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Static and dynamic modifications to photon absorption: The effects of surrounding chromophores

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ABSTRACT

This Letter investigates the influence, on the molecular absorption of light, of surrounding chromophores. Two novel rate contributions are identified – one vanishing for a medium with no static dipole moment. The other, dynamic term is used to model a system of primary absorbers and secondary chromophores distributed in a host medium. Further modification provides a basis for modelling a case where the medium is, itself, marginally absorptive, thus accounting for optical losses as the input propagates through the surrounding host. The results facilitate tailoring of secondary chromophore and host effects in the pursuit of materials with specific absorption features.

1. Introduction

It is well-known that the optical properties of atoms and molecules can be influenced by their electronic environment. Local field effects on spontaneous emission rates within nanostructured photonic materials for example are familiar, and have been well summarized [1]. Optical processes, including resonance energy transfer are similarly dependent on the local environment of molecular chromophores [2–4]. Many biological systems are known to contain complex organizations of molecules with absorption bands shifted due to the electronic influence of other, nearby optical centres. For instance, in widely studied light-harvesting complexes, there are two identifiable forms of the photosynthetic antenna molecule bacteriochlorophyll, with absorption bands centred on 800 and 850 nm; it has been shown that the most efficient forms of energy transfer between the two occurs when there is a neighbouring carotenoid species 5–7. Until now, research on the broader influence of a neighbouring, off-resonant, molecule on photon absorption has mostly centred on the phenomenon of induced circular dichroism, where both quantum electrodynamic (QED) calculations [8–10] and experimental procedures [11–13] predict and verify that a chiral mediator confers the capacity for an achiral acceptor to exhibit circular differential absorption.

In this Letter, we investigate the influence of one or more secondary chromophores, to be labelled *M*, on the absorption of light by a primary absorber molecule, *A*. The secondary species is assumed to have an electronic energy level that is slightly above the input photon energy – i.e. its optical absorption is blue-shifted compared to the primary absorber – to rule out *M* as a competing acceptor. It emerges that there is a dynamic contribution to the absorption rate that can be extended by integrating over all possible positions and orientations of the mediators, thereby modelling a continuous medium in which both absorbers and secondary chromophores are embedded. Further refinement enables this model to account for a wider range of materials in which, like the biological materials mentioned above, the primary absorbers and the secondary species are distributed within a marginally absorptive host material with its own optical characteristics. Developing such a theory is shown to provide wider links with both the molecular and bulk properties of materials.

2. Background theory

Molecular QED is the analytical tool of choice for analysis of the interactions of light with molecules, and their electromagnetic interactions with each other [10,14]. Quantizing the whole system under consideration, particles and fields alike, this formulation of theory introduces the virtual photon to describe the couplings between particles of matter [15,16]. Where molecules are not in direct contact, all intermolecular interactions must be mediated by virtual photon exchange; ensuring a fully retarded, causal framework. In such a framework, the non-relativistic Hamiltonian is promoted to operator form and, for a system comprised of interacting molecules, indexed by ξ, is exactly expressible as:

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$$H = H_{\text{radiation}} + \sum_{\xi} H_{\text{matter}}(\xi) + \sum_{\xi} H_{\text{interaction}}(\xi), \tag{1}$$

where the sum over the discrete index, ξ, denotes the individual optical centres. Furthermore, the rate, Γ_{fi}, of an identified transition process is given by the Fermi 'Golden Rule'. For a system proceeding from initial state i to final state f:

$$\Gamma_{fi} = 2\pi\hbar^{-1}\rho_f |M_{fi}|^2 \tag{2}$$

where $\hbar$ is the reduced Planck's constant, ρ_f is the density of states, and M_{fi} is the quantum amplitude for the event. A process consisting of N interactions is described by Nth-order perturbation theory, such that its quantum amplitude M_{fi} is given by the Nth term of the perturbation expansion [17]:

$$M_{fi} = \langle f|H_{int}|i\rangle + \sum_{r} \frac{\langle f|H_{int}|r\rangle\langle r|H_{int}|i\rangle}{(E_i - E_r)} + \sum_{r,s} \frac{\langle f|H_{int}|s\rangle\langle s|H_{int}|r\rangle\langle r|H_{int}|i\rangle}{(E_i - E_r)(E_i - E_s)} + \dots \tag{3}$$

Elementary absorption by individual chromophores generally entails the annihilation of single photons, and is accordingly represented by the first order term in Eq. (3). The analysis of optical processes involving two or more coupled centres – electronically distinct in the sense of being separated beyond significant wavefunction overlap – invokes higher order terms; it is these that formally require a QED treatment cast in terms of virtual photon coupling. Since every discrete molecular transition is a local matter-radiation interaction event, for each exchange of a virtual photon there has to be one photon creation and one corresponding photon annihilation event.

In the following, we first develop in precise QED terms, the mathematical modelling of photon absorption, and then extend this analysis to a medium-modified case. In every case the initial and final system states are given by:

$$|i\rangle = |\psi_0^{(A)};\psi_0^{(M)}\rangle|n(\mathbf{k},\eta)\rangle; \tag{4}$$

$$|f\rangle = |\psi_\alpha^{(A)};\psi_0^{(M)}\rangle|(n-1)(\mathbf{k},\eta)\rangle; \tag{5}$$

where ψ designates the wavefunction of either the acceptor, A, or inert mediator, M. Moreover, the subscript of ψ corresponds to either: the electronic ground state 0, or the excited state α (in the case of A). The radiation is modelled as a number state of wave-vector $\mathbf{k}$ and polarization label η, with photon population given by n. Moreover, the photon energy is necessarily such that $E_\alpha - E_0 \equiv E_{\alpha 0} \approx \hbar ck$.

3. Locally modified absorption

The probability amplitude for the process of photon absorption, modified by the presence of a secondary chromophore is given by the sum of three terms:

$$M_{fi} = M_{fi}^{(A)} + M_{fi}^{(MA)} + M_{fi}^{(AM)}, \tag{6}$$

where $M_{fi}^{(A)}$ is the amplitude for absorption by the acceptor molecule, A, alone; the second term, $M_{fi}^{(MA)}$, corresponds to the mediator molecule absorbing a photon and then transferring the energy to the acceptor molecule, and $M_{fi}^{(AM)}$ denotes the absorption of a photon by A, which then interacts with M. Each of the three possible configurations is represented diagrammatically in Figure 1.

According to the Feynman prescription, the contributions to the matrix element are terms corresponding to all topologically distinct Feynman diagrams, examples of which are displayed in Figure 2 [18]. We determine the rate from the Fermi rule, equation (2), which now depends on the square modulus of Eq. (6):

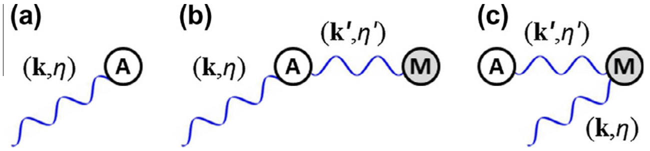

Figure 1. Diagrams (a), (b) and (c) represent the *A*, *AM* and *MA* absorption configurations respectively. The input photon is labelled with wave-vector **k** and polarization η: ($\mathbf{k}'$,η') represents the mode of a virtual photon mediator between molecular centres. All diagrams represent *A* and *M* in arbitrary positions relative to each other.

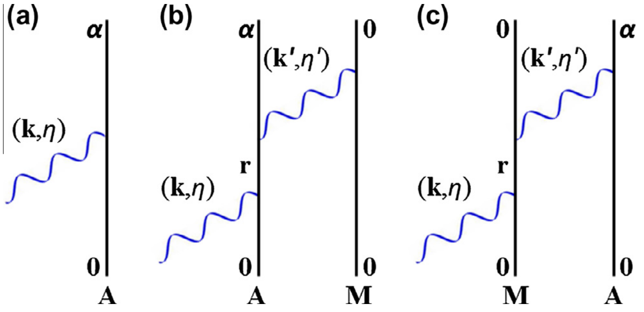

Figure 2. Example Feynman diagrams for the medium-independent (a), static (b), and dynamic (c) absorption events described by first- and third-order perturbation theory. The molecular virtual intermediate state is labelled *r*.

$$|M_{fi}|^2 = \underbrace{\left|M_{fi}^{(A)}\right|^2}_{(1)} + \underbrace{\left|M_{fi}^{(MA)}\right|^2}_{(2)} + \underbrace{\left|M_{fi}^{(AM)}\right|^2}_{(3)} + 2\Re e\left\{\underbrace{M_{fi}^{(A)}\overline{M_{fi}^{(MA)}}}_{(4)} + \underbrace{M_{fi}^{(A)}\overline{M_{fi}^{(AM)}}}_{(5)} + \underbrace{M_{fi}^{(MA)}\overline{M_{fi}^{(AM)}}}_{(6)}\right\}, \tag{7}$$

in which numbering has been introduced so that terms may be tackled individually. The leading order term is term (1), which corresponds to absorption in the absence of the mediator. The terms (2) and (3) are obtained from third-order perturbation theory, and are therefore small in comparison to term (1), which implies that term (6) is also small. Thus, the first correction terms to the absorption rate are terms (4) and (5).

3.1. Medium-independent absorption

Firstly, we calculate the leading order term, where no other molecule is involved. In the electric dipole approximation, the interaction Hamiltonian is given by $H_{int} = -\varepsilon_0^{-1}\boldsymbol{\mu}\cdot\mathbf{d}^{\perp}$, with the transverse electric field given by:

$$\mathbf{d}^{\perp}(\mathbf{r}) = i\sum_{\mathbf{k},\eta}\left(\frac{\hbar ck\varepsilon_0}{2V}\right)^{\frac{1}{2}}\left\{\mathbf{e}^{(\eta)}(\mathbf{k})\,a^{(\eta)}(\mathbf{k})\mathrm{e}^{\mathrm{i}\mathbf{k}\cdot\mathbf{r}} - \bar{\mathbf{e}}^{(\eta)}(\mathbf{k})\,a^{\dagger(\eta)}(\mathbf{k})\mathrm{e}^{-\mathrm{i}\mathbf{k}\cdot\mathbf{r}}\right\}. \tag{8}$$

where V is the quantization volume, while $\mathbf{e}^{(\eta)}(\mathbf{k})$and $a^{(\eta)}(\mathbf{k})$ are the polarization vector and photon annihilation operator respectively for a mode with polarization η and wave-vector k. The right-most term in Eq. (8) is the Hermitian conjugate of the term on the left, with $a^{\dagger(\eta)}(k)$defined as the photon creation operator. Thus, we have:

$$M_{fi}^{(A)} = \langle f|H_{int}|i\rangle = -i\left(\frac{n\hbar ck}{2V\varepsilon_0}\right)^{\frac{1}{2}}\boldsymbol{\mu}^{(A)\alpha 0}\cdot\mathbf{e}^{(\eta)}(\mathbf{k})\mathrm{e}^{\mathrm{i}\mathbf{k}\cdot\mathbf{r}_A}, \tag{9}$$

where $\mathbf{r}_A$ is the position vector of the acceptor molecule. We assume the wavefunctions are real. The square modulus of the above – term (1) from Eq. (7) – is:

$$\left|M_{fi}^{(A)}\right|^2 = \left(\frac{n\hbar ck}{2V\varepsilon_0}\right)\left|\boldsymbol{\mu}^{(A)\alpha 0}\cdot\mathbf{e}^{(\eta)}(\mathbf{k})\right|^2, \tag{10}$$

which, by substituting into the Fermi rule and performing a three-dimensional isotropic rotational average [10,19,20], yields:

$$\langle\Gamma^{(A)}\rangle = \left(\frac{\pi nck\rho_f}{3V\varepsilon_0}\right)\left|\boldsymbol{\mu}^{(A)\alpha 0}\right|^2. \tag{11}$$

This well-known result [10] is presented for later comparison with the modifications to the rate introduced by secondary (mediator) chromophores.

3.2. Static correction term

To begin calculation of the correction terms, we compute $M_{fi}^{(AM)}$from third-order perturbation theory. The third term of Eq. (3) and a programme of contour integration delivers a contribution to the quantum amplitude as dependent on a molecular interaction tensor:

$$M_{fi}^{(AM)} = -i\left(\frac{n\hbar ck}{2V\varepsilon_0}\right)^{\frac{1}{2}} e_j^{(\eta)}\alpha_{jk}^{A(\alpha 0)}V_{kl}(k,R_{MA})\mu_l^{M(00)}, \tag{12}$$

where R_{MA} is the distance between the absorber and secondary chromophore and $V_{ij}(k,R_{MA})$ is the general form of the fully retarded dipole–dipole interaction tensor given as [21,22]:

$$V_{ij}(k,R) = \frac{e^{ikR}}{4\pi\varepsilon_0 R^3}\left[(1-ikR)(\delta_{ij}-3\hat{R}_i\hat{R}_j)-k^2R^2(\delta_{ij}-\hat{R}_i\hat{R}_j)\right]. \tag{13}$$

In Eq. (12), the polarizability tensor for the acceptor model is labelled $\alpha_{ij}^{A(\alpha 0)}$ which is duly presented in the following general form:

$$\alpha_{ij}^{\xi(\alpha 0)} = \sum_r\left\{\frac{\mu_i^{\xi(\alpha r)}\mu_j^{\xi(r0)}}{(E_{\xi(r0)}-\hbar ck)}+\frac{\mu_j^{\xi(\alpha r)}\mu_i^{\xi(r0)}}{(E_{\xi(r\alpha)}+\hbar ck)}\right\}. \tag{14}$$

The static interference term of the probability – term (5) of Eq. (7) – follows as:

$$2\Re e\left\{M_{fi}^{(A)}\overline{M_{fi}^{(AM)}}\right\} = \Re e\left\{-\frac{n\hbar ck}{V\varepsilon_0}e_i^{(\eta)}\overline{e}_j^{(\acute{\eta})}\mu_i^{A(\alpha 0)}\overline{\mu}_i^{M(00)}\overline{\alpha}_{jk}^{A(\alpha 0)}\bar{V}_{kl}(k,R_{MA})\right\} \tag{15}$$

Depending explicitly on $\bar{\mu}_l^{M(00)}$, we now assume that the secondary chromophores have no static dipole moment, causing this term to vanish.

3.3. Dynamic correction term

To begin calculation of the remaining correction term, we compute $M_{fi}^{(MA)}$, as before, from third-order perturbation theory, which delivers this term of the quantum amplitude as:

$$M_{fi}^{(MA)} = -i\left(\frac{n\hbar ck}{2V\varepsilon_0}\right)^{\frac{1}{2}} e_j^{(\eta)}\alpha_{jk}^{M(00)}V_{kl}(k,R_{MA})\mu_l^{A(\alpha 0)}, \tag{16}$$

where $\alpha_{ij}^{M(00)}$is the polarizability tensor for the molecule M. Thus, term (4) from Eq. (7) becomes:

$$2\Re e\left\{M_{fi}^{(A)}\overline{M_{fi}^{(MA)}}\right\} = \Re e\left\{-\frac{n\hbar ck}{V\varepsilon_0}e_i^{(\eta)}\bar{e}_j^{(\eta')}\mu_i^{(A)\alpha 0}\bar{\mu}_l^{A(\alpha 0)}\bar{\alpha}_{jk}^{M(00)}\bar{V}_{kl}(k,R_{MA})\right\}, \tag{17}$$

It is worth noting that in the multipolar formulation of QED the interaction tensor can be generalized to couplings between electric and magnetic multipoles of any order [23–25]. Therefore, the form of Eq. (17) can be modified to permit calculation of modifications to absorption in a medium with strong magnetic dipole or electric quadrupole transition moments. In fact, it is through involvement of the magnetic transition dipole moments that an achiral molecule may display induced circular dichroism in the presence of a neighboring chiral molecule [9].

4. Absorption modified by secondary chromophores in a host medium

We now turn attention to the case of a material in which there is a distribution of secondary chromophores, variously located at different distances from, and relative orientations with respect to, each primary absorber. Represented by Figure 3, it is to be assumed that both species are held within a host matrix that is essentially transparent in the wavelength region of interest, and which can to that extent be represented as a continuous medium characterized by a refractive index n_ω with a non-zero but essentially negligible imaginary component (the assumption is to be revised in Section 4.1.). The presence of this host medium introduces a modification to the equations given in the previous section.

First, assuming for simplicity that the group velocity is equal to the phase velocity c/n_ω, the electric displacement field expansion of Eq. (8) is adapted to the following form [17,26,27]:

$$\tilde{\mathbf{d}}^{\perp}(\boldsymbol{r}) = i\sum_{\mathbf{k},\eta}\left(\frac{\hbar ck\varepsilon_0}{2V}\right)^{\frac{1}{2}}\left(\frac{n_\omega^2+2}{3n_\omega}\right)\left\{\mathbf{e}^{(\eta)}(\mathbf{k})a^{(\eta)}(\mathbf{k})\mathrm{e}^{\mathrm{i}\mathbf{k}\cdot\mathbf{r}}-\bar{\mathbf{e}}^{(\eta)}(\mathbf{k})a^{\dagger(\eta)}(\mathbf{k})\mathrm{e}^{-\mathrm{i}\mathbf{k}\cdot\mathbf{r}}\right\}. \tag{18}$$

The matrix element for absorption independent of M is accordingly also modified as:

$$\tilde{M}_{fi}^{(A)} = -i\left(\frac{n\hbar ck}{2V\varepsilon_0}\right)^{\frac{1}{2}}\left(\frac{n_\omega^2+2}{3n_\omega}\right)\boldsymbol{\mu}^{(A)\alpha 0}\cdot\mathbf{e}^{(\eta)}(\mathbf{k})\mathrm{e}^{\mathrm{i}\mathbf{k}\cdot\mathbf{r}_A}, \tag{19}$$

Furthermore, the transfer tensor given in Eq. (13), which is the form appropriate for species interacting in a vacuum, also now accommodates the effects of the continuous surrounding medium:

$$\tilde{V}_{ij}(n_\omega k,\mathbf{R}_{MA}) = \frac{1}{n_\omega^2}\left(\frac{n_\omega^2+2}{3}\right)^2 V_{ij}(n_\omega k,\mathbf{R}_{MA}). \tag{20}$$

Therefore the host-influenced equivalent of Eq. (16) is duly:

$$\tilde{M}_{fi}^{(MA)} = -i\left(\frac{n\hbar ck}{2V\varepsilon_0}\right)^{\frac{1}{2}}\left(\frac{n_\omega^2+2}{3n_\omega}\right)e_j^{(\eta)}\alpha_{jk}^{M(00)}\tilde{V}_{kl}(n_\omega k,R_{MA})\mu_l^{A(\alpha 0)}, \tag{21}$$

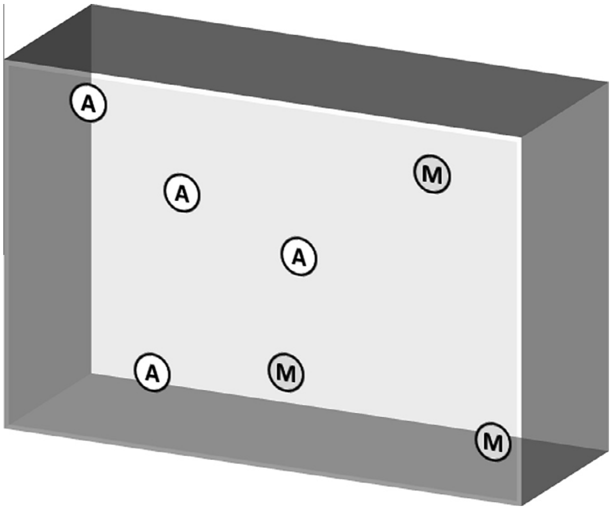

Figure 3. Representation of a system of primary and secondary chromophores incorporated within a host matrix (the latter depicted as a notional cube for illustrative purposes only). All components of the continuous host media display negligible absorption in the wavelength region of both *A* and *M*.

To be clear, we are assuming that the surroundings, characterized by n_ω, are comprised of neither A nor M. Now, the effects of every secondary chromophore in the system must be taken into account. To effect an analytically tractable calculation, and to avoid unnecessarily complicated results, we assume that the secondary species have random orientations; this justifies performing a three-dimensional isotropic rotational average with respect to the orientation of M. Substituting Eq. (13) and (20) into (17) and enacting the rotational average, enables the expression to be written as:

$$\begin{aligned}2\Re e\left\{\tilde{M}_{fi}^{(A)}\overline{\tilde{M}_{fi}^{(MA)}}\right\} = \Re e\Bigg\{&-\frac{In_\omega}{12c\pi\varepsilon_0^2}\sum_M\frac{e^{-i\bar{n}_\omega kR_{MA}}}{R_{MA}^3}\left(\frac{n_\omega^2+2}{3n_\omega}\right)\left(\frac{\bar{n}_\omega^2+2}{3\bar{n}_\omega}\right)^3\\ &\bar{\alpha}_{\lambda\lambda}^{M(00)}\times(\mathbf{e}\cdot\boldsymbol{\mu}^{A(\alpha0)})[(1+i\bar{n}_\omega kR_{MA})\\ &\times\left((\bar{\mathbf{e}}\cdot\bar{\boldsymbol{\mu}}^{A(\alpha0)})-3\left(\bar{\mathbf{e}}\cdot\hat{\mathbf{R}}_{MA}\right)(\bar{\boldsymbol{\mu}}^{A(\alpha0)}\cdot\hat{\mathbf{R}}_{MA})\right)\\ &-\bar{n}_\omega^2k^2R_{MA}^2\{(\bar{\mathbf{e}}\cdot\bar{\boldsymbol{\mu}}^{A(\alpha0)})-(\bar{\mathbf{e}}\cdot\hat{\mathbf{R}}_{MA})(\bar{\boldsymbol{\mu}}^{A(\alpha0)}\cdot\hat{\mathbf{R}}_{MA})\}],\end{aligned} \quad (22)$$

where Greek subscripts denote laboratory-frame co-ordinates. The pre-factor has been cast in terms of mean irradiance I, where $I = \frac{n\hbar c^2k}{n_\omega V}$.

To aid interpretation of the mathematical result, let us assume that the input radiation propagates at an angle γ to the dipole moment of the acceptor molecule. Working in spherical coordinates with r, ϕ and θ being the radial, azimuthal and polar coordinates respectively, we model a continuous medium by re-expressing the sum over all mediators as the product of the mediator concentration, C_M and an integral over all positions of M.

$$\begin{aligned}\Re e\Bigg\{&-\frac{In_\omega C_M}{12c\pi\varepsilon_0^2}\int\int\int\frac{e^{-i\bar{n}_\omega kR_{MA}}}{R_{MA}^3}\left(\frac{n_\omega^2+2}{3n_\omega}\right)\left(\frac{\bar{n}_\omega^2+2}{3\bar{n}_\omega}\right)^3\bar{\alpha}_{\lambda\lambda}^{M(00)}.|\boldsymbol{\mu}^{A(\alpha0)}|^2\\ &\times cos\gamma\Big[1+(i\bar{n}_\omega kR_{MA})(cos\gamma-3cos(\theta-\gamma)cos\theta)-\bar{n}_\omega^2k^2R_{MA}^2\\ &(cos\gamma-cos(\theta-\gamma)cos\theta)]R_{MA}^2sin\theta\partial\theta\partial\phi\partial R_{MA}\Bigg\}\end{aligned} \quad (23)$$

where the integration is performed over every point in $\mathbb{R}^3$ by a triple integral with standard limits, and $R_{MA}^2\sin(\theta)d\theta d\phi dR_{MA}$ is the volume element [28]. Implementing the θ integral, the R-independent terms and others that are dependent on R^{-1} all vanish, and further integration over the azimuthal angular coordinate introduces a factor of 2π. By imposing a minimum distance, $R_{\min}$, between the acceptor molecule and the mediator molecules in the continuum we can use the following identity:

$$\int_{R_{\min}}^{\infty}e^{-i\bar{n}_\omega kR_{MA}}R_{MA}\,\partial R_{MA} = \frac{e^{-i\bar{n}_\omega kR_{\min}}(i\bar{n}_\omega kR_{\min}+1)}{\bar{n}_\omega^2k^2}. \quad (24)$$

Given that the wavenumber is real and the overbar denotes complex conjugation, this identity is valid for $\Im m(n_\omega) > 0$, i.e. when the medium has at least a marginal absorption over the wavelength range of concern – which in practice will always be the case. Before developing this further, we first take the first two terms of a power series expansion of the exponential $e^{-i\bar{n}_\omega kR}$, such that Eq. (24) is re-expressed as:

$$\int_{R_{\min}}^{\infty}e^{-i\bar{n}_\omega kR_{MA}}R_{MA}\,\partial R_{MA} = R_{\min}^2+\frac{1}{\bar{n}_\omega^2k^2}. \quad (25)$$

We then obtain the following medium-induced correction to the absorption rate:

$$2\Re e\left\{\frac{In_\omega C_M(1+\bar{n}_\omega^2k^2R_{\min}^2)\cos^2\gamma}{9c\varepsilon_0^2}\left(\frac{n_\omega^2+2}{3n_\omega}\right)\left(\frac{\bar{n}_\omega^2+2}{3\bar{n}_\omega}\right)^3\bar{\alpha}_{\lambda\lambda}^{M(00)}|\boldsymbol{\mu}^{A(\alpha0)}|^2\right\}. \quad (26)$$

The zeros of Eq. (26) can be readily identified as $\gamma = m\pi - \pi/2$, where m represents any integer value. Now, we can take the limit when $R_{\min}$ tends to zero. This assumption is readily shown to have minimal impact on the quantitative values delivered by the above expression – based on an optical input where $k = 10^7m^{-1}$, the value of $R_{\min}$ would realistically need to exceed 100 nm before delivering a 1% additive contribution to the overall result of Eq. (26). Finally, by rotational averaging with respect to the propagation angle of the input radiation or, equivalently, the orientation of the absorber molecule A, we obtain:

$$2\Re e\left\{\tilde{M}_{FI}^{(A)}\overline{\tilde{M}_{FI}^{(MA)}}\right\} = \Re e\left\{\frac{2In_\omega C_M}{27c\varepsilon_0^2}\left(\frac{n_\omega^2+2}{3n_\omega}\right)\left(\frac{\bar{n}_\omega^2+2}{3\bar{n}_\omega}\right)^3\bar{\alpha}_{\lambda\lambda}^{M(00)}|\boldsymbol{\mu}^{A(\alpha0)}|^2\right\}. \quad (27)$$

It is now possible to compare the free-field term and the dynamic correction. It is clear that for the modification of absorption to become significant, the medium requires a polarizability tensor with large diagonal components. The transition dipole of the acceptor molecule does not affect the ratio of these two terms, since the square modulus of this vector appears in both the free-space expression, Eq. (10), and the dynamic correction, Eq. (27).

4.1. Absorption modified by secondary chromophores in an absorptive host medium

In the previous section, photon absorption at a primary chromophore has been shown to be modified by the proximity of a secondary chromophore. Assuming the secondary mediators to be non-polar, the lead correction to the absorption process was expressed as either Eqs. (17), (27), representing isolated systems or those embedded within a host material, respectively. The theory in the previous section is consistent with the concept that radiative loss as light propagates through the host medium is minimal, *i.e.* the host is essentially transparent for photons of energy $\hbar\omega$. By revisiting this assumption, equations of wider application are now to be derived for a system in which the primary and secondary chromophores are held within a host material that exhibits more significant absorptive loss. The lead matrix element contribution – term 4 in Eq. (7) – is now developed from Eq. (23) upon the substitution of $n_\omega = n'_\omega - in''_\omega$ for all cases of n_ω. Here, n'_ω is the real part of the refractive index and n''_ω is a small but non-zero constant, physically representing a host with low optical density. Hence, we obtain:

$$\begin{aligned}2\Re e\Bigg\{&\frac{Ik^2C_M(n'_\omega-in''_\omega)(n'_\omega+in''_\omega)^2\cos^2\gamma}{9c\varepsilon_0^2}\left(\frac{(n'_\omega-in''_\omega)^2+2}{3(n'_\omega-in''_\omega)}\right)\\ &\left(\frac{(n'_\omega+in''_\omega)^2+2}{3(n'_\omega+in''_\omega)}\right)^3\int_{R_{\min}}^{\infty}e^{-i(n'_\omega+in''_\omega)kR_{MA}}R_{MA}\partial R_{MA}\bar{\alpha}_{\lambda\lambda}^{M(00)}|\boldsymbol{\mu}^{A(\alpha0)}|^2\Bigg\}\end{aligned} \quad (28)$$

In the above expression, separate integrations over θ and ϕ have already been implemented, again delivering a result dependent on R^{-1}, however the integration over R now requires an alternative identity to that employed in Eq. (24), namely:

$$\int_{R_{\min}}^{\infty}e^{-i(n'_\omega+in''_\omega)kR_{MA}}R_{MA}\,\partial R_{MA} = \frac{e^{-i(n'_\omega+in''_\omega)kR_{\min}}(i(n'_\omega+in''_\omega)kR_{\min}+1)}{k^2(n'^2_\omega+2in'_\omega n''_\omega-n''^2_\omega)}. \quad (29)$$

Again using the first two terms of a power series expansion of the exponential $e^{-i(n'_\omega+in''_\omega)kR}$, equation (29) can be re-expressed as:

$$\int_{R_{\min}}^{\infty}e^{-i(n'_\omega+in''_\omega)kR_{MA}}R_{MA}\,\partial R_{MA} = R_{\min}^2+\frac{1}{k^2(n'^2_\omega+2in'_\omega n''_\omega-n''^2_\omega)}. \quad (30)$$

Substituting the right hand side of Eq. (30) into (28), and performing the rotational average with respect to the propagation angle of the input radiation, the emerging expression is equivalent to:

$$2\Re e\left\{\frac{IC_M\left(n_\omega'^2+2\right)^3}{3^7 c\varepsilon_0^2\left(n_\omega'^6+4in_\omega'^5 n_\omega''\right)}\left[n_\omega'^3\left(n_\omega'^2+2\right)\left(1+n_\omega'^2k^2R_{\min}^2\right)\right.\right.$$
$$\left.\left.+in_\omega'^2 n_\omega''\left(\left(5n_\omega'^2+2\right)+n_\omega'^2k^2R_{\min}^2\left(7n_\omega'^2+6\right)\right)\right]\bar{\alpha}_{\lambda\lambda}^{M(00)}\left|\boldsymbol{\mu}^{A(\alpha 0)}\right|^2\right\}. \qquad (31)$$

Since n_ω'' is small, all terms that are non-linear in n_ω'' in the above and any subsequent expression are negligible, and can thus be discarded. Following a geometric series expansion, Eq. (31) is re-expressible as:

$$2\Re e\left\{\frac{IC_M\left(n_\omega'^2+2\right)^3}{3^7 c\varepsilon_0^2 n_\omega'^4}\left[n_\omega'\left(n_\omega'^2+2\right)\left(1+n_\omega'^2k^2R_{\min}^2\right)\right.\right.$$
$$\left.\left.+in_\omega''\left(\left(n_\omega'^2-6\right)+n_\omega'^2k^2R_{\min}^2\left(3n_\omega'^2-2\right)\right)\right]\bar{\alpha}_{\lambda\lambda}^{M(00)}\left|\boldsymbol{\mu}^{A(\alpha 0)}\right|^2\right\}, \qquad (32)$$

Continuing with the procedure established in the previous section, as $R_{\min}$ tends to zero, the final expression for the correction to the absorption rate – in an absorptive host medium, follows as:

$$2\Re e\left\{\tilde{M}_{fi}^{(A)}\overline{\tilde{M}_{fi}^{(MA)}}\right\}=\frac{2IC_M\left|\boldsymbol{\mu}^{A(\alpha 0)}\right|^2\left(n_\omega'^2+2\right)^3}{3^7 c\varepsilon_0^2 n_\omega'^4}\left[n_\omega'\left(n_\omega'^2+2\right)\alpha_{\lambda\lambda}'^{M(00)}\right.$$
$$\left.+n_\omega''\left(n_\omega'^2-6\right)\alpha_{\lambda\lambda}''^{M(00)}\right], \qquad (33)$$

The preceding result is expressed as a sum of both real and imaginary contributions, having implemented a re-expression of the molecular polarizability tensor such that $\bar{\alpha}_{\lambda\lambda}^{M(00)}=\alpha_{\lambda\lambda}'^{M(00)}-i\alpha_{\lambda\lambda}''^{M(00)}$. All non-zero, real and imaginary terms in Eq. (32) have been collated with $\alpha_{\lambda\lambda}'^{M(00)}$ and $\alpha_{\lambda\lambda}''^{M(00)}$, which respectively represent the real and imaginary parts of $\bar{\alpha}_{\lambda\lambda}^{M(00)}$. It is rewarding to note that in the limit where $\alpha_{\lambda\lambda}''^{M(00)}$ and n'' are zero, Eq. (33) reduces to the earlier result (27). Notably, the extent to which the difference is significant depends on a product of terms representing low-level absorption by both the host and the secondary chromophore species *M*. Lastly, it is interesting to note that while the presented results are analytically tractable, the broadly analogous modification of resonance energy transfer through interaction with a secondary chromophore is not as tractable, requiring the use of numerical methods [29,30].

5. Conclusion

Using a fully quantized radiation formalism it has been shown that, in a host material containing two or more types of molecular chromophore, the rate of single photon absorption by a primary chromophore is significantly influenced by others that absorb at a shorter wavelength. Corrections to the absorption rate are predicted – and subsequently characterized – as a result of intermolecular coupling between the primary and secondary centres. Upon the basis that such coupling is mediated by virtual photons, the lead correction term to the photon absorption rate emerges as a quantum interference contribution, dependent on the molecular polarizability of the molecular mediators. In considering the more experimentally feasible conditions where such a system of primary and secondary chromophores is incorporated within a host matrix or molecular scaffold, the dependence on the refractive index of the surrounding molecular environment is duly identified. Finally, the effect of partial absorption by the host itself is accommodated, to give a result of wider applicability.

In application to the most complex types of optical media, determining the optimum criteria for modified optical absorption will require account to be taken of other, possibly competing acceptors; it can be anticipated that the emerging result will exhibit a sensitive dependence on the ratio of acceptors to mediators. To further extend the analysis, it may also be desirable to model the set of mediators as having some alignment preference. Such a situation would require use of weighted rotational averaging [31], with explicit calculation of the static correction terms if the chromophores are polar; this may demand the implementation of computational techniques. The prospect represents scope for future work.

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