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A quantum electrodynamical theory of three-center energy transfer for upconversion and downconversion in rare earth doped materials

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Three-center energy transfer affords the basic mechanism for a variety of multiphoton processes identified within materials doped with rare earths. Addressing the theory using quantum electrodynamics, general results are obtained for systems in which the fundamental photophysics engages three ions. Distinct cooperative and accretive mechanistic pathways are identified and the theory is formulated to elicit their role and features in energy transfer phenomena of pooling upconversion, sensitization, and downconversion or quantum cutting. It is shown that although the two mechanisms play significant roles in pooling and cutting, only the accretive mechanism is responsible for sensitization processes. Both mechanisms are shown to invoke Raman selection rules, which govern transitions of the mediator ions in the accretive mechanisms and transitions of the acceptor ions in the cooperative mechanisms. The local, microscopic level results are used to gauge the lattice response, encompassing concentration and structural effects. Attention is drawn to a general implication of implementing a multipolar description for the optical properties of doped solid-state ionic materials. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1323958]

I. INTRODUCTION

From the early days of photophysics it has been known that the electronic energy of an excited donor species can migrate to a nearby acceptor without a requirement for wave function overlap. The process, generally known as resonance energy transfer (RET), was first shown by Förster[1] to be a Coulombic interaction with a distance dependence following an inverse sixth power law, over separations in the order of tens of Ångströms. Today Förster energy transfer is a topic of great significance in a large variety of photophysical systems, for example occupying a crucial role in the delivery of excitation energy to the reaction center in photosynthesis.[2,3] As the distance between donors and acceptors is increased, RET acquires an increasingly radiative emission-absorption character, ultimately under the jurisdiction of an inverse square law—a feature which exerts a significant effect on fluorescence within optically thick samples, through the reabsorption of emitted photons.[4] Both these processes and their interplay are fully encompassed within the unified theory formulated by Andrews,[5] following ground-breaking quantum-mechanical work by Avery[6] and also by Gomberoff and Power[7] alongside the classical treatment by Kuhn.[8] At distances shorter than the Förster regime, inside wave function overlap, energy transfer is dominated by an exchange mechanism due to Dexter.[9]

It is widely acknowledged that resonance energy transfer plays a highly important role in the photophysics of rare earth or lanthanide (Ln^{3+}) doped crystals (also glasses and vitroceramics). The relative positioning of the lanthanide energy levels generally affords excellent opportunities for the design of materials to invoke not only conventional RET, but also higher order effects.[10–12] One of the main thrusts of our research concerns the identification of features in the theory underlying such effects as fall under the umbrella term of *upconversion* (in which low-frequency photoexcitation energy is converted to a higher frequency), often designed as a basis for laser emission.[13] Through the necessary involvement of three ions rather than two (the donor and acceptor in conventional RET), this process shares common theoretical ground with *sensitization*, where a dopant assists the conveyance of excitation between donor and acceptor, and also *quantum cutting* (degenerate downconversion), which is formally the time-inverse of upconversion. All of these phenomena are commonly studied in materials doped with rare earths.

In this paper, development of the general theory allows a consistent treatment of all the above processes, allowing elucidation of their common features and highlighting of their fundamental differences. The following section establishes an identity for the singular role in each process of the third ion with respect to the two other participants. In each case the processes of initial donor excitation and subsequent acceptor fluorescence, entailing conventional and physically separable mechanisms, are outside the scope of our discussion. Section III contains a detailed formulation of the general mechanisms for three-center energy transfer, and the application of these mechanisms to lanthanide-doped systems is elucidated in Sec. IV. In Sec. V the implications of symmetry selection rules are considered; finally, a quantification of lattice distributional factors is presented in Sec. VI.

II. PERSPECTIVE ON THREE-CENTER ENERGY TRANSFER

A. Backdrop

A variety of photophysical processes involving the rare earths were initially proposed by Dexter[14] and

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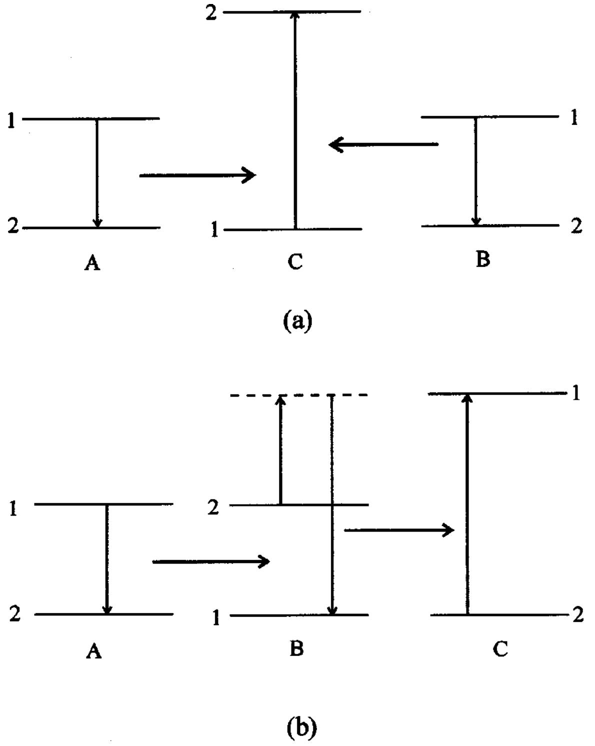

FIG. 1. Energy level diagrams for three-center energy pooling: (a) cooperative mechanism, (b) accretive mechanism.

Bloembergen[15] in the 1950's, suggesting the deployment of RET to relay excitation between lanthanide ions in various media. In practice, it was with the development of laser technology in the 1960's that the predicted higher-order effects were experimentally observed. Alongside such technological advancements, pioneering work by Brown and Shand[16] first realized infrared (IR) quantum counter action (IRQC) in physical systems containing Pr^{3+}, Dy^{3+}, Er^{3+}, and Ho^{3+}. The IRQC system involved the *upconversion* of IR photons to the visible via their ''addition,'' facilitated by the excited energy levels of each rare earth. It was here too that one of the first instances of the *sensitization* of rare earth ions was accredited. Esterowitz *et al.*[17] considered a system containing two different ionic species, wherein pump IR photons were absorbed by a sensitizer Yb^{3+} ion (the donor) which, following a degree of internal relaxation, transferred its excitation to a Ho^{3+} ion (the acceptor), utilizing RET. In order to yield the observed fluorescence the acceptor was required to be either in an excited state, or to be subsequently excited by a second pump. Auzel[18] has conveniently and succinctly summarized the energetic intricacies of one-, two-, and three-body photophysical processes for the lanthanides. As the present work is primarily concerned with three-body interactions, we identify and represent three such categories (*vide infra*) of ABC systems, following Auzel, in Figs. 1–3.

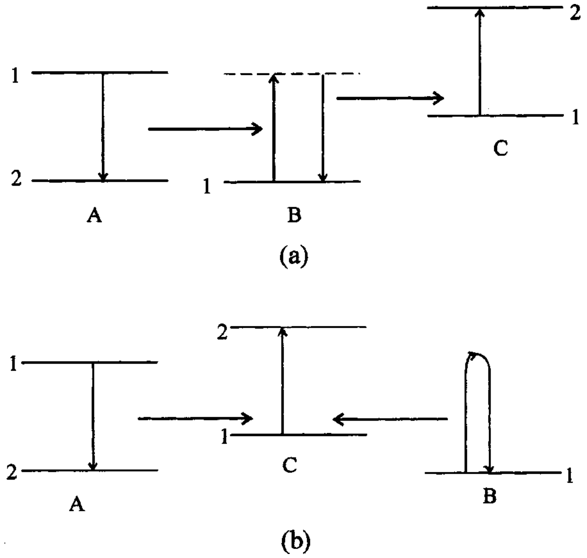

FIG. 2. Energy level diagrams for sensitization: (a) accretive, (b) cooperative (defunct in this case, see text).

B. Pooling processes

The pooling of excitation energy from a number of donors at a single acceptor is a process identifiable (under various guises) in rare earth photophysics; the essential energetics are shown in Fig. 1. Here we focus on the case where the transfer of energy from two excited donors (A* and B*) promotes an acceptor (C) to a state with approximately twice the energy of the initial excitation, a process commonly but not invariably categorized as *upconversion*. Two-photon upconversion has been identified in the literature under many aliases: *(i) two-photon APTE*[19] (*Addition de Photons par Transferts d'Energie*) whereby isolated ions (usually Yb^{3+}) transfer their energy one photon at a time (via RET) to an amenable acceptor, mediated by conveniently spaced acceptor energy levels. This process is also known as *sequential* or *stepwise upconversion; (ii) cooperative sensitization*,

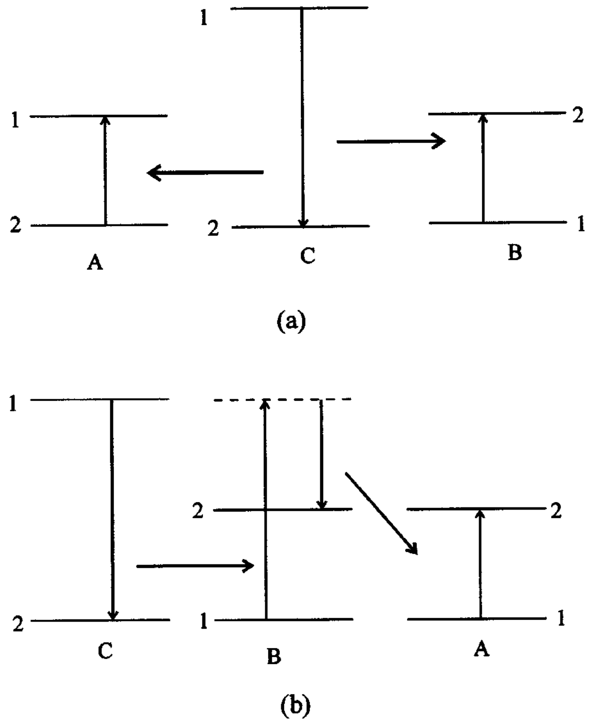

FIG. 3. Energy level diagrams for quantum cutting: (a) cooperative, (b) accretive.

whereby the same net effect as two-photon APTE is achieved but there is no suitable energy level to accommodate the initial transfer step. This process can be thought of as two concurrent RET processes accommodated by the mediation of a virtual level within the acceptor. This process is also known as *cooperative upconversion*.

Miyakawa and Dexter[20] compared and contrasted the probabilities of the APTE and cooperative mechanisms of energy pooling in systems where the energy of emitted photons was approximately double that of an incident beam. Building upon early work by Ovsyakin and Feofilov[21] with BaF_2 co-doped crystals, it was shown that two donor Yb^{3+} ions (pre-excited using a $\sim 1\ \mu m$ microwave beam, invisible to Tm^{3+}) undergoing ${}^2F_{7/2} \rightarrow {}^2F_{5/2}$ transitions could simultaneously transfer their excitation, via the cooperative sensitization mechanism, to a Tm^{3+} ion. This induced the Tm^{3+}:${}^3H_6 \rightarrow {}^1G_4$ transition (approximately twice the energy of Yb^{3+}:${}^2F_{7/2} \rightarrow {}^2F_{5/2}$), yielding a subsequent visible fluorescence. Reappraisal of the same system in the 1990's within a $LiYF_4$ substrate by Huber *et al.*[22] led to the postulation of similar effects (along with APTE).

Further observations using co-doped alkaline metal rare earth fluorides were reported by Seelbinder and Wright,[23] identifying energy pooling from two Yb^{3+} ions to Tb^{3+} and there resulting in ${}^7H_6 \rightarrow {}^5D_4$ excitation. The process was also observed in Yb/Er co-doped barium-thorium fluoride glasses by Yeh *et al.*,[24] and in $KYb_{0.8}Eu_{0.2}(WO_4)_2$ by Strek *et al.*[25] The transfer dynamics of the former system (alongside others containing Yb/Er and also Pr/Tb) were the subject of work subsequently undertaken by Chua and Tanner.[26] Using the Judd–Ofelt formalism,[27,28] they considered an extension of the previously formulated, nonradiative mechanisms to regimes where radiative transfer is the dominant protagonist.

Three-body energy pooling is by no means limited to systems containing more than one species of rare earth ion. Occurrence of the process has been identified (Lee *et al.*[29] and Lezama *et al.*[30]) in systems involving three Pr^{3+} ions previously excited to the ${}^1D_2$ level, with simultaneous energy transfer from two of them resulting in the transition ${}^1D_2 \rightarrow {}^1S_0$ at the third. An identical isoionic process has been suggested (Jouart and Mary[31]) as an explanation for both green and red emissions from Er^{3+} in fluorite-type crystals.

C. Sensitization processes

Here we identify systems where a rare earth ion exhibits similar properties to the bridging species frequently encountered in the transfer dynamics of multichromophore arrays.[32–34] In this process, as shown in Fig. 2, the excitation of a donor ion (A*) engages with a bridging species (B), with the resultant deposition of a modified energy at an acceptor (C). The acceptor may or may not be in an excited state to begin with. Once again, the label ''upconversion'' is common for such observations, but here it is termed *sensitization* to distinguish it from the pooling processes described in the previous section.

The usual *bridge* in sensitization is the Yb^{3+} ion, whose ${}^2F_{7/2} \rightarrow {}^2F_{5/2}$ transition serves to induce novel photophysical effects in a variety of donor-acceptor pairs. Zhang *et al.*[35] identified its role in mediating red emission from Ho^{3+}: ${}^5F_5 \rightarrow {}^5I_7$, allowing access to ${}^5F_4$, ${}^5S_2$ degenerate manifolds in a second, excited Ho^{3+} ion—the ensuing relaxation resulting in green emission. Similarly the role of Yb^{3+} in mediating excitation transfer between two identical, excited rare earth ions, has been expounded for Pr^{3+},[36] and also Tm^{3+} in vitroceramics containing Ge[37] and Te.[38] This sensitization of ions has again been investigated by Jouart and Mary[31] for the Er^{3+}: ${}^4F_{9/2} \rightarrow {}^4S_{15/2}$ emission bridged by Tm^{3+}. Very recently a system was reported by Qui *et al.*[39] involving not two but three different dopants. The highly complex photophysics proposed involves initial excitation of the ${}^2H_{9/2}$, ${}^4F_{5/2}$ level of Nd^{3+} via pumping at 800 nm, relaxation of this state then facilitating the familiar Yb^{3+}: ${}^2F_{7/2} \rightarrow {}^2F_{5/2}$ transition. Subsequent sensitized upconversion populates the ${}^5D_4$ state of Tb^{3+}, through which visible emission at 490 nm is emergent.

D. Degenerate downconversion

Some of the most recent processes to be observed in the area of rare earth ion energy transfer involve the realization of systems postulated back in the infancy of the subject. Dexter[14] suggested systems that could exhibit quantum yields greater than unity. The mechanism comprised simultaneous transfer of excitation to two acceptors from a single donor, with each transfer carrying approximately half the energy of excitation of the donor, as illustrated in Fig. 3. The initial excitation, usually due to the absorption of a violet ultraviolet (VUV) photon, leads to the emission of two visible photons. First proposed as the inverse of cooperative upconversion, the quantum optical nature of the phenomenon has more recently earned it the sobriquet *quantum cutting* and has been reported in the visible region by Wegh *et al.*, both from Gd^{3+} in $LiYF_4$[40] and Eu^{3+} in $LiGdF_4$.[41] A more complex analogue in $LiGdF_4$ has also been observed where cutting is facilitated by Gd^{3+} with emission from both Er^{3+} and Tb^{3+}.[42] Early examples of the process operating outside the visible, involving Pr^{3+} and Tm^{3+}, were reported by Sommerdjink *et al.*[43] and Piper *et al.*,[44] respectively.

E. Distinction from competing processes

The nature of most lanthanide-doped systems lends itself to an extensive range of complex photophysical behavior, so that for unambiguous identification of the processes of interest here it is important to identify and dispel the possibility of other interactions that might result in similar excitation–relaxation within the lattice. First, with three-center energy pooling, the means of instigation along with the observable of the process (prior illumination followed by the detection of short-wavelength fluorescence from the acceptor) potentially implicates other competing effects. The most obvious culprits for alternative mechanisms would be direct two-photon excitation of the acceptor or two-photon excitation of a single donor followed by excitation transfer to the acceptor.[45] However, by suitable choice of wavelengths for both donor and acceptor, away from regions amenable to two-photon effects, we can safely assume little or no direct multi-excitation localized at any single ion within the lattice. Second, with sensitization processes, simple RET from the donor to acceptor could, in principle, readily account for the subsequent luminescence. However, in practice the relevant fluorescence emission is not observed in systems where the bridge (invariably a species different to both donor and acceptor) is not present as a dopant, thus supporting its role as presented here. Similar remarks can be made concerning quantum cutting, where in the cases of interest, absence of the supporting ions can extinguish the effect—which could otherwise have been considered to involve the optically excited ions alone.

III. QED FORMALISM

The three-body energy transfer processes described above have not escaped theoretical treatments. For example, both Fong and Diestler[46] and Kushida[47] have considered systems comprising three interacting dipoles in the context of cooperative up-conversion (pooling) in Ln^{3+} doped crystals or glasses. In this paper the various processes described in the previous section are for the first time the subject of a fundamental treatment using quantum electrodynamics (QED).[48,49] Previously we have delineated the general framework for a QED theory of three-center energy pooling, with particular regard to its role in complex molecular systems.[50–52] One facet of these initial investigations has been the identification of two competing pathways for pooling: (i) A *cooperative* mechanism, whereby donor excitations are directly and concertedly delivered to the acceptor (embracing both APTE and cooperative upconversion); (ii) an *accretive* mechanism involving the transient acquisition by one donor of both excitation energies, through coupling with an intermediate virtual state. Here, we develop the fundamental theory for application to crystalline materials, with the full detail of the accretive mechanism being presented explicitly for the first time.

Before proceeding further, some comment should be made concerning the chosen deployment of quantum electrodynamical principles for the development of theory in the present context. The application to lanthanide-doped materials requires the representation of energy transfer between optical centers which are host or guest ions embedded in the lattice. Each energy release and uptake transition involves energy levels modified by the local crystal field, and each is commonly described with reference to multipolar selection rules. (In this paper we shall limit discussion to the common case of electric dipole transitions, our formalism nonetheless being readily adaptable to other cases.) Although the salient transitions occur within ionic species, the unit cell or local environment where each ion is located has overall electrical neutrality; as a result, utilization of the multipolar Hamiltonian effects an exact cancellation of all longitudinal (Coulombic) couplings, as has been shown elsewhere.[53,54] In other words there is no *longitudinal* coupling between the optical centers. It also worth remarking that in the counterpart semiclassical theory there is no formal basis for establishing the gauge transformations which properly lead to multipolar development.[55]

An important implication follows. In multipolar quantum electrodynamics, representation of the electromagnetic coupling between distinct optical centers entails the interaction of each of them with the vacuum radiation field. This principle underpins all QED calculations of resonance energy transfer—whether in a simple system involving a single donor and acceptor, or in more intricate systems as here. Each energy release and uptake transition entails the creation and annihilation (respectively, or *vice versa*) of one virtual photon, the propagation of which is subject to an interplay of quantum uncertainty and retarded causality.[56] The role of the virtual photons is to convey the electromagnetic coupling. Since the virtual photons are not observed, calculations based on this protocol require summation of their properties over all electromagnetic modes. The application of this QED method ensures results that are properly causal, and correctly satisfy time-reversal symmetry.

At simplest, energy transfer processes can be depicted in terms of virtual photons propagating *in vacuo*, neglecting any electronic influence of the intervening medium. Such an approach can, however, lead to inaccurate values for the transfer rates. Because of the inverse square law which governs long-range behavior, such an approach also admits the possibility of infinite donor decay rates, associated with the possibility of coupling to all remote acceptors.[57] To obviate these problems the influence of the medium should where practicable be included in the calculations from the outset, through a *dressing* of the virtual photons involved. Specifically, the resulting medium-dressed photons, termed *polaritons*, are quanta of a dynamical subsystem comprising the radiation field (empty at the start of each process) and the normal modes of the medium.[58,59] To identify the role of each such polariton in the various interactions to be considered below, each is distinguished by its pair of wave vector and polarization labels as follows: $(\mathbf{p},\lambda)$ and $(\mathbf{p}',\lambda')$ signify polaritons exchanged by C with A and B, respectively, and $(\mathbf{p}'',\lambda'')$ denotes a polariton exchanged between A and B.

The full Hamiltonian for such a three-center energy pooling system can be adequately described by partitioning into subsystems, one containing the operators for the three ions participating in the interaction, and the other subsystem the remaining operators for the surrounding medium and the radiation field (which together comprise the *polariton bath*). Such a Hamiltonian can be written as

$$H=H_0+V, \tag{3.1}$$

with

$$H_0=H_{\mathrm{bath}}+\sum_{\xi=\mathrm{A,B,C}} H^{\xi}_{\mathrm{mol}}, \tag{3.2}$$

$$V=\sum_{\xi=\mathrm{A,B,C}} H^{\xi}_{\mathrm{int}}, \tag{3.3}$$

and

$$H_{\mathrm{bath}}=H_{\mathrm{rad}}+\sum_{\xi\neq\mathrm{A,B,C}} (H^{\xi}_{\mathrm{mol}}+H^{\xi}_{\mathrm{int}}). \tag{3.4}$$

In the above equations, H_{rad} is the second-quantized radiation field Hamiltonian and, for each molecule ξ, H^{ξ}_{mol} and H^{ξ}_{int} are the corresponding molecular and molecule-field coupling Hamiltonians, respectively. For distances beyond wave function overlap, and for the transitions to be considered, it is valid to use the electric dipole approximation in which the latter operator is defined by

$$H_{\rm int}^{\xi} = -\epsilon_0^{-1}\boldsymbol{\mu}(\xi)\cdot\mathbf{d}^{\perp}(\mathbf{R}_{\xi}), \tag{3.5}$$

with $\boldsymbol{\mu}(\xi)$ being the electric dipole moment operator and $\mathbf{R}_{\xi}$ the position vector for species ξ. As discussed elsewhere, the electric displacement field operator, $\mathbf{d}^{\perp}(\mathbf{R}_{\xi})$, can be cast in terms of a mode expansion either in the usual vacuum formulation or as modified by the influence of the surrounding medium in a host or solvent ''bath''.[60,61] For precision we utilize the latter expansion for the polariton-mediated exchange, explicitly featuring local field and other refractive corrections and given by

$$\mathbf{d}^{\perp}(\mathbf{R}_{\xi}) = \mathrm{i}\sum_{\mathbf{p}}\sum_{m}\sum_{\lambda=1}^{2}\left(\frac{\epsilon_0\hbar\omega_p^{(m)}v_g^{(m)}}{2cV_0 n^{(m)}}\right)^{1/2}\left(\frac{(n^{(m)})^2+2}{3}\right) \times[\mathbf{e}^{(\lambda)}(\mathbf{p})P_{\mathbf{p},m,\lambda}e^{\mathrm{i}\mathbf{p}\cdot\mathbf{R}_{\xi}}-\overline{\mathbf{e}}^{(\lambda)}(\mathbf{p})P^{\dagger}_{\mathbf{p},m,\lambda}e^{-\mathrm{i}\mathbf{p}\cdot\mathbf{R}_{\xi}}]. \tag{3.6}$$

Expression (3.6) embraces a summation over modes for virtual polaritons characterized by a wave-vector **p**, polarization λ and an additional index, *m*, indicating branches of polariton dispersion (as appropriate for excitation propagation within a dispersive medium). Moreover, **e** represents the polariton polarization unit vector ($\overline{\mathbf{e}}$ being its complex conjugate), P and $P^{\dagger}$ are polariton annihilation and creation Bose operators, respectively, and V_0 is the quantization volume. Also,

$$n^{(m)} \equiv n(\omega_p^{(m)})$$

is the refractive index of the molecular medium and

$$v_g^{(m)} = c\left\{\frac{d[\omega n(\omega)]}{d\omega}\right\}^{-1}\Bigg|_{\omega=\omega_p^{(m)}} = \frac{d\omega_p^{(m)}}{dp}$$

is the group velocity, both quantities deriving from the polariton frequency $\omega_p^{(m)} = cp/n(\omega_p^{(m)})$.

It is known that there are three distinct pathways for the energy pooling form of three-center energy transfer,[50,51] but the link between them is not immediately apparent. When the full three-center transfer system is cast in a recently devised diagrammatic form embracing the complete set of Feynman diagrams,[50] the inherent interconnection between all three mechanistic paths becomes obvious (see Fig. 4). By their nature, each of the contributing pathways entails four distinct polariton interactions, a pair (creation and annihilation) for each energy transfer. Since the interaction operator is linear in the polariton creation and annihilation operators, the probability amplitude or *matrix element*, M_{fi}, for any such four-event process is described by the fourth-order term in the time-dependent perturbation expansion

$$M_{fi} = \sum_{\mathcal{P}}\frac{\langle r_4^1|H_{\rm int}|r_3^{m''}\rangle\langle r_3^{m''}|H_{\rm int}|r_2^{m'}\rangle\langle r_2^{m'}|H_{\rm int}|r_1^{m}\rangle\langle r_1^{m}|H_{\rm int}|r_0^{1}\rangle}{(E_{r_0^1}-E_{r_1^m})(E_{r_0^1}-E_{r_2^{m'}})(E_{r_0^1}-E_{r_3^{m''}})}, \tag{3.7}$$

where the initial and final system states, here for internal consistency labeled $|r_0^1\rangle$ and $|r_4^1\rangle$, are bridged by virtual

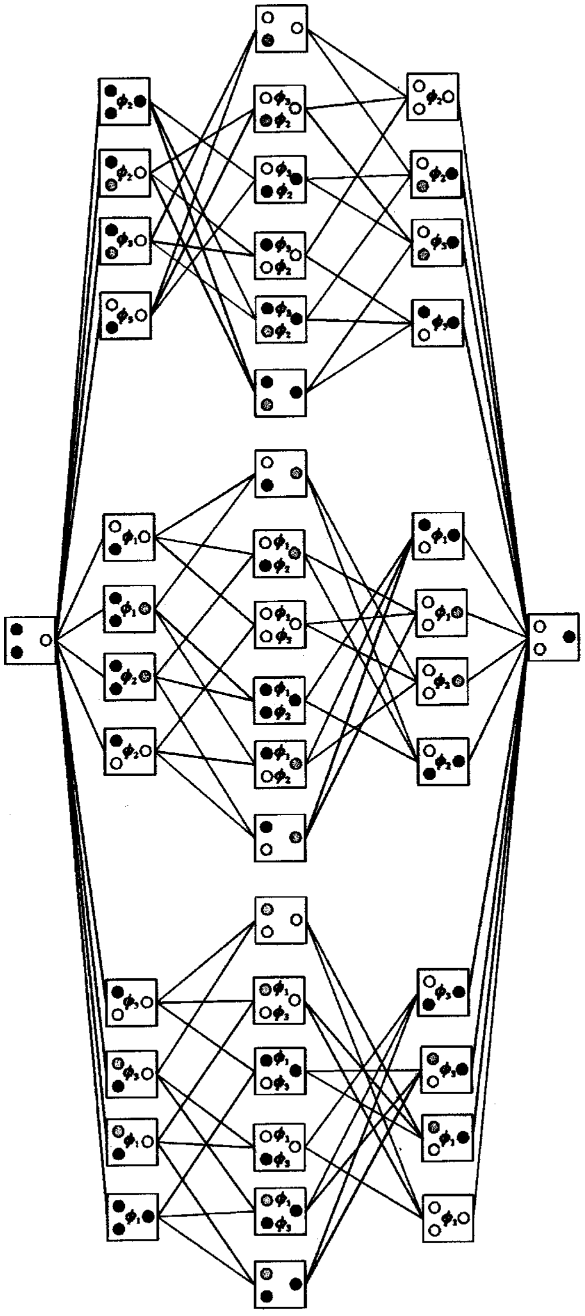

FIG. 4. Complete box diagram for three-body energy pooling. The top and bottom sections represent accretive pathways, the middle section cooperative pathways.

states $|r_1^m\rangle$, $|r_2^m\rangle$, and $|r_3^{m''}\rangle$, m being a label to differentiate states of different polariton occupancy, and $\mathcal{P}$ representing a valid path, i.e., one of the routes through Fig. 4 (*vide infra*). In general the system states, $|n\rangle$, have energy E_n and take the form $|n\rangle = |\mathrm{A}_n;\mathrm{B}_n;\mathrm{C}_n\rangle|\sigma_n\rangle$, with the subscripts on A, B, and C pertaining to ionic states and on σ, excited states of the bath accessible through one operation of the polariton creation operator on the bath ground-state vector $|0\rangle$. In Fig. 4, as in all such diagrams, initial and final system states are represented by boxes on the far left and far right, respectively. For generality we impose the initial and final conditions $|r_0^1\rangle = |\mathrm{A}_1;\mathrm{B}_1;\mathrm{C}_1\rangle|0\rangle$ and $|r_4^1\rangle = |\mathrm{A}_2;\mathrm{B}_2;\mathrm{C}_2\rangle|0\rangle$. The only constraint is that each ion initially resides in state 1, finally progressing to state 2. The physical distinction between the processes of upconversion, sensitization, and downconversion will emerge later when energetic and state constraints are imposed on $|r_0^1\rangle$ and $|r_4^1\rangle$. The intervening columns in the diagram represent a set of intermediate system states (r_1^m, $r_2^{m'}$, and $r_3^{m''}$ from left to right) connected by links which can be thought of as valid operations by H_{int} on a preceding state. Within this diagram there are three specific regions (top, middle, and bottom) with each region comprising twenty-four routes from $|r_0^1\rangle$ to $|r_4^1\rangle$. Each route is equivalent to one time-ordering as rendered by a traditional Feynman diagram. Collectively each set of twenty-four routes is indicative of an individual three-center energy migration mechanism. The central region (representing the cooperative mechanism) entails ionic states identical to those in both accretive pathways (top and bottom), but the system states differ in the polariton mode occupancy.

In order to compute contributions to Eq. (3.7) it is necessary to consider each pathway $\mathcal{P}$ individually. With a focus on accretive pathways, the box diagram for energy being accrued at B (the mechanism here termed ''acc1'') is shown in Fig. 5—itself a component of Fig. 4 (the uppermost system). We note in passing that both accretive mechanism diagrams are, by symmetry, identical in form—the counterpart to the mechanism currently under scrutiny (i.e., where energy is accrued at A, termed ''acc2'') is obtained by exchanging B↔A in the key box and implementing $p' \rightarrow p$ where necessary. It is calculationally expedient to number each set of intermediate states, for example, the first set is labeled r_1^1 to r_1^4 from top to bottom hence $m=1 \ldots 4$. Implementation of a previously expounded methodology[50] allows computation of all twenty-four contributions to the $acc1$ matrix element, M_{fi}^{acc1}. For example, the ''first'' route, $r_0^1 \rightarrow r_1^1 \rightarrow r_2^1 \rightarrow r_3^1 \rightarrow r_4^1$, results in an expression given by

$$M_{fi}^{(1)}=\sum_m \left(\frac{\hbar\omega_{p'}^{(m)} v_g^{(m)}}{2\epsilon_0 c V_0 n^{(m)}}\right)\left(\frac{\hbar\omega_{p''}^{(m)} v_g^{(m)}}{2\epsilon_0 c V_0 n^{(m)}}\right)\left(\frac{(n^{(m)})^2+2}{3}\right)^4 \times\sum_b \sum_{\mathbf{p}',\mathbf{p}'',l'l''} \frac{\mu_l^{21(\mathrm{A})}\mu_l^{21(\mathrm{C})}\mu_k^{2b(\mathrm{B})}\mu_j^{b1(\mathrm{B})}\overline{e}_i^{(l'')}(\mathbf{p}'')e_j^{(l'')}(\mathbf{p}'')e^{i\mathbf{p}''\cdot\mathbf{R}''}\overline{e}_k^{(l')}(\mathbf{p}')e_l^{(l')}(\mathbf{p}')e^{-i\mathbf{p}'\cdot\mathbf{R}'}}{(E_{12}^{\mathrm{A}}-\tilde{\Pi}'')(E_{12}^{\mathrm{A}}+\tilde{E}_{1b}^{\mathrm{B}})(E_{12}^{\mathrm{A}}+E_{12}^{\mathrm{B}}-\tilde{\Pi}')}. \tag{3.8}$$

Here we introduce the notation $E_{xy}^{\xi}=E_x^{\xi}-E_y^{\xi}$ for ion energy differences, and $\Pi^{(','')}$ for the energy of a polariton $\hbar c p^{(','')}$; for the transition dipoles, $\mu^{xy(\xi)}=\langle x|\mu^{(\xi)}|y\rangle$, and the interionic separation vectors are denoted by $\mathbf{R}'=\mathbf{R}_{\mathrm{C}}-\mathbf{R}_{\mathrm{B}}$ and $\mathbf{R}''=\mathbf{R}_{\mathrm{B}}-\mathbf{R}_{\mathrm{A}}$. Equation (3.8) is to be understood as effecting implied summation over repeated Cartesian (subscript) indices. Furthermore, here and in the following, resonance features are properly accommodated in the matrix elements by the tildes placed over particular energy denominator contributions. Two types of resonance modification need to be applied. The first reflects the finite lifetime of each virtual state, ζ, through which an ion ξ progresses, phenomenologically implemented by a modification of the corresponding energy, $\tilde{E}_{1\zeta}^{\xi}=E_{1\zeta}^{\xi}+\mathrm{i}\Gamma_{\zeta}$. This has the effect of giving the state a Lorentzian profile, Γ_{ζ} representing its half width at half maximum (HWHM) linewidth. The constancy of sign for this first form of damping is determined by principles of time-reversal symmetry.[62] Second, imaginary infinitesimals have to be added to the polariton energies to circumvent spurious singularities in effecting the sum over polariton wave vectors. Thus we write $\tilde{\Pi}^{(','')}=\Pi^{(','')}+\mathrm{i}s$ with $s\rightarrow+0$.[63]

By following recognized techniques whose application to conventional RET is described in detail elsewhere,[63] the summation of all twenty-four $acc1$ contributions, including the one given by (3.8), leads to the total $acc1$ matrix element. This, after extensive algebraic manipulation, can be written as

$$M_{fi}^{\text{acc1}}=\mu_1^{21(\mathrm{A})}V_{ij}(n|\pm\omega_{12}^{\mathrm{A}}|,\mathbf{R}'')\alpha_{jk}^{21(\mathrm{B})}(\pm\omega_{12}^{\mathrm{A}}\pm\omega_{12}^{\mathrm{B}},\mp\omega_{12}^{\mathrm{A}}) \times V_{kl}(n|\pm\omega_{12}^{\mathrm{A}}\pm\omega_{12}^{\mathrm{B}}|,\mathbf{R}')\mu_l^{21(\mathrm{C})}. \tag{3.9a}$$

Here, the principle of energy conservation leads to the identity $E_{12}^{\mathrm{A}}+E_{12}^{\mathrm{B}}=E_{21}^{\mathrm{C}}$, where $E_{12}^{\mathrm{A}}=\hbar\omega_{12}^{\mathrm{A}}$ and $E_{12}^{\mathrm{B}}=\hbar\omega_{12}^{\mathrm{A}}$. In (3.9a) and the following the energies are replaced by frequencies to assuage complications arising from presenting the modulus of wave vectors in the arguments. Proceeding by similar means we determine the matrix element for the $acc2$ accretive mechanism as

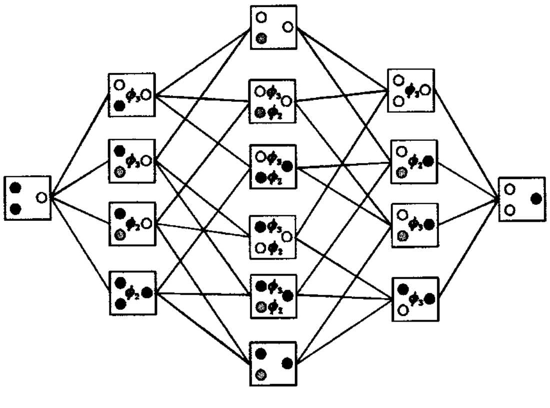

FIG. 5. Box diagram showing accretive three-body energy transfer mediated by ion B.

$$M_{fi}^{\mathrm{acc2}}=\mu_i^{21(\mathrm{B})}V_{ij}(n|\pm\omega_{12}^{\mathrm{B}}|,\mathbf{R}'')\,\alpha_{jk}^{21(\mathrm{A})}(\pm\omega_{12}^{\mathrm{A}}\pm\omega_{12}^{\mathrm{B}},\mp\omega_{12}^{\mathrm{B}})\times V_{kl}(n|\pm\omega_{12}^{\mathrm{A}}\pm\omega_{12}^{\mathrm{B}}|,\mathbf{R})\,\mu_l^{21(\mathrm{C})}, \tag{3.9b}$$

introducing $\mathbf{R}=\mathbf{R}_{\mathrm{C}}-\mathbf{R}_{\mathrm{A}}$. Finally we recast the matrix element for the cooperative pathway[50] in general terms as

$$M_{fi}^{\mathrm{coop}}=\mu_i^{21(\mathrm{A})}V_{ij}(n|\pm\omega_{12}^{\mathrm{A}}|,\mathbf{R})\,\alpha_{jk}^{21(\mathrm{C})}(\mp\omega_{12}^{\mathrm{A}},\mp\omega_{12}^{\mathrm{B}})\times V_{kl}(n|\pm\omega_{12}^{\mathrm{B}}|,\mathbf{R}')\,\mu_l^{21(\mathrm{B})}. \tag{3.9c}$$

It is worth noting that the ± signs are chosen with respect to the direction of flow of energy within the system, accommodating upconversion and downconversion by a simple choice of sign (*vide infra*).

The results of (3.9) are concise and contain two second-rank tensors, whose properties we now delineate. The generalized two-photon interaction tensor, $\alpha^{21(\xi)}(\omega_1,\omega_2)$, has a form given by

$$\alpha_{ij}^{21(\xi)}(\mp\omega_1,\mp\omega_2)=\sum_{\zeta}\left\{\frac{\mu_i^{2\zeta(\xi)}\mu_j^{\zeta 1(\xi)}}{(\tilde{E}_{1\zeta}\pm\hbar\omega_1)}+\frac{\mu_j^{2\zeta(\xi)}\mu_i^{\zeta 1(\xi)}}{(\tilde{E}_{1\zeta}\pm\hbar\omega_2)}\right\}. \tag{3.10}$$

Within the accretive mechanisms of Eqs. (3.9a) and (3.9b), the two-photon interaction tensor is of the same nonsymmetric form as the tensor which supports all forms of electronic Raman scattering (see Sec. V for a discussion of the corresponding selection rules). Conversely, for the cooperative pathway of Eqs. (3.9c) and (3.10) presents a result which has the index-symmetric form of a (single-beam) two-photon interaction tensor. The cooperative mechanism has a distinct advantage over a conventional two-photon absorption at the acceptor. The photon flux needed to doubly excite a single molecule may be of a similar order to that required to excite two donors sufficiently close to the acceptor to initiate the cooperative mechanism, but the relative longevity of singly (compared to doubly) excited sites proves to be a deciding factor. The different roles of this tensor reflect the different ways for energy transfer to be effected. The scatteringlike behavior in accretive mechanisms owes its origin to the excitation at either donor being passed on to the acceptor, via a second donor as a mediator to the process, whereas the cooperative mechanism may be thought of as simple, mediation-free, dual interaction at C.

In Eq. (3.9) we also identify the second-rank, index-symmetric, retarded resonance electric dipole-electric dipole coupling tensor, $\mathbf{V}(n\omega,\mathbf{r})$. Its general form, which fully accommodates effects of the intervening transfer medium, is given by

$$V_{ij}(n\omega,\mathbf{r})=\frac{1}{n^2}\left(\frac{n^2+2}{3}\right)^2\frac{e^{\mathrm{i}(n/c)\omega r}}{4\pi\epsilon_0 r^3}\left\{\left(1-\mathrm{i}\frac{n}{c}\omega r\right)\times(\delta_{ij}-3\hat{r}_i\hat{r}_j)-\left(\frac{n}{c}\omega r\right)^2(\delta_{ij}-\hat{r}_i\hat{r}_j)\right\}, \tag{3.11}$$

where ω relates to the effective transferral frequency of an energy $\hbar\omega$, and $\mathbf{r}$ is the relative displacement vector of the connected transition electric dipoles. The behavior of Eq. (3.11) necessarily approaches that of the vacuum case when the refractive index of the medium, n, approaches 1, reducing the effect of the Lorentz premultiplier to unity. In any real dispersive medium, however, the imaginary part of the refractive index elicits a real exponential decay component from within the phase factor. Furthermore, it is in Eq. (3.11) that the power of the unified theory is apparent, as the result is applicable to all post-overlap distances. The short-range ($n\omega r\ll 1$) and long-range ($n\omega r\gg 1$) limits lead to r^{-3} and r^{-1} distance dependence in the coupling itself (and hence, r^{-6} and r^{-2} in the transfer rate which goes as the square of the matrix element). Note, however, that in the results of Eq. (3.9) there are two resonance coupling tensors which, though each of the form of (3.11), exhibit different interionic vector arguments. For example, in result (3.9a) we observe an inverse cubic dependence on both of the relative displacements R' and R''. Each result (3.9a)–(3.9c) is controlled by two of the three interionic distances quantities R, R', and R''.[52]

IV. APPLICATIONS

In this section we demonstrate how the several distinct classes of rare earth interactions described in Sec. II can be described by the general pooling theory delineated in Sec. III, and how the cooperative and accretive pathways figure in the various processes. The processes are readily distinguished by the nature of the initial and final states; the main mechanisms and sources of experimental data are presented in Table I.

A. Upconversion

Although its nomenclature correctly suggests that the cooperative mechanism is the major contributor to upconversion processes (cooperative sensitization) as previously expounded,[49] the accretive mechanism nonetheless plays an auxiliary role whose importance is primarily determined by the relative positions of the ions involved.[50] Assuming that A and B begin in excited states and each progresses to its ground state (indicated by 0), thereby promoting C from its ground state to an excited state, we set the form of the energy identity as $E_{12}^{\mathrm{A}}+E_{12}^{\mathrm{B}}=\hbar\omega_{12}^{\mathrm{A}}+\hbar\omega_{12}^{\mathrm{B}}$. By imposing these constraints in (3.9) we recover previously calculated results.[50] Explicitly, these are

$$M_{fi}^{\mathrm{coop}}=\mu_i^{01(\mathrm{A})}V_{ij}(n\omega_{12}^{\mathrm{A}},\mathbf{R})\,\alpha_{jk}^{20(\mathrm{C})}(-\omega_{12}^{\mathrm{A}},-\omega_{12}^{\mathrm{B}})\times V_{kl}(n\omega_{12}^{\mathrm{B}},\mathbf{R}')\,\mu_l^{01(\mathrm{B})}, \tag{4.1a}$$

for the cooperative pathway, alongside

$$M_{fi}^{\mathrm{acc1}}=\mu_i^{01(\mathrm{A})}V_{ij}(n\omega_{12}^{\mathrm{A}},\mathbf{R}'')\,\alpha_{jk}^{01(\mathrm{B})}(\omega_{12}^{\mathrm{A}}+\omega_{12}^{\mathrm{B}},-\omega_{12}^{\mathrm{A}})\times V_{kl}(n(\omega_{12}^{\mathrm{A}}+\omega_{12}^{\mathrm{B}}),\mathbf{R}')\,\mu_l^{20(\mathrm{C})}, \tag{4.1b}$$

$$M_{fi}^{\mathrm{acc2}}=\mu_i^{01(\mathrm{B})}V_{ij}(n\omega_{12}^{\mathrm{B}},\mathbf{R}'')\,\alpha_{jk}^{01(\mathrm{A})}(\omega_{12}^{\mathrm{A}}+\omega_{12}^{\mathrm{B}},-\omega_{12}^{\mathrm{B}})\times V_{kl}(n(\omega_{12}^{\mathrm{A}}+\omega_{12}^{\mathrm{B}}),\mathbf{R})\,\mu_l^{20(\mathrm{C})}, \tag{4.1c}$$

for the accretive, the total matrix element being the sum of all three. In the present formulation, the electronic influence of the host is fully accommodated within the results with due reverence to equation (3.11).

TABLE I. Table of transitions between lanthanide dopant ions in crystal field environs: i-energy pooling, ii-two photon APTE, iii-sensitization, iv-quantum cutting.

A (Transition)	B (Transition)	C (Transition)	Type	References
$Yb^{3+}(^2F_{5/2}\rightarrow{}^2F_{7/2})$	$Yb^{3+}(^2F_{5/2}\rightarrow{}^2F_{7/2})$	$Tb^{3+}(^7H_6\rightarrow{}^5D_4)$	i	18, 23, 26
$Yb^{3+}(^2F_{5/2}\rightarrow{}^2F_{7/2})$	$Yb^{3+}(^2F_{5/2}\rightarrow{}^2F_{7/2})$	$Tm^{3+}(^3H_6\rightarrow{}^1G_4)$	i, ii	21, 22
$Yb^{3+}(^2F_{5/2}\rightarrow{}^2F_{7/2})$	$Yb^{3+}(^2F_{5/2}\rightarrow{}^2F_{7/2})$	$Eu^{3+}(^5D_0\rightarrow{}^7F_0)$	i	25
$Pr^{3+}(^1D_2\rightarrow{}^3H_4)$	$Pr^{3+}(^1D_2\rightarrow{}^3H_4)$	$Pr^{3+}(^1D_2\rightarrow{}^1S_0)$	i	29, 30
$Yb^{3+}(^2F_{5/2}\rightarrow{}^2F_{7/2})$	$Yb^{3+}(^2F_{5/2}\rightarrow{}^2F_{7/2})$	$Ho^{3+}(^5I_8\rightarrow{}^5S_2,{}^5F_4)$	ii	13, 21
$Yb^{3+}(^2F_{5/2}\rightarrow{}^2F_{7/2})$	$Yb^{3+}(^2F_{5/2}\rightarrow{}^2F_{7/2})$	$Er^{3+}(^4I_{15/2}\rightarrow{}^4F_{7/2})$	ii	18, 19, 21, 24, 26
$Pr^{3+}(^3P_0\rightarrow{}^1G_4)$	$Yb^{3+}(^2F_{7/2}\rightarrow{}^2F_{7/2})$	$Pr^{3+}(^3H_4\rightarrow{}^1G_4)$	iii	36
$Er^{3+}(^4I_{13/2}\rightarrow{}^4I_{15/2})$	$Tm^{3+}(^3H_6\rightarrow{}^3H_6)$	$Er^{3+}(^4I_{11/2}\rightarrow{}^4F_{9/2})$	iii	31
$Ho^{3+}(^5F_5\rightarrow{}^5I_7)$	$Yb^{3+}(^2F_{7/2}\rightarrow{}^2F_{7/2})$	$Ho^{3+}(^5I_6\rightarrow{}^5S_2,{}^5F_4)$	iii	35
$Tm^{3+}(^3F_4\rightarrow{}^3H_4)$	$Yb^{3+}(^2F_{7/2}\rightarrow{}^2F_{7/2})$	$Tm^{3+}(^3H_6\rightarrow{}^3H_4)$	iii	37, 38
$Nd^{3+}(^4F_{3/2}\rightarrow{}^4F_{11/2})$	$Yb^{3+}(^2F_{7/2}\rightarrow{}^2F_{7/2})$	$Tb^{3+}(^5D_4\rightarrow{}^5D_1)$	iii	39
$Eu^{3+}(^7F_1\rightarrow{}^5D_0)$	$Eu^{3+}(^7F_1\rightarrow{}^5H_J)$	$Gd^{3+}(^6G_J\rightarrow{}^8S_{7/2})$	iv	41
$Tb^{3+}(^5D_3\rightarrow{}^7F_J)$	$Er^{3+}(^4S_{7/2}\rightarrow{}^4I_{15/2})$	$Er^{3+}(4f^{10}5d\rightarrow{}^4S_{3/2})$	iv	42
$Pr^{3+}(^3H_4\rightarrow{}^3P_2)$	$Pr^{3+}(^3H_4\rightarrow{}^3P_2)$	$Pr^{3+}(^1S_0\rightarrow{}^3H_4)$	iv	43

B. Sensitization

Rare earth sensitization is implicated in a variety of photophysical processes, as the donor (or acceptor) may relax to (or initially be in) a state other than the ground state. The nature of each process determines that the role of the bridge remains immutable, however—starting and finishing, as it does, in the ground state. Here we focus on the case where the acceptor is in some pre-excited state 1 and the donor relaxes to the ground state. (The case where the acceptor is excited from the ground state was the subject of earlier work by Craig and Thirunamachandran.[32]) By stipulating the donor as species A, the bridge as B and acceptor as C, noting that $E_{12}^{\mathrm{B}}=0$, we may rewrite (3.9) as

$$M_{fi}^{\mathrm{acc1}}=\mu_i^{01(\mathrm{A})}V_{ij}(n\omega_{12}^{\mathrm{A}},\mathbf{R}'')\alpha_{jk}^{00(\mathrm{B})}(\omega_{12}^{\mathrm{A}},-\omega_{12}^{\mathrm{A}})\times V_{kl}(n\omega_{12}^{\mathrm{A}},\mathbf{R}')\mu_l^{21(\mathrm{C})},\tag{4.2a}$$

$$M_{fi}^{\mathrm{acc2}}=\mu_i^{00(\mathrm{B})}V_{ij}(0,\mathbf{R}'')\alpha_{jk}^{01(\mathrm{A})}(0,-\omega_{12}^{\mathrm{A}})\times V_{kl}(n\omega_{12}^{\mathrm{A}},\mathbf{R}')\mu_l^{21(\mathrm{C})},\tag{4.2b}$$

and

$$M_{fi}^{\mathrm{coop}}=\mu_i^{01(\mathrm{A})}V_{ij}(n\omega_{12}^{\mathrm{A}},\mathbf{R})\alpha_{jk}^{21(\mathrm{C})}(-\omega_{12}^{\mathrm{A}},0)V_{kl}(0,\mathbf{R}')\mu_l^{00(\mathrm{B})}.\tag{4.2c}$$

In Eqs. (4.2b) and (4.2c) we identify a static dipole moment term, μ^{00}. If the lanthanide ions themselves were considered spherical[64] with a uniform electronic distribution they would exhibit no permanent dipole—but even in a more distorting crystal field environment which substantially shifts the center of charge, the moment would usually be small. We, therefore, deduce that the sensitization process is in general purely accretive by nature, with a quantum amplitude as described by expression (4.2a), a proposition that is further expounded in Sec. V. In any event, it may be noted that, as discussed previously,[51] the relative disposition of the three ions in the lattice may favor one mechanism over the other. Certain triad geometries impose a large bias toward the cooperative mechanism, and in this case (for sensitization) we may assume negligible three-center transfer from such configurations. For example in a linear A-C-B configuration the cooperative mechanism is dominant and this would suggest little involvement in rare earth sensitization processes.

C. Downconversion

For downconversion (quantum cutting) the results are of a similar form to those for energy pooling upconversion, different only in a reversal of the energy flow; hence $E_{12}^{\mathrm{A}}+E_{12}^{\mathrm{B}}=-\hbar\omega_{12}^{\mathrm{A}}-\hbar\omega_{12}^{\mathrm{B}}$. Thus we obtain the results

$$M_{fi}^{\mathrm{coop}}=\mu_i^{20(\mathrm{A})}V_{ij}(n\omega_{12}^{\mathrm{A}},\mathbf{R})\alpha_{jk}^{01(\mathrm{C})}(\omega_{12}^{\mathrm{A}},\omega_{12}^{\mathrm{B}})\times V_{kl}(n\omega_{12}^{\mathrm{B}},\mathbf{R}')\mu_l^{20(\mathrm{B})},\tag{4.3a}$$

for the cooperative pathway and

$$M_{fi}^{\mathrm{acc1}}=\mu_i^{20(\mathrm{A})}V_{ij}(n\omega_{12}^{\mathrm{A}},\mathbf{R}'')\alpha_{jk}^{20(\mathrm{B})}(\omega_{12}^{\mathrm{A}},-\omega_{12}^{\mathrm{A}}-\omega_{12}^{\mathrm{B}})\times V_{kl}(n(\omega_{12}^{\mathrm{A}}+\omega_{12}^{\mathrm{B}}),\mathbf{R}')\mu_l^{01(\mathrm{C})},\tag{4.3b}$$

$$M_{fi}^{\mathrm{acc2}}=\mu_i^{20(\mathrm{B})}V_{ij}(n\omega_{12}^{\mathrm{B}},\mathbf{R}'')\alpha_{jk}^{20(\mathrm{A})}(\omega_{12}^{\mathrm{B}},-\omega_{12}^{\mathrm{A}}-\omega_{12}^{\mathrm{B}})\times V_{kl}(n(\omega_{12}^{\mathrm{A}}+\omega_{12}^{\mathrm{B}}),\mathbf{R})\mu_l^{01(\mathrm{C})},\tag{4.3c}$$

for the two accretive mechanisms. Here, the interplay between site geometry and optical selection rules will determine the dominant contributory mechanism.

V. SELECTION RULES

This section focuses on the symmetry implications associated with the two-photon interaction tensor (3.10) in triple-ion energy transfer processes. It is clear that the tensor plays an important role in pooling, sensitization and cutting, representing the electronic parameters involved—either where mediation occurs (in the case of accretive mechanisms) or where maximum energy is deposited, or from whence it emanates (in cooperative systems for pooling and cutting, respectively). The following discourse is primarily concerned with identifying differences between the scattering and two-photon absorption/emission analogues of the two-photon tensor. To fully investigate the tensor it is useful to implement its decomposition into irreducible components.[65] In general

$$\alpha_{ij}^{21(\xi)}(\mp\omega_1,\mp\omega_2)\equiv\alpha_{ij}=\alpha_{ij}^{(0)}+\alpha_{ij}^{(1)}+\alpha_{ij}^{(2)}, \tag{5.1}$$

where the components of $\alpha_{ij}^{(0)}$, $\alpha_{ij}^{(1)}$, and $\alpha_{ij}^{(2)}$ (the weight 0, 1, and 2 parts of, respectively) transform under the operations of the full rotation group SO(3) as a scalar, an antisymmetric pseudo-vector and a traceless symmetric second-rank tensor, respectively. The irreducible tensors can be explicitly written as

$$\alpha_{ij}^{(0)}=\tfrac{1}{3}\delta_{ij}\alpha_{kk}, \tag{5.2a}$$

$$\alpha_{ij}^{(1)}=\tfrac{1}{2}(\alpha_{ij}-\alpha_{ji}), \tag{5.2b}$$

$$\alpha_{ij}^{(2)}=\tfrac{1}{2}(\alpha_{ij}+\alpha_{ji})-\tfrac{1}{3}\delta_{ij}\alpha_{kk}. \tag{5.2c}$$

Ionic transitions at sites undergoing two-photon interactions are subject to site symmetry selection rules which render components of each irreducible part of α_{ij} either zero or nonzero, such that the symmetry of each allowed transition is characterized by its combination of allowed weights. Of these permutations only six generally occur[66]—three relate to transitions which contain representations of the totally symmetric representation of the ionic site point group: $2^+\{012\}$, $2^+\{02\}$, $2^+\{0\}$—and another three, nontotally symmetric product representations: $2^+\{12\}$, $2^+\{1\}$, $2^+\{2\}$. Here, the notation denotes tensor rank (with superscript indicating parity) and braced numbers show the allowed weight combination.

A. Pooling and cutting processes

In symmetry terms, the three-center processes of energy pooling and quantum cutting are equivalent, since the selection rules which apply to any transition also apply to its inverse. Both processes are accordingly addressed in this subsection: For clarity the text will focus on pooling, with the cutting analogue, if applicable, appearing in brackets. For example, species A and B are both donors (acceptors) in the cooperative scheme for energy pooling (quantum cutting).

There are intrinsic differences in the symmetry rules for the cooperative and accretive pathways of pooling and cutting. It can be seen from (5.2b) that a symmetric two-photon absorption (emission) tensor, such as that involved in the cooperative mechanism for pooling (cutting), necessarily has a zero contribution from its weight 1 part irrespective of the transition symmetry. However, a nonsymmetric two-photon tensor, which features in accretive pathways, is permitted a full quota of irreducible components, though any weight may disappear on symmetry grounds. Cooperative transitions thus suffer a spectroscopic restriction due to nullity of the antisymmetric term. Further symmetry implications can arise for accretive pathways as a result of the fact that A and B are almost invariably chemically identical, and their transitions equivalent; consequently those transitions must be allowed by both 2^+ and 1^- selection rules. Clearly, in centrosymmetric species, a combination such as $1^-\{1\},2^+\{0\}$ is forbidden; however, many crystallographic point groups afford irreducible representations conducive to suitable transitions. A full list is shown in Table II.

B. Sensitization

The process of sensitization is permitted only by the first accretive mechanism, as shown in Sec. IV, establishing the sole means for energy migration to occur from A to C. Here the symmetry selection rules are essentially trivial, and are reported here for completeness. The role of B is passive in the sense that this ion begins and ends in its ground state, though experiment shows that its presence is essential for transfer to occur. The totally symmetric product of the initial and final irreducible representations of the site point group determines that only classes $2^+\{012\}$, $2^+\{02\}$, $2^+\{0\}$ are feasible. However, the pseudo-vector term is again zero due to the symmetric nature of the tensor, which is of conventional polarizability form. Thus, only classes $2^+\{02\}$ and $2^+\{0\}$ arise, as indicated in Table II.

VI. TRANSFER RATES

For any given system the three-center energy transfer rate Γ may be determined from Fermi's Golden Rule

$$\Gamma=\frac{2\pi}{\hbar}|M_{fi}|^2\rho, \tag{6.1}$$

where ρ is the density of final states for the acceptor and M_{fi} is the total matrix element for the process. In the downconversion case when there are *two* acceptors, the appropriate density of states is a convolution of the state densities for each acceptor.[67] In each instance of three-center energy transfer the matrix element M_{fi} is explicitly given by

$$M_{fi}=M_{fi}^{\mathrm{acc1}}+M_{fi}^{\mathrm{acc2}}+M_{fi}^{\mathrm{coop}}, \tag{6.2}$$

where the full cooperative and accretive matrix elements are given by Eq. (3.9). An important feature and distinction between the quantum amplitudes of (6.2) is the dependence of each on two different energy coupling tensors, the general case of which is explicitly given by Eq. (3.11). In the total matrix element (6.2), M_{fi}^{acc1} involves a direct parametric dependence on both $\mathbf{R}'$ and $\mathbf{R}''$, M_{fi}^{acc2} depends on $\mathbf{R}$ and $\mathbf{R}''$, and M_{fi}^{coop} on $\mathbf{R}$ and $\mathbf{R}'$. At this stage we recall that retardation effects are only significant over distances which are comparatively large compared to the energy-equivalent wavelength. Recognizing this permits the assumption that transfer between physically distant ions will be obviated by dissipative effects—see Eq. (3.11) and subsequent comments. Calculation therefore proceeds on the general basis of an r^{-3} factor for each interionic transfer tensor.

For both upconversion and downconversion Eq. (6.2) invokes all three contributing pathways. Exhibiting the direct functional dependence explicitly, the rate of (6.1) can be expanded to yield

TABLE II. Table showing pertinent point groups with allowed transitions for three-body energy transfer processes.

	Pooling/Cutting		Sensitization
	Cooperative	Accretive	Accretive
C_1	$A:2^+\{02\}$	$A:1^-\{1\},2^+\{012\}$	$A:2^+\{02\}$
C_s	$A':2^+\{02\}$	$A':1^-\{1\},2^+\{012\}$ $A'':1^-\{1\},2^+\{12\}$	$A':2^+\{02\}$
C_i	$A_g:2^+\{02\}$	n/a	$A_g:2^+\{02\}$
C_2	$A:2^+\{02\}$ $B:2^+\{2\}$	$A:1^-\{1\},2^+\{012\}$ $B:1^-\{1\},2^+\{12\}$	$A:2^+\{02\}$
C_3	$A:2^+\{02\}$ $E:2^+\{2\}$	$A:1^-\{1\},2^+\{012\}$ $E:1^-\{1\},2^+\{12\}$	$A:2^+\{02\}$
C_4	$A:2^+\{02\}$ $B,E:2^+\{2\}$	$A:1^-\{1\},2^+\{012\}$ $E:1^-\{1\},2^+\{12\}$	$A:2^+\{02\}$
D_2	$A:2^+\{02\}$ $B_1,B_2,B_3:2^+\{2\}$	$B_1,B_2,B_3:1^-\{1\},2^+\{12\}$	$A:2^+\{02\}$
D_3	$A_1:2^+\{02\}E:2^+\{2\}$	$A_2:1^-\{1\},2^+\{1\}$ $E:1^-\{1\},2^+\{2\}$	$A_1:2^+\{02\}$
S_4	$A:2^+\{02\}$ $B,$ $E:2^+\{2\}$	$A:1^-\{1\},2^+\{012\}$ $E:1^-\{1\},2^+\{12\}$	$A:2^+\{02\}$
S_6	$A_g:2^+\{02\}E_g:2^+\{2\}$	n/a	$A_g:2^+\{02\}$
C_{2v}	$A_1:2^+\{02\}$ $A_2,B_1,B_2:2^+\{2\}$	$A_1:1^-\{1\},2^+\{012\}$ $B_2,B_3:1^-\{1\},2^+\{12\}$	$A_1:2^+\{02\}$
C_{3v}	$A_1:2^+\{02\}$ $E:2^+\{2\}$	$A_1:1^-\{1\},2^+\{02\}$ $E:1^-\{1\},2^+\{12\}$	$A_1:2^+\{02\}$
C_{4v}	$A_1:2^+\{02\}$ $B_1,B_2,E:2^+\{2\}$	$A_1:1^-\{1\},2^+\{02\}$ $E:1^-\{1\},2^+\{12\}$	$A_1:2^+\{02\}$
C_{5v}	$A_1:2^+\{02\}$ $E_1,E_2:2^+\{2\}$	$A_1:1^-\{1\},2^+\{02\}$ $E_1:1^-\{1\},2^+\{12\}$	$A_1:2^+\{02\}$
C_{6v}	$A_1:2^{2+}\{02\}$ $E_1,E_2:2^+\{2\}$	$A_1:1^-\{1\},2^+\{02\}$ $E_1:1^-\{1\},2^+\{12\}$	$A_1:2^+\{02\}$
D_{2h}	$A_g:2^+\{02\}$ $B_{1g},B_{2g},B_{3g}:2^+\{2\}$	n/a	$A_g:2^+\{02\}$
D_{3h}	$A_1':2^+\{02\}$ $E',E'':2^+\{2\}$	$E':1^-\{1\},2^+\{2\}$	$A_1':2^+\{02\}$
D_{4h}	$A_{1g}:2^+\{02\}$ $B_{1g},B_{2g},E_g:2^+\{2\}$	n/a	$A_{1g}:2^+\{02\}$
D_{5h}	$A_1':2^+\{02\}$ $E_2',E_1'':2^+\{2\}$	n/a	$A_1':2^+\{02\}$
D_{6h}	$A_{1g}:2^+\{02\}$ $E_{1g}:\{12\}$ $E_{2g}:2^+\{2\}$	n/a	$A_{1g}:2^+\{02\}$
D_{8h}	$A_{1g}:2^+\{02\}$ $E_{1g}:\{12\}$ $E_{2g}:2^+\{2\}$	n/a	$A_{1g}:2^+\{02\}$
T	$A:2^+\{0\}E,$ $T:2^+\{2\}$	$T:1^-\{1\},2^+\{12\}$	$A:2^+\{0\}$
T_h	$A_g:2^+\{0\}$ $E_g,T_g:2^+\{2\}$	n/a	$A_g:2^+\{0\}$
T_d	$A_g:2^+\{0\}$ $E_g,T_2:2^+\{2\}$	$T_2:1^-\{1\},2^+\{12\}$	$A_1:2^+\{0\}$
O	$A_1:2^+\{0\}$ $E,T_2:2^+\{2\}$	$T_1:1^-\{1\},2^+\{1\}$	$A_1:2^+\{0\}$
O_h	$A_{1g}:2^+\{0\}$ $E_g,T_{2g}:2^+\{2\}$	n/a	$A_{1g}:2^+\{0\}$
C_{2h}	$A_g:2^+\{02\}$ $B_g:2^+\{2\}$	n/a	$A_g:2^+\{02\}$
C_{3h}	$A':2^+\{02\}$ $E',E'':2^+\{2\}$	$E':1^-\{1\},2^+\{2\}$	$A':2^+\{02\}$
C_{4h}	$A_g:2^+\{02\}$ $B_g,E_g:2^+\{2\}$	n/a	$A_g:2^+\{02\}$
D_{2d}	$A_1:2^+\{02\}$ $B_1,B_2,E:2^+\{2\}$	$B:1^-\{1\},2^+\{2\}$ $E:2^+\{12\}$	$A_1:2^+\{02\}$
D_{3d}	$A_{1g}:2^+\{02\}$ $E_g:2^+\{2\}$	n/a	$A_{1g}:2^+\{02\}$
D_{4d}	$A_1:2^+\{02\}$ $E_2,E_3:2^+\{2\}$	n/a	$A_1:2^+\{02\}$
D_{5d}	$A_{1g}:2^+\{02\}$ $E_{1g},E_{2g}:2^+\{2\}$	n/a	$A_{1g}:2^+\{02\}$
D_{6d}	$A_1:2^+\{02\}$ $E_2,E_5:2^+\{2\}$	n/a	$A_1:2^+\{02\}$
$C_{\infty v}$	$A_1:2^+\{02\}$ $E_1,E_2:2^+\{2\}$	$A_1:2^+\{02\}$ $E_1:2^+\{12\}$	$A_1:2^+\{02\}$
$D_{\infty v}$	$\Sigma^+:2^+\{02\}$	n/a	$\Sigma^+:2^+\{02\}$

$$\begin{aligned}\Gamma=\frac{2\pi\rho}{\hbar}\{&|M_{fi}^{\mathrm{acc1}}(\mathbf{R}',\mathbf{R}'')|^2+|M_{fi}^{\mathrm{acc2}}(\mathbf{R},\mathbf{R}'')|^2\\&+|M_{fi}^{\mathrm{coop}}(\mathbf{R},\mathbf{R}')|^2\\&+2\,\mathrm{Re}(M_{fi}^{\mathrm{acc1}}(\mathbf{R}',\mathbf{R}'')\bar{M}_{fi}^{\mathrm{acc2}}(\mathbf{R},\mathbf{R}'')\\&+M_{fi}^{\mathrm{acc1}}(\mathbf{R}',\mathbf{R}'')\bar{M}_{fi}^{\mathrm{coop}}(\mathbf{R}',\mathbf{R}')\\&+M_{fi}^{\mathrm{acc2}}(\mathbf{R},\mathbf{R}'')\bar{M}_{fi}^{\mathrm{coop}}(\mathbf{R},\mathbf{R}'))\},\end{aligned}\tag{6.3}$$

where the first three rate components are diagonal contributions from each pathway matrix element multiplied by its complex conjugate. The second three components represent quantum interference between different three-center energy transfer pathways. For sensitization processes, we have only one viable mechanistic pathway, and the rate is explicitly

$$\Gamma=\frac{2\pi}{\hbar}|M_{fi}^{\mathrm{acc1}}(\mathbf{R}',\mathbf{R}'')|^2\rho.\tag{6.4}$$

An important feature of the diagonal elements of (6.3) and the single term in (6.4) is their dependence on the modulus squared of the pertinent coupling tensors. As each such tensor is governed by an inverse cubic dependence on both interionic vectors, the associated rate contributions acquire an inverse sixth power dependence on each interionic distance.

Complications arise with the cross terms within (6.3). It is no longer simply a case of considering two (independent) but of three (interdependent) interionic vectors, *vide infra*.

To instigate the application of the fundamental ionic triad rate results to any real crystal, it is necessary to identify a distributional weighting factor for each of the three-center rate components.[68] In the following, we derive the appropriate result for a simple cubic lattice of unit cell length a, with donors or acceptors potentially occupying any site. For any set of three sites within the lattice, whether they be in a local neighborhood or not, there is an associated probability of finding three ions in suitable electronic states to initiate a three-center transfer process. An ensemble response for transfer within the lattice may then be obtained by summing contributions from all such combinations (here assuming a random distribution within the lattice).

First we consider the diagonal terms contributing to (6.2) and (6.3). The ensemble result must be tempered by accommodating the number of ions A, B, and C, per unit cell which are residing in their initial electronic states. The quantities are assigned as c_{A_1}, c_{B_1}, and c_{C_1}, respectively (for example, in upconversion these concentrations relate to two excited and one ground-state species). In conventional units, the corresponding concentrations per unit volume are $C_{\mathrm{A}_1}=a^{-3}c_{\mathrm{A}_1}$, $C_{\mathrm{B}_1}=a^{-3}c_{\mathrm{B}_1}$, and $C_{\mathrm{C}_1}=a^{-3}c_{\mathrm{C}_1}$, respectively. It is important to note that each diagonal rate component has only two inverse sixth power interionic distance factors. Although the two distances are independent of each other, we must ensure that any triad where two or three ions share identical lattice sites are discounted. Allowing for all these restrictions, we can write the following lattice sums:

$$\sum_{\text{lattice}} R^{-6}R'^{-6} \to \eta c_{\mathrm{A}_1} c_{\mathrm{B}_1} c_{\mathrm{C}_1}^2 a^{-12} = \eta C_{\mathrm{A}_1} C_{\mathrm{B}_1} C_{\mathrm{C}_1}^2, \tag{6.5a}$$

$$\sum_{\text{lattice}} R^{-6}R''^{-6} \to \eta c_{\mathrm{A}_1}^2 c_{\mathrm{B}_1} c_{\mathrm{C}_1} a^{-12} = \eta C_{\mathrm{A}_1}^2 C_{\mathrm{B}_1} C_{\mathrm{C}_1}, \tag{6.5b}$$

$$\sum_{\text{lattice}} R'^{-6}R''^{-6} \to \eta c_{\mathrm{A}_1} c_{B_1}^2 c_{\mathrm{C}_1} a^{-12} = \eta C_{\mathrm{A}_1} C_{\mathrm{B}_1}^2 C_{\mathrm{C}_1}, \tag{6.5c}$$

with a numerical factor η, derived from Pythagorean sums, taking the explicit value of 64.39. The calculation of η (and its more intricate analogue σ, see below) is to be described elsewhere.[69] The lattice weightings of Eqs. (6.5a)–(6.5c) relate directly to the diagonal rate contributions $|M_{fi}^{\text{coop}}|^2$, $|M_{fi}^{\text{acc2}}|^2$, and $|M_{fi}^{\text{acc1}}|^2$, respectively, with differences reflecting the concentration factors for each of the participating ions in their appropriate initial states.

When considering the off-diagonal, quantum interference terms in Eq. (6.3) it is no longer simply the case of considering two independent interionic distance; we now have all three present in every contribution. We can no longer define the systems in terms of independent variables as any one interionic vector can be described as a difference of the other two. Three types of summation arise from the cross terms of (6.3). These are

$$\sum_{\text{lattice}} R^{-3}R'^{-3}R''^{-6} \to \sigma C_{\mathrm{A}_1}^{3/2} C_{\mathrm{B}_1}^{3/2} C_{\mathrm{C}_1}, \tag{6.6a}$$

$$\sum_{\text{lattice}} R^{-6}R'^{-3}R''^{-3} \to \sigma C_{\mathrm{A}_1}^{3/2} C_{\mathrm{B}_1} C_{\mathrm{C}_1}^{3/2}, \tag{6.6b}$$

$$\sum_{\text{lattice}} R^{-3}R'^{-6}R''^{-3} \to \sigma C_{\mathrm{A}_1} C_{\mathrm{B}_1}^{3/2} C_{\mathrm{C}_1}^{3/2}, \tag{6.6c}$$

introducing the numerical factor σ, whose value proves to be 35.81. Specifically, the lattice factors of Eqs. (6.6a)–(6.6c) relate to the quantum interference terms $M_{fi}^{\text{acc2}}\bar{M}_{fi}^{\text{coop}}$, $M_{fi}^{\text{acc1}}\bar{M}_{fi}^{\text{acc2}}$, and $M_{fi}^{\text{acc1}}\bar{M}_{fi}^{\text{coop}}$, respectively, with differences again arising in their dependence on ionic concentrations. The fact that σ is approximately half the value of η (its diagonal-term counterpart) is compensated by the factor of 2 multiplying each off-diagonal term in (6.3). This indicates that the quantum interference terms have, for the case of ions randomly disposed on a cubic lattice, an equal physical significance to the diagonal terms.

VII. CONCLUSION

In this paper we have identified varying processes which fall under the umbrella term of three-center energy transfer. In the field of lanthanide doped materials best suited to these effects, and where various descriptors have been applied to these forms of energy transfer, we have shown that every one can be fully interpreted in terms of accretive and/or cooperative mechanisms. We have established the detailed form of the quantum electrodynamical framework which supports these mechanisms, eliciting their role and features in the energy transfer phenomena of pooling upconversion, sensitization, and downconversion of quantum cutting. It has been proved that, although the two mechanisms play significant roles in pooling and cutting, only the accretive mechanism is responsible for sensitization processes. Both mechanisms have been shown to invoke Raman selection rules, which govern transitions of the mediator ions in the accretive mechanisms and transitions of the acceptor ions in cooperative mechanisms. Finally, we have shown that in real materials, the lattice parameters associated with the various rate components ensure that diagonal and quantum interference terms have broadly comparable significance in three-center energy transfer.

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