

## Laser-assisted resonance-energy transfer

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The process of laser-assisted resonance-energy transfer (LARET) is described and analyzed within the framework of molecular quantum electrodynamics. LARET is a higher-order perturbative contribution to the familiar spontaneous dipole-dipole mechanism for resonance-energy transfer, in which an auxiliary laser field is applied specifically to stimulate the energy transfer. The frequency of the auxiliary beam is chosen to be off-resonant with any molecular transition frequencies in order to eliminate direct photoabsorption by the interacting molecules. Here consideration is given to the general case where the energy exchange takes place between two uncorrelated molecular species, as for example in a molecular fluid, or a system in which the molecules are randomly oriented. In the ensuing calculations it is necessary to implement phase-weighted averaging in tandem with standard isotropic averaging procedures. Results are discussed in terms of a laser intensity-dependent mechanism for energy transfer. Identifying the applied field regime where LARET should prove experimentally significant, transfer rate increases of up to 30% are predicted on reasonable estimates of the molecular parameters. Possible detection techniques are discussed and analyzed with reference to illustrative models.

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### I. INTRODUCTION

The process whereby electronic energy transfers from excited atoms or molecules to ground-state species is a well-established facet of ultrafast photochemistry. Resonance-energy transfer (RET) exercises an important role in the photodynamics of multichromophoric assemblies [1,2], interlayer and intralayer excitation transport in Langmuir-Blodgett films [3,4], and it mediates the storage and migration of energy in photosynthetic systems [5–7] spawning recent interest in man-made antenna devices [8,9]. It also affords an important tool for the determination of molecular architecture, where it is used mainly to determine either site separation distances or conformational changes within large biological structures, through its use as a so-called “spectroscopic ruler” [10–16]. In such systems RET exerts its major effect over distances of the order of tens of Angströms, where radiationless (Förster) energy migration occurs without significant overlap between the wave functions of the participating donor and acceptor species. Governed by dipole-dipole coupling, the process is characterized by a well-known inverse sixth-power dependence on the donor-acceptor separation [17]. At substantially longer distances, radiative energy transfer becomes a more significant means of energy dispersal, and represents an important mechanism for the reabsorption of photons emitted in optically thick samples [18]. Here the associated inverse square distance dependence, which counts against the significant involvement of any individual well-separated donor-acceptor pair, is partially offset (subject to dissipative corrections) by the quadratic growth with distance of the number of possible

acceptors for any initially excited donor.

A somewhat less familiar quantum-field approach to RET was first essayed in pioneering studies by Avery [19] concurrently with Gomberoff and Power [20]. Such approaches do not differentiate between transfer by *radiative* and *radiationless* mechanisms, as these are both necessarily incorporated within a common theory as asymptotic limits. With time, recognition of this unification of previously differentiated regimes has shown that the two processes are simply twin aspects of a single mechanism [21–25]. Such *unified theory* discussions have revealed that at distances intermediary to the asymptotic limits, the energy-transfer rate embraces one or more additional contributions associated with quantum interference. For disordered systems the major additional contribution exhibits an inverse fourth-power dependence on donor-acceptor distance and proves to play as important a role as both the radiative and radiationless mechanisms [23]. The unified theory has also proved amenable to the inclusion of nondipolar coupling effects associated with LMO (localized molecular orbital) interactions through the involvement of charge transfer, thereby offering a seamless extension of Förster theory into regions of strong orbital overlap [26,27]. The recent use of quantum electrodynamics (QED) in research on condensed-matter RET processes [28,29] has led to the formulation of modified radiation-field operators which fully take into account the effects of an intervening medium [30,31].

In this context we have recently drawn attention to the nonlinearities which attach to the fundamental process of energy transfer at high laser intensities [32,33]. Specifically we have shown that, following conventional excitation of the donor species, the transfer rate can be appreciably modified by the propagation of an auxiliary laser beam through the donor-acceptor system. Since a sizable rate enhancement can be engineered under suitable conditions, we have termed the effect laser-assisted resonance-energy transfer (LARET). Essentially, it entails the coupled absorption and stimulated

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emission of photons from and into the applied beam, the overall process accomplishing the same net transfer of energy as in RET. We show that the transfer rate equations thereby exhibit corrections of linear and quadratic dependence on the auxiliary laser irradiance  $I$  as can be represented by the leading terms in the equation,

$$\Gamma = \Gamma_{\text{RET}} + \Gamma_{\text{LARET}} = \Gamma_{\text{RET}} + \Gamma' I + \Gamma'' I^2 + \dots, \quad (1.1)$$

highlighting the form of the intensity dependence. In our earlier work we limited discussion to an outline of the quantum electrodynamical mechanisms for LARET, restricting attention to short-range transfer between a donor and acceptor with fixed mutual orientation. Here we extend the theory to accommodate systems with arbitrary separation, lifting orientation restrictions. Our object is the identification and evaluation of the explicit form of the coefficients  $\Gamma'$  and  $\Gamma''$  in Eq. (1.1).

As a semantic preliminary, we add a note of caution with regard to nomenclature. Reported here is an optical phenomenon markedly different from another higher-order process commonly coined “laser-induced resonance-energy transfer” [34–36]. In the latter, acceptor excited states are accessed by simultaneous transfer of excitation from a preexcited donor, *and* absorption of radiation at a suitable resonant laser frequency. The principle difference from the LARET process being considered here is that the laser field is utilized to bridge the frequency mismatch between the donor and acceptor, and so suffers absorptive losses. In LARET, however, the field plays a quasipassive role. The title “laser-induced energy transfer” has also recently been employed to describe what is essentially conventional laser excitation of a donor and subsequent laser-induced fluorescence from a compatible acceptor [37].

## II. THEORETICAL FORMULATION

The framework of quantum electrodynamics [38] in which both radiation and matter are treated quantum mechanically, lends itself well to the representation of RET, a spontaneous process. The corresponding time-ordered diagrams are given in Fig. 1, where a donor molecule ( $A$ ) in an electronically excited state  $|\alpha\rangle$  (of energy  $\hbar c q$ ) transfers its excitation to an acceptor ( $B$ ). The acceptor, initially in the electronic ground state, thereby undergoes a transition to an electronically excited state  $|\beta\rangle$ . The interaction is facilitated by the interchange of virtual photons, *vide infra*. Viewing the transfer process in these terms, LARET represents an embellishment of the RET process entailing interactions with an auxiliary laser field (defined as comprising, both initially and finally,  $n$  photons with wave vector  $\mathbf{k}$  and polarization  $\lambda$ ). The same net energy is transferred from the donor to the acceptor as in RET.

Laser-assisted resonance-energy transfer can be described with the aid of 96 time-ordered diagrams of the form shown in Figs. 2 and 3, in addition to those shown in Fig. 1. These graphs account for all possible time orderings of the interactions over a full range of distances beyond wave-function overlap. Previously [23] we explicated the short-range (static) asymptote of the interaction, for a molecule in a rigid

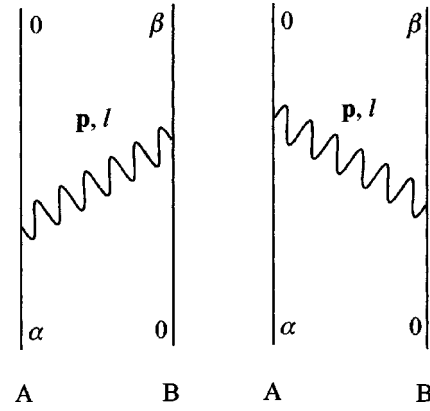


FIG. 1. Time-ordered diagrams representing resonance-energy transfer between a donor  $A$  and acceptor  $B$ . On each molecular worldline, Greek symbols identify molecular electronic excited states, with 0 the corresponding ground state. The transfer is mediated by the virtual photon  $(\mathbf{p}, l)$ .

geometry, considerably simplifying the calculation to a sum represented by 12 diagrams. As in RET, LARET is mediated by the exchange of virtual photons (deemed as such since they are not observed), summed over all possible wave vectors and polarizations. As a consequence of the uncertainty principle these virtual photons have a high uncertainty in energy, associated with their short propagation time. Furthermore, due to the fully retarded nature of the theory from which they emerge, as transfer distances increase so does the real character of these photons, as is reflected in a progressively radiative character to the energy-transfer process.

The full Hamiltonian  $H$  for LARET is given by

$$H = H_{\text{mol}}^A + H_{\text{mol}}^B + H_{\text{int}}^A + H_{\text{int}}^B + H_{\text{rad}}, \quad (2.1)$$

where  $H_{\text{mol}}^\xi$  is the molecular Hamiltonian for molecule  $\xi$  and  $H_{\text{rad}}$  represents the second-quantized radiation field. Within the electric dipole approximation utilized here, the molecule-field coupling Hamiltonian  $H_{\text{int}}^\xi$  is explicitly

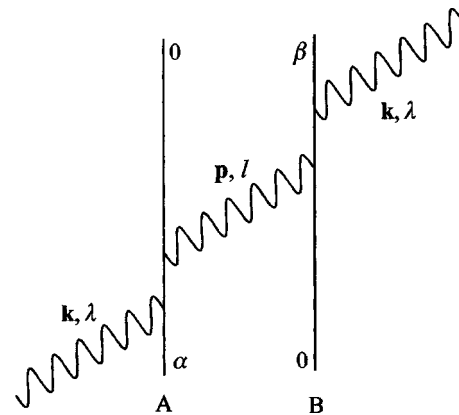


FIG. 2. One of 24 time orderings representing one type of LARET process where both donor and acceptor interact with the auxiliary beam. A mirror-case entails photonic annihilation and creation at the opposite molecule to that shown.

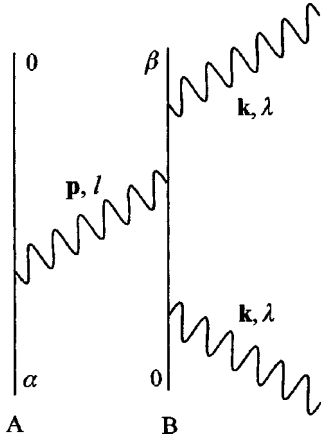


FIG. 3. One of 24 time orderings representative of LARET interactions where only the donor  $A$  interacts with the auxiliary beam. Again another process can be identified in which both laser molecule interactions occur at the acceptor  $B$ .

$$H_{\text{int}}^{\xi} = \varepsilon_0^{-1} \boldsymbol{\mu}(\xi) \cdot \mathbf{d}^{\perp}(\mathbf{R}_{\xi}), \quad (2.2)$$

with  $\boldsymbol{\mu}(\xi)$  the electric dipole moment operator and  $\mathbf{R}_{\xi}$  the position vector for molecule  $\xi$ . The transverse electric displacement field operator  $\mathbf{d}^{\perp}(\mathbf{R}_{\xi})$  can be expressed in terms of a mode expansion either in the traditional vacuum formulation [38] or through the incorporation of media influences, in a form appropriate for a system embedded in a host or solvent ‘‘bath’’ [30,31]. For presentational simplicity Eq. (2.3) addresses the vacuum expansion in terms of photons of wave vector  $\mathbf{p}$  and polarization  $l$

$$\begin{aligned} \mathbf{d}^{\perp}(\mathbf{R}_{\xi}) = & \sum_{\mathbf{p}, l} \left( \frac{\hbar c p \varepsilon_0}{2V} \right)^{1/2} i [\mathbf{e}^{(l)}(\mathbf{p}) a^{(l)}(\mathbf{p}) e^{i\mathbf{p} \cdot \mathbf{R}_{\xi}} - \bar{\mathbf{e}}^{(l)}(\mathbf{p}) \\ & \times a^{\dagger(l)}(\mathbf{p}) e^{-i\mathbf{p} \cdot \mathbf{R}_{\xi}}], \end{aligned} \quad (2.3)$$

where  $\mathbf{e}$  is the electric-field unit vector ( $\bar{\mathbf{e}}$  being its complex conjugate),  $a$  and  $a^{\dagger}$  are annihilation and creation operators, respectively, and  $V$  is the quantization volume.

For any photophysical process we can define the quantum probability amplitude or *matrix element*,  $M_{FI}$ , connecting the initial,  $|I\rangle$ , to the final,  $|F\rangle$ , system states.  $M_{FI}$  is expressible through the time-dependent perturbation expansion,

$$M_{FI} = \sum_{m=1}^{\infty} M_{FI}^{(m)}, \quad (2.4)$$

where  $m$  is the number of photonic interactions (real or virtual). For conventional energy transfer, leading contributions to the matrix element are associated with  $m=2$ , indicative of the two interactions depicted in each of the graphs of Fig. 1. These contributions are quantified by second-order perturbation results summed over virtual intermediate states  $|S\rangle$ , signifying virtual photon propagation,

$$M_{FI}^{(2)} = \sum_R \frac{\langle F | H_{\text{int}} | S \rangle \langle S | H_{\text{int}} | I \rangle}{(E_I - E_S)}. \quad (2.5)$$

In Eq. (2.5)  $E_N$  is the energy of the system state  $|N\rangle$ , comprising products of both molecular and radiation states  $|N\rangle = |n_{(\text{mol})}\rangle |n_{(\text{rad})}\rangle$ .

Considering next the effects on the energy-transfer process manifest through interaction with an auxiliary beam, the lowest-order contribution to effect a rate modification will be due to two extra laser-molecule interactions, as depicted in Figs. 2 and 3, associated with the case  $m=4$  in Eq. (2.4). The matrix element which accounts for these corrections is a fourth-order perturbational result summing over three intermediate states  $S$ ,  $T$ , and  $U$ ,

$$M_{FI}^{(4)} = \sum_{R,S,T} \frac{\langle F | H_{\text{int}} | U \rangle \langle U | H_{\text{int}} | T \rangle \langle T | H_{\text{int}} | S \rangle \langle S | H_{\text{int}} | I \rangle}{(E_I - E_S)(E_I - E_T)(E_I - E_U)}. \quad (2.6)$$

The intermediate states contained in Eq. (2.6) envelop all four basic forms of LARET interaction due to interplay of the external fields with either solely  $A$  or solely  $B$  (Fig. 3), or sequentially with both (Fig. 2).

The duly modified rate  $\Gamma$  for the energy-transfer process (viz., LARET) can be ascertained using Fermi’s golden rule with constituents as given in Eq. (2.4) with  $m=2,4,\dots$ . The even constraint on the value of  $m$  is a result of the nature of LARET; every energy transfer entails at least two photonic interactions and, in order for the auxiliary laser field to remain unperturbed overall, each molecule-field photonic annihilation needs to be twinned with a creation and vice versa. The LARET rate can therefore be expressed as

$$\Gamma = \frac{2\pi\rho}{\hbar} \left| \sum_{m'=1}^{\infty} M_{FI}^{(2m')} \right|^2, \quad (2.7)$$

where  $\rho$  is the density of molecular states of the acceptor molecule. Only the second and fourth orders of the perturbation play a significant part in the LARET effect as the series rapidly converges, making higher contributions,  $m' \geq 3$ , negligible.

### III. RESULTS

Recognizing the insignificance of higher-order contributions to the rate given by Eq. (2.7) allows us to write, in a more explicit form, the LARET matrix element  $M^{\text{LARET}}$ ,

$$M^{\text{LARET}} = M^{(2)} + \sum_{j=1}^4 M_j^{(4)}. \quad (3.1)$$

Adopting the convention of implied summation over repeated indices, the calculated matrix element contributions to Eq. (3.1) are given by

$$M^{(2)} = -\mu_i^{0\alpha(A)} V_{ij}(q, \mathbf{R}) \mu_j^{\beta 0(B)}, \quad (3.2)$$

$$\begin{aligned} M_1^{(4)} = & -\frac{n\hbar ck}{2\varepsilon_0 V} e_i^{(\lambda)}(\mathbf{k}) \alpha_{ij}^{0\alpha(A^+)}(k) V_{jk}((q+k), \mathbf{R}) \\ & \times \alpha_{kl}^{\beta 0(B^-)}(k) \bar{e}_l^{(\lambda)}(\mathbf{k}) e^{-i\mathbf{k} \cdot \mathbf{R}}, \end{aligned} \quad (3.3a)$$

$$M_2^{(4)} = -\frac{n\hbar ck}{2\varepsilon_0 V} \bar{e}_i^{(\lambda)}(\mathbf{k}) \alpha_{ij}^{0\alpha(A^-)}(k) V_{jk}((q-k), \mathbf{R}) \\ \times \alpha_{kl}^{\beta_0(B^+)}(k) e_l^{(\lambda)}(\mathbf{k}) e^{i\mathbf{k}\cdot\mathbf{R}}, \quad (3.3b)$$

$$M_3^{(4)} = -\frac{n\hbar ck}{2\varepsilon_0 V} \bar{e}_i^{(\lambda)}(\mathbf{k}) e_l^{(\lambda)}(\mathbf{k}) \beta_{ijl}^{0\alpha(A)}(k) V_{jk}(q, \mathbf{R}) \mu_k^{\beta_0(B)}, \quad (3.3c)$$

$$M_4^{(4)} = -\frac{n\hbar ck}{2\varepsilon_0 V} \bar{e}_i^{(\lambda)}(\mathbf{k}) e_l^{(\lambda)}(\mathbf{k}) \beta_{ijl}^{\beta_0(B)}(k) V_{jk}(q, \mathbf{R}) \mu_i^{0\alpha(A)}, \quad (3.3d)$$

where we define the intermolecular vector  $\mathbf{R} \equiv \mathbf{R}_B - \mathbf{R}_A$ ,  $\mu^{xy(\xi)} \equiv \langle x | \mu(\xi) | y \rangle$ , and  $\mathbf{V}(p, \mathbf{R})$  is the index-symmetric, complex, and fully retarded intermolecular transfer tensor [38] of the form

$$V_{ij}(p, \mathbf{R}) = \frac{\exp(ipR)}{(4\pi\varepsilon_0 R^3)^2} [(1-ipR)(\delta_{ij} - 3\hat{R}_i \hat{R}_j) \\ - (pR)^2 (\delta_{ij} - \hat{R}_i \hat{R}_j)]. \quad (3.4)$$

In our initial investigations [33] it was considered pertinent in establishing the process to treat only the case of small donor-acceptor separations ( $qR \ll 1$ ), thus reducing Eq. (3.4) to its short-range limit with  $R^{-3}$  distance dependence. Here, by generalizing the result, we not only naturally incorporate the short-range limit but also accommodate larger values of  $q$  and  $R$  which will exhibit retardation effects. To this end, it will prove useful to introduce the notation  $q_{\pm} = q \pm k$  for the arguments of the intermolecular transfer contained in the first two terms of Eq. (3.3). With further reference to Eq. (3.4), the detailed form of any dissipative and refractive modifications explicitly given elsewhere [28–31] can serve only to enhance LARET, as a premultiplier (greater than unity) is introduced. Dependent on the refractive index of the medium over which energy transfer takes place, this factor arises from the involvement of *dressed* virtual photons as effectors of the energy migration. Although deemed unnecessarily complicated here, such effects should, in general, not be neglected and form rich ground for future work.

Returning to Eqs. (3.3a)–(3.3d), the generalized polarizabilities  $\alpha^{fi(\xi\pm)}(k)$  and hyperpolarizabilities  $\beta^{fi(\xi)}(k)$  appearing therein are defined as

$$\alpha_{ij}^{fi(\xi\pm)}(k) = \sum_s \left\{ \frac{\mu_i^{fs} \mu_j^{si}}{(E_{sf} \pm \hbar ck - i\Gamma_s)} + \frac{\mu_j^{fs} \mu_i^{si}}{(E_{si} \mp \hbar ck - i\Gamma_s)} \right\} \quad (3.5)$$

and

$$\beta_{ijk}^{fi(\xi)}(k) = \sum_{s,t} \left\{ \frac{\mu_i^{ft} \mu_j^{ts} \mu_k^{si}}{(E_{si} - \hbar ck - i\Gamma_s)(E_{tf} - \hbar ck - i\Gamma_t)} \right. \\ + \frac{\mu_i^{ft} \mu_k^{ts} \mu_j^{si}}{(E_{sf} - i\Gamma_s)(E_{tf} - \hbar ck - i\Gamma_t)} \\ + \frac{\mu_j^{ft} \mu_i^{ts} \mu_k^{si}}{(E_{si} - \hbar ck - i\Gamma_s)(E_{ti} - i\Gamma_t)} \\ + \frac{\mu_k^{ft} \mu_j^{ts} \mu_i^{si}}{(E_{si} + \hbar ck - i\Gamma_s)(E_{tf} + \hbar ck - i\Gamma_t)} \\ + \frac{\mu_k^{ft} \mu_i^{ts} \mu_j^{si}}{(E_{sf} - i\Gamma_s)(E_{tf} + \hbar ck - i\Gamma_t)} \\ \left. + \frac{\mu_j^{ft} \mu_k^{ts} \mu_i^{si}}{(E_{si} + \hbar ck - i\Gamma_s)(E_{ti} - i\Gamma_t)} \right\}, \quad (3.6)$$

respectively. Here both molecular tensors employ the energy difference notation  $E_{xy} \equiv E_x - E_y$ , along with the proper accommodation of resonance behavior through the inclusion of imaginary energy addenda in the denominators. The addenda,  $i\Gamma_n$ , signal the existence of molecular state lifetimes associated with the intermediate states  $|n_{(\text{mol})}\rangle$ , the sign consistent with time-reversal symmetry [39].

As a result of Eqs. (2.7) and (3.1) the rate for the LARET process can be written as

$$\Gamma = \frac{2\pi}{\hbar} |M^{\text{LARET}}|^2 \rho \quad (3.7)$$

with the modulus-squared part yielding 25 contributions expressible as the sum of 15 terms contained by Eq. (3.8),

$$|M^{\text{LARET}}|^2 = |M^{(2)}|^2 + \sum_{i=1}^4 |M_i^{(4)}|^2 + 2 \operatorname{Re} M^{(2)} \sum_{i=1}^4 \bar{M}_i^{(4)} \\ + 2 \operatorname{Re} \sum_{i=1}^3 \sum_{j=i+1}^4 M_i^{(4)} \bar{M}_j^{(4)}. \quad (3.8)$$

Here matrix element initial- and final-state subscripts have been suppressed for brevity. The first two terms of Eq. (3.8) contribute diagonal elements to the LARET rate and the latter two, off diagonal or cross terms. All 15 contributions need to be rotationally averaged, the implementation of which is outlined below. Each result is primarily judged on its dependence on the auxiliary laser intensity  $I(\mathbf{k})$ , where  $I(\mathbf{k}) \equiv n\hbar c^2 k/V$ .

For the case of energy transfer in fixed coordinate systems, such as chromophores held in crystal-lattice points or suspended in either a molecular cage or matrix, the results for the static, short-range limit (as given previously [33]) are perfectly valid. Here we address the more general case of randomly oriented or freely rotating chromophores, as in a molecular fluid. This case requires rotational averaging of the rate given by Eq. (3.7). To deal with the 15 terms that arise is acutely complex since, in general, three consecutive averages are necessary, two to decouple the donor and ac-

ceptor from their respective displacement vectors, and a third to decouple that vector from the auxiliary field. The detailed methods have been elaborated previously in connection with cooperative absorption processes [40,41]. To allow clarity during this passage, many explicit definitions of parameters have been removed to the Appendix. Nevertheless, full calculational methods are outlined and the full results are presented below.

The results we concern ourselves with fall into two distinct calculational categories, invoking isotropic and phase-weighted averages. The weighted terms only arise from off-diagonal contributions involving  $M_1^{(4)}, M_2^{(4)}$  (or a mixture of both) through the phase factors evident in Eqs. (3.3a) and (3.3b). The other rate contributions, which are calculated using standard isotropic average methods [42], afford a convenient place to start our analysis. The fully rotationally averaged diagonal contributions contained in the first two terms of Eq. (3.8) are as follows. Firstly,

$$\langle \Gamma(2:\bar{2}) \rangle = \frac{2\pi\rho_f}{9\hbar} |\boldsymbol{\mu}^{(A)}|^2 |\boldsymbol{\mu}^{(B)}|^2 |\mathbf{V}(q, \mathbf{R})|^2, \quad (3.9)$$

where the argument  $(2:\bar{2})$  here introduced and utilized henceforth signifies the rate contribution calculated from the product of matrix elements  $M^{(2)}\bar{M}^{(2)}$ , angular brackets indicating a fully averaged result. The result given in Eq. (3.9) is the familiar, laser intensity-independent, rate for RET. It can be regarded as a useful benchmark against which all other contributions are to be compared. Furthermore, explicitly

$$|\mathbf{V}(q, \mathbf{R})|^2 = V_{ij}(q, \mathbf{R}) \bar{V}_{ij}(q, \mathbf{R}) \\ = \frac{2}{(4\pi\epsilon_0 R^3)^2} (3 + q^2 R^2 + q^4 R^4). \quad (3.10)$$

The right-hand side of Eq. (3.10) can be thought of as an excitation transfer function serving to assimilate retardation effects within the standard Förster-type energy-transfer result. The structure of Eq. (3.10) plays an intrinsic part in our investigations at a later stage, and is worthy of expansion here. The calculations of cross terms arising from Eq. (3.8) produce disparate energy-transfer tensor contractions, similar in form to Eq. (3.10), including  $V_{ij}(q, \mathbf{R}) \bar{V}_{ij}(q_{\pm}, \mathbf{R})$  and  $V_{ij}(q_{\pm}, \mathbf{R}) \bar{V}_{ij}(q_{\mp}, \mathbf{R})$  *inter alia*. These contributions, which occur through the contraction of tensors with differing wave-vector arguments, engender complex results, the form of which has been detailed (again in connection with cooperative absorption) elsewhere [43]. The short- and long-range limits of such contractions are reported fully in the Appendix.

Returning to the averages, along with the result given by Eq. (3.9) we have a further four diagonal results arising from the first sum embedded in Eq. (3.8). The nature of these results immediately reveals them to be dependent on the square of the laser intensity, signifying contributions to the  $\Gamma'' I^2$  term in Eq. (1.1). The results are as follows: firstly,

$$\langle \Gamma(4_1:\bar{4}_1) \rangle = \frac{\pi I^2(\mathbf{k})\rho}{27\,000\hbar c^2 \epsilon_0^2} (4\pi\epsilon_0 R^3)^{-2} (10(3 + q_+^2 R^2 + q_+^4 R^4) \\ \times [\{\Sigma_1^{(\alpha\bar{\alpha})}(A_+^+) + 3\Sigma_2^{(\alpha\bar{\alpha})}(A_+^+) + \Sigma_3^{(\alpha\bar{\alpha})}(A_+^+)\} \Sigma_2^{(\alpha\bar{\alpha})}(B_-^-) + \Sigma_2^{(\alpha\bar{\alpha})}(A_+^+) \{\Sigma_1^{(\alpha\bar{\alpha})}(B_-^-) + \Sigma_3^{(\alpha\bar{\alpha})}(B_-^-)\}] \\ + 2\{(3 - |\mathbf{e} \cdot \mathbf{e}|^2)(3 + q_+^2 R^2) + (1 + 3|\mathbf{e} \cdot \mathbf{e}|^2)q_+^4 R^4\} \{\Sigma_1^{(\alpha\bar{\alpha})}(A_+^+) \Sigma_3^{(\alpha\bar{\alpha})}(B_-^-) + \Sigma_3^{(\alpha\bar{\alpha})}(A_+^+) \Sigma_1^{(\alpha\bar{\alpha})}(B_-^-)\} \\ + \{(1 + 3|\mathbf{e} \cdot \mathbf{e}|^2)(3 + q_+^2 R^2) + (7 + |\mathbf{e} \cdot \mathbf{e}|^2)q_+^4 R^4\} \{\Sigma_1^{(\alpha\bar{\alpha})}(A_+^+) \Sigma_1^{(\alpha\bar{\alpha})}(B_-^-) + \Sigma_3^{(\alpha\bar{\alpha})}(A_+^+) \Sigma_3^{(\alpha\bar{\alpha})}(B_-^-)\}), \quad (3.11)$$

wherein, to avoid overlong expressions obscuring the underlying physics, we have defined sums of product molecular polarizabilities as

$$\Sigma_1^{(\alpha\bar{\alpha})}(\xi_{\mp}^{\pm}) = 4\alpha_{\lambda\lambda}^{(\xi_{\pm}^{\pm})} \bar{\alpha}_{\mu\mu}^{(\xi_{\mp}^{\mp})} - \alpha_{\lambda\mu}^{(\xi_{\pm}^{\pm})} \bar{\alpha}_{\lambda\mu}^{(\xi_{\mp}^{\mp})} - \alpha_{\lambda\mu}^{(\xi_{\pm}^{\pm})} \bar{\alpha}_{\mu\lambda}^{(\xi_{\mp}^{\mp})}, \\ \Sigma_2^{(\alpha\bar{\alpha})}(\xi_{\mp}^{\pm}) = -\alpha_{\lambda\lambda}^{(\xi_{\pm}^{\pm})} \bar{\alpha}_{\mu\mu}^{(\xi_{\mp}^{\mp})} + 4\alpha_{\lambda\mu}^{(\xi_{\pm}^{\pm})} \bar{\alpha}_{\lambda\mu}^{(\xi_{\mp}^{\mp})} - \alpha_{\lambda\mu}^{(\xi_{\pm}^{\pm})} \bar{\alpha}_{\mu\lambda}^{(\xi_{\mp}^{\mp})}, \\ \Sigma_3^{(\alpha\bar{\alpha})}(\xi_{\mp}^{\pm}) = -\alpha_{\lambda\lambda}^{(\xi_{\pm}^{\pm})} \bar{\alpha}_{\mu\mu}^{(\xi_{\mp}^{\mp})} - \alpha_{\lambda\mu}^{(\xi_{\pm}^{\pm})} \bar{\alpha}_{\lambda\mu}^{(\xi_{\mp}^{\mp})} + 4\alpha_{\lambda\mu}^{(\xi_{\pm}^{\pm})} \bar{\alpha}_{\mu\lambda}^{(\xi_{\mp}^{\mp})},$$

and where, bearing in mind Eq. (3.5), argumentative  $\pm$  superscripts and subscripts relate to the frequency dependence of the molecular polarizability and its

(overbarred) complex conjugate, respectively. Such parameters are recurrent in this work due to the fourth-rank rotational average that spawns them in more than one rate contribution. Also, within Eq. (3.11), we identify internal products of identical polarizations manifest as  $|\mathbf{e} \cdot \mathbf{e}|^2$  which have the values of unity or zero for plane or circularly polarized light, respectively. It is interesting to see that, by symmetry, the contribution  $\langle \Gamma(4_2:\bar{4}_2) \rangle$  is identical in form to the result of Eq. (3.11). However, we must take care and recognize that, in  $\langle \Gamma(4_2:\bar{4}_2) \rangle$ , the transformations  $q_+ \rightarrow q_-$ , and  $\alpha^{(\xi_{\pm}^{\pm})} \leftrightarrow \alpha^{(\xi_{\mp}^{\mp})}$  have taken place. Continuing, the next diagonal term,  $\langle \Gamma(4_3:\bar{4}_3) \rangle$ , can be expressed as

$$\begin{aligned} \langle \Gamma(4_3 : \bar{4}_3) \rangle &= \frac{\pi I^2 \rho |\boldsymbol{\mu}^{(B)}|^2 |\mathbf{V}(q, \mathbf{R})|^2}{540 \hbar \varepsilon_0^2 c^2} \{ (3 - |\mathbf{e} \cdot \mathbf{e}|^2) \\ &\quad \times (\beta_{\lambda\mu\lambda}^{(A)} \bar{\beta}_{\nu\mu\nu}^{(A)}) + 2(2|\mathbf{e} \cdot \mathbf{e}|^2 - 1) \beta_{\lambda\mu\nu}^{(A)} \bar{\beta}_{\nu\mu\lambda}^{(A)} \} \end{aligned} \quad (3.12)$$

with a similar expression for  $\langle \Gamma(4_4 : \bar{4}_4) \rangle$  obtainable, again by symmetry, following the molecular label substitution  $A \leftrightarrow B$ .

The off-diagonal rate contributions are contained in the latter two sums of Eq. (3.8). We first concentrate on the third

term, embracing those results linearly dependent on the auxiliary laser intensity, together relating to the  $\Gamma' I$  term in Eq. (1.1). It is here, however, that averaging complications arise through cross-term contributions containing elements  $M_1^{(4)}$  and  $M_2^{(4)}$  and their associated phase factors  $e^{\mp i \mathbf{k} \cdot \mathbf{R}}$ , respectively. Such phase factors require that we utilize phase-weighted isotropic averaging techniques [44] to give a full and proper description. These methods introduce  $n$ th-order spherical Bessel functions,  $j_n(x)$ ,  $0 \leq n \leq 5$ , into our expressions. As a result of index symmetry within Eq. (3.4) only even,  $n=0, 2$ , and 4, spherical Bessel functions survive. Acknowledging this, the linearly intensity-dependent terms can be expressed as

$$\begin{aligned} \langle \Gamma(2 : \bar{4}_1) \rangle &= \frac{\pi I(\mathbf{k}) \rho}{36 \hbar \varepsilon_0 c} \text{Re} \{ (\varepsilon_{\lambda\sigma\omega} \mu_{\lambda}^{(A)} \bar{\alpha}_{\sigma\omega}^{(A+)}) (\mu_{\lambda}^{(B)} \bar{\alpha}_{\Sigma\Omega}^{(B)} \varepsilon_{\Lambda\Sigma\Omega}) \} \\ &\quad \times \left( \left[ \frac{1}{3} j_0(kR) \{ V_{ij}(q, \mathbf{R}) \bar{V}_{ij}(q_+, \mathbf{R}) - V_{ii}(q, \mathbf{R}) \bar{V}_{jj}(q_+, \mathbf{R}) \} \right] \right. \\ &\quad - \frac{1}{2} j_2(kR) \left[ \{ V_{ii}(q, \mathbf{R}) \bar{V}_{jk}(q_+, \mathbf{R}) \hat{R}_j \hat{R}_k - \frac{1}{3} V_{ii}(q, \mathbf{R}) \bar{V}_{jj}(q_+, \mathbf{R}) \} \right. \\ &\quad \left. \left. + \{ V_{ij}(q, \mathbf{R}) \bar{V}_{kk}(q_+, \mathbf{R}) \hat{R}_i \hat{R}_j - \frac{1}{3} V_{ii}(q, \mathbf{R}) \bar{V}_{jj}(q_+, \mathbf{R}) \} \right] \right. \\ &\quad \left. - 2 \{ V_{ij}(q, \mathbf{R}) \bar{V}_{ik}(q_+, \mathbf{R}) \hat{R}_j \hat{R}_k - \frac{1}{3} V_{ij}(q, \mathbf{R}) \bar{V}_{ij}(q_+, \mathbf{R}) \} \right), \end{aligned} \quad (3.13)$$

where lower- and upper-case Greek indices refer to the rotationally invariant frames of molecules  $A$  and  $B$ , respectively. As with earlier results,  $\langle \Gamma(2 : \bar{4}_2) \rangle$  can be derived from Eq. (3.13) by application of the same transformation used on Eq. (3.11) to effect the corresponding change in the wave-vector arguments and molecular polarizabilities. The remaining two averages in the third term of the sum of component matrix elements are calculated using the standard isotropic averaging methods as there are no complicating phase factors in elements  $M_3^{(4)}$  or  $M_4^{(4)}$ . Explicitly,

$$\langle \Gamma(2 : \bar{4}_3) \rangle = \frac{\pi I(\mathbf{k}) |\boldsymbol{\mu}^{(B)}|^2 |V_{ij}|^2 \rho}{27 \hbar c \varepsilon_0} \text{Re}(\mu_{\lambda}^{(A)} \bar{\beta}_{\lambda\mu\mu}^{(A)}), \quad (3.14)$$

with  $\langle \Gamma(2 : \bar{4}_4) \rangle$  obtainable by the molecular substitution  $A \leftrightarrow B$ , mirroring the treatment of Eq. (3.12).

Finally we return to the other  $\Gamma'' I^2$  contributions to the LARET rate equation (1.1). Dependent on the square of the laser intensity, these are the six contributions embraced by the final term in the general matrix element equation, Eq. (3.8). Once more it is necessary to use the phased-averaging technique for terms incorporating  $M_1^{(4)}$  and  $M_2^{(4)}$ . Sequentially the results unfold as

$$\begin{aligned} \langle \Gamma(4_1 : \bar{4}_2) \rangle &= \frac{\pi I^2(\mathbf{k}) \rho}{900 \hbar c^2 \varepsilon_0^2} \text{Re} \{ \{ \Sigma_1^{(\alpha\bar{\alpha})}(A_+) + \Sigma_3^{(\alpha\bar{\alpha})}(A_+) \} \{ \Sigma_1^{(\alpha\bar{\alpha})}(B_+) + \Sigma_3^{(\alpha\bar{\alpha})}(B_+) \} \} \\ &\quad \times \left[ \frac{1}{30} j_0(2kR) \{ 3 V_{ii}^+ \bar{V}_{jj}^- + V_{ij}^+ \bar{V}_{ij}^- + |\mathbf{e} \cdot \mathbf{e}|^2 (3 V_{ij}^+ \bar{V}_{ij}^- - V_{ii}^+ \bar{V}_{jj}^-) \} + \frac{1}{14} j_2(2kR) \right. \\ &\quad \times \{ (3 - 2|\mathbf{e} \cdot \mathbf{e}|^2) (V_{ii}^+ \bar{V}_{jk}^- \hat{R}_j \hat{R}_k + V_{ij}^+ \bar{V}_{ik}^- \hat{R}_i \hat{R}_j - \frac{2}{3} V_{ij}^+ \bar{V}_{ij}^-) + 2(3|\mathbf{e} \cdot \mathbf{e}|^2 - 1) (V_{ij}^+ \bar{V}_{ik}^- \hat{R}_j \hat{R}_k - \frac{1}{3} V_{ij}^+ \bar{V}_{ij}^-) \} \\ &\quad \left. + \frac{1}{8} j_4(2kR) (2 + |\mathbf{e} \cdot \mathbf{e}|^2) \{ V_{ij}^+ \bar{V}_{kl}^- \hat{R}_i \hat{R}_j \hat{R}_k \hat{R}_l - \frac{1}{7} (V_{ii}^+ \bar{V}_{jk}^- \hat{R}_j \hat{R}_k + 4 V_{ij}^+ \bar{V}_{ik}^- \hat{R}_i \hat{R}_k + V_{ij}^+ \bar{V}_{kk}^- R_i R_j) \right. \\ &\quad \left. + \frac{1}{35} (V_{ii}^+ \bar{V}_{jj}^- + 2 V_{ij}^+ \bar{V}_{ij}^-) \right] + \left[ \{ \Sigma_1^{(\alpha\bar{\alpha})}(A_+) + \Sigma_3^{(\alpha\bar{\alpha})}(A_+) \} \Sigma_2^{(\alpha\bar{\alpha})}(B_+) + \Sigma_2^{(\alpha\bar{\alpha})}(A_+) \{ \Sigma_1^{(\alpha\bar{\alpha})}(B_+) \right. \\ &\quad \left. + \Sigma_3^{(\alpha\bar{\alpha})}(B_+) \} \right] |\mathbf{e} \cdot \mathbf{e}|^2 \left\{ \frac{1}{3} j_0(2kR) V_{ij}^+ \bar{V}_{ij}^- + \frac{1}{2} j_2(2kR) (V_{ij}^+ \bar{V}_{ik}^- \hat{R}_j \hat{R}_k - \frac{1}{3} V_{ij}^+ \bar{V}_{ij}^-) \right\} \\ &\quad + \Sigma_2^{(\alpha\bar{\alpha})}(A_+) \Sigma_2^{(\alpha\bar{\alpha})}(B_+) |\mathbf{e} \cdot \mathbf{e}|^2 j_0(2kR) V_{ij}^+ \bar{V}_{ij}^-, \end{aligned} \quad (3.15)$$

where arguments associated with the radiation energy-transfer tensors have been suppressed, utilizing the notation  $V_{ij}^+ \bar{V}_{ij}^- \equiv V_{ij}(q_+, \mathbf{R}) \bar{V}_{ij}(q_-, \mathbf{R})$  to clarify their contraction with the intermolecular unit vector  $\hat{\mathbf{R}}$  (full expressions are contained within the Appendix). Continuing,

$$\begin{aligned} \langle \Gamma(4_1: \bar{4}_3) \rangle = & \frac{I^2(\mathbf{k}) \pi \rho}{180 \hbar c^2 \varepsilon_0^2} \text{Re}(\alpha_{ij}^{(B-)} \bar{\mu}_k^{(B)} \varepsilon_{ijk}) \{ (\alpha_{\pi\rho}^{(A+)} \bar{\beta}_{\tau\sigma\sigma}^{(A)} \varepsilon_{\pi\rho\tau}) S_+(1) + (\alpha_{\pi\rho}^{(A+)} \bar{\beta}_{\tau\sigma\tau}^{(A)} \varepsilon_{\pi\rho\sigma}) S_+(2) + (\alpha_{\pi\rho}^{(A+)} \bar{\beta}_{\tau\tau\sigma}^{(A)} \varepsilon_{\pi\rho\sigma}) S_+(3) \\ & + (\alpha_{\pi\rho}^{(A+)} \bar{\beta}_{\tau\sigma\rho}^{(A)} \varepsilon_{\pi\tau\sigma}) S_+(4) + (\alpha_{\pi\rho}^{(A+)} \bar{\beta}_{\tau\rho\sigma}^{(A)} \varepsilon_{\pi\tau\sigma}) S_+(5) + (\alpha_{\pi\rho}^{(A+)} \bar{\beta}_{\rho\tau\sigma}^{(A)} \varepsilon_{\pi\tau\sigma}) S_+(6) \}, \end{aligned} \quad (3.16)$$

where composite radiation tensor parameters  $S_{\pm}(n)$ , again introduced for conciseness, are reported explicitly in the Appendix. The contribution from  $\langle \Gamma(4_1: \bar{4}_4) \rangle$  takes the form of Eq. (3.16) following the molecular label substitution  $A \leftrightarrow B$ . Similarly, we calculate

$$\begin{aligned} \langle \Gamma(4_2: \bar{4}_3) \rangle = & \frac{I^2(\mathbf{k}) \pi \rho}{180 \hbar c^2 \varepsilon_0^2} \text{Re}(\alpha_{\lambda\mu}^{(B+)} \bar{\mu}_\nu^{(B)} \varepsilon_{\lambda\mu\nu}) \{ (\alpha_{\pi\rho}^{(A-)} \bar{\beta}_{\tau\sigma\sigma}^{(A)} \varepsilon_{\pi\rho\tau}) S_-(3) + (\alpha_{\pi\rho}^{(A-)} \bar{\beta}_{\tau\sigma\tau}^{(A)} \varepsilon_{\pi\rho\sigma}) S_-(2) + (\alpha_{\pi\rho}^{(A-)} \bar{\beta}_{\tau\tau\sigma}^{(A)} \varepsilon_{\pi\rho\tau}) S_-(1) \\ & - (\alpha_{\pi\rho}^{(A-)} \bar{\beta}_{\tau\sigma\rho}^{(A)} \varepsilon_{\pi\tau\sigma}) S_-(6) - (\alpha_{\pi\rho}^{(A-)} \bar{\beta}_{\tau\rho\sigma}^{(A)} \varepsilon_{\pi\tau\sigma}) S_-(5) - (\alpha_{\pi\rho}^{(A-)} \bar{\beta}_{\rho\tau\sigma}^{(A)} \varepsilon_{\pi\tau\sigma}) S_-(4) \} \end{aligned} \quad (3.17)$$

with  $\langle \Gamma(4_2: \bar{4}_4) \rangle$  derivable from Eq. (3.17), again with  $A \leftrightarrow B$ . Finally,

$$\begin{aligned} \langle \Gamma(4_3: \bar{4}_4) \rangle = & \frac{\pi I^2(\mathbf{k}) \rho}{13500 \hbar c^2 \varepsilon_0^2} \text{Re}(4 \pi \varepsilon_0 R^3)^{-2} (10(3 + q^2 R^2 + q^4 R^4) \\ & \times [ \{ \Sigma_1^{(\beta\bar{\mu})}(A) + 3 \Sigma_2^{(\beta\bar{\mu})}(A) + \Sigma_3^{(\beta\bar{\mu})}(A) \} \Sigma_2^{(\beta\bar{\mu})}(B) + \Sigma_2^{(\beta\bar{\mu})}(A) \{ \Sigma_1^{(\beta\bar{\mu})}(B) + \Sigma_3^{(\beta\bar{\mu})(B)} \} ] \\ & + 2 \{ (3 - |\mathbf{e} \cdot \mathbf{e}|^2)(3 + q^2 R^2) + (1 + 3|\mathbf{e} \cdot \mathbf{e}|^2) q^4 R^4 \} \{ \Sigma_1^{(\beta\bar{\mu})}(A) \Sigma_3^{(\beta\bar{\mu})}(B) + \Sigma_3^{(\beta\bar{\mu})}(A) \Sigma_1^{(\beta\bar{\mu})}(B) \} \\ & + \{ (1 + 3|\mathbf{e} \cdot \mathbf{e}|^2)(3 + q^2 R^2) + (7 + |\mathbf{e} \cdot \mathbf{e}|^2) q^4 R^4 \} \{ \Sigma_1^{(\beta\bar{\mu})}(A) \Sigma_1^{(\beta\bar{\mu})}(B) + \Sigma_3^{(\beta\bar{\mu})}(A) \Sigma_3^{(\beta\bar{\mu})}(B) \} \end{aligned} \quad (3.18)$$

using similar definitions for the sums of product molecular parameters as introduced in Eq. (3.11). In Eq. (3.18) however, the fourth-rank average contains contributions from a third-rank hyperpolarizability tensor along with a transition dipole moment, as opposed to the two second-rank (both polarizability) tensor contributions of Eq. (3.11). This completes our total of 15, fully averaged, contributions to the rate of LARET.

#### IV. DISCUSSION

We have derived in Sec. III a fully rotationally averaged expression for the rate of laser-assisted resonance-energy transfer incorporating all possible intermolecular separations, representative of the bulk response from a molecular fluid or isotropic environment. This, together with the theory previously developed for fixed molecular orientation [33] completes a comprehensive fundamental study of the nonlinear effect coined LARET. However, to demonstrate the physical and experimental significance of our results we submit them to a numerical analysis. By implementing conservative estimates for molecular parameters,  $\mu^{(A)} \approx \mu^{(B)} \approx 10^{-29}$  C m for transition dipole moment magnitudes and  $\alpha^{(A)} \alpha^{(B)} \approx \beta^{(A)} \mu^{(B)} \approx \beta^{(B)} \mu^{(A)} \approx 10^{78}$  C<sup>4</sup> m<sup>2</sup> J<sup>-2</sup> for tensor products, we can estimate the relative magnitude of the effect with increasing laser intensity.

It is useful to ascertain the strength of the LARET effect

with respect to that of the fiducial RET. Inspection of the averaged contributions to the LARET rate as denoted by  $\langle \Gamma(2: \bar{4}_1) \rangle$ ,  $\langle \Gamma(2: \bar{4}_2) \rangle$ ,  $\langle \Gamma(4_1: \bar{4}_3) \rangle$ ,  $\langle \Gamma(4_1: \bar{4}_4) \rangle$ ,  $\langle \Gamma(4_2: \bar{4}_3) \rangle$ , and  $\langle \Gamma(4_2: \bar{4}_4) \rangle$  invites pertinent questions about the symmetry of each molecular species. Within these particular expressions, the contraction of the antisymmetric Levi-Civita tensor with relevant molecular tensors ensures that each term can only survive if each chromophore is chiral, as shown below. Each contraction entails factors of the form

$$\varepsilon_{ijk} \mu_i^\xi \alpha_{jk}^\xi \equiv \mu_i^\xi T_i, \quad (4.1)$$

with  $T_i$  indicating the Levi-Civita polarizability contraction relating to both  $A$  and  $B$  in the relevant expressions. Recognizing the polar nature of the dipole moment vector, along with the axial nature of  $\mathbf{T}$ , imposes stringent conditions for the scalar product of the two not to vanish identically. Such an achievement is only possible if  $\xi$  is chiral (optically active). Such considerations are unimportant for the other LARET contributions as the remaining results contain no tensor contractions of the form of Eq. (4.1). Consequently, if the donor and acceptor molecules are optically active, the rates are calculated using all terms—conversely, if either of the two species has an improper axis of rotation then the rate is determined by a reduced sum. Assuming that the primary contributions occur in the short-range limit

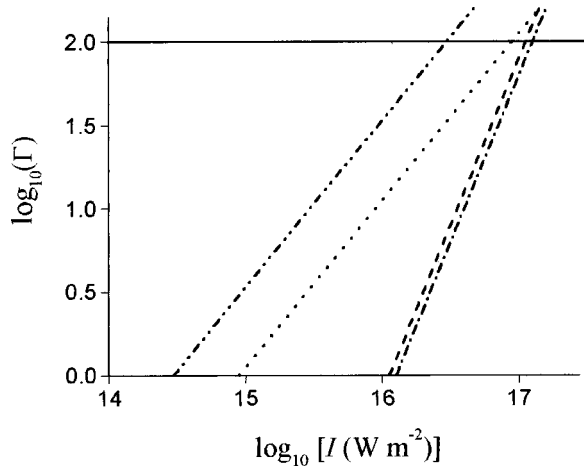


FIG. 4. Log-log plot of the Förster rate (normalized to 100) and additional laser-dependent contributions. Rates enhanced for optically active (OA) molecules are depicted together with those calculated for molecules with higher symmetry. Specifically,  $\langle \Gamma(2:2) \rangle$  (—),  $\langle \Gamma(2:4) \rangle$  (····),  $\langle \Gamma_{\text{OA}}(2:4) \rangle$  (— · — · — ·),  $\langle \Gamma(4:4) \rangle$  (— · — · — ·), and  $\langle \Gamma_{\text{OA}}(4:4) \rangle$  (— — —).

where  $kR \ll 1$  readily allows calculation of the laser-dependent terms to compare with the Förster rate.

Modifications to the rate of energy transfer can be illustrated by means of the log-log plots of Fig. 4. Normalizing the Förster rate to a value of 100 allows comparison with the relative magnitudes of each laser-dependent (LARET) contribution to RET (i.e., energy transfer in the absence of the auxiliary field). Figure 4 exhibits the terms linearly and quadratically dependent on auxiliary laser intensity, not only for optically active molecules but also those with higher symmetry. It is immediately apparent that, at intensities less than  $10^{13} \text{ W m}^{-2}$ , the transfer is Förster dominated. However, for focused laser intensities approaching  $10^{16} \text{ W m}^{-2}$  ( $10^{12} \text{ W cm}^{-2}$ ), the theory predicts optimum rate enhancements of  $\sim 10\%$  for achiral species and  $\sim 30\%$  for chiral molecules. This significantly impinges on the validity of theoretical results calculated using Förster's original theory without modification. Interestingly, as Fig. 4 illustrates, it is the terms linearly dependent on the laser intensity that play the dominant role in regimes readily accessible by standard commercial benchtop apparatus.

The results outlined above are not reliant upon any auxiliary beam resonance enhancement. That is, the initial excitation of the donor takes place prior to the application of any auxiliary laser field involved in stimulation of the energy transfer. The condition of exact resonance with the auxiliary beam is counterproductive since it would implement direct excitation by the laser, thus obscuring the more subtle influence on energy transfer of LARET. Ensuring off-resonance

laser operation decreases that excited states kinetics for both donor and acceptor species will follow familiar fluorescence decay profiles. Considering for simplicity an ensemble of donor-acceptor pairs with constant intermolecular separation, and at this stage ignoring orientational features, the rates associated with the excited state decay of both donor and acceptor molecules can be represented as follows [45]:

$$\frac{d}{dt} \rho_A^* = -(k_F^A + k_{\text{RET}} + k_{\text{NR}}^A) \rho_A^*, \quad (4.2)$$

$$\frac{d}{dt} \rho_B^* = k_{\text{RET}} \rho_A^* - (k_F^B + k_{\text{NR}}^B) \rho_B^*, \quad (4.3)$$

where  $\rho_\xi^*$  is the excited-state population density of the molecule  $\xi$ , and rate constants  $k$  carry subscripts relating to the fluorescence ( $F$ ), resonance-energy transfer (RET), and non-radiative intramolecular relaxation (NR) excited-state decay pathways. By considering the system to be initially excited, at time  $t=0$ , by an extremely short pulse of light (i.e., a  $\delta$  function pulse), then solutions to Eqs. (4.2) and (4.3) can be written as

$$\rho_A^*(t) = \rho_A^*(0) \exp[-(k_F^A + k_{\text{RET}}^A + k_{\text{NR}}^A)t] \quad (4.4)$$

and

$$\rho_B^*(t) = k_{\text{RET}} \rho_A^*(0) \times \frac{\exp[-(k_F^A + k_{\text{RET}}^A + k_{\text{NR}}^A)t] - \exp[-(k_F^B + k_{\text{NR}}^B)t]}{k_F^B + k_{\text{NR}}^B - k_F^A - k_{\text{RET}}^A - k_{\text{NR}}^A}. \quad (4.5)$$

We have assumed in Eq. (4.5) that, immediately following the excitation pulse, no acceptor molecules are directly excited. Equations (4.4) and (4.5) reveal the characteristic kinetics shown by the fluorescence of the donor and acceptor molecules, respectively.

Correct representation of the increased rate invoked by LARET requires incorporation of an additional term,  $k_{\text{LARET}}$ , into the kinetics of the donor molecule, through  $k_{\text{RET}} \rightarrow k'_{\text{RET}} = k_{\text{RET}} + k_{\text{LARET}}$ . Such a modification allows us to rewrite Eq. (4.2) as

$$\frac{d}{dt} \rho_A^* = -(k_F^A + k_{\text{RET}} + k_{\text{LARET}} + k_{\text{NR}}^A) \rho_A^*; \quad (4.6)$$

moreover, the LARET donor and acceptor kinetics now take the form

$$\rho_A^*(t) = \rho_A^*(0) \exp[-(k_F^A + k_{\text{RET}} + k_{\text{LARET}} + k_{\text{NR}}^A)t] \quad (4.7)$$

and

$$\rho_B^*(t) = (k_{\text{RET}} + k_{\text{LARET}}) \rho_A^*(0) \frac{\exp[-(k_F^A + k_{\text{RET}} + k_{\text{LARET}} + k_{\text{NR}}^A)t] - \exp[-(k_F^B + k_{\text{NR}}^B)t]}{k_F^B + k_{\text{NR}}^B - k_F^A - k_{\text{RET}} - k_{\text{LARET}} - k_{\text{NR}}^A}, \quad (4.8)$$



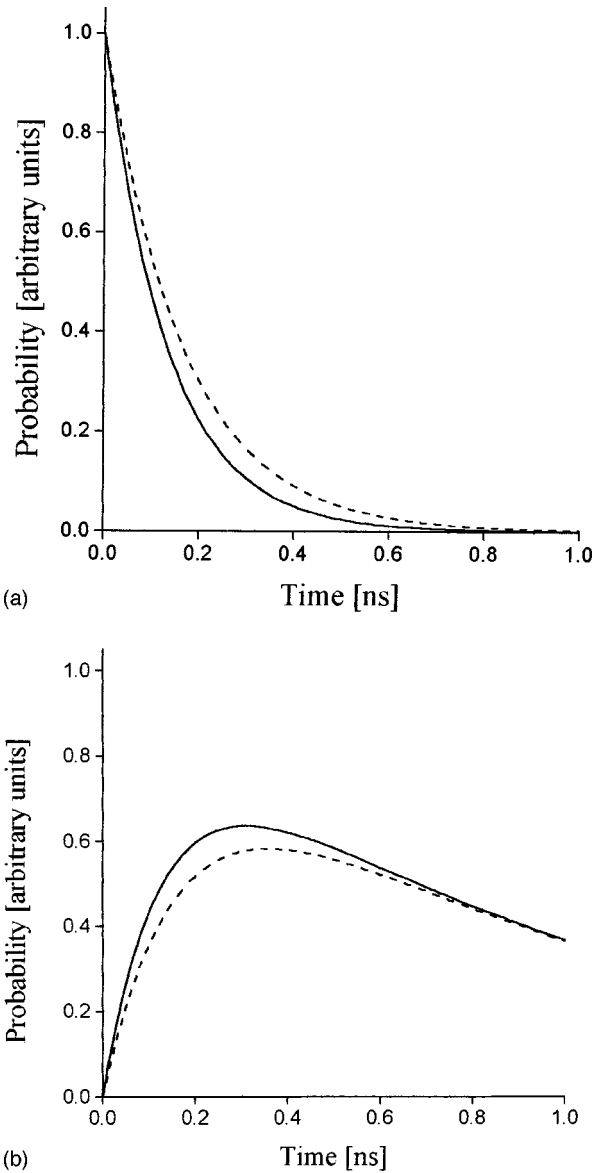


FIG. 5. Solid lines represent the kinetic profiles of fluorescence for donor (a) and acceptor (b) in the presence of an off-resonant auxiliary laser field. The laser pulse is assumed to be only a slowly varying function over the time scale illustrated, and is assigned an intensity of  $10^{16} \text{ W m}^{-2}$  ( $10^{12} \text{ W cm}^{-2}$ ). The molecular parameters are as given in the text and the dotted lines represent normal energy-transfer kinetics in the absence of the field.

respectively. As implied in Fig. 4, an increase in auxiliary field intensity augments the rate of LARET. Due to the magnitude of the intensities required, only a single pulse will generally be available during the total fluorescence decay of the acceptor. If, for example, the auxiliary laser pulse width is of a nanosecond time scale, then its intensity can be considered constant throughout the fluorescence lifetime and Eqs. (4.7) and (4.8) are valid. Figure 5(a) illustrates the case of such a pulse, the solid line highlighting the decrease in donor fluorescence. Equally, Fig. 5(b) shows the associated increase in acceptor fluorescence. Each effect exhibits the increase in the energy-transfer rate due to LARET, as com-

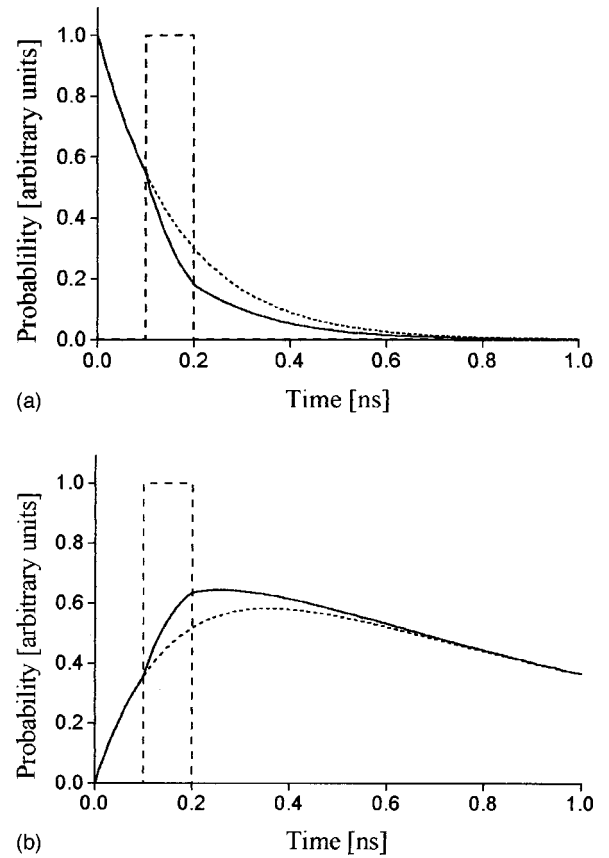


FIG. 6. On introducing a square pulse of finite duration (100 ps) the kinetic profiles clearly illustrate the LARET effect being switched on as the pulse appears. Results are modeled using the parameters in the text and a pulse intensity of  $5 \times 10^{16} \text{ W m}^{-2}$  ( $5 \times 10^{12} \text{ W cm}^{-2}$ ). Once more the dotted line illustrates the standard.

pared to the normal RET rates calculated through Eqs. (4.4) and (4.5) (dotted lines).

In the case where yet higher intensities are obtained by further reducing the pulse duration, as, for example, by using a picosecond pulse, then  $k_{\text{LARET}}$  is evidently modulated by a time-dependent function  $f(t)$ . Such a temporal modulation of  $k_{\text{LARET}}$  can be neatly illustrated by introducing a 100 ps square pulse during the fluorescence lifetime of the donor. Figure 6 clearly shows the onset of the LARET effect, as the pulse is switched on, and the subsequent decay following its removal. By adopting a pulse shape of the form  $f(t) = \text{sech}^2[\omega(t-t') + \phi]$ , where  $\omega^{-1}$  is proportional to the pulse width of the auxiliary beam and  $\phi$  is an arbitrary phase factor, we are able to derive more experimentally realistic analytical expressions. In this case the donor decay is properly represented by

$$\rho_A^*(t) = \rho_A^*(0) \exp \left[ - (k_F^A + k_{\text{RET}} + k_{\text{NR}}^A) t - \frac{k_{\text{LARET}}}{\omega} \{ \tanh[\omega(t-t')] + \tanh(\omega t') \} \right], \quad (4.9)$$

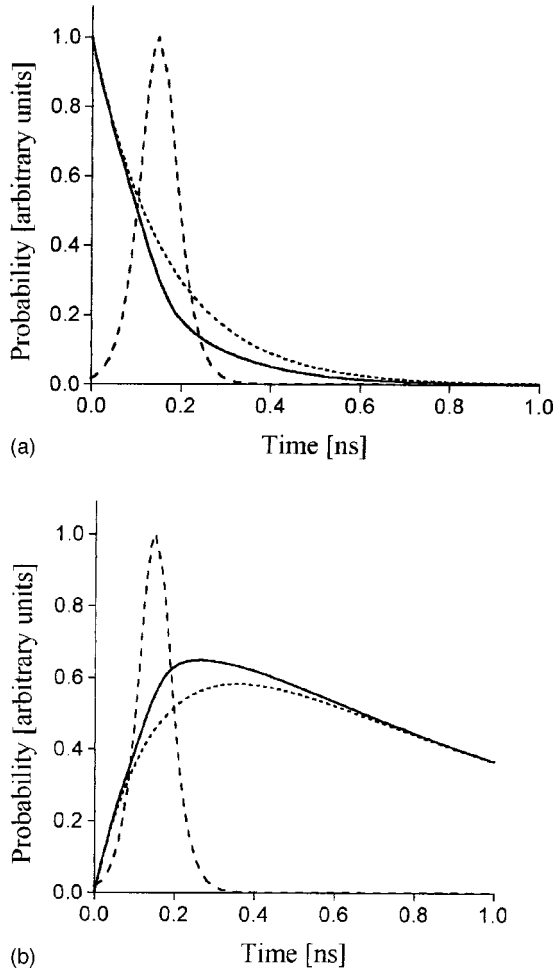


FIG. 7. Analytical results of Eqs. (4.9) and (4.10) model more closely a real experimental profile. The FWHM pulse width is 100 ps with the same peak intensity as in Fig. 6, all other terms and parameters remaining the same.

which in turn modifies the acceptor fluorescence profile such that

$$\begin{aligned} \rho_B^*(t) = & \rho_A^*(0) \left( \exp[-(k_F^A + k_{NR}^A)t] \right. \\ & - \exp\left[-(k_F^A + k_{NR}^A + k_{RET})t\right] \\ & - \frac{k_{LARET}}{\omega} \left( \left( \frac{\exp[\omega(t-t')]^2 - 1}{\exp[\omega(t-t')]^2 + 1} \right) \right. \\ & \left. \left. + \left( \frac{\exp[(\omega t')]^2 - 1}{\exp[(\omega t')]^2 + 1} \right) \right) \right). \end{aligned} \quad (4.10)$$

Equations (4.9) and (4.10) lead to the solid line traces shown in Figs. 7(a) and 7(b), respectively. The pulse  $\text{sech}^2[\omega(t-t')]$  is modeled as 100 ps full width at half maximum (FWHM) and the dotted line traces again represent the fiducial equations (4.4) and (4.5). In all cases we have modeled the donor and acceptor molecules to have similar natural lifetimes, specifically  $\tau = 1$  ns, the energy-transfer (ET) rate

constant is taken as  $k_{ET} = 5 \text{ ns}^{-1}$  and  $k_{LARET} = 1.5 \text{ ns}^{-1}$  ( $10^{12} \text{ W cm}^{-2}$ ) and  $5 \text{ ns}^{-1}$  ( $5 \times 10^{12} \text{ W cm}^{-2}$ ) for the nano-second and picosecond pulses, respectively.

The perturbations on the standard RET acceptor fluorescence kinetic profiles illustrated in Figs. 5–7 represent model evidence of LARET. The simple substitution of conservative values for salient parameters leads to measurable results. The experimental realization of LARET can be envisaged through a modification of conventional detection techniques, as standard single-photon timing procedures are likely to prove unprofitable. A suitable choice of the donor-acceptor pair, combined with utilization of a time-gated amplifier (boxcar integrator) to record the fluorescence in real time, should make detection a relatively simple task.

## V. CONCLUSION

We have calculated the rate of energy transfer between two uncorrelated chromophores in an isotropic environment in the presence of a quasipassive (i.e., nonresonant) auxiliary laser field. It has been found, using perturbational methods, that the transfer rate exhibits an enhancement due to higher-order interactions with the field. Equation (1.1) serves to pigeonhole the results;  $\Gamma_{RET}$  is representative of the rate of unembellished energy migration,  $\Gamma'I$  is the leading contribution to the LARET effect, and  $\Gamma''I^2$  only plays a supporting role. The latter only dominates at intensities sufficient to induce photodestruction.

We have found that at relatively low laser intensities ( $I < 10^9 \text{ W cm}^{-2}$ ), the higher-order effects are negligible. However, at suitably higher laser intensities, for example those readily available from a focused, mode-locked or  $Q$ -switched laser ( $I \sim 10^{12} \text{ W cm}^{-2}$ ), we have calculated energy-transfer rate enhancements of up to 30%. Interestingly, for a fully isotropic system, the rate is dependent upon the molecular symmetry and the maximum increase is only obtainable if each of the chromophores undergoing energy exchange is chiral. The experimental realization of this effect is envisaged through direct measurement of the excited-state kinetics of either the donor or acceptor. Using realistic molecular parameters we have modeled the real-time fluorescence profiles as a guide to experimentalists for both constant and pulsed auxiliary fields.

To conclude, we offer a potential use for LARET as a methodology for the detection of energy transfer. In multi-chromophore systems with complex photophysical dynamics, many processes may contribute to the emergence of a fluorescence signal, and it is often difficult to separate the contributory factors. The results expounded here indicate that when a suitable intense auxiliary laser field is present, the associated change in the temporal profiles of the donor and acceptor fluorescence may serve to identify energy transfer even within such a system. Provided that conditions are chosen to obviate any alternative nonlinear effects, as, for example, might be associated with two-photon or cooperative resonances, LARET offers a means for the identification of resonance-energy transfer within complex systems.

## ACKNOWLEDGMENTS

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## APPENDIX

Here in terms of general wave vectors  $p$  and  $p'$ , we report the short-range ( $pR \ll 1$  and  $p'R \ll 1$ ) and long-range ( $pR \gg 1$  and  $p'R \gg 1$ ) limits of the energy-transfer tensors alluded to in Ref. [23] [Eqs. (25)–(28)]. Sequentially,

$$V_{ii}(p, \mathbf{R}) \bar{V}_{jj}(p', \mathbf{R}) = \frac{2}{(4\pi\epsilon_0 R^3)^2} \times \begin{cases} 2p^2 p'^2 R^4 & \text{short range} \\ \exp[-i\{(p' - p)R\}] (2p^2 p'^2 R^4) & \text{long range,} \end{cases} \quad (\text{A1})$$

$$V_{ij}(p, \mathbf{R}) \bar{V}_{ij}(p', \mathbf{R}) = \frac{2}{(4\pi\epsilon_0 R^3)^2} \times \begin{cases} 3 & \text{short range} \\ \exp[-i\{(p' - p)R\}] (2p^2 p'^2 R^4) & \text{long range,} \end{cases} \quad (\text{A2})$$

$$V_{ii}(p, \mathbf{R}) \{ \bar{V}_{jk}(p', \mathbf{R}) \hat{R}_j \hat{R}_k \} = \frac{2}{(4\pi\epsilon_0 R^3)^2} \times \begin{cases} 2p^2 R^2 & \text{short range} \\ \exp[-i\{(p' - p)R\}] (2ipp'R^3) & \text{long range,} \end{cases} \quad (\text{A3})$$

$$\{ V_{ij}(p, \mathbf{R}) \hat{R}_i \hat{R}_j \} \bar{V}_{kk}(p', \mathbf{R}) = \frac{2}{(4\pi\epsilon_0 R^3)^2} \times \begin{cases} 2p'^2 R^2 & \text{short range} \\ \exp[-i\{(p' - p)R\}] (-2ipp'^2 R^3) & \text{long range,} \end{cases} \quad (\text{A4})$$

and

$$\{ V_{ij}(p, \mathbf{R}) \hat{R}_j \} \{ \bar{V}_{ik}(p', \mathbf{R}) \hat{R}_k \} = \frac{2}{(4\pi\epsilon_0 R^3)^2} \times \begin{cases} 2 & \text{short range} \\ \exp[-i\{(p' - p)R\}] (2pp'R^2) & \text{long range.} \end{cases} \quad (\text{A5})$$

Equation (A2) properly reduces to the short- and long-range limits of (3.10) when  $p = p'$ . Next, defining

$$\nu_1^{(\pm)} = V_{ii}(q \pm k, \mathbf{R}) \bar{V}_{jj}(q, \mathbf{R}),$$

$$\nu_2^{(\pm)} = V_{ij}(q \pm k, \mathbf{R}) \bar{V}_{ij}(q, \mathbf{R}),$$

$$\nu_3^{(\pm)} = V_{ii}(q \pm k, \mathbf{R}) \bar{V}_{jk}(q, \mathbf{R}) \hat{R}_j \hat{R}_k,$$

$$\nu_4^{(\pm)} = V_{ij}(q \pm k, \mathbf{R}) \bar{V}_{kk}(q, \mathbf{R}) \hat{R}_i \hat{R}_j,$$

$$\nu_5^{(\pm)} = V_{ij}(q \pm k, \mathbf{R}) \bar{V}_{ik}(q, \mathbf{R}) \hat{R}_j \hat{R}_k,$$

$$\nu_6^{(\pm)} = V_{ij}(q \pm k, R) \bar{V}_{kl}(q, R) \hat{R}_i \hat{R}_j \hat{R}_k \hat{R}_l,$$

we can report the following forms of  $S_{\pm}(n)$ :

$$\begin{aligned} S_{\pm}(1) &= \frac{1}{3} j_0(kR) (1 - 2|\mathbf{e} \cdot \mathbf{e}|^2) (\nu_2^{(\pm)} - \nu_1^{(\pm)}) + j_2(kR) \\ &\times [ \{ (\nu_4^{(\pm)} - \frac{1}{3} \nu_1^{(\pm)}) - (\nu_5^{(\pm)} - \frac{1}{3} \nu_2^{(\pm)}) \} \\ &- \frac{1}{2} |\mathbf{e} \cdot \mathbf{e}|^2 \{ (\nu_3^{(\pm)} - \frac{1}{3} \nu_1^{(\pm)}) + (\nu_4^{(\pm)} - \frac{1}{3} \nu_1^{(\pm)}) \\ &- 4(\nu_5^{(\pm)} - \frac{1}{3} \nu_2^{(\pm)}) \} ], \end{aligned}$$

$$\begin{aligned} S_{\pm}(2) &= (2 + |\mathbf{e} \cdot \mathbf{e}|^2) \frac{1}{3} j_0(kR) (\nu_2^{(\pm)} - \nu_1^{(\pm)}) + \frac{1}{2} j_2(kR) \\ &\times [ \{ (\nu_3^{(\pm)} - \frac{1}{3} \nu_1^{(\pm)}) + (\nu_4^{(\pm)} - \frac{1}{3} \nu_1^{(\pm)}) \\ &- 2(\nu_5^{(\pm)} - \frac{1}{3} \nu_2^{(\pm)}) \} + \frac{1}{2} |\mathbf{e} \cdot \mathbf{e}|^2 \{ (\nu_3^{(\pm)} - \frac{1}{3} \nu_1^{(\pm)}) \\ &+ (\nu_4^{(\pm)} - \frac{1}{3} \nu_1^{(\pm)}) - 2(\nu_5^{(\pm)} - \frac{1}{3} \nu_2^{(\pm)}) \} ], \end{aligned}$$

$$\begin{aligned} S_{\pm}(3) &= \frac{1}{3} j_0(kR) (\frac{1}{3} |\mathbf{e} \cdot \mathbf{e}|^2 - 1) (\nu_2^{(\pm)} - \nu_1^{(\pm)}) - j_2(kR) \\ &\times [ \{ \frac{1}{2} (\nu_3^{(\pm)} - \frac{1}{3} \nu_1^{(\pm)}) + (\nu_4^{(\pm)} - \frac{1}{3} \nu_1^{(\pm)}) \\ &- \frac{3}{2} (\nu_5^{(\pm)} - \frac{1}{3} \nu_2^{(\pm)}) \} - \frac{1}{2} |\mathbf{e} \cdot \mathbf{e}|^2 \{ (\nu_4^{(\pm)} - \frac{1}{3} \nu_1^{(\pm)}) \\ &- (\nu_5^{(\pm)} - \frac{1}{3} \nu_2^{(\pm)}) \} ], \end{aligned}$$

$$\begin{aligned} S_{\pm}(4) &= \frac{1}{3} j_0(kR) (1 - 2|\mathbf{e} \cdot \mathbf{e}|^2) (\nu_2 - \nu_1) + j_2(kR) \\ &\times [ (\nu_3^{(\pm)} - \frac{1}{3} \nu_1^{(\pm)}) - (\nu_5^{(\pm)} - \frac{1}{3} \nu_2^{(\pm)}) \\ &- \frac{1}{2} |\mathbf{e} \cdot \mathbf{e}|^2 \{ 3(\nu_3^{(\pm)} - \frac{1}{3} \nu_1^{(\pm)}) + (\nu_4^{(\pm)} - \frac{1}{3} \nu_1^{(\pm)}) \\ &- 2(\nu_5^{(\pm)} - \frac{1}{3} \nu_2^{(\pm)}) \} ], \end{aligned}$$

$$\begin{aligned} S_{\pm}(5) &= \frac{1}{2} j_2(kR) (1 - |\mathbf{e} \cdot \mathbf{e}|^2) \{ (\nu_4^{(\pm)} - \frac{1}{3} \nu_1^{(\pm)}) \\ &- (\nu_3^{(\pm)} - \frac{1}{3} \nu_1^{(\pm)}) \}, \end{aligned}$$

$$\begin{aligned} S_{\pm}(6) &= \frac{1}{2} j_0(kR) (1 - \frac{1}{3} |\mathbf{e} \cdot \mathbf{e}|^2) (\nu_2^{(\pm)} - \nu_1^{(\pm)}) + j_2(kR) \\ &\times [ \{ (\nu_3^{(\pm)} - \frac{1}{3} \nu_1^{(\pm)}) + \frac{1}{2} (\nu_4^{(\pm)} - \frac{1}{3} \nu_1^{(\pm)}) \\ &- \frac{3}{2} (\nu_5^{(\pm)} - \frac{1}{3} \nu_2^{(\pm)}) \} - \frac{1}{2} |\mathbf{e} \cdot \mathbf{e}|^2 \{ (\nu_3^{(\pm)} - \frac{1}{3} \nu_1^{(\pm)}) \\ &- (\nu_5^{(\pm)} - \frac{1}{3} \nu_2^{(\pm)}) \} ]. \end{aligned}$$

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