Resonance energy transfer and interface forces: Quantum electrodynamical analysis

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ABSTRACT

On the propagation of radiation with a suitably resonant optical frequency through a dense chromophoric system – a doped solid for example – photon capture is commonly followed by one or more near-field transfers of the resulting optical excitation, usually to closely neighboring chromophores. Since the process results in a change to the local electronic environment, it can be expected to also shift the electromagnetic interactions between the participant optical units, producing modified inter-particle forces. Significantly, it emerges that energy transfer, when it occurs between chromophores or particles with electronically dissimilar properties (such as differing polarizabilities), engenders hitherto unreported changes in the local potential energy landscape. This paper reports the results of quantum electrodynamical calculations which cast a new light on the physical link between these features. The theory also elucidates a significant relationship with Casimir-Polder forces; it transpires that there are clear and fundamental links between dispersion forces and resonance energy transfer. Based on the results, we highlight specific effects that can be anticipated when laser light propagates through an interface between two absorbing media. Both steady-state and pulsed excitation conditions are modeled and the consequences for interface forces are subjected to detailed analysis.

Keywords: energy transfer, electronic excitation, surface forces, optomechanical forces, Casimir forces, quantum electrodynamics

1. INTRODUCTION

Establishing a link between the mechanical effects of off-resonant optical radiation, and the electronic effects produced by light at resonant frequencies, is theoretically straightforward – though intricate. Essentially, one such connection can be demonstrated by determining the dispersion properties of the individual particles involved. Specifically, their linear susceptibility or polarizability values are properties which, while on the one hand entail the detuning-weighted absorption cross-sections for resonance frequencies; on the other hand link with the leading (quadratic) dependence of any mechanical coupling with the oscillatory fields of off-resonant light. It is not surprising that a technically much more challenging issue, that of establishing any linkage between mechanical and electronic effects that involve *two*-particle interactions, has received relatively little attention. However, there is good reason to consider that there are significant relationships to explore.

When radiation propagates through a system comprising two or more chemically distinct components – such as a doped solid or a multichromophore molecular system for example – photon capture by one of those components will occur if the optical frequency is suitable. Once that material component is promoted to an electronic excited state, its local electronic environment is thereby modified, and one necessary result is a change in the form of interactions with near-neighbor particles. When the pair interaction energies shift in value, the associated force fields also undergo change, and some motion can be expected as the system becomes accommodated to the new potential energy landscape. If the absorbed energy then transfers to a neighboring chromophore of another species, so that the latter acquires the excitation, the local electronic environment suffers further change and once again a compensating motion can be expected to occur. The detail of these processes is the subject of the following analysis, based on a robust quantum electrodynamical theory.

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To begin, a succinct treatment of the London pair potential is given in Section 2, in which the dependence on the electronic state of the interacting particles is explicitly delivered. In Section 3, a steady-state solution for the behavior of the system as described above is given. Since the adaptation to subtly changing force fields is most readily tested in an ensemble, rather than in individual particle pairs, the results are applied to an experimentally meaningful system in which the two components between which energy is transferred are arrayed on parallel planes in close proximity. In Section 4 the theory is further developed in order to elicit the dynamical behavior. Here, the developing response of the system is ascertained as a function of time, following initial excitation by a realistically shaped pulse of laser light. Possible developments of the theory are then discussed in the final Conclusion.

2. THE LONDON POTENTIAL

2.1. Derivation

The attractive force between neutral particles, at distances beyond significant wavefunction overlap, owes its origin to the well-known Casimir-Polder potential [1]. When ascertained by quantum electrodynamical analysis, this potential can be considered the result of a coupling between molecular polarizations that are induced by vacuum field fluctuations [2]. Although the long-range behavior of this potential runs with the inverse *seventh* power of the inter-particle distance R, the shorter-range form that operates over distances where the effects are most pronounced exhibits an R^{-6} asymptotic behavior, known as the London potential. The latter is itself the attractive component of the Lennard-Jones potential. Although the London potential is usually considered as an interaction between molecules in their ground states, a potential of similar form may also be derived by QED for molecules in excited states [3]. Recently, another force attributed to resonance energy transfer (RET) has also been proposed [4], being considered a consequence of interaction with the field emitted by a decay transition in a donor. The latter potential was, however, already embedded in previous derivations and described as a 'contribution from real photons' [5] – a term present even when there are no transition levels suitably disposed for RET to occur

The London potential, which can be recovered as the short-range limit of a full quantum electrodynamical analysis, can be more readily determined by directly exploiting the near-field, essentially unretarded form of pair coupling between a donor A and an acceptor B. In the short-range, an energy shift corresponding to this interaction is determined by standard methods through second-order perturbation theory, and the result is given by;

$$\Delta E = \sum_S \frac{\langle \Lambda | \mathbf{W}_{AB} | S \rangle \langle S | \mathbf{W}_{AB} | \Lambda \rangle}{E_\Lambda - E_S} \quad , \tag{1}$$

where $|S\rangle$ is an intermediate or virtual state of the system (two particles plus the vacuum radiation field) and $|\Lambda\rangle$ represents the unperturbed basis state. The near-zone energy transfer operator, applicable above, is explicitly written as;

$$\mathbf{W}_{AB} = \frac{\mu_i^A \mu_j^B}{4\pi\varepsilon_0 R^3} \left(\delta_{ij} - 3\hat{R}_i \hat{R}_j \right) \quad . \tag{2}$$

Here, $\boldsymbol{\mu}^\xi$ is the dipole moment operator, which operates on the states of particle ξ, and $\mathbf{R}$ is the intermolecular separation vector; summation over repeated Cartesian indices is also implemented. Inserting equation (2) into (1), with the state of each molecule fully specified, the following expression emerges;

$$\Delta E(A^a B^b) = \sum_{r,s} \frac{\langle A^a; B^b | \mathbf{W}_{AB} | A^r; B^s \rangle \langle A^r; B^s | \mathbf{W}_{AB} | A^a; B^b \rangle}{E_a^A + E_b^B - E_r^A - E_s^B}$$

$$= \frac{1}{16\pi^2 \varepsilon_0^2 R^6} \left[\frac{\mu_i^{ar(A)} \mu_j^{bs(B)} \mu_k^{ra(A)} \mu_l^{sb(B)} \left(\delta_{ij} - 3\hat{R}_i \hat{R}_j \right) \left(\delta_{kl} - 3\hat{R}_k \hat{R}_l \right)}{E_{ar}^A + E_{bs}^B} \right] , \tag{3}$$

where $\left|A^a\right\rangle$ and $\left|B^b\right\rangle$ are general molecular states – also $\left|A^r\right\rangle$ and $\left|B^s\right\rangle$ are virtual states. In this expression a more concise notation is introduced for the transition dipole moment components so that, for example, we write $\mu_i^{ar(A)} = \left\langle a\left|\mu_i^A\right|r\right\rangle$. By performing an isotropic average on the result that emerges from equation (3), the following result is ascertained;

$$\Delta E(A^a B^b) = -\frac{1}{24\pi^2 \varepsilon_0^{\,2} R^6} \sum_{r,s} \frac{\left|\boldsymbol{\mu}_A^{ar}\right|^2 \left|\boldsymbol{\mu}_B^{bs}\right|^2}{E_{ra}^A + E_{sb}^B} \quad , \tag{4}$$

which reduces to the well-known London formula when a and b are ground levels.

2.2. Three- or two-level systems

Consider the London potential between two three-level molecules, A and B, whose optically significant states are $\left|A^0\right\rangle$, $\left|A^\alpha\right\rangle$ and $\left|A^{\alpha*}\right\rangle$, and $\left|B^0\right\rangle$, $\left|B^\beta\right\rangle$ and $\left|B^{\beta*}\right\rangle$, respectively. If both molecules are in the ground states ($\left|A^0\right\rangle$ and $\left|B^0\right\rangle$), equation (4) for the pair interaction energy may be written as;

$$\Delta E(A^0 B^0) = -\frac{1}{24\pi^2 \varepsilon_0^{\,2} R^6} \left(-\left|\boldsymbol{\mu}_A^{00}\right|^2 \left(\frac{\left|\boldsymbol{\mu}_B^{0\beta}\right|^2}{E_{\beta0}^B} + \frac{\left|\boldsymbol{\mu}_B^{0\beta*}\right|^2}{E_{\beta*0}^B} \right) - \left|\boldsymbol{\mu}_B^{00}\right|^2 \left(\frac{\left|\boldsymbol{\mu}_A^{0\alpha}\right|^2}{E_{\alpha0}^A} + \frac{\left|\boldsymbol{\mu}_A^{0\alpha*}\right|^2}{E_{\alpha*0}^A} \right) \right.$$
$$\left. - \left(\frac{\left|\boldsymbol{\mu}_A^{0\alpha}\right|^2 \left|\boldsymbol{\mu}_B^{0\beta}\right|^2}{E_{\alpha0}^A + E_{\beta0}^B} + \frac{\left|\boldsymbol{\mu}_A^{0\alpha*}\right|^2 \left|\boldsymbol{\mu}_B^{0\beta}\right|^2}{E_{\alpha*0}^A + E_{\beta0}^B} + \frac{\left|\boldsymbol{\mu}_A^{0\alpha}\right|^2 \left|\boldsymbol{\mu}_B^{0\beta*}\right|^2}{E_{\alpha0}^A + E_{\beta*0}^B} + \frac{\left|\boldsymbol{\mu}_A^{0\alpha*}\right|^2 \left|\boldsymbol{\mu}_B^{0\beta*}\right|^2}{E_{\alpha*0}^A + E_{\beta*0}^B} \right) \right) \quad ; \tag{5}$$

similar expressions can be obtained if one or both of the molecules are excited. For instance; when A is in the state $\left|A^\alpha\right\rangle$, and B is in the state $\left|B^{\beta*}\right\rangle$, the result given by equation (5) requires modification only by the replacement of $\left|A^0\right\rangle$ with $\left|A^\alpha\right\rangle$, $\left|B^0\right\rangle$ with $\left|B^{\beta*}\right\rangle$, and *vice versa*. If only two levels are considered, equation (5) may be simplified as follows;

$$\Delta E(A^0 B^0) = -\frac{1}{24\pi^2 \varepsilon_0^{\,2} R^6} \left(\frac{\left|\boldsymbol{\mu}_A^{00}\right|^2 \left|\boldsymbol{\mu}_B^{0\beta}\right|^2}{E_{\beta0}^B} + \frac{\left|\boldsymbol{\mu}_B^{00}\right|^2 \left|\boldsymbol{\mu}_A^{0\alpha}\right|^2}{E_{\alpha0}^A} + \frac{\left|\boldsymbol{\mu}_A^{0\alpha}\right|^2 \left|\boldsymbol{\mu}_B^{0\beta}\right|^2}{E_{\alpha0}^A + E_{\beta0}^B} \right) \quad . \tag{6}$$

More specifically, for non-polar molecules where $\boldsymbol{\mu}_A^{00} = \boldsymbol{\mu}_B^{00} = 0$, we have;

$$\Delta E(A^0 B^0) = -\frac{1}{24\pi^2 \varepsilon_0^{\,2} R^6} \left(\frac{\left|\boldsymbol{\mu}_A^{0\alpha}\right|^2 \left|\boldsymbol{\mu}_B^{0\beta}\right|^2}{E_{\alpha0}^A + E_{\beta0}^B} \right) \quad . \tag{7}$$

In order to progress from the pair result to macroscopic systems such as parallel arrays, it is necessary to determine the ensemble average (*ave*) interaction potential effective between all particle pairs in the system, and the result is therefore given by;

$$\Delta E_{ave} = \sum_{a,b} N_a' N_b'' \Delta E(A^a B^b) \quad , \tag{8}$$

where N_a' is the fractional population of A in the state a, and N_b'' is the population of B in state b. The net interaction is determined by the relative populations of all states, which now invite more detailed consideration.

3. STEADY STATE

Let us consider a system that allows observation of the separation between two assemblies of the different materials, in close contact, as a function of the excited populations of their components. In order to avoid contributions arising from the material expansion (in consequence of the increase of vibrational energy through dissipative losses), the system should be kept at constant temperature. Under such conditions, it is appropriate to first entertain a system in which net rates of particle excitation and decay are the same, so that the excited populations are constant.

Suppose we have two planar assemblies of particles, A and B, placed adjacent to each other and in parallel. In general they are attracted towards each other by Van der Waals dispersion forces, and repelled by intermolecular electronic repulsion. These two forms of interaction potential, operating between the molecules of A and B, then determine the separation of the assemblies. When molecules of the assembly of particles A are excited by a monochromatic beam of constant intensity I, they may acquire excitation energy and also transfer it to molecules of the assembly B (the molecules of the latter assembly B are assumed to be off-resonant with respect to the throughput radiation). Under these conditions, the fractional populations of excited molecules in the layers A and B, $i.e.$ $N'_\alpha(t)$ and $N''_\beta(t)$ respectively, are subject to the following time evolution equations;

$$\frac{dN'_\alpha(t)}{dt} = I\sigma^{(A)}\left(1 - N'_\alpha(t)\right) - N'_\alpha\left(\Gamma_A + \Gamma'_A\right) + N''_\beta\Gamma_B \quad, \tag{9}$$

$$\frac{dN''_\beta(t)}{dt} = N''_\beta(t) - N''_\beta\left(\Gamma_B + \Gamma'_B\right) + N'_\alpha\Gamma_A \quad, \tag{10}$$

where Γ_A and Γ_B are the rates of energy transfer from A to B and from B to A, respectively, while Γ'_A and Γ'_B are the rates of energy loss by the system (by spontaneous emission, for example) from assemblies A and B, respectively. Also, in the above equations, $\sigma^{(A)}$ is the fractional increase in excitation of molecules of A per unit irradiance. To avoid optically induced forces between molecules in the interacting surfaces, the light used should not be polarized. If the system reaches a steady state, and $\Gamma_B \gg \Gamma'_B$ (as may be expected if Γ'_B is the rate of spontaneous emission of the molecules in the layer B, and the overlap between the emission spectrum of B and absorption spectrum of A is not too small), the solutions of the equations (9) and (10) can be written as;

$$N'_\alpha = I\sigma^{(A)} \frac{1}{\left(\Gamma'_A + I\sigma^{(A)}\right) + \dfrac{\Gamma_A}{\Gamma_B}\Gamma'_B} \quad, \tag{11}$$

$$N''_\beta = I\sigma^{(A)} \frac{1}{\Gamma'_B + \dfrac{\Gamma_B}{\Gamma_A}\left(\Gamma'_A + I\sigma^{(A)}\right)} \quad. \tag{12}$$

Let us now assume that the molecules of both assemblies, A and B, with the states $\left|A^0\right\rangle$ and $\left|A^\alpha\right\rangle$, and $\left|B^0\right\rangle$ and $\left|B^\beta\right\rangle$, respectively, are non-polar. For simplicity we can also assume that each surface has its components arrayed on the vertices of a square lattice, such that the position vector of any molecule in B respect to another, on its interacting surface, can be generalized as $\hat{x}nl + \hat{y}ml$, with n and m being positive or negative integers and l the lattice constant. In these conditions, if there is a total of N molecules in the interacting surface of A, the net interaction potential may be written as;

$$\Delta E_{ave} = -N\sum_{a,b}\sum_{r,s}\frac{N'_a N''_b}{24\pi^2\varepsilon_0^2}\frac{\left|\mu(A)\right|^2\left|\mu(B)\right|^2}{E_{ar} + E_{bs}}\sum_{n=-\infty}^{\infty}\sum_{m=-\infty}^{\infty}\frac{1}{(d^2 + (nl)^2 + (ml)^2)^3} \quad. \tag{13}$$

Here, $R^2 = d^2 + (nl)^2 + (ml)^2$ has been employed and a equates to 0 or α with $b = 0$ or β. The intermolecular electronic *repulsion* is approximated as an inverse-12 power potential dependence on the particles separations, as in the usual Lennard-Jones potential; this potential is assumed to be independent of the excitation, and is given by;

$$\Delta E_R \cong N \sum_{n=-\infty}^{\infty} \sum_{m=-\infty}^{\infty} \frac{K}{(d^2 + (nl)^2 + (ml)^2)^6} . \tag{14}$$

A generalized expression, similar to the Lennard-Jones potential, is obtained by summing the potentials in (13) and (14);

$$\Delta E = N \sum_{n=-\infty}^{\infty} \sum_{m=-\infty}^{\infty} \frac{K}{(d^2 + (nl)^2 + (ml)^2)^6}$$
$$- N \sum_{n=-\infty}^{\infty} \sum_{m=-\infty}^{\infty} \frac{|\boldsymbol{\mu}(A)|^2 |\boldsymbol{\mu}(B)|^2}{24\pi^2 \varepsilon_0^2 (d^2 + (nl)^2 + (ml)^2)^3} \left(\frac{(1 - N_\beta'' - N_\alpha')}{E_{\alpha 0} + E_{\beta 0}} + \frac{N_\alpha' - N_\beta''}{E_{\alpha 0} - E_{\beta 0}} \right) , \tag{15}$$

with $N_0' = 1 - N_\alpha'$ and $N_0'' = 1 - N_\beta''$. If the sum of the potentials given by equations (13) and (14) is attractive, the assemblies move towards a relative displacement where the total force is zero. When the summations in equation (15) are approximated as continuous integrals, this separation may be expressed as;

$$d = d_0 \left((1 - N_\beta'' - N_\alpha') + \frac{1 + E_{\beta 0} / E_{\alpha 0}}{E_{\beta 0} / E_{\alpha 0} - 1} (N_\alpha' - N_\beta'') \right)^{-1/6} , \tag{16}$$

where

$$d_0 = \left(\frac{|\boldsymbol{\mu}(A)|^2 |\boldsymbol{\mu}(B)|^2}{24 K \pi^2 \varepsilon_0^2} \left(\frac{1}{E_{\alpha 0} + E_{\beta 0}} \right) \right)^{-1/6} , \tag{17}$$

the parameter d_0 being the separation of the assemblies when there is no excitation. Fig. 1 shows the variation of the equilibrium spacing, relative to its ground-state value, as a function of laser irradiance. It is notable that the degree of contraction, which levels off at high intensities, is strongly influenced by the relative spacing of molecular energy levels.
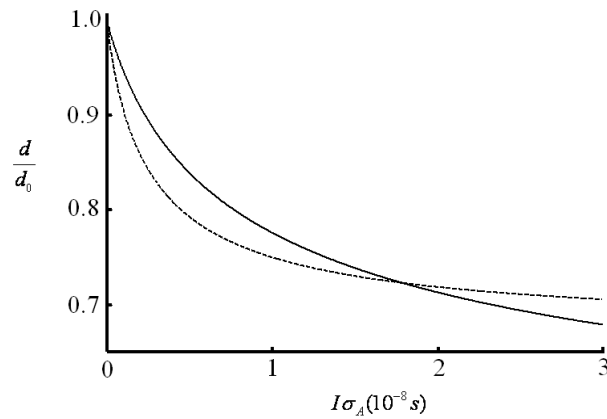

Figure 1. Separation between the assemblies, d, as a function of the irradiance, I. For both curves it is assumed that $\Gamma_B' = \Gamma_C' = 1/10^{-8} s$; in the solid curve $\Gamma_A / \Gamma_B = 1/10$, and $E_{\beta 0} / E_{\alpha 0} = 2$; and in the dashed curve $\Gamma_A / \Gamma_B = 10$, and $E_{\beta 0} / E_{\alpha 0} = 0.5$.

4. DYNAMICS

This Section examines the dynamics, the initial aim being to approximately represent the time-dependence of the populations of the α and β states, expressed as the fractional populations N'_α and N''_β. Using the result, equation (8) can be employed to deliver a time-dependent solution for ΔE_{ave}. In order to accurately evaluate N'_α and N''_β, a photophysical model is required that will encompasses all of the most prominent donor-acceptor events that follow pulsed laser excitation of *A*. This model represents a number of distinct, stepwise processes that can populate or depopulate the various excited energy levels involved; the solution of the rate equations for those populations determines the time-evolution of the state populations which determine the overall pair interaction energy. Such a system of processes is represented by the Jablonski diagram, Fig. 2.
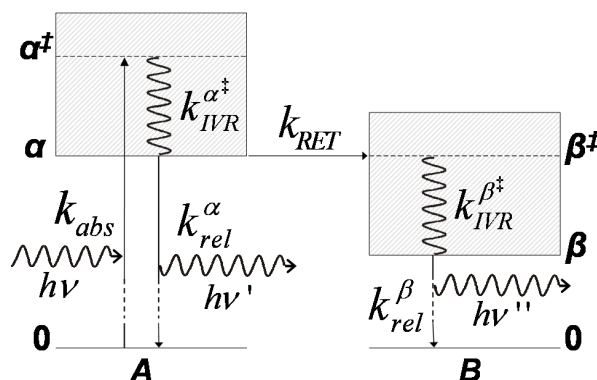

Figure 2. A Jablonski diagram (energy increasing vertically) showing the key processes in laser energy absorption, relaxation and transfer between an interacting pair of molecules, *A* and *B*. The textured boxes represent accessible continua of vibrational levels.

The first step in the sequence of interactions is the laser-induced excitation of *A* by photon absorption (*abs*) from 0 to $\alpha^\ddagger$ – the latter generally a vibrationally excited level of the electronically excited state α. The corresponding rate coefficient, k_{abs}, itself has a time variation through its dependence on the excitation laser profile – which in the study below is to be modeled by a Gaussian shape. The laser wavelength is considered to be resonant only to the transition between 0 and $\alpha^\ddagger$ – the energies of $\alpha^\ddagger$ and $\beta^\ddagger$ relative to 0 are necessarily different. Following excitation to $\alpha^\ddagger$, relaxation to the lowest level of α is achieved by ultrafast intramolecular vibrational redistribution (IVR). Further decay routes are then possible, principally direct relaxation back to 0 (*rel*) or transfer of energy to *B*, the latter effecting the excitation of level $\beta^\ddagger$ by resonant energy transfer (RET). (In the former case it may be considered that the rate coefficient k_{rel}^α accommodates the effects of intramolecular relaxation and spontaneous radiative emission of energy from α). When, as a result of RET, any molecule *B* acquires excitation energy directly into the state $\beta^\ddagger$, the immediate effect is once again an IVR process – which in this case populates the lowest energy excited state for *B*, i.e. β. Crucially, the directional efficiency of RET between *A* and *B* is exponentially dependent on a spectroscopic gradient [6]; since the energy (relative to the corresponding electronic ground state) of α is greater than β, it can be assumed that back transfer is negligible and hence need not be considered in these calculations. The final stage of the overall process occurs with the decay of *B* from β to its ground state, again allowing for both intramolecular relaxation and the spontaneous emission of energy.

4.1. Expressing N'_α and N''_β

The total rate of excitation to α is expressible as in the form of a sum over all routes of excitation to, and decay from α; from Fig. 2 we have:

$$\frac{\mathrm{d}}{\mathrm{d}t}N'_\alpha = k^{\alpha\ddagger}_{IVR}N'_{\alpha\ddagger} - k^\alpha_{rel}N'_\alpha - k_{RET}N'_\alpha. \tag{18}$$

The population of α is dependent on $k^{\alpha\ddagger}_{IVR}$, given that $k^{\alpha\ddagger}_{IVR} \gg k_{abs}$, $N'^A_0 \gg N'_{\alpha\ddagger}$ and the timescale for excitation to $\alpha^\ddagger$ is assumed to be short with respect to the laser pulse duration.. It is possible to express (18) in the form of an analytically solvable differential equation:

$$\frac{\mathrm{d}}{\mathrm{d}t}N'_\alpha = k_{abs} - N'_\alpha\left(k_{abs} + k_{rel} + k_{RET}\right). \tag{19}$$

Similarly the rate of formation of N''_β is again expressible in terms of fractional populations:

$$\frac{\mathrm{d}}{\mathrm{d}t}N''_\beta = k^{\beta\ddagger}_{IVR}N''_{\beta\ddagger} - k^\beta_{rel}N''_\beta . \tag{20}$$

Under the conditions $k^{\beta\ddagger}_{IVR} \gg k_{RET}$ and $N'_\alpha \gg N''_{\beta\ddagger}$, the formation of β is dominated by k_{RET}, and the previously determined solution for N'_α yields the following expression for the time-dependent variation in N''_β:

$$\frac{\mathrm{d}}{\mathrm{d}t}N''_\beta = k_{RET}N'_\alpha - k^\beta_{rel}N''_\beta \tag{21}$$

The constants of integration for both solutions (19) and (21) are determined by setting the physically reasonable initial condition that N'_α and N''_β are zero at time zero, i.e. excluding excitation by intrinsic thermal energy, all molecules are in the ground state prior to the laser pulse.

The modelled fractional populations for α and β are shown in Fig. 3, plotted on an arbitrary timescale. The maximum value of N'_α has been set by adjustment of the laser intensity profile maximum to a value of 0.5. For this set of results, k_{RET} accounts for the majority of the total decay of α relative to k^α_{rel}. Such a condition represents a short-range interaction between A and B, where RET is assumed the dominant decay process for α.
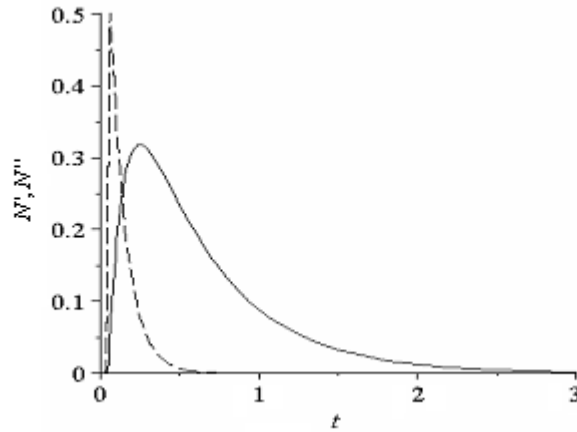
Figure 3. Predicted N''_β (solid line) and N'_α (dashed line) profiles following laser excitation. Gaussian parameters set for a laser pulse FWHM = 1 and maximum of N'_α as 0.5 at $t = 5$. Arbitrary values of k_{RET} and k^α_{rel} are chosen such that k_{RET} accounts for 80% of the total, and k^α_{rel} and k^β_{rel} are equal.

4.2. Total system energy

In a similar manner, the net interaction energy during the process is given by:

$$\Delta E_{ave} = -\sum_{a,b}\sum_{r,s}\frac{N'_a N''_b}{24\pi^2 \varepsilon_0{}^2 R^6}\frac{\left|\boldsymbol{\mu}(A)\right|^2 \left|\boldsymbol{\mu}(B)\right|^2}{E_{ra}+E_{sb}}\quad,\tag{22}$$

where N'_a and N''_b are the time-dependent quantities determined in the previous sub-section. In the case of a three-level RET system, the summations over levels a and b exclude a as $\left|\alpha^*\right\rangle$ or b as $\left|\beta^*\right\rangle$ since the latter states are never populated. In determining numerical results from (22), the value of R is taken as 1 nm and the transition dipole moments for A and B are assumed to be similar in magnitude, their values both taken as 1×10^{-29} C m. Fig. 4 exhibits the final result, for the evolution of the pair potential energy of interaction as a function of time.

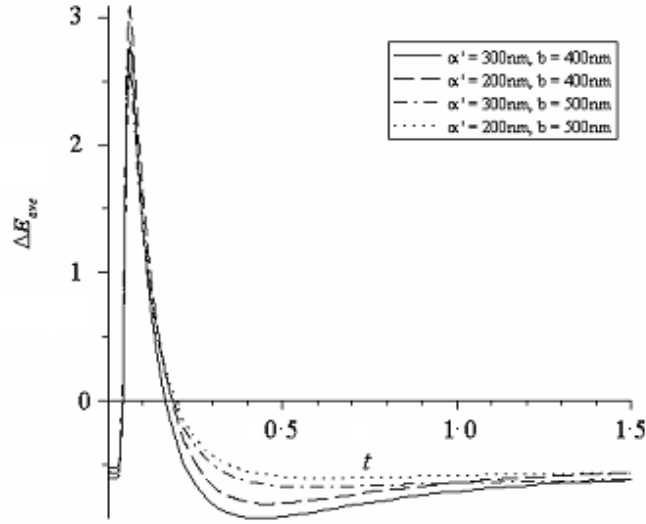**Figure 4.** ΔE_{ave} profiles as defined by (8) and (22). For all cases $\alpha = 350$ nm and $\beta^* = 355$ nm. Profiles plotted against an arbitrary time-scale, consistent with Fig. 3.

By extension, it is interesting to determine an expression for the London force between two parallel arrays composed of N molecules. First, ΔE_{ave} per unit area is found for the transfer of energy from an arbitrary excited molecule in the donor array to molecules in the acceptor array, i.e. an similar expression to equation (13), given as;

$$\Delta E_{ave} = -\frac{NA}{24\pi^3\varepsilon_0{}^2}\sum_{a,b}\sum_{r,s}N'_a N''_b \frac{\left|\boldsymbol{\mu}_A^{ar}\right|^2 \left|\boldsymbol{\mu}_B^{bs}\right|^2}{E_{ra}^A+E_{sb}^B}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\frac{1}{\left(d^2+(nl)^2+(ml)^2\right)^3}\mathrm{d}(n)\mathrm{d}(m)$$

$$= -\frac{NA}{48\pi^2\varepsilon_0{}^2 l^2 d^4}\sum_{a,b}\sum_{r,s}N'_a N''_b \frac{\left|\boldsymbol{\mu}_A^{ar}\right|^2 \left|\boldsymbol{\mu}_B^{bs}\right|^2}{E_{ra}^A+E_{sb}^B}\quad,\tag{23}$$

with A as the cross-sectional area of the acceptor array. In equation (23), the double integration over nl and ml is a suitable approximation for a summation over all molecules in the acceptor array. The London force between these two arrays is found through $\mathbf{F}_{ave}=-\left(\partial\Delta E_{ave}/\partial d\right)\hat{\mathbf{n}}$, where $\hat{\mathbf{n}}$ is the normal to the plane of the donor array. Thus, the following is determined from (23);

$$\mathbf{F}_{ave} = -\frac{NA}{48\pi^3 \varepsilon_0^{\,2} d^5} \sum_{a,b} \sum_{r,s} N_a' N_b'' \frac{\left|\boldsymbol{\mu}_A^{ar}\right|^2 \left|\boldsymbol{\mu}_B^{bs}\right|^2}{E_{ra}^A + E_{sb}^B} \hat{\mathbf{n}} \quad . \tag{24}$$

Plots of $\mathbf{F}_{ave}$ against t will be of equivalent form to the curves shown in Fig. 4.

5. CONCLUSION

This paper has presented a detailed analysis of the possibility of optically effecting a modification of the London force between neutral molecules, through photon absorption and emission by molecular pairs, and through the engagement of resonance transfer of energy between them. The theory has been developed, and the results modeled, for both steady-state and pulsed excitation conditions. In considering the practical issues that will need to be addressed in measurements and applications, one obvious issue will be the need to obviate and/or effectively distinguish (for example by time-gating) any effect produced by molecular motions − especially since heating will be produced as a result of the vibrational relaxation; this is a subject of ongoing research. To further consolidate this work, a general theory should be developed to address both short- and long-range regions, without the assumption of isotropic averaging. Furthermore to accommodate other effects, consistent with the involvement of high-power laser light, it will be interesting to consider the possible contributory effects of optically induced pair forces [6-10], and optically controlled resonance energy transfer − the latter mechanism recently proposed as a basis for all-optical switching [11-14] − operating on fundamentally similar principles to those presented in this work.

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