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Thermal quenching of fluorescence in condensed media

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ABSTRACT

Environmental factors strongly affect the features of the electromagnetic spectra of fluorescent compounds hosted by material media. The shape of the absorption and emission peaks, their characteristic asymmetry and breadth, the Stokes shift and quantum yield are generally temperature dependent and heavily influenced by both the local and extended physical properties of the medium. The theoretical method used before to obtain the lineshape function is extended here to other terms of the interaction energy between the optically sensitive orbital and the hosting medium, which become significant when the spectral feature is broad. An analytical expression for the temperature dependent decay rate by non-radiative processes is obtained by this way. Comparison with experiment on thermal quenching gives agreement within the experimental uncertainty. The solvent polarity, its protic or aprotic character, hydrogen bonds, proximity effects and presence of quenchers are expected to enter through the coupling constants of the corresponding energy terms.

1. Introduction

Fluorescence is characterized by the wide frequency spectrum displayed by the emitted light, which may occupy a substantial part of the visible spectrum, and its occurrence at frequencies significantly lower than those at which absorption takes place. The latter occurs in a frequency range as broad as emission. A fluorescent spectral feature is generally associated to transitions between two specific states of a bonding electronic orbital which take or release a well defined energy amount [1–3]. What widens and shifts the spectral line is principally the coupling of the optically responsive orbital of the fluorophore, as is usually called the fluorescent chemical compound when hosted by a different material medium, with the acoustic vibrational modes of the hosting medium. Fluorescence is thus related with a large strength of this coupling [4].

A recently published fully quantal theoretical approach to the problem provides a general expression for the line shape function valid for spectral lines of any width or, equivalently, any strength of the coupling of the electronic degrees of freedom with the radiation field [4–6]. The theoretical framework assumes that the electronic orbital undergoing the transition couples with the elementary excitations of the material medium through the conformational change of the molecule. Despite the striking success attained in the accurate reproduction of the experimentally observed lineshapes, the theory fails in predicting the right temperature dependence of the fluorescent yield. The predicted quantum yield is always unity, independent of the temperature and particularities of the hosting medium, which contradicts observations. This communication amends the point showing that the shortcoming comes from dropping a term of the system Hamiltonian which becomes significant when the coupling of the electronic and configurational variables become strong enough, as occurs in fluorescent molecules. This term does not contain variables of the radiation field and gives rise to a non-radiative decay channel which competes with the radiative contribution. The properties of the latter are not altered, but only the area of the spectral feature. The correction yields a closed-form equation for thermal quenching which exhibits very good agreement with experiment.

The material medium hosting the fluorescent orbital has acoustic modes of vibration extending over its whole volume, whose frequencies are linear in the wavenumbers and form a quasi-continuum with no ground state energy gap. On the contrary, optical and molecular vibration modes, and any kind of localized excitation, have finite energy and are expected to contribute less than the acoustic modes, or produce a distinguishable spectral component. Liquid solvents can support only longitudinal acoustic waves, which do not give a complete account of the degrees of freedom of the system. The problem of the collective dynamical variables of liquids is quite old [7], but has no clear-cut solution yet. Recent *ab initio* molecular dynamics simulations indicate that the remaining degrees of freedom are local configurational excitations in the atomic connectivity network [8]. By their

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local character these excitations should have an energy gap. It is assumed here that longitudinal phonons are the only relevant low energy excitations in liquid media, keeping in mind that this description may be not always complete.

2. The Hamiltonian

The Hamiltonian of the condensed phase interacting with the electromagnetic radiation field is written as [4–6]

$$H = H_0 + H_1 + H_2 + H_3 + H_4, \tag{1}$$

where

$$H_0 = \sum_q \hbar\omega_q \left(a_q^\dagger a_q + \frac{1}{2} \right) + \sum_\ell \epsilon_\ell c_\ell^\dagger c_\ell + \sum_{q\ell} g_{q\ell} c_\ell^\dagger c_\ell (a_q - a_{\bar{q}}^\dagger) \tag{2}$$

$$H_1 = \sum_{\ell \neq \ell'} \sum_q g_{q\ell'\ell} c_{\ell'}^\dagger c_\ell (a_q - a_{\bar{q}}^\dagger) \tag{3}$$

$$H_2 = \sum_{\nu\vec{k}} \hbar c k \eta_{\nu\vec{k}}^\dagger \eta_{\nu\vec{k}} \tag{4}$$

$$H_3 = \sum_{\ell'\ell\nu\vec{k}} Q_{\ell'\ell\nu\vec{k}} c_{\ell'}^\dagger c_\ell (\eta_{\nu\vec{k}} - \eta_{\nu(-\vec{k})}^\dagger) \tag{5}$$

$$H_4 = \sum_{\ell'\ell q\nu\vec{k}} R_{\ell'\ell q\nu\vec{k}} c_{\ell'}^\dagger c_\ell (a_q - a_{\bar{q}}^\dagger)(\eta_{\nu\vec{k}} - \eta_{\nu(-\vec{k})}^\dagger). \tag{6}$$

H_0 is the Hamiltonian of the molecule in the condensed material medium, a_q is a phonon operator of mode q, with angular frequency ω_q, the mode propagating in the opposite direction is denoted $\bar{q}$. The fermion operator $c_\ell^\dagger$ creates a localized one-electron state, index ℓ characterizes both the molecular site and the excitation state. The operator $c_\ell^\dagger c_\ell$ accounts for the occupancy of the one-electron state ℓ. By the hermiticity of H_0, the diagonal matrix elements $g_{q\ell}$ between the local one-electron basis functions satisfy $g_{\bar{q}\ell}^* = -g_{\bar{q}\ell}$.

The term H_1 collects the terms proportional to the off-diagonal matrix elements $g_{q\ell'\ell}$ between the local one-electron basis functions. The terms in $g_{q\ell'\ell}$, $\ell' \neq \ell$, contribute to hybridize the electronic states by effect of the distortion produced by the excitation of the local bond. The neglection of H_1 is usually referred to as Condon approximation. However, fluorescence is characterized by strong electron–phonon couplings and it will be shown in the next sections that H_1 may be large enough to produce notorious effects.

The remaining three terms, H_2, H_3 and H_4, are the Hamiltonian of the free electromagnetic field and its interaction with the electronic bonds ℓ. The bosonic operators $\eta_{\nu\vec{k}}^\dagger$ create photons with well defined momentum $\hbar\vec{k}$ and polarization index ν, and the coefficients appearing in H_3 are written explicitly in Gauss units as

$$Q_{\ell'\ell\nu\vec{k}} = \frac{e}{m}\sqrt{\frac{2\pi\hbar}{ckV}}\hat{e}_{\nu\vec{k}} \cdot \vec{p}_{\vec{k}\ell'\ell}, \tag{7}$$

where e/m is the specific charge of the electron, V the volume occupied by the system, $\hat{e}_{\nu\vec{k}}$ the polarization unit vector of the photon, and

$$\vec{p}_{\vec{k}\ell'\ell} = -i\hbar \int d^3\vec{r} \langle \ell' | \vec{r} \rangle e^{i\vec{k}\cdot\vec{r}} \nabla \langle \vec{r} | \ell \rangle, \tag{8}$$

where $\langle \vec{r} | \ell \rangle$ and $\langle \vec{r} | \ell' \rangle$ are wave functions of the local electronic orbital undergoing the transition. They are stationary states of the electron moving in the field of the ions fixed at the equilibrium sites they have when the whole system is in its ground state.

3. The lineshape

The coefficient $g_{q\ell}$ vanishes when ℓ corresponds to the ground state of a molecular orbital. Hence the third term in the right hand side of Eq. (2) vanishes when the binding electrons are all in their ground states. In this situation the Hamiltonian H_0 decouples into an harmonic part for the nuclear variables and an electronic one, in the spirit of the Born–Oppenheimer approximation. The excitation of a one-electron state ℓ switches on the linear term of H_0 coupling the nuclear and electronic variables.

The energy spectrum and stationary states of H_0 can be derived exactly replacing the new Bose operators [4,5]

$$b_q^\dagger = a_q^\dagger + \sum_\ell \frac{g_{q\ell}}{\hbar\omega_q} c_\ell^\dagger c_\ell, \tag{9}$$

which excite nuclear vibrations around equilibrium positions which are displaced with respect to the equilibrium configuration taken by the system when all the electronic quantum numbers have the ground state values. Details of the procedure can be found in the literature [4,5], however a brief review of the results is given here, mainly for the sake of defining the notation and for recalling some ideas which will be important for interpreting the forthcoming results.

The eigenvalues and eigenvectors of H_0 read

$$E_{\ell\{n_q\}} = \sum_{\{n_q\}} \hbar\omega_q \left(n_q + \frac{1}{2} \right) + \epsilon_\ell - \sum_q \frac{|g_{q\ell}|^2}{\hbar\omega_q}, \quad n_q = 0, 1, 2, \ldots. \tag{10}$$

$$|\ell\{n_q\}\rangle = \prod_q \frac{\left(b_q^\dagger\right)^{n_q}}{\sqrt{n_q!}} \exp\left[\sum_q \frac{g_{q\ell}}{\hbar\omega_q} (b_q + b_{\bar{q}}^\dagger) \right] c_\ell^\dagger |00\rangle \tag{11}$$

when only one electronic orbital is excited to the state ℓ. Here $|00\rangle$ denotes the ground state of the system, with no vibrational and no electronic excitations. With some work it can be shown that [5]

$$\langle \ell'\{n_q + \mu_q\} | c_{\ell'}^\dagger c_\ell | \ell\{n_q\} \rangle = \prod_q \sqrt{\frac{n_q!}{(n_q + \mu_q)!}} \exp\left(-\frac{1}{2}|G_{q\ell'\ell}|^2 \right) |G_{q\ell'\ell}|^{\mu_q} L_{n_q}^{\mu_q}\left(|G_{q\ell'\ell}|^2 \right), \tag{12}$$

where $G_{q\ell'\ell} = (g_{q\ell'} - g_{q\ell})/\hbar\omega_q$ and $L_n^\mu(x)$ is the generalized Laguerre polynomial of the variable x in standard notation.

Neglecting by the time being H_1 and H_4, Fermi's golden rule applied to the linear interaction term H_3 between the optically sensitive orbital and the radiation field gives for the probability per unit time of a transition between the stationary states (11), concurrent with the creation or annihilation of a single photon $(\nu, \vec{k})$. Replacing in golden's rule the interaction term H_3 and Eq. (12), expressing the δ-function by its integral representation, and then summing over all the initial excitation numbers n_q and the final ones $n_q + \mu_q$, weighting the former with their thermodynamic probabilities, it is obtained that

$$w_{\ell'\ell\nu\vec{k}} = \frac{4\pi^2 e^2}{m^2 c^2 k} |\hat{e}_{\nu\vec{k}} \cdot \vec{p}_{\vec{k}\ell'\ell}|^2 J_{\nu\vec{k}} F_{\ell'\ell}(\hbar c k; T), \tag{13}$$

where $J_{\nu\vec{k}}$ represents the density of flux of $(\nu\vec{k})$ photons and [5]

$$F_{\ell'\ell}(\hbar c k; T) = \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} dt \exp\left\{ \sum_q |G_{q\ell'\ell}|^2 \times \left[-\coth\left(\frac{\hbar\omega_q}{2k_B T} \right) \left(1 - \cos(\omega_q t) \right) + i \sin(\omega_q t) \right] \right\} \times \exp\left(i \frac{E_{\ell'\ell} - \hbar c k}{\hbar} t \right), \tag{14}$$