Chemical Physics Letters 595–596 (2014) 151–155

Contents lists available at ScienceDirect

Chemical Physics Letters

journal homepage: www.elsevier.com/locate/cplett

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

Matt M. Coles, Jamie M. Leeder, David L. Andrews [*]

School of Chemistry, University of East Anglia, Norwich NR4 7TJ, United Kingdom

ARTICLE INFO

Article history:
Received 20 December 2013
In final form 21 January 2014
Available online 31 January 2014

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:

---

[*] Corresponding author.
E-mail address: d.l.andrews@uea.ac.uk (D.L. Andrews).

http://dx.doi.org/10.1016/j.cplett.2014.01.028
0009-2614/© 2014 The Authors. Published by Elsevier B.V.

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

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):

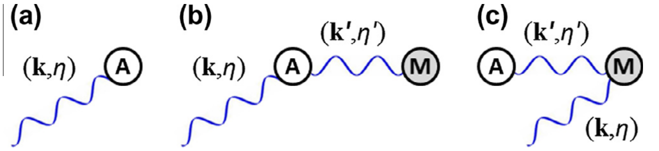

Figure 1. Diagrams (a), (b) and (c) represent the A, AM and MA absorption configurations respectively. The input photon is labelled with wave-vector $\mathbf{k}$ and polarization η: ($\mathbf{k}'$,η') represents the mode of a virtual photon mediator between molecular centres. All diagrams represent A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

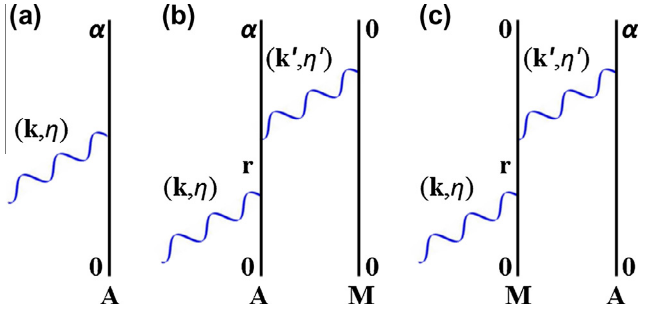

Figure 2. Example Feynman diagrams for the medium-independent (a), static (b), and dynamic (c) absorption events described by first- and third-order perturbation theory. The molecular virtual intermediate state is labelled r.

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

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: