB}|a''0\mu'\rangle}{\delta_{a''}-\delta_a+\epsilon_{0\mu'}-\epsilon_{0\mu}} + \sum_{\substack{b''\mu''\\ \mu''\neq 0 \text{ when } b''=0}} \langle b''\mu''|\underline{M}^{(1)}(B)|0\mu'\rangle \frac{\langle a0\mu|H'_{AB}|a'b''\mu''\rangle}{\epsilon_{b''\mu''}-\epsilon_{0\mu}+\delta_{a'}-\delta_a} \\
& + \sum_{a''\neq a'} \langle a|\underline{D}^{(1)}(A)|a''\rangle \frac{\langle a''0\mu|H'_{AB}|a'0\mu'\rangle}{\delta_{a''}-\delta_{a'}+\epsilon_{0\mu}-\epsilon_{0\mu'}} + \sum_{\substack{b''\mu''\\ \mu''\neq \mu' \text{ when } b''=0}} \langle 0\mu|\underline{M}^{(1)}(B)|b''\mu''\rangle \frac{\langle ab''\mu''|H'_{AB}|a'0\mu'\rangle}{\epsilon_{b''\mu''}-\epsilon_{0\mu'}+\delta_a-\delta_{a'}} \Bigg) \; .
\end{aligned}
\tag{2.13}
$$

If the initial state $|a0\mu\rangle$ is of lower energy than the final state $|a'0\mu'\rangle$, then the effect is cooperative absorption if both ions make upward transitions, or is simultaneous absorption and transfer if one ion makes an upward transition and the other a downward transition of less energy. Similarly, if the initial state $|a0\mu\rangle$ is of higher energy than the final state $|a'0\mu'\rangle$ then the effect is cooperative luminescence if both ions make downward transitions or is simultaneous emission and transfer if one ion makes an upward transition and the other a downward transition of greater energy.

III. NUMERICAL RESULTS

In Sec. II the theory of several ion-pair effects was rewritten to include a center which undergoes only vibrational transitions. In the specific system we consider here, center A is a tripositive RE ion and center B is an OH^- ion where both are imagined to be impurity centers in a solid. We derive approximate expressions for the squared matrix elements appearing in the results for the effects previously discussed.

Estimates of matrix elements and sums over excited states for RE ions are made using the methods employed by Kushida[22] in estimating the magnitudes of ion-pair effects involving electronic states of RE ions. A scalar theory is developed by averaging over the orientations of RE and OH^- ions. Further, for RE transitions, we average the matrix elements over the components of the initial and final states, that is the structure of a level, J, and the details of the population of sublevels are ignored, as an approximation, for the purpose of evaluating matrix elements. The details of these and further approximations are expanded upon in what follows.

Experimental results for OH^- impurities in the alkali halides are used to obtain numerical estimates of matrix elements and sums over excited states to make clear the order of magnitudes involved. It is important that one realizes that the parameters we use do not exactly characterize the OH^- stretching vibration in all environments. For example, our numerical estimates would certainly need modification to be applied to effects involving OH vibrations in aqueous solutions.

A. Energy transfer

We estimate the squared matrix element appearing in the energy-transfer rate,

$$
P_{AB}=\frac{2\pi}{\hbar}\sum_{if}\frac{e^{-E_i/kT}}{Q}|\langle a_i0\mu|H_{AB}'|a_f'0\mu'\rangle|^2\int f_{a_ia_f}(E)F_{0\mu0\mu'}(E)\,dE \; . \tag{3.1}
$$

The sum is over the components of the RE-ion's initial- and final-state manifolds. A Boltzmann factor has been included to account for the thermal distribution of energy among the initial-state levels. Also $Q\equiv\sum_i e^{-E_i/kT}$. The methods to be employed in deriving an approximate expression for Eq. (3.1), as applied to energy transfer between RE ions, have been reviewed by Watts.[4]

The following expansion formula is used to write the electron-electron portion of the interaction energy as a multipole expansion[25]:

$$\frac{1}{|\vec{r}_i(A)-\vec{R}-\vec{r}_j(B)|}=\sum_{\substack{k_1k_2\\q_1q_2}}\left(\frac{1}{R^{k_1+k_2+1}}\right)C^{k_1k_2}_{q_1q_2}(\Theta,\Phi)\,r_i^{k_1}(A)\,C^{(k_1)}_{q_1}(\theta_i,\phi_i)\,r_j^{k_2}(B)\,C^{(k_2)}_{q_2}(\theta_j,\phi_j)\ ,$$

$$C^{k_1k_2}_{q_1q_2}(\Theta,\Phi)=(-1)^{k_1}\left(\frac{[2(k_1+k_2)+1]!}{(2k_1)!(2k_2)!}\right)^{1/2}\begin{pmatrix}k_1 & k_2 & (k_1+k_2)\\ q_1 & q_2 & -(q_1+q_2)\end{pmatrix}[C^{k_1+k_2}_{q_1+q_2}(\Theta,\Phi)]^*\ . \tag{3.2}$$

The electron-nuclear interaction is expanded similarly to obtain the following expansion for the electrostatic interaction energy, written to include the electric moments of the center B nuclei:

$$H'_{AB}=\frac{1}{\kappa}\sum_{\substack{k_1k_2\\q_1q_2}}\left(\frac{e^2}{R^{k_1+k_2+1}}\right)C^{k_1k_2}_{q_1q_2}(\Theta,\Phi)\,D^{(k_1)}_{q_1}(A)\,M^{(k_2)}_{q_2}(B)\ . \tag{3.3}$$

We use this multipole expansion and an expanded notation for the states of the RE ion to write the squared matrix element of H'_{AB} as follows:

$$\left|\frac{1}{\kappa}\sum_{\substack{k_1k_2\\q_1q_2}}\left(\frac{e^2}{R^{k_1+k_2+1}}\right)C^{k_1k_2}_{q_1q_2}(\Theta,\Phi)\,\langle 4f^N\psi JM|D^{(k_1)}_{q_1}(A)|4f^N\psi'J'M'\rangle\langle 0\mu|M^{(k_2)}_{q_2}|0\mu'\rangle\right|^2\ . \tag{3.4}$$

While it is possible to estimate the value of this expression for a specific crystalline geometry, a more general expression can be derived if we make the following approximations. Upon integrating the squared matrix element over Θ and Φ, many of the cross terms in the square of the sum over k_1, k_2, q_1, and q_2 vanish because of the orthogonality of the spherical harmonic in $C^{k_1k_2}_{q_1q_2}(\Theta,\Phi)$. Cross terms which do not vanish, that is those terms for which $k_1+k_2=k_1'+k_2'$ but $k_1\neq k_1'$ and $k_2\neq k_2'$, are ignored.[4] (See Sec. III B.) If the square of the 3-j symbol appearing in $C^{k_1k_2}_{q_1q_2}(\Theta,\Phi)$ is replaced by its average value, the squared matrix element becomes

$$|\langle a_i0\mu|H_{AB}'|a_f'0\mu'\rangle|^2=\frac{1}{\kappa^2}\sum_{k_1k_2}\left(\frac{e^2}{R^{k_1+k_2+1}}\right)^2\frac{[2(k_1+k_2)]!}{(2k_1+1)!(2k_2+1)!}$$
$$\times\sum_{q_1}|\langle 4f^N\psi JM|D^{(k_1)}_{q_1}(A)|4f^N\psi'J'M'\rangle|^2|\langle 0\mu|\underline{M}^{(k_2)}(B)|0\mu'\rangle|^2\ . \tag{3.5}$$

In estimating the transfer probability we average the squared matrix element of H'_{AB} over the quantum numbers M and M'. An approximate expression for the energy-transfer rate is then

$$P_{AB}=\frac{2\pi}{\hbar}\left[\frac{1}{\kappa^2}\sum_{k_1k_2}\left(\frac{e^2}{R^{k_1+k_2+1}}\right)^2\frac{[2(k_1+k_2)]!}{(2k_1+1)!(2k_2+1)!}\,\frac{|\langle 4f^N\psi J||D^{(k_1)}(A)||4f^N\psi'J'\rangle|^2}{(2J+1)(2J'+1)}\right.$$
$$\left.\times|\langle 0\mu|\underline{M}^{(k_2)}(B)|0\mu'\rangle|^2\right]\rho_E\ , \tag{3.6}$$

where

$$\rho_E=\sum_{if}\frac{e^{-E_i/kT}}{Q}\int f_{a_ia_f'}(E)\,F_{0\mu0\mu'}(E)\,dE\ .$$

It should be noted that Kushida[22] includes the factor $1/(2J'+1)$ in the overlap integral while we do not.

For odd k, matrix elements of $\underline{D}^{(k)}$ between $4f$ states of RE ions would be zero except for the configuration mixing caused by the crystal field. Reduced matrix elements of $\underline{D}^{(1)}$ can be estimated from the electric dipole contribution to the oscillator strength of optical transitions between $4f$ levels using the equation

$$f_{\mathrm{ed}}(J \rightarrow J') = \frac{2m\omega}{3\hbar}\frac{1}{(2J+1)} \times |\langle 4f^N\psi J \| D^{(1)} \| 4f^N\psi' J'\rangle|^2 \quad . \quad (3.7)$$

We calculate $f_{\mathrm{ed}}(J \rightarrow J')$ using Judd-Ofelt[26,27] intensity parameters reported in the literature. We use values of f_{ed} given for specific RE hosts here to estimate the order of magnitude of $P_{AB}^{(d-d)}$, realizing that the forced electric dipole oscillator strength is sensitive to the environment of the RE ion. Riseberg and Weber,[2] and Peacock[28] have recently reviewed the work done on the intensities of intraconfigurational RE transitions.

For even k, the reduced matrix elements of $\underline{D}^{(k)}$ between intermediate coupling states for the $4f$ levels of RE ions are calculated using the following equation:

$$\langle 4f^N\psi J \| D^{(k)} \| 4f^N\psi' J'\rangle = \langle 4f|r^k|4f\rangle \langle f \| C^{(k)} \| f\rangle \times \langle f^N\psi J \| U^{(k)} \| f^N\psi' J'\rangle \quad . \quad (3.8)$$

Reduced matrix elements of the unit tensor operators, $\underline{U}^{(k)}$, have been tabulated for many RE transitions.[29] The radial matrix elements are taken from Judd's[26] work. The reduced matrix element of $\underline{C}^{(k)}$ can be evaluated by standard tensor operator techniques.[30]

The dipole matrix element for the $00 \rightarrow 01$ transition of the OH^- ion is estimated using Wedding and Klein's[10] experimentally determined oscillator strengths and the equation

$$f = \frac{2m_{\mathrm{OH}}\omega}{3\hbar} |\langle 00|\underline{M}^{(1)}|01\rangle|^2 \quad . \quad (3.9)$$

Here, m_{OH} is the reduced mass of the OH^- ion. In the alkali halides a typical oscillator strength for the OH^- stretching absorption is 5×10^{-3} from which we estimate

$$|\langle 00|\underline{M}^{(1)}|01\rangle|^2 = 2.6 \times 10^{-4} a_0^2 \quad .$$

The effect of the large mass in Eq. (3.9) is to reduce $|\langle 00|M^{(1)}|01\rangle|^2$ by about three orders of magnitude from what it would be for an electronic transition of comparable oscillator strength.

In the following paragraphs we make numerical estimates of Eq. (3.6) for transfer involving several specific RE transitions which are in near resonance with OH^- transitions from the ground state to the fundamental or first overtone bands. While the energies and linewidths of these transitions are not known by the authors for a system incorporating RE and OH^- impurities, we consider transitions where the integral over lineshape functions could be sizable.

Although we leave the density-of-states factor undetermined in our calculations, we make crude guesses as to what it might be. First one should note that for the way have chosen to define ρ_E, the lineshape functions for transitions from the RE ion's initial-state manifold, to each of the $2J'+1$ components of the final state, have unit area so that the total area for the entire band, $J \rightarrow J'$, is $2J'+1$. We characterize roughly the RE and OH^- transitions as follows for the purpose of estimating ρ_E. The widths reported by Wedding and Klein[10] for OH^- in the alkali halides are taken to be appropriate here. At helium or nitrogen temperature, we assume that the RE-ion's transitions originate from the lowest Stark component of the initial state J, and terminate at $2J'+1$ components of the final state J', giving rise to a band of $2J'+1$ sharp lines. We also take these lines to have widths much narrower than the OH^- band's width and splittings that are large enough so that good overlap with the OH^- band is possible for only one Stark component. Then, for perfect overlap of one of the $2J'+1$ δ-function-like RE lineshape functions and a Gaussian, OH^- lineshape function, ρ_E is approximately equal to the reciprocal of the OH^- band's full width at half maximum (FWHM). ρ_E is reduced by a factor of 100 if the peaks of the lineshape functions are split by about 1.3 times the FWHM of the OH^- band.

We estimate the OH^- band's FWHM to be 1–2 cm^{-1} at 4 °K, 10–20 cm^{-1} at 77 °K, and 50–75 cm^{-1} at 290 °K from a graph of OH^- widths for various alkali halide hosts as a function of temperature.[10] At helium temperature, perfect overlap would give a ρ_E of about $1(1/\mathrm{cm}^{-1})$. At nitrogen temperature, perfect overlap would give a ρ_E of about $0.1(1/\mathrm{cm}^{-1})$ to $0.05(1/\mathrm{cm}^{-1})$ with ρ_E being reduced by a factor of 0.01 if the lineshape function peaks are split by 15–25 cm^{-1}.

At room temperature, we do not characterize the RE transitions as above but rather take a transition, $J \rightarrow J'$, to give a Gaussian shaped band of area $2J'+1$ with a FWHM of about 75 cm^{-1}. For perfect overlap with an OH^- band with a 75 cm^{-1} FWHM, ρ_E is about $10^{-2}(1/\mathrm{cm}^{-1}) \times (2J'+1)$. If the peaks of the RE and OH^- bands are split by 100 cm^{-1} at room temperature, ρ_E is reduced by a factor of about 0.1.

It should be clear here that ρ_E is temperature dependent just as for energy transfer between centers making purely electronic transitions. If the overlap between emission and absorption bands is very good, then increasing temperature tends to broaden these bands and decrease ρ_E. If the overlap is not good, as it is often the case, broadening bands increases overlap and thereby increases ρ_E.

We realize that we have characterized RE and OH^- transitions crudely but the estimates of ρ_E we have made should help one understand the significance of the energy-transfer rates we report without the spectroscopic data necessary to calculate ρ_E properly. In the following ρ_E always has units of $1/\mathrm{cm}^{-1}$.

We report estimates of energy-transfer rates for dipole-dipole and quadrupole-dipole processes when the transfer involves the OH^- stretching fundamental. The dipole matrix elements for intraconfigurational RE transitions are only weakly allowed so that quadrupole-dipole processes, unless disallowed, are expected to dominate for small separations. We remark that smaller separations are possible for RE, OH^- pairs than RE pairs because here OH^- would replace a liganding ion. In say LaF_3, about 2.5 Å is possible for RE, OH^- pairs compared to about 3.7 Å for RE pairs. Transfer processes involving RE moments of higher order than quadrupole have been estimated and are small with respect to the quadrupole-dipole rates estimated here but could be of importance for RE transitions which are not quadrupole allowed as they are comparable in magnitude to the dipole-dipole rates at small separations.

1. *Direct transfer for* Dy^{3+}, OH^- *pairs*

We consider direct transfer for a Dy^{3+}, OH^- pair first. The ${}^6H_{13/2}$ level of Dy^{3+} normally exhibits luminescence at about 3500 cm^{-1} in going to the ${}^6H_{15/2}$ ground state. Energy transfer to OH^- should quench this luminescence at room temperature.

For a dipole-dipole process we estimate

$$P_{AB}^{(d-d)}=7\times10^{13}(a_0/R)^6(\rho_E/\kappa^2)\ \mathrm{sec}^{-1}$$

using Eq. (3.6). To obtain this result we have estimated the electric dipole contribution to the oscillator strength of the ${}^6H_{13/2}\rightarrow{}^6H_{15/2}$ transition from the Judd-Ofelt intensity parameters reported for Dy^{3+} in solutions by Carnall *et al.*[31] From

$$f_{\mathrm{ed}}({}^6H_{13/2}\rightarrow{}^6H_{15/2})=1.0\times10^{-6}$$

we get

$$|\langle 4f^{9\,6}H_{13/2}||D^{(1)}||4f^{9\,6}H_{15/2}\rangle|^2=1.5\times10^{-3}a_0^2$$

using Eq. (3.7).

For a quadrupole-dipole process we estimate that

$$P_{AB}^{(q-d)}=3\times10^{16}(a_0/R)^8(\rho_E/\kappa^2)\ \mathrm{sec}^{-1}$$

using Eq. (3.6). To obtain this result we have calculated

$$|\langle 4f^{9\,6}H_{13/2}||D^{(2)}||4f^{9\,6}H_{15/2}\rangle|^2=0.5a_0^4$$

using Eq. (3.8) with

$$|\langle f^{9\,6}H_{13/2}||U^{(2)}||f^{9\,6}H_{15/2}\rangle|^2=0.2457$$

as given by Carnall *et al.*[31] and $\langle 4f|r^2|4f\rangle=0.972a_0^2$.[26]

At a separation of 2.5 Å

$$P_{AB}^{(q-d)}=1\times10^{11}(\rho_E/\kappa^2)\ \mathrm{sec}^{-1}$$

and

$$P_{AB}^{(d-d)}=6\times10^{9}(\rho_E/\kappa^2)\ \mathrm{sec}^{-1}\ ,$$

with the quadrupole-dipole transfer rate dominating. The overlap integral could be very small and still allow significant energy transfer compared to the spontaneous emission probability of about 20 sec^{-1} for $Dy^{3+}({}^6H_{13/2})$ estimated from the Judd-Ofelt intensity parameters. The possibility of back transfer is discussed in Sec. IV.

2. *Direct transfer for* Er^{3+}, OH^- *pairs and* Er^{3+}, OD^- *pairs*

Energy transfer to OH^- can also occur from a RE ion which makes a transition between excited states. The lowest component of the Er^{3+}, ${}^4I_{11/2}$ manifold is above the ${}^4I_{13/2}$ manifold by 3477 cm^{-1} to 3698 cm^{-1} in LaF_3.[32] We estimate the probability of energy transfer from Er^{3+}, making a transition ${}^4I_{11/2}\rightarrow{}^4I_{13/2}$, to OH^- as follows.

For a dipole-dipole process we estimate

$$P_{AB}^{(d-d)}=2\times10^{13}(a_0/R)^6(\rho_E/\kappa^2)\ \mathrm{sec}^{-1}\ .$$

We have used the Judd-Ofelt intensity parameters reported by Weber[33] for $LaF_3{:}Er^{3+}$ to calculate $f_{\mathrm{ed}}=2.4\times10^{-7}$ and then from Eq. (3.7) we obtain

$$|\langle 4f^{11\,4}I_{11/2}||D^{(1)}||4f^{11\,4}I_{13/2}\rangle|^2=2.6\times10^{-4}a_0^2.$$

For a quadrupole-dipole process we estimate that

$$P_{AB}^{(q-d)}=2\times10^{15}(a_0/R)^8(\rho_E/\kappa^2)\ \mathrm{sec}^{-1}\ .$$

To obtain this result we have calculated

$$|\langle 4f^{11\,4}I_{11/2}||D^{(2)}||4f^{11\,4}I_{13/2}\rangle|^2=2.7\times10^{-2}a_0^4$$

using

$$|\langle f^{11\,4}I_{11/2}||U^{(2)}||f^{11\,4}I_{13/2}\rangle|^2=0.021$$

as given by Weber[33] and $\langle 4f|r^2|4f\rangle=0.831a_0^2$.

For a 2.5-Å RE, OH^- pair separation, the quadrupole-dipole transfer rate is $1\times10^{10}(\rho_E/\kappa^2)\ \mathrm{sec}^{-1}$ and the dipole-dipole rate is $1\times10^{9}(\rho_E/\kappa^2)\ \mathrm{sec}^{-1}$. These rates, if compared to the observed lifetime of the ${}^4I_{11/2}$ state of 11 msec in LaF_3 (Ref. 33) in the absence of OH^-, show that transfer to OH^- should quench the ${}^4I_{11/2}$ luminescence.

If instead of adding OH^-, one substitutes OD^-, RE transitions which are in near resonance with the OH^- stretching energy of about 3600 cm^{-1} will not be with the OD^- stretching energy of about 2600 cm^{-1}. We expect that luminescence from an excited state which is strongly quenched by transfer to OH$^-$ might not be for OD$^-$. Further, there might be transitions which are in resonance with the OD$^-$ energy and luminescence associated with these excited states will be more strongly quenched by OD$^-$ than OH$^-$.

In Er^{3+} the transition, $^4F_{9/2} \rightarrow {}^4I_{9/2}$, has an energy of about 2700–3000 cm^{-1} for transitions from the lowest Stark component of $^4F_{9/2}$ to the components of $^4I_{9/2}$. Transfer to OD$^-$ might quench the luminescence of Er^{3+}($^4F_{9/2}$). We estimate

$$P_{AB}^{(d-d)} = 1 \times 10^{12}(a_0/R)^6(\rho_E/\kappa^2)\ \text{sec}^{-1}$$

and

$$P_{AB}^{(q-d)} = 7 \times 10^{15}(a_0/R)^8(\rho_E/\kappa^2)\ \text{sec}^{-1}\ .$$

We have calculated the RE matrix elements using again the Judd-Ofelt intensity parameters and the reduced matrix elements of the unit tensor operators reported by Weber.[33] The OD$^-$ dipole matrix element has been estimated using Eq. (3.9) with an oscillator strength, $f = 2.5 \times 10^{-3}$, that is about what is observed by Wedding and Klein[10] for OD$^-$ in a number of alkali-halide hosts.

For a pair separation of 2.5 Å,

$$P_{AB}^{(d-d)} = 1 \times 10^{9}(\rho_E/\kappa^2)\ \text{sec}^{-1}$$

and

$$P_{AB}^{(q-d)} = 3 \times 10^{10}(\rho_E/\kappa^2)\ \text{sec}^{-1}\ .$$

The lifetime of Er^{3+}($^4F_{9/2}$) in LaF$_3$ in the absence of OH$^-$ is observed to be 0.75 msec. We expect there to be significant energy transfer to OD$^-$ thereby quenching Er^{3+}($^4F_{9/2}$) luminescence.

3. Transfer to OH$^-$ *overtone for* Pr^{3+}, OH$^-$ *pairs*

The energy of a RE transition may be in near resonance with an overtone band of the OH$^-$ ion. We consider the excitation of the first overtone of OH$^-$ by energy transfer from an excited RE ion. We show that an OH$^-$ quadrupole moment matrix element may be more effective than a dipole moment matrix element, which is nonzero because of the ion's vibrational and electrical anharmonicities, in providing coupling to the first overtone.

The ratio of Eq. (3.6) written for a quadrupole-dipole process to (3.6) written for a quadrupole-quadrupole process is

$$\frac{P_{AB}^{(q-d)}}{P_{AB}^{(q-q)}} = 0.36R^2\frac{|\langle 00|\underline{M}^{(1)}|02\rangle|^2}{|\langle 00|\underline{M}^{(2)}|02\rangle|^2}\ . \qquad (3.10)$$

The area of the first overtone band for the OH$^-$ stretch in KBr:KOH has been observed to be $\frac{1}{400}$ of the main band area by Wedding and Klein[10] from which we estimate $\langle 00|\underline{M}^{(1)}|02\rangle|^2 = 3 \times 10^{-7}a_0^2$. We estimate $|\langle 00|\underline{M}^{(2)}|02\rangle|^2 = 8 \times 10^{-4}a_0^4$ using a theoretical calculation made by Cade[34] of the free OH$^-$ ion's quadrupole moment. We find the second derivative of the quadrupole moment with respect to the O-H bond length to be $1.14e$ in the ion's center of mass coordinate system. For $R = 2.5$ Å, we estimate Eq. (3.10) to be 3×10^{-3} so that the OH$^-$ ion's quadrupole moment matrix element provides much stronger coupling than the dipole moment matrix element provides.

As a specific example, we consider the $^1D_2 \rightarrow {}^1G_4$ transition in Pr^{3+}. In LaF$_3$, the energy differences for the lowest component of the $^1D_2$ level and the components of the $^1G_4$ level are between about 6300 cm^{-1} and 7100 cm^{-1},[35] and include the energy of the first OH$^-$ overtone band in KBr:KOH which has been observed to be about 7060 cm^{-1}.[10] We estimate the transfer probabilities

$$P_{AB}^{(d-d)} = 5 \times 10^{10}(a_0/R)^6(\rho_E/\kappa^2)\ \text{sec}^{-1}\ ,$$

$$P_{AB}^{(d-q)} = 2 \times 10^{14}(a_0/R)^8(\rho_E/\kappa^2)\ \text{sec}^{-1}\ ,$$

$$P_{AB}^{(q-d)} = 6 \times 10^{14}(a_0/R)^8(\rho_E/\kappa^2)\ \text{sec}^{-1}\ ,$$

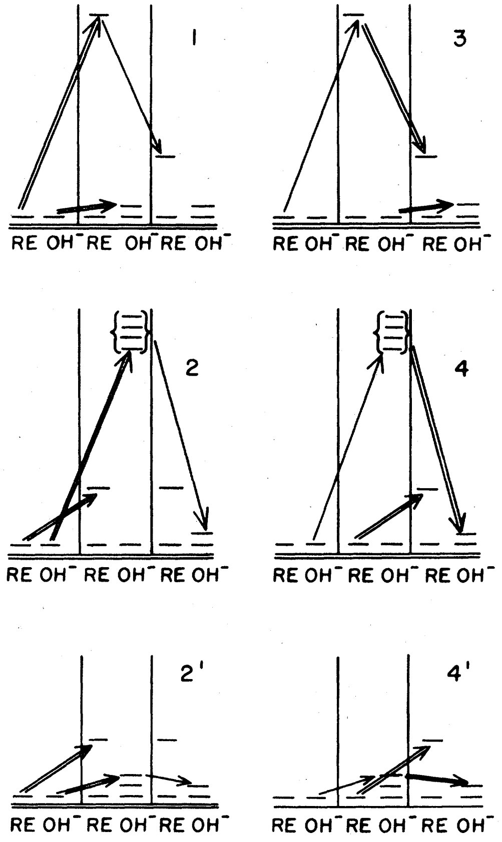

FIG. 2. Schematic representation of initial, intermediate, and final states for a cooperative absorption process. Double arrows correspond to electrostatic interactions, single arrows to radiative matrix elements.

and

$$P_{AB}^{(q-q)}=5\times 10^{18}(a_0/R)^{10}(\rho_E/\kappa^2)\ \mathrm{sec}^{-1}$$

from Eq. (3.6) where we have used Eqs. (3.7) and (3.8) to estimate the necessary RE matrix elements from the work of Weber[36] and Krupke[37] on LaF$_3$:Pr^{3+}. At 2.5 Å, $P_{AB}^{(q-q)}=8\times 10^{11}(\rho_E/\kappa^2)$ sec^{-1} and is larger than the rates estimated for other processes by at least three orders of magnitude. The observed lifetime of Pr^{3+}($^1D_2$) in LaF$_3$ has been observed to be 520 μsec,[36] in the absence of OH$^-$, so that transfer to OH$^-$ should quench the $^1D_2$ luminescence.

B. Cooperative effects

Approximate expressions are derived here for the squared radiative dipole moment matrix element for cooperative optical transition processes involving RE, OH$^-$ ion pairs. We use these expressions to make numerical estimates of the squared matrix elements for the effects involving specific RE and OH$^-$ transitions.

In deriving the expressions below, we include those excited states which we believe may make the dominant contributions to the squared matrix element. The squares of those terms in the matrix element that involve the RE-ion's excited configurations, the OH$^-$-ion's vibronic excited states, and the OH$^-$-ion's vibrational excited states are treated separately. If any one of these sets of excited states does not make a dominant contribution to the cooperative transition matrix element, there may be additions or cancellations between terms which are ignored here. Figure 2 is a schematic representation of the contributions to the cooperative transition matrix element considered here.

The first and third terms of Eq. (2.13) involve sums over excited configurations of the RE ion. We treat these terms using the methods employed by Kushida.[22] Expanding H'_{AB} in a multipole expansion and expanding the notation for RE states, we find the first term to be

$$\sum_{\substack{n'l'\\ \psi''J''M''}}\frac{1}{\kappa}\sum_{\substack{k_1k_2\\ q_1q_2}}\left(\frac{e^2}{R^{k_1+k_2+1}}\right)C_{q_1q_2}^{k_1k_2}(\Theta,\Phi)\,\langle 4f^{N-1}(n'l')\psi''J''M''|D_p^{(1)}(A)|4f^N\psi'J'M'\rangle$$
$$\times\frac{\langle 4f^N\psi JM|D_{q_1}^{(k_1)}(A)|4f^{N-1}(n'l')\psi''J''M''\rangle\,\langle 0\mu|M_{q_2}^{(k_2)}(B)|0\mu'\rangle}{E(4f^{N-1}(n'l')\psi''J''M'')-E(4f^N\psi JM)+\epsilon_{0\mu'}-\epsilon_{0\mu}}\ . \qquad (3.11)$$

The approximation methods introduced by Judd[26] and Ofelt[27] to calculate the oscillator strengths of optical transitions between levels of the $4f$ configuration in RE ions are used to simplify the evaluation of the sum over excited states. Peacock[28] has reviewed the theory of RE transition intensities and has included a didactic discussion of the tensor operator techniques and discussion of the validity of the Judd-Ofelt approximations. In this approximation an average energy denominator is introduced. This allows the following closure relationship to be used to sum the contributions from the excited configuration:

$$\sum_{J''M''\psi''}\langle 4f^N\psi JM|D_{q_1}^{(k_1)}|4f^{N-1}(n'l')\psi''J''M''\rangle\,\langle 4f^{N-1}(n'l')\psi''J''M''|D_p^{(1)}|4f^N\psi'J'M'\rangle$$
$$=\sum_{\lambda}(-1)^{q_1+p}(2\lambda+1)\begin{pmatrix}k_1 & \lambda & 1\\ q_1 & -(q_1+p) & p\end{pmatrix}\begin{Bmatrix}1 & \lambda & k_1\\ f & l' & f\end{Bmatrix}\langle 4f|r|n'l'\rangle\,\langle 4f|r^{k_1}|n'l'\rangle$$
$$\times\langle f||C^{(1)}||l'\rangle\,\langle l'||C^{(k_1)}||f\rangle\,\langle f^N\psi JM|U_{p+q_1}^{(\lambda)}|f^N\psi'J'M'\rangle\ . \qquad (3.12)$$

Here $\underline{U}^{(\lambda)}$ is a unit tensor operator. The third term of Eq. (3.13) can be treated similarly so that together the first and third terms contribute

$$\frac{1}{\kappa}\sum_{\substack{k_1k_2\\ q_1q_2}}\sum_{\lambda\ \mathrm{even}}\left(\frac{e^2}{R^{k_1+k_2+1}}\right)\Bigg[C_{q_1q_2}^{k_1k_2}(\Theta,\Phi)(-1)^{-q_1-p}(2\lambda+1)\Xi(k_1,\lambda)\begin{pmatrix}k_1 & \lambda & 1\\ q_1 & -(q_1+p) & p\end{pmatrix}$$
$$\times\langle f^N\psi JM|U_{p+q_1}^{(\lambda)}|f^N\psi'J'M'\rangle\,\langle 0\mu|M_{q_2}^{(k_2)}(B)|0\mu'\rangle\Bigg]\ ,$$

where

$$\Xi(k_1,\lambda)=2\sum_{n'l'}\begin{Bmatrix}1 & \lambda & k_1\\ f & l' & f\end{Bmatrix}\langle 4f|r|n'l'\rangle\,\langle 4f|r^{k_1}|n'l'\rangle\,\langle f||C^{(1)}||l'\rangle\,\langle l'||C^{k_1}||f\rangle/\Delta(n'l')\ . \tag{3.13}$$

Here $\Delta(n'l')$ is the average energy denominator for configuration $n'l'$. Contributions from odd λ terms cancel between the first and third terms of Eq. (2.13) upon introduction of an average energy denominator.

While we could estimate the squared magnitude of the expression above for a specific geometry, averaging out the dependence of the relative orientations of the ions allows a simpler expression to be derived. Written for dipole-dipole coupling, the contribution of the first and third terms to the square magnitude of Eq. (3.13) becomes

$$(10e^4/3\kappa^2R^6)\,\Xi^2(1,2)\,|\langle 0\mu|\underline{M}^{(1)}(B)|0\mu'\rangle|^2\,|\langle l^N\psi J||U^{(2)}||l^N\psi'J'\rangle|^2/(2J+1)\ ,$$

where (3.14)

$$\Xi(1,2)=2\sum_{n'l'}\begin{Bmatrix}1 & 2 & 1\\ f & l' & f\end{Bmatrix}\langle 4f|r|n'l'\rangle^2\,\langle f||C^{(1)}||l'\rangle\,\langle l'||C^{(1)}||f\rangle/\Delta(n'l')\ .$$

In obtaining this expression, we have summed over the polarization index of the radiative dipole moment operator, summed over the components of the RE-ion's final-state manifold, and averaged over the components of the RE-ion's initial-state manifold.

We derive approximate expressions for the squares of the second and fourth terms of Eq. (2.13) in the next paragraphs. We assume that the OH$^-$ ion has one most important electronic excited state similar to that observed in the alkali halides although we realize that this may not be correct. We label this electronic excited state 1 below and estimate its contribution to the squared matrix element.

We expand H'_{AB} to write the second term of Eq. (2.13) as follows:

$$\frac{1}{\kappa}\sum_{\mu''}\langle 1\mu''|\underline{M}^{(1)}(B)|0\mu'\rangle\sum_{\substack{k_1k_2\\ q_1q_2}}\left[\frac{e^2}{R^{k_1+k_2+1}}\right]C^{k_1k_2}_{q_1q_2}(\Theta,\Phi)\,\langle a|D^{(k_1)}_{q_1}(A)|a'\rangle$$
$$\times\langle 0\mu|M^{(k_2)}_{q_2}|1\mu''\rangle/(\epsilon_{1\mu''}-\epsilon_{0\mu}+\delta_{a'}-\delta_a)\ . \tag{3.15}$$

The part of the electric moment that depends on the nuclear coordinates does not contribute to matrix elements of the type $\langle 0\mu|\underline{M}^{(k)}|1\mu'\rangle$ because the electronic wave functions of the ground and excited states are orthogonal. We write these matrix elements as the product of an electronic matrix element and a Franck-Condon factor;

$$\frac{1}{\kappa}\langle 1|\underline{M}^{(1)}(B)|0\rangle\sum_{\substack{k_1k_2\\ q_1q_2}}\left[\frac{e^2}{R^{k_1+k_2+1}}\right]C^{k_1k_2}_{q_1q_2}(\Theta,\Phi)\,\langle a|D^{k_1}_{q_1}(A)|a'\rangle\,\langle 0|M^{(k_2)}_{q_2}(B)|1\rangle\sum_{\mu''}\frac{\langle\mu|\mu''\rangle\,\langle\mu''|\mu'\rangle}{(\epsilon_{1\mu''}-\epsilon_{0\mu}+\delta_{a'}-\delta_a)}\ . \tag{3.16}$$

If the splitting of the OH$^-$-ion's excited-state vibrational manifold is ignored, this expression is equal to zero because the excited-state's vibrational wave functions comprise a complete set and the ground-state's vibrational wave functions are orthogonal. Therefore, we approximate the sum of Franck-Condon factors, so as to account for this cancellation without ignoring the splitting, by placing the $|10\rangle$ state at its energy level and by considering the remaining states to be degenerate at the $|11\rangle$ level. For $\mu=0$ and $\mu'=1$ ($\mu=1$ and $\mu'=0$ gives the same result) this is done as follows:

$$\sum_{\mu''}\frac{\langle 0|\mu''\rangle\,\langle\mu''|1\rangle}{\epsilon_{1\mu''}+\delta_{a'}-\delta_a}\approx\sum_{\mu''}\frac{\langle 0|\mu''\rangle\,\langle\mu''|1\rangle}{\epsilon_{10}+\delta_{a'}-\delta_a}\times\left[1-\frac{\mu''\Delta}{\epsilon_{10}+\delta_{a'}-\delta_a}\right]\ .$$

The leading term of this expression vanishes. Further, because the product of Franck-Condon factors decreases rapidly for increasing μ'', it makes little difference if we ignore the splitting of vibrational levels with $\mu'' > 1$. Then the closure relationship may be used, i.e.,

$$-\sum_{\mu''\neq 0} \langle 0|\mu''\rangle\langle\mu''|1\rangle = \langle 0|0\rangle\langle 0|1\rangle \ .$$

$$\sum_{\mu''} \frac{\langle 0|\mu''\rangle\langle\mu''|1\rangle}{\epsilon_{1\mu''}+\delta_{a'}-\delta_a} \approx -\sum_{\mu''\neq 0} \frac{\Delta\langle 0|\mu''\rangle\langle\mu''|1\rangle}{(\epsilon_{10}+\delta_{a'}-\delta_a)^2}$$

$$\approx \frac{\Delta\langle 0|0\rangle\langle 0|1\rangle}{(\epsilon_{10}+\delta_{a'}-\delta_a)^2} \ . \qquad (3.17)$$

Here Δ is the spacing of the vibrational levels which we have taken to be roughly equal for the ground and excited OH^- electronic states.

The fourth term of Eq. (2.13) can be treated similarly. For RE transition energies of 1 eV or more and the assumed 6 eV excited-state energy of the OH^- ion, different energy denominators make it reasonable to neglect the smaller of the second and fourth terms with respect to the other. Therefore, we consider the square of each separately. For transitions on the OH^- ion between the $|00\rangle$ and $|01\rangle$ states, an approximate expression for the contribution of the larger of the second and fourth terms to the square magnitude of (2.13), written for quadrupole-dipole coupling, is

$$\left(\frac{e^4}{\kappa^2 R^8}\right) |\langle 0|\underline{M}^{(1)}(B)|1\rangle|^4 |\langle 0|0\rangle|^2 |\langle 0|1\rangle|^2$$

$$\times\left(\frac{\Delta}{(\epsilon_{10}-|\delta_a-\delta_{a'}|)^2}\right)^2$$

$$\times\frac{|\langle 4f^N\psi J||D^{(2)}(A)||4f^N\psi' J'\rangle|^2}{2J+1} \ . \qquad (3.18)$$

In obtaining this expression, we have, as usual, averaged over the relative orientations of the ions, summed over the polarization index of the radiative dipole moment operator, averaged over the components of the RE-ion's initial state, and summed over the components of the RE-ion's final state.

The vibrational excited states of the OH^- ion in its ground electronic state also contribute to the sums in the second and fourth terms of Eq. (2.13). We derive an approximate expression for the fourth term so that we may show later that vibrational intermediate states are unimportant. [See Eq. (3.21).]

We write the fourth term of Eq. (2.13) as follows where we have restricted the sum to the vibrational excited states and expanded H_{AB}':

$$\frac{1}{\kappa}\sum_{\mu''\neq\mu'} \langle 0\mu|\underline{M}^{(1)}(B)|0\mu''\rangle$$

$$\times\sum_{\substack{k_1k_2\\q_1q_2}} \left(\frac{e^2}{R^{k_1+k_2+1}}\right) C^{k_1k_2}_{q_1q_2}(\Theta,\Phi)$$

$$\times\frac{\langle 0\mu''|\underline{M}^{(k_2)}_{q_2}(B)|0\mu'\rangle\langle 0|D^{(k_1)}_{q_1}(A)|a'\rangle}{\epsilon_{0\mu''}-\epsilon_{0\mu'}+\delta_a-\delta_{a'}} \ .$$

$$(3.19)$$

For transitions between the $|00\rangle$ and $|01\rangle$ states of the OH^- ion, we consider only the $\mu''=2$ term in the sum over excited states because this should give the dominant contribution assuming that the energy denominator is nonzero for the other μ''. With these simplifications and approximations similar to those we have made above, the squared contribution of the fourth term is

$$\frac{1}{\kappa^2}\sum_{k_1k_2}\left(\frac{e^2}{R^{k_1+k_2+1}}\right)^2 \frac{[2(k_1+k_2)]!}{(2k_1+1)!(2k_2+1)!}$$

$$\times|\langle 0\mu|\underline{M}^{(1)}(B)|02\rangle|^2|\langle 02|M^{(k_2)}_{q_2}(B)|0\mu'\rangle|^2$$

$$\times\frac{|\langle 4f^N\psi J||D^{(k_1)}(A)||4f^N\psi' J'\rangle|^2}{(2J+1)(\epsilon_{02}-\epsilon_{0\mu'}+\delta_a-\delta_{a'})^2} \ . \qquad (3.20)$$

The second term could be treated in much the same way.

In the following subsections, we use Eqs. (3.14) and (3.18) to estimate squared matrix elements for the cooperative absorption and cooperative transfer and emission processes and their inverses. In our estimates Eqs. (3.14) and (3.18) give the dominant dipole-dipole and quadrupole-dipole contributions respectively, to the squared matrix element. As we have remarked previously, RE, OH^- pair separations may be as small as about 2.5 Å. At this separation our dipole-dipole and quadrupole-dipole estimates are of the same magnitude. We show that these do not interfere as follows.

We discuss what cross terms have been neglected to arrive at our approximate expressions. Squaring Eq. (2.13) doubles the number of summation indices. One could introduce the multipole expansion (3.3) and average the square magnitude of Eq. (2.13) over Θ and Φ before separating into terms summed over RE and OH^- excited states. The orthonormality relationship for the spherical harmonic in $C^{k_1k_2}_{q_1q_2}(\Theta,\Phi)$ causes those terms for which $k_1+k_2\neq k_1'+k_2'$ to vanish. Further we ignore cross terms for which $k_1\neq k_1'$ and $k_2\neq k_2'$ to arrive at our expressions.

This means that after performing the averages over Θ and Φ, cross terms between the dipole-dipole and quadrupole-dipole terms vanish, so that here, there is no interference between those contributions to the squared matrix element which we believe are largest. Now one could separate the resulting expression into terms summed over RE and OH^- excited states, neglecting cross terms, and proceed to our final expressions.

Here we find Eqs. (3.18) and (3.14) to give squared radiative dipole matrix elements of the same order of magnitude in spite of the fact that Eq. (3.18) involves higher-order mulitpole coupling and that there is cancellation of the greater part of the contribution of the OH^- electronic state. This is so because the dipole matrix element for the OH^- stretching transition appearing in Eq. (3.14) is small compared to matrix elements for electronic transitions. The squared matrix element for the OH^- vibrational transition is reduced from that of an electronic transition by the ratio of an electronic mass to the OH^- reduced mass. Further, an oscillator strength of 5×10^{-3} implies an oscillating effective charge of only 0.07 e. While there is not much one can do about the large mass, the squared matrix element for the OH stretching vibration in the bulk of liquid water say, is about a factor of 100 greater than that we have used. An increased OH vibrational matrix element would allow Eq. (3.18) to be ignored as one might have expected. As we have already stressed, the matrix elements we have used are not generally applicable for OH stretching vibration in all environments.

The contributions of coupling mechanisms other than dipole-dipole for Eq. (3.14) and quadrupole-dipole for Eq. (3.18) have been estimated for cases where we thought they might be of importance. In the systems we have investigated and in the framework of the approximations we have made here other coupling mechanisms give contributions reduced by a factor of at least about 5 (usually more like 10) with respect to those of Eqs. (3.14) and (3.18) for pair separations of 2.5 Å.

We discuss further details of the evaluation of Eqs. (3.14) and (3.18). The first and third terms of Eq. (2.13) are shown schematically in Fig. 2. In both terms the excited configuration is connected to the $4f$ configuration by a radiative dipole moment matrix element. Therefore, only the d and g excited configurations are considered. We estimate $\Xi(1,2)$ by placing the $5d$ states at $\Delta(5d)$ and by placing all remaining d states including split shells at $\Delta(6d)$.[38] These average energy denominators are estimated from Dieke's diagram[32] of the relative positions of the free ion configurations. The g states are all placed at $\Delta(5g)$ where we linearly interpolate Judd's[26] estimate of the $5g$ energy denominator over the series of RE ions and remove his correction for ions in complexes by adding $10^5\ \text{cm}^{-1}$ to his reported energies. Radial matrix elements and reduced matrix elements of tensor operators are estimated as in the energy-transfer calculations.

In evaluating Eq. (3.18) we take ϵ_{10} to be 6 eV and $\Delta=3600\ \text{cm}^{-1}$. The oscillator strength of the uv absorption band of the OH^- ion in the alkali halides is typically about 0.12,[11] from which we estimate $|\langle 0|\underline{M}^{(1)}(B)|1\rangle|^2=0.8a_0^2$. The emission spectrum for uv excitation at about 6 eV as observed by Patterson and Kabler[12] in KBr:KOH shows bands corresponding to transitions from an excited electronic state to the vibrational levels of the ground electronic state. We estimate roughly that $|\langle 0|0\rangle|^2=1$ and $|\langle 1|0\rangle|^2=0.1$.

To finish this section, we compare the expression derived for the terms summed over OH^- excited vibronic states to those derived for these same terms summed over the OH^- excited vibrational states. The ratio of Eq. (3.18) to Eq. (3.20), both written for a quadrupole-dipole process, is

$$\frac{|\langle 1|\underline{M}^{(1)}(B)|0\rangle|^4|\langle 0|0\rangle|^2|\langle 0|1\rangle|^2[\Delta/(\epsilon_{10}-|\delta_a-\delta_{a'}|)^2]^2}{|\langle 02|\underline{M}^{(1)}(B)|01\rangle|^2|\langle 00|\underline{M}^{(1)}(B)|02\rangle|^2/(\epsilon_{02}-\epsilon_{01}+\delta_{a'}-\delta_a)^2}\ . \tag{3.21}$$

We take 5 eV for the energy denominator on top and 0.5 eV for the energy denominator on the bottom. The matrix element, $|\langle 00|\underline{M}^{(1)}(B)|02\rangle|^2$, is estimated as in the energy-transfer calculations from the observed area of the first OH^- overtone band. We estimate this ratio, Eq. (3.21), to be about 10^4.

We also estimate the ratio of Eqs. (3.18) to (3.20) with Eq. (3.18) written for quadrupole-dipole coupling and Eq. (3.20) written for quadrupole-quadrupole coupling because the quadrupole moment matrix element of the OH^- ion may give better coupling than the dipole moment matrix element for the $|00\rangle$ and $|02\rangle$ states. The ratio is

$$\frac{|\langle 1|\underline{M}^{(1)}(B)|0\rangle|^4|\langle 0|0\rangle|^2|\langle 0|1\rangle|^2[\Delta/(\epsilon_{10}-|\delta_a-\delta_{a'}|)^2]^2}{(14/5R^2)|\langle 02|\underline{M}^{(1)}(B)|01\rangle|^2|\langle 00|\underline{M}^{(2)}(B)|02\rangle|^2/(\epsilon_{02}-\epsilon_{01}+\delta_{a'}-\delta_a)^2}\ . \tag{3.22}$$

We estimate $|\langle 00|\underline{M}^{(2)}(B)|02\rangle|^2$ as before from the theoretical calculation of Cade.[34] We find the ratio (3.22) to be about 10^2.

We find that we may neglect the sum over the vibrational excited states with respect to the sum over the vibronic states even with the cancellation of the greater part of the latter. Increased OH vibrational matrix elements could make Eqs. (3.20) and (3.18) of comparable magnitudes. However, in this case Eq. (3.14) is also enhanced so that we believe that it is unlikely that the contributions of vibrational excited states could be of importance.

1. *Cooperative absorption and simultaneous emission and transfer for* Tb^{3+}, OH^- *ion pairs*

We estimate the squared radiative dipole moment matrix elements for the cooperative absorption process and the simultaneous emission and energy-transfer process for a Tb^{3+}, OH^- pair. The oscillator strength or spontaneous emission probability is then calculated for a nearest-neighbor pair and an estimate is made of the ratio of emission band areas for a two-center transition to that of the corresponding electronic, Tb^{3+} transition. The Tb^{3+} states $^5D_4$ and ^7F_J, $J=2$ to 6, are of particular interest, the $^5D_4$ state being about 20500 cm^{-1} above the $^7F_6$ ground state.

We consider first the following cooperative absorption process. Tb^{3+} and OH^-, initially in their ground states, make simultaneous transitions $^7F_6 \rightarrow {}^5D_4$ and $00 \rightarrow 01$ by the absorption of a photon. The dipole-dipole and quadrupole-dipole coupling contributions to the squared radiative dipole moment matrix element are $1.1\times10^{-7}\ a_0^8/\kappa^2R^2$ and $7.4\times10^{-6}\ a_0^{10}/\kappa^2R^8$ respectively from Eqs. (3.14) and (3.17). Here and in the following the sources of radial matrix elements and energy denominators are as given in the paragraph preceding Eq. (3.21). We have used the values

$$\Delta(5d)=0.8\times10^5\ \text{cm}^{-1},\quad \Delta(5g)=2.9\times10^5\ \text{cm}^{-1}\ ,$$

$$\Delta(6d)=2.1\times10^5\ \text{cm}^{-1},\quad \langle 4f|r|5d\rangle=0.71a_0\ ,$$

$$\langle 4f|r^2|4f\rangle=1.04a_0^2\ ,$$

and the reduced matrix element,

$$|\langle f^{8}\,{}^7F_6||U^{(2)}||f^{8}\,{}^5D_4\rangle|^2=6.6\times10^{-4}\ ,$$

as given by Kuboniwa and Hoshina.[39]

We take $R=2.5$ Å and $\kappa^2=10$ ($n\approx1.8$) to estimate the oscillator strength $f=3\times10^{-13}$ from the sum of the contributions to the squared matrix element given above for simultaneous $Tb^{3+}(^7F_6\rightarrow{}^5D_4)$ and $OH^-(00\rightarrow01)$ transitions using the following equation:

$$f=\frac{2m\omega}{3\hbar}|\langle a00|\underline{D}^{(1)}(A)+\underline{M}^{(1)}(B)|a'01\rangle|^2\ . \quad (3.23)$$

Here $\hbar\omega$ is the energy of the absorbed light and m is the electronic mass. A factor accounting for the degeneracy of the initial state has already been included in our expressions for the squared matrix element.

The cooperative absorption process could be detected by $Tb^{3+}(^5D_4)$ emission upon excitation of the two-center band. We do not estimate the intensity of emitted light because we expect $Tb^{3+}(^5D_4)$ to be depopulated not only by radiative but also by radiationless processes (especially the presence of OH^-). We can estimate the ratio of excitation band areas for direct and two-center excitations however, because the nonradiative decay rate will be the same for both excitations. (We ignore the fact that the OH^- ion is excited in the two-center absorption process because we expect it to dissipate its energy very quickly.) We consider a Tb^{3+} ion with one and just one OH^- nearest neighbor and we neglect two-center absorption processes involving more distant OH^- ions. The ratio of the areas of the excitation bands for direct and two-center excitations will be given then by the ratio of the transition rates for the direct and two-center absorptions which, for equal intensity excitations, is equal to the ratio of the oscillator strengths divided by the transition energies. A typical oscillator strength for a $Tb^{3+}(^7F_6\rightarrow{}^5D_4)$ transition[40] is about 3×10^{-8} from which we estimate the ratio of emission band areas to be 10^{-5}. Although small, the cooperative excitation may be detectable because excitation in the absence of OH^- should be essentially zero.

Excited Tb^{3+} may make a $^5D_4\rightarrow{}^7F_{J'}$, $J'=0$ to 6, transition by the simultaneous emission of a photon and energy transfer to a nearby OH^- ion which makes a $00\rightarrow01$ transition. For Tb^{3+} final states with $J'=2$ to 6 our treatment of this emission process is much the same as that of the two-center absorption process we have just discussed. Transitions involving $J'=0, 1$ final states are not discussed here because these require a somewhat different treatment involving weaker electric multipole coupling than for $J'=2$ to 6.

The results for the Tb^{3+}, OH^- emission and transfer process are given in Table I. We have used the reduced matrix elements of the unit tensor operator tabulated by Kuboniwa and Hoshina[39] and the values of average energy denominators and radial matrix elements given in the preceeding paragraphs to evaluate Eqs. (3.14) and (3.18). The spontaneous emission probability is calculated using the equation

$$A=\frac{4e^2\omega^3}{3\hbar c^3}\chi|\langle a00|\underline{D}^{(1)}(A)+\underline{M}^{(1)}(B)|a'01\rangle|^2\ . \quad (3.24)$$

Here, $\hbar\omega$ is the energy of the emitted photon and $\chi=\frac{1}{9}n(n^2+2)^2$. (We have taken $\chi=5$, for $n\approx1.8$.) As with the oscillator strength, Eq. (3.23), a factor accounting for the degeneracy of the initial-state level has been included in Eqs. (3.14) and (3.18).

The ratio of quantum yields for a two-center emission process and the corresponding electronic RE emission process is given by the ratio of the spontaneous emission probabilities. This ratio for simultaneous $\mathrm{Tb}^{3+}({}^5D_4 \rightarrow {}^7F_3)$ and $\mathrm{OH}^-(00 \rightarrow 01)$ transitions is estimated to be 10^{-5} for a Tb^{3+} ion with one OH^- neighbor at $R = 2.5$ Å in a crystal with an index of refraction of about $n = 1.8$. We have estimated the $\mathrm{Tb}^{3+}({}^5D_4 \rightarrow {}^7F_3)$ spontaneous emission probability to be about 30 sec^{-1} from the Judd-Ofelt intensity parameters and magnetic dipole emission probability reported by Weber *et al.*[41] Again, this small intensity should be measurable because in the absence of OH^- there should be essentially no emission at 12 600 cm^{-1}.

We wish to stress that the experiments suggested in this section and Sec. III B 2 can be performed for RE, OD^- pairs as well as RE, OH^- pairs. Substitution of OD^- for OH^- should shift a two-center emission or absorption band by about 1000 cm^{-1} because of the difference in stretching energies. This shift should aid greatly in the identification of the effects we propose.

2. *Cooperative absorption, simultaneous emission and transfer, and their inverses for* Yb^{3+}, OH^- *pairs*

We estimate the squared radiative dipole moment matrix elements for two-center absorption and emission processes involving Yb^{3+}, OH^--ion pairs. Oscillator strengths or spontaneous emission probabilities are calculated for a nearest-neighbor pair.

The excited $\mathrm{Yb}^{3+}({}^2F_{5/2})$ level is at an energy of 1×10^4 cm^{-1} above the ${}^2F_{7/2}$ ground-state level. Yb^{3+} and OH^-, initially in their ground states, can absorb a photon to make simultaneous ${}^2F_{7/2} \rightarrow {}^2F_{5/2}$ and $00 \rightarrow 01$ transitions. Using Eqs. (3.14) and (3.18) we estimate the squared radiative dipole moment matrix element for such a process to be $9.4 \times 10^{-6}(a_0^8/\kappa^2R^6)$ and $2.7 \times 10^{-4}(a_0^{10}/\kappa^2R^8)$ for dipole-dipole and quadrupole-dipole coupling respectively. We have used the values

$$\langle 4f|r|5d\rangle = 0.551\,a_0, \quad \langle 4f|r^2|4f\rangle = 0.691\,a_0^2 \;,$$

$$\Delta(5d) = 1.0 \times 10^5\ \mathrm{cm}^{-1}, \quad \Delta(6d) = 2.3 \times 10^5\ \mathrm{cm}^{-1} \;,$$

$$\Delta(5g) = 3.2 \times 10^5\ \mathrm{cm}^{-1} \;,$$

and

$$|\langle f^{13}\,{}^2F_{7/2}||U^{(2)}||f^{13}\,{}^2F_{5/2}\rangle|^2 = \tfrac{6}{49} \;.$$

Our expressions (3.14) and (3.18) are cast in a form such that other two-center optical processes involving the same levels have the same estimate of the squared radiative dipole moment matrix element as that for cooperative absorption if corrected by a factor to account for the reversed roles of initial and final states in emission processes. We take $R = 2.5$ Å and $K^2 = 10$ to estimate oscillator strengths and spontaneous emission probabilities from the sum of the dipole-dipole and quadrupole-dipole contributions. The oscillator strength for the cooperative absorption process is estimated to be $f = 8 \times 10^{-12}$. We have used Eq. (3.23) with $\hbar\omega = 13600$ cm^{-1}, the sum of the Yb^{3+} and OH^- transition energies. The same estimate for the squared matrix element is used to calculate the oscillator strength of the process in which Yb^{3+}, initially in its ground state, is excited to its ${}^2F_{5/2}$ state by simultaneous photon absorption and energy transfer from an excited OH^- ion. The energy of the absorbed photon, $\hbar\omega = 6400$ cm^{-1}, is that of the Yb^{3+} transition less the energy of the OH^- stretching excitation. We have used Eq. (3.23) to calculate $f = 4 \times 10^{-12}$ for this process.

For emission processes the squared matrix element given above is multiplied by $(2J'+1)/(2J+1)$ ($\frac{8}{6}$ for Yb^{3+}). An excited Yb^{3+} ion and an OH^- ion in its ground state can make simultaneous ${}^2F_{5/2} \rightarrow {}^2F_{7/2}$ and $00 \rightarrow 01$ transitions, emitting a photon. For this simultaneous emission and transfer process we estimate $A = 7 \times 10^{-4}$ sec^{-1}. We have used Eq. (3.24)

TABLE I. Energies, matrix elements, and spontaneous emission probabilities for simultaneous $\mathrm{Tb}^{3+}({}^5D_4 \rightarrow {}^7F_{J'})$ and $\mathrm{OH}^-(00 \rightarrow 01)$ transitions.

J'	$\hbar\omega$ (10^3 cm^{-1})	$\vert\langle a00\vert\underline{D}^{(1)}(A)+\underline{M}^{(1)}(B)\vert a'01\rangle\vert^2$		A for $R = 2.5$ Å and $\kappa^2 = 10$ (10^{-3} sec^{-1})
		$d-d$ ($10^{-7}a_0^8/\kappa^2R^6$)	$q-d$ ($10^{-5}a_0^{10}/\kappa^2R^8$)	
6	16.9	1.5	0.66	0.2
5	14.9	34	15	3
4	13.6	0.78	0.34	0.05
3	12.6	6.3	2.7	0.3
2	12.0	2.1	0.90	0.1

with the energy of the emitted photon, $\hbar\omega = 6400$ cm^{-1}, and $\chi = 5$. If Yb^{3+} and OH^- are both excited initially then a cooperative luminescence process is possible with light being emitted at $\hbar\omega = 13\,600$ cm^{-1}. We estimate $A = 7 \times 10^{-3}$ sec^{-1} for this process. Experiments involving OH^- ions in vibrationally excited initial states, such as the cooperative luminescence experiment suggested here, would require intense excitation at 3600 cm^{-1} to maintain a high population of excited OH^-.

IV. CONCLUSION

In this paper we have taken the point of view used to explain effects involving RE-ion pairs to discuss effects involving RE, OH^- pairs and to estimate the strength of these effects for several specific transitions. While we have used parameters which describe RE and OH^- impurities in specific crystals, we expect these effects to be observable in a wide range of materials including glasses and liquids. Further, similar effects may be observed with other centers which have high-energy vibrational modes. In the following paragraphs we make further comments about possible experiments involving the energy-transfer and two-center transition processes we have proposed.

We have estimated the rate of energy transfer to OH^- to be several orders of magnitude larger than the radiative decay rates of RE excited states, even for only fair overlap of RE and OH^- transition energies. We expect therefore, energy-transfer processes involving dilute concentrations of OH^- to be easy to observe but perhaps not always easy to characterize unambiguously. Several luminescence quenching processes involving centers with internal vibrational modes are possible; for example there are processes involving direct transfer to the fundamental mode or to overtone modes and phonon-assisted process. It may not be easy to add a dilute concentration of OH^- or OD^- to a RE-doped material and identify the mechanisms by which particular levels are depopulated and luminescence quenched simply by the consideration of energy matching for the RE and OH^- (or OD^-) transitions (as we have proposed for Er^{3+}, OH^- pairs). These are, of course, only possible pitfalls. Crystals containing dilute concentrations of trivalent RE ions and OH^- ions have not been studied previously to the knowledge of the authors although in glasses doped with RE ions, the problem seems to be getting OH^- out, not in.[15] An experiment in which the lifetimes of the excited states of say Er^{3+} were measured, perhaps in a glass in which Er^{3+} luminescence is observed in the absence of OH^-, and with dilute concentrations of OH^- or OD^- added would surely be of interest.

Riseberg and Weber,[2] as an example of how relaxation phenomena may be used in laser design, discuss how the $Tb^{3+}(^5D_4)$ level is populated by optical pumping of levels above $^5D_3$ and how a concentration quenching mechanism allows the $^5D_3$ to $^5D_4$ gap to be bridged in a laser made by Jensen *et al.*[42] We remark that a dilute concentration of OH^- or OD^- added to a material including Tb^{3+} and without high-energy lattice modes would bridge the $^5D_3$ to $^5D_4$ by energy transfer to OH^- or OD^-. The $^5D_4 \rightarrow {}^7F_J$ transitions would be affected less by the addition of OH^- or OD^- because a larger number of stretching quanta are needed to bridge this gap.

The two-center optical transition probabilities we have calculated for nearest-neighbor RE, OH^- pairs may be compared to those calculated by Kushida[22] for nearest-neighbor RE pairs. For a cooperative absorption process involving a pair of Yb^{3+} ions at nearest-neighbor sites, Kushida has estimated an oscillator strength of $f = 1 \times 10^{-11}$. For a pair of excited Yb^{3+} ions, he has estimated the spontaneous emission probability for a cooperative luminescence process to be $A = 2.6 \times 10^{-2}$ sec^{-1}. For both processes, dipole-quadrupole and quadrupole-dipole coupling provide the dominant interaction mechanism. For a nearest-neighbor Yb^{3+}, OH^- pair we have estimated $f = 8 \times 10^{-12}$ and $A = 7 \times 10^{-3}$ sec^{-1} for cooperative absorption and cooperative luminescence processes respectively. Although these differ by only a small factor from Kushida's estimates for these processes involving an Yb^{3+} pair, differences in the method of calculation should be noted. We have included a factor $1/\kappa^2 = 0.1$ in our estimates of squared matrix elements to account for the screening of the Coulomb interaction in a dielectric medium. While we include this factor for nearest-neighbor ion pairs, we note that perhaps it does not belong for such small separations. Kushida has not included such a factor in his estimates and if we were to ignore it also, our estimates of transition probabilities would be larger than those of Kushida by a factor of about 3 to 10.

In the consideration of RE, OH^- pairs and vibrational excitations of the OH^- ion, intermediate states of the OH^- ion have required a treatment different from that for the RE ion. For the purpose of making an order-of-magnitude estimate of the contribution of OH^- intermediate states to transition probabilities for cooperative optical processes, we have neglected all but the lowest-lying electronic excited state of the OH^- ion and its vibrational manifold and have taken this state to be characterized by what is observed for OH^- impurities in alkali-halide hosts. A comparison of our results with those of Kushida should not be taken too seriously because different approximations involving a different (vibronic) type of excited state have been made and found to be important.

Further, while the transition probabilities we predict are of about the same size as those estimated by Kushida, this circumstance alone does not determine that a process involving a RE, OH^- pair can be observed as easily as a process involving a RE-ion pair for the following reasons. The presence of OH^- tends to quench the RE luminescence one might hope to observe. It might be difficult to observe luminescence associated with a two-center optical process in, say, Pr^{3+} where the energies of only one or two OH^- stretching quanta separate electronic levels. Further, because we expect the lifetimes of the vibrational OH^- excited state to be small[43] compared to RE excited-state lifetimes of milliseconds, effects in which OH^- need be populated initially will be more difficult to observe than the corresponding effects involving RE-ion pairs. Up-conversion processes involving RE, OH^- ion pairs, while possible, would be relatively inefficient. Operationally it is usually perhaps more significant to consider the OH^- ion as an energy sink. We remark here that up-conversion processes could perhaps be observed if the OH^- ion were pumped with, say, an infrared laser.

As mentioned in the Introduction, straightforward experiments involving crystals which have already been studied, namely the hydrated RE salts and the RE trihydroxides, could be done to observe the two-center optical transitions we have proposed. The large gap, RE transitions $Gd^{3+}(^6P_{7/2} \rightarrow {}^8S_{7/2})$, $Tb^{3+}(^5D_4 \rightarrow {}^7F_J)$, and $Eu^{3+}(^5D_0 \rightarrow {}^7F_J)$ are of particular interest because the excited states are not depopulated by nonradiative processes as quickly as for transitions involving smaller RE excitation energies so that the effects we propose might have appreciable quantum yields. Further, dilute concentrations of D_2O or OD could be introduced in crystals made with H_2O or OH and vice versa, so that the interactions of dynamically decoupled OD or OH oscillators with RE ions could be studied.

We believe experiments involving Tb^{3+} would be simplest because excitation energies of interest are in the visible or near ultraviolet and the luminescence to be detected is in the visible. The gaps above and below $Tb^{3+}(^5D_4)$ aid further the observation of the effects we propose. Two-center optical transitions give rise to much weaker absorption and emission bands than those normally observed for electronic RE transitions and therefore, a two-center band must be well separated from purely electronic bands if it is not to be masked. Estimates of the emitted intensity associated with two-center transitions compared to that associated with electronic RE transitions such as we have made for Tb^{3+} should be helpful in deciding whether specific experiments are feasible.

The study of the optical properties of RE ions in a variety of systems has provided a probe of the local structure of the ion's environment. Some techniques exploit the luminescence quenching process involving OH. For example, the luminescence of trivalent lanthanides which have been added to biological systems has been of recent interest. One idea of Horrocks *et al.*[44] has been to measure the luminescence decay constant of a RE ion which is bonded to a macromolecule thereby extracting information about the RE-ion's environment. As a preliminary experiment, they have determined the number of water molecules surrounding a RE ion in several solutions. The techniques of luminescence spectroscopy, as a probe of the structure of oxidic catalysts has recently been reviewed by Pott and Stork.[45] One idea discussed involves determining whether metal ions are on the surface or in the bulk of an oxidic system by whether they are coordinated to OH ions as determined by luminescence quenching.

The two-center optical transitions we have proposed provide the possibility of observing spectral structure associated with specific intramolecular vibrational modes of centers near RE ions. This provides a very powerful probe of the RE-ion's environment. With the observation of RE, OH^- pair transitions not only is it possible to identify OH^- as a near neighbor of the RE ion unambiguously, one can also measure the spectrum of the OH^- stretching vibration for OH^- ions in the immediate neighborhood of the RE ion. In experiments involving the spectra of RE ions in aqueous solution,[20] motivated by this work, information has been extracted about the nature of the hydrogen bonding between solvation shells of RE ions from the measurement of the OH stretching energy for water molecules in the first solvation shell of the RE ion.

The lineshape of the two-center band associated with a RE parent state J would be the convolution of the RE band's $J \rightarrow J'$ lineshape and the OH^- band's lineshape if all RE sublevels were degenerate. In the theory we have developed, we have ignored the details of the structure of the bands arising from RE transitions $J \rightarrow J'$. Therefore, for RE transitions with obvious structure, it will not be possible to determine the details of the OH^- band's lineshape from a measurement of the two-center band's lineshape unless the OH^- band is much broader than the RE band. For some transitions of interest this may be the case so that the OH^- band's lineshape, for those OH^- ions near RE ions, may be extracted from the lineshape of two-center bands.

Subsequent to the preparation of this manuscipt we have been informed of a paper by Sierro[46] in which OH^- impurities are believed to occupy Gd^{3+} nearest-neighbor sites in CaF_2. In the ESR spectrum of Gd^{3+} lines are observed and assigned to Gd^{3+} at sites for which the crystalline field symmetry has been altered by the substitution of OH^- for F^-. Other more recent ESR studies of RE ions with OH^- nearest neighbors are cited by Heist.[47] Unfortunately these authors do not include information about the infrared or ultraviolet spectra of the OH^- ion.

We have also become aware of work[48] in which vibronic bands involving RE ions and H_2O molecules have been observed.

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$$\langle 4f|r^t|5d\rangle \langle 4f|r|5d\rangle \approx \langle 4f|r^{t+1}|4f\rangle \ ,$$

even if one were to perform a closure over all configurations $4f^{N-1}nd$ and to include also contributions from closed shells it would make little difference in the result. For $t=1$, the case of interest here, the approximate equality above is not valid for the radial matrix elements Judd has estimated so that while d states other than $5d$ make only a small contribution, we include them.

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