Optically Switched Energy Transfer: Twin-Beam Off-Resonance Control

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It is shown that, in the optical near field, the interaction of two polarized laser beams with different frequencies can promote a transfer of energy between suitably placed donor and acceptor particles, through a process that is rigorously forbidden in the absence of the laser light. The mechanism, which operates through stimulated Raman scattering by the donor-acceptor pair, is identified and characterized by quantum electrodynamical calculation. The results suggest efficiency levels comparable to conventional resonance energy transfer. Optical switching applications are envisaged.

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Much of the current interest in the transfer of energy between atoms, or between nanoscale clusters, stems from technical innovations allowing such processes to occur in essentially static local environments—in contrast to primarily collision-induced transfer in atomic gases. Prominent examples of such systems are cold atoms [1–3], emitters in microcavities [4,5], and quantum dots [6,7]. Some of this interest is fuelled by recent advances in processes that additionally engage the transfer of spin [8–10]. In the more established field of doped solids, too, there is renewed interest in connection with the nonparametric process of energy transfer frequency up-conversion (reviewed in Ref. [11]). In these and other systems where stably localized participants exchange electronic excitation, new opportunities arise for the optical control of energy transfer.

Here it is shown that in the optical near field, at the intersection of two polarized laser beams having differing frequencies, it is possible to promote a transfer of energy (between suitably placed donor and acceptor particles) that is *forbidden* in the absence of the laser light. The effect operates through a mechanism of stimulated Raman scattering—one radiation mode suffers the absorption of a photon, and the other mode stimulated emission. However, in contrast to conventional stimulated Raman, the sites of photon annihilation and creation are not the same; each event is involved in the separate transitions undergone by the donor and acceptor particles.

The analysis is based on quantum electrodynamics (QED). In the Power-Zienau-Woolley formulation [12], there is no longitudinal component to the electromagnetic fields, and any ostensibly radiationless transfer can be understood in terms of vacuum fluctuations and virtual photon propagation between the donor and acceptor particles [13–16]. Conventional resonance energy transfer (RET) is generally based on transition electric dipole coupling; the creation and annihilation of the virtual photon thus incur linear electric interactions with the vacuum radiation field, and the full process invokes second-order time-dependent perturbation theory. It has previously been shown that the propagation of a single beam of off-resonant laser light through an RET system can enhance allowed transfer processes by a concerted fourth-order interaction, in which the annihilation and stimulated emission of laser light represent additional interactions [17].

Let the two laser beams $m = 1, 2$ be designated by optical modes with n_m photons of wave vector $\boldsymbol{k}_m$, polarization vector $\boldsymbol{e}_m$, and optical circular frequency ω_m. Both frequencies are off-resonant with respect to all donor and acceptor transitions. The donor A at position $\boldsymbol{R}_A$ undergoes decay to the ground state from an initial electronic level α, and the acceptor B at $\boldsymbol{R}_B$ is promoted to a level β. The energy mismatch persists only during the lifetime of the virtual photon propagation and is finally compensated in overall energy conservation:

$$E_\beta^B - E_0^B = E_\alpha^A - E_0^A + \hbar(\omega_1 - \omega_2). \tag{1}$$

Although the process is less amenable to semiclassical interpretation, it can be loosely described in such terms: The difference frequency of the two optical waves supplies a quantum of energy that, compensating for the mismatch between the donor decay and acceptor uptake in energy, enables a transfer of excitation to occur between the two particles.

The energetics of the process are depicted in Fig. 1. In principle, the optical coupling can result in the population of a level β in B either higher than level α in A (as shown) or lower, according to the sign of $(\omega_1 - \omega_2)$. Here attention first focuses on the case where the annihilation of photon from beam 1 engages with the decay of the donor atom/particle A, stimulated emission of a beam 2 photon simultaneously engaging with excitation of the acceptor B. It is taken that $\omega_1 > \omega_2$, the difference exceeding both excited state linewidths; the corresponding shift in energy

between the initial donor level and the excitation-acquiring acceptor level precludes energy transfer in the absence of the two beams. This energetic constraint is reinforced by the difference in optical selection rules, as two-photon conditions apply to both the donor decay and the acceptor excitation transition.

The transfer rate for the process is determined by the Fermi rule [18] $\Gamma = (2\pi/\hbar)|M|^2\rho(E_\beta)$, where M is the quantum amplitude and $\rho(E_\beta)$ the density of acceptor states at energy E_β. The result is secured through textbook methods of QED [19], developing the quantum amplitude as a sum of 24 distinct fourth-order perturbation contributions, each associated with a different time ordering. The calculation is expedited by a recently developed state-sequence method [20,21] that casts the complete set of time orderings, each having a distinct Feynman diagram, in a single, complete diagrammatic representation. The results are summed, and the usual integrations carried out over virtual photon wave vectors and polarizations, giving the first term in Eq. (2) below. The other term in (2) arises from similar calculations on another 24 time orderings having interchanged sites of $\boldsymbol{k}_1$ absorption and $\boldsymbol{k}_2$ emission. The full result, cast in the usual form of implied summation over repeated indices, is thus

$$M = \frac{\hbar c(n_1 n_2 k_1 k_2)^{1/2}}{2\varepsilon_0 V}[e_{1i}\bar{e}_{2l}\alpha_{ij}^{0\alpha(A)}(k_1)V_{jk}((q+k_1),(\boldsymbol{R}_B-\boldsymbol{R}_A))\alpha_{kl}^{\beta 0(B)}(-k_2)e^{i(\boldsymbol{k}_1\cdot\boldsymbol{R}_A-\boldsymbol{k}_2\cdot\boldsymbol{R}_B)} + e_{1i}\bar{e}_{2l}\alpha_{ij}^{\beta 0(B)}(k_1)V_{jk}((k_2-q),(\boldsymbol{R}_A-\boldsymbol{R}_B))\alpha_{kl}^{0\alpha(A)}(-k_2)e^{i(\boldsymbol{k}_2\cdot\boldsymbol{R}_A-\boldsymbol{k}_1\cdot\boldsymbol{R}_B)}]. \quad (2)$$

Here e_{mi} designates the ith component of the polarization vector e_m (an overbar denoting complex conjugation, for circular polarizations), $q \equiv (E_\alpha - E_0)/\hbar c$, the scalar V is the quantization volume, and the coupling tensor [15] (representing the retarded interaction of transition dipoles) is given by

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

In the present context, the coupling can accurately be approximated by its near-field asymptote $V_{ij}(\boldsymbol{R}) \approx (4\pi\varepsilon_0 R^3)^{-1}(\delta_{ij}-3\hat{\boldsymbol{R}}_i\hat{\boldsymbol{R}}_j)$, and, for application in this region, the phase factors in Eq. (2) can also be dropped.

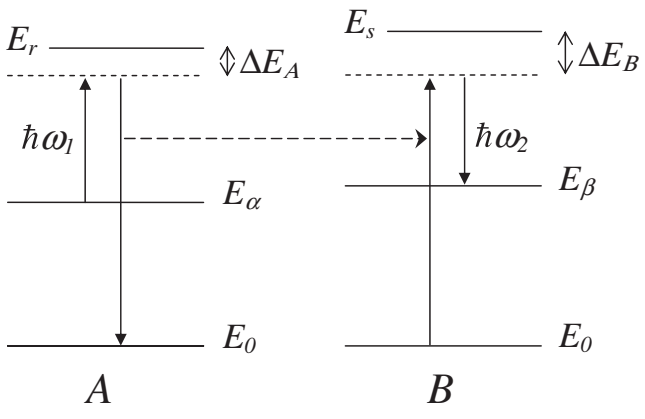

FIG. 1. Energetics scheme for optically switched transfer of energy from donor A to acceptor B. Solid-head arrows denote four transitions coupling the donor decay $\alpha \rightarrow 0$ and acceptor excitation $0 \rightarrow \beta$, laser interactions denoted by the photon energies. Dotted lines denote virtual states, the closest real states E_r and E_s offset in energy by ΔE_A and ΔE_B. The dashed line signifies energy transfer.

The second rank response tensor $\alpha^{0a(A)}(k_1)$ in Eq. (2) is a generalized polarizability of standard form [17]:

$$\alpha_{ij}^{0\alpha(A)}(k_1) = \sum_r\left\{\frac{\mu_i^{0r}\mu_j^{r\alpha}}{(\tilde{E}_{r0}+\hbar ck_1)} + \frac{\mu_j^{0r}\mu_i^{r\alpha}}{(\tilde{E}_{r\alpha}-\hbar ck_1)}\right\}, \quad (4)$$

accommodating the usual sum over states; the result for $\alpha^{\beta 0(B)}(-k_2)$ follows by simple substitution. To a good approximation, let it be assumed that these sums are limited to the three states that determine the most prominent optical features. As depicted in Fig. 1, for the donor A, these are the states denoted $|0\rangle$, $|\alpha\rangle$, $|r\rangle$ and, for the acceptor B, $|0\rangle$, $|\beta\rangle$, $|s\rangle$. For atomic (or other nonpolar) systems, the following results emerge:

$$\alpha_{ij}^{0\alpha(A)}(k_1) \approx \frac{\mu_j^{0r}\mu_i^{r\alpha}}{\Delta\tilde{E}_A} + \frac{\mu_i^{0r}\mu_j^{r\alpha}}{\tilde{E}_r - E_0 + \hbar ck_1},$$
$$\alpha_{kl}^{\beta 0(B)}(-k_2) \approx \frac{\mu_k^{\beta s}\mu_l^{s0}}{\Delta\tilde{E}_B} + \frac{\mu_l^{\beta s}\mu_k^{s0}}{\tilde{E}_s - E_0 + \hbar ck_2}, \quad (5)$$

where each $\boldsymbol{\mu}$ is a transition electric dipole, for example, $\mu^{r\alpha} = \langle r|\hat{\mu}|\alpha\rangle$, and ΔE_A, ΔE_B are the resonance offsets as illustrated in Fig. 1. The tildes in Eqs. (4) and (5) serve as a reminder to add to the excited state energies, in the case of near-resonance conditions, imaginary terms to accommodate damping. The present analysis focuses on off-resonant conditions, and the energies are taken as real. In the expressions for each tensor in Eq. (5), the first term will certainly dominate, typically by an order of magnitude or more, and, to a good approximation, the second terms can be dropped. Equally, the tensors featured in the second term of Eq. (2) are much less significant in magnitude, and they too can be neglected—as physical intuition suggests.

The ensuing result for the rate of energy transfer, obtained from the Fermi rule, is succinctly expressible as follows:

$$\Gamma = \frac{\rho I_1 I_2}{32\pi\hbar c^2 \varepsilon_0^4 R^6} |e_{1i}\bar{e}_{2l}\alpha_{ij}^{0\alpha(A)}(k_1)(\delta_{jk} - 3\hat{R}_i\hat{R}_j) \times \alpha_{kl}^{\beta 0(B)}(-k_2)|^2. \quad (6)$$

Here $\boldsymbol{R}$ is the displacement vector ($\boldsymbol{R}_B$-$\boldsymbol{R}_A$), and the result is cast in terms of the irradiances I_1 and I_2 of the two beams. The sharp R^{-6} dependence of the rate is a motif commonly associated with standard RET; in both cases, it signifies that near-field energy transfer occurs primarily between closely neighboring particles, a feature that allows exploitation without significant cross talk in array implementations [22]. In the present case, it is also evident that energy transfer can take place only if *both* beams are present, signifying a simple logic operation.

To exactly determine the efficiency of the process for a specific system requires knowledge of the generalized polarizability components, and these are not available in the current literature. However, an assessment can be based on observing that the result is not dissimilar in form from the standard result for short-range resonance energy transfer, between particles with energetically matched excited states, due to transition dipole coupling [14]. Normal RET and the optically induced process cannot both occur in the same particle pair, because they have different energetics—but the relative magnitude of the corresponding efficiencies gives a practical guide to the experimental viability of the optically switched case. The comparison can be effected on the basis of three-level models for the donor and acceptor, assuming the state sums in the generalized polarizabilities are limited to the electronic states nearest in energy to the virtual levels indicated in Fig. 1; let us assume the offsets are ΔE_A, ΔE_B and that μ_A and μ_B signify typical transition dipole moments of A and B. Then it becomes evident that, compared to RET, twin-beam optical switching introduces a relative rate factor that is given by $I_1 I_2 (\mu_A \mu_B / c\varepsilon_0 \Delta E_A \Delta E_B)^2$.

For example, with $I_1 = I_2 = 10^{12}$ W cm^{-2}, $\mu_A = \mu_B = 5$ D, and $\Delta E_A/hc = \Delta E_B/hc = 200$ cm^{-1}, the ratio of efficiencies is 4.4×10^3; i.e., the optically switched mechanism is substantially *more* efficient than conventional RET. Even at a significantly lower level of intensity, 8×10^{10} W cm^{-2} (routinely attainable with femtosecond laser instrumentation) and with a more sizable detuning of 500 cm^{-1}, the relative efficiency of 0.7 suggests an optically induced transfer efficiency having the same order of magnitude as normal RET. Among the widely extensive applications of the latter process, many appear to offer considerable scope for quantum information processing based on the resonant coupling of qubit pairs [23]. The opportunities for electromagnetically controlling the interactions among the basis states $|00\rangle$, $|0\beta\rangle$, $|\alpha 0\rangle$, $|\alpha\beta\rangle$ in the present analysis therefore appear propitious for realizable applications in quantum computation—conceivably in a quantum-dot implementation [24]. Specifically, each pair of suitably tailored, sufficiently dissimilar quantum dots furnishes excited states whose coupling through the Förster interaction can be put entirely under optical control; this will greatly extend the scope to exploit entangled interactions with other neighboring particles or particle pairs [25].

In conclusion, two further developments may be anticipated. One is the possibility of exploring an alternative form of optically switched energy transfer. Again based on stimulated Raman scattering by the donor-acceptor pair, but in contrast to the mechanism described above, the absorption of beam 1 and stimulated emission of beam 2 will here occur at the *same* site (either the donor or the acceptor) such that three-photon selection rules are associated with the corresponding transition. One other intriguing possibility is the engagement of spin transfer in optically activated transfer between quantum dots, where circular beam polarizations can be expected to play a significant determining role (see, for example, Ref. [10]). A full analysis of these cases is currently underway.

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