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Mechanism for Optical Enhancement and Suppression of Fluorescence

David S. Bradshaw and David L. Andrews*

Nanostructures and Photomolecular Systems, School of Chemical Sciences, University of East Anglia, Norwich NR4 7TJ, United Kingdom

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When fluorescence from electronically excited states follows the absorption of radiation, the emission spectrum is often a key to identification of the excited species. It now emerges that passing off-resonant laser light through such an electronically excited system may enhance or suppress the fluorescent emission. This report establishes the mechanism and theory for this optical control of spontaneous fluorescence, derived by quantum electrodynamical analysis. Experimental techniques to detect the enhanced signal are also proposed.

When light of a suitable wavelength passes through any chemically complex system, the primary result of ultraviolet/visible absorption is the electronic excitation of individual molecules or chromophores. Typically, relaxation processes produce an ultrafast but partial degradation of the acquired energy, and any subsequent fluorescence occurs from the lowest vibrational level of the electronic excited state. As is well-known, the throughput of a laser beam in such photoactivated systems produces stimulated emission when the optical frequency matches the emission, a phenomenon that has recently found clever analytical applications in stimulated emission depletion spectroscopy.[1−6] It now emerges that the intensity and directional character of such fluorescence may also be significantly influenced by a completely *off*-resonant probe laser beam of sufficient intensity, through a nonlinear optical coupling mechanism. In this report, the nature of this coupling is described in detail, and its characteristics are analyzed using a quantum electrodynamical framework. It is shown how the process depends on the detailed spectral properties of each fluorophore, and possible applications are identified.

When fluorescence occurs by spontaneous emission, the process generally involves a single matter−photon interaction and its standard theory is cast in terms of first-order time-dependent perturbation theory. When no light is present, in particular, once any radiation responsible for the initial electronic excitation has passed out of the system, higher order (odd-rank) correction terms are insignificant and denote only self-energy corrections. However, this is no longer the case when the activated system is subject to a throughput of laser light. The delivery of radiation with a frequency to match the fluorescence allows stimulated emission to occur; the emission is still a first-order interaction but, in the language of quantum electrodynamics (QED), its probability is weighted by the occupation number of the input radiation mode. A quite different form of interaction is possible using a probe laser with an optical frequency at which the system is transparent. There is no net absorption or stimulated emission, but elastic forward-scattering events do occur: photons are annihilated and created into the same radiation mode (which thus emerges unchanged). Such events can engage by nonlinear coupling with the fluorescence emission, and the effect is to modify the transition moment for fluorescence decay. This mechanism entails three matter-photon interactions, i.e., third-order perturbation theory.

The intensity of fluorescence, $I'(\Omega')$, (or power per unit solid angle) follows from the Fermi Rule rate[7] multiplied by the energy of a fluorescence photon, $\hbar ck'$.[8] Hence, the net intensity is determined from $I'(\Omega')\,\mathrm{d}\Omega' = 2\pi\rho ck'|M^{(1)} + M^{(3)}|^2$, where $M^{(1)}$ and $M^{(3)}$ are the quantum amplitudes for the first- and third-order interaction processes, respectively, and the density of radiation states is $\rho = (k^2V/8\pi^3\hbar c)\,\mathrm{d}\Omega$.[9] The effects to be considered below depend on the relative signs of the first- and third-order amplitudes; a common sign will lead to fluorescence enhancement, opposite signs its suppression. The criteria determining the specific outcome for a given system will emerge by analyzing the detailed form of the result. To proceed, the following is found for a given emission polarization:

$$I'(\Omega') = \left(\frac{ck'^4}{8\pi^2\varepsilon_0}\right)[e'_i e'_j \mu_i^{0\alpha}\mu_j^{0\alpha} + (I/c\varepsilon_0)e'_i e_j e_k e'_l \chi_{ijk}^{0\alpha}(\omega';-\omega,\omega)\mu_l^{0\alpha} + (I^2/4c^2\varepsilon_0^2)e'_i e_j e_k e'_l e_m e_n \chi_{ijk}^{0\alpha}(\omega';-\omega,\omega)\chi_{lmn}^{0\alpha}(\omega';-\omega,\omega)] \quad (1)$$

where the fluorescence-decay transition dipole moment is designated by the shorthand notation $\boldsymbol{\mu}^{0\alpha} = \langle 0|\boldsymbol{\mu}|\alpha\rangle$, in which $|\alpha\rangle$ denotes the excited matter state and $|0\rangle$ the ground state. The nonlinear transition susceptibility $\chi_{ijk}{}^{0\alpha}(\omega';-\omega,\omega)$ is defined below. In eq 1, the implied summation convention for repeated Cartesian tensor indices is used, and I is the irradiance of the laser probe, with $\mathbf{e}'$ and $\mathbf{e}$ representing the polarization vectors of fluorescence and probe photons, respectively. For simplicity, all photons are assumed linearly polarized.

The initial term on the right-hand side in eq 1 corresponds to spontaneous emission (the usual one-photon transition, intrinsic to the system and independent of the probe laser beam), while the last term signifies a coupling of the elastically forward-scattered probe beam with the fluorescence emission, a three-

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* To whom correspondence should be addressed. E-mail: d.l.andrews@uea.ac.uk.

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photon event. The second term, linear in I, represents a quantum interference of these two concurrent processes; in the context of absorption processes such interference between one- and three-photon transitions have been the subject of both theoretical and experimental interest, particularly regarding phase control applications.[10,11] In general, it may be assumed that the leading term in (1) is nonzero and the second term is the leading correction. The relative sign of this correction will partly depend on the orientations of the relevant transition dipoles relative to the optical polarization vectors; one ensuing consequence of engagement with the probe beam is therefore a modification to the fluorescence anisotropy, an issue we return to below. First, however, it is instructive to focus on the optical dispersion, identifying conditions that will be most expedient for detection of the effect.

The third-order nonlinear optical transition tensor, whose components are written as $\chi_{ijk}{}^{0\alpha}(\omega';-\omega,\omega)$, describes the material property that determines the decay coupling to the nonresonant probe beam. The tensor was first introduced in the context of laser-induced circular dichroism,[12] and in a generalized form it has also been shown to play a role in the dynamics of assisted energy transfer.[13] The sum-over-states form, explicitly exhibiting the frequency dispersion, is as follows:

$$\begin{aligned}\chi_{ijk}^{0\alpha}(\omega';-\omega,\omega) = {} & \sum_{r}\sum_{s\neq\alpha}\left(\frac{\mu_i^{0s}\mu_j^{sr}\mu_k^{r\alpha}}{\tilde{E}_{s\alpha}(\tilde{E}_{r\alpha}-\hbar\omega)}+\frac{\mu_i^{0s}\mu_k^{sr}\mu_j^{r\alpha}}{\tilde{E}_{s\alpha}(\tilde{E}_{r\alpha}+\hbar\omega)}\right)+ \\ & \sum_{r}\sum_{s}\left(\frac{\mu_j^{0s}\mu_i^{sr}\mu_k^{r\alpha}}{(\tilde{E}_{s\alpha}-\hbar\omega+\hbar\omega')(\tilde{E}_{r\alpha}-\hbar\omega)}+ \right. \\ & \left. \frac{\mu_k^{0s}\mu_i^{sr}\mu_j^{r\alpha}}{(\tilde{E}_{s\alpha}+\hbar\omega+\hbar\omega')(\tilde{E}_{r\alpha}+\hbar\omega)}\right)+ \\ & \sum_{r\neq0}\sum_{s}\left(\frac{\mu_j^{0s}\mu_k^{sr}\mu_i^{r\alpha}}{(\tilde{E}_{s\alpha}-\hbar\omega+\hbar\omega')(\tilde{E}_{r\alpha}+\hbar\omega')}+ \right. \\ & \left. \frac{\mu_k^{0s}\mu_j^{sr}\mu_i^{r\alpha}}{(\tilde{E}_{s\alpha}+\hbar\omega+\hbar\omega')(\tilde{E}_{r\alpha}+\hbar\omega')}\right) \end{aligned} \qquad (2)$$

where ω is the probe beam frequency, r and s are intermediate matter states, $E_{xy} = E_x - E_y$ is an energy difference between two such states (for example $E_{\alpha0} \equiv \hbar\omega' \equiv \hbar ck'$) and the transition moments are defined in the same manner as $\boldsymbol{\mu}^{0\alpha}$. The tildes serve as a reminder to add to the excited state energies, in the case of near-resonance conditions, imaginary terms that accommodate damping.

Considering the dependence of the fluorescence signal on the optical frequency of the probe beam, it is evident that the denominators within the susceptibility of eq 2 are the primary factors determining the degree of enhancement or suppression of the fluorescent emission. These factors are ultimately determined by the relative positioning of the fluorophore energy levels, relative to the magnitude of the probe photon energy. To discover more, we focus on the common case where the initially activated level $|\alpha\rangle$ is the lowest electronic excited state, assuming the same spin multiplicity as the ground state. It may also be assumed that the probe light is delivered with a tunable beam of frequency $\omega < \omega'$, precluding excitation from the ground state to higher electronic levels. Under such conditions it is readily apparent that the third term of eq 2, in effecting the sums over states $|r\rangle$ and $|s\rangle$, yields a denominator with the smallest magnitude. The maximum effect is achieved if the fluorophore has an electronic state $|\sigma\rangle$ positioned at an energy approximately $\hbar\omega$ above state $|\alpha\rangle$, as illustrated by Figure 1.

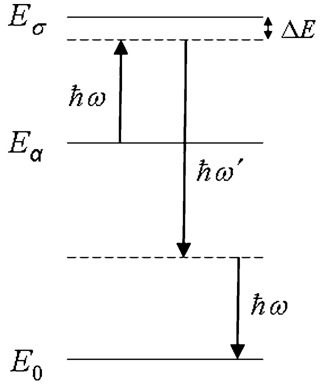

Figure 1. Optimum energetics for off-resonant laser-controlled fluorescence. Levels E_σ and E_0 denote ground and first excited electronic states, respectively, and E_0 is a state of higher energy, each represented by a solid line. Dotted lines denote virtual states, directed arrows exhibiting coupled transitions between the electronic states.

The major contribution to eq 2 then represents an approximate value for the susceptibility, and we have

$$\chi_{ijk}^{0\alpha}(\omega';-\omega,\omega) \approx \sum_{s}\frac{|\boldsymbol{\mu}^{0\alpha}|^3}{(\tilde{E}_{s0}-\hbar\omega)\Delta\tilde{E}} \qquad (3)$$

where $\Delta\tilde{E} = \tilde{E}_{\sigma\alpha} - \hbar\omega$, and it is assumed that the relevant transition dipole components have broadly similar magnitudes and direction, simply represented as $|\boldsymbol{\mu}^{0\alpha}|$. The terms that contribute most to the susceptibility tensor arise for $s = 0$ and α, and therefore eq 3 may be simplified to

$$\chi_{ijk}^{0\alpha}(\omega';-\omega,\omega) \approx \frac{|\boldsymbol{\mu}^{0\alpha}|^3}{\hbar\omega\Delta\tilde{E}}\left(\frac{2\omega-\omega'}{\omega'-\omega}\right) \qquad (4)$$

On analysis of eq 4, for $\omega < \omega'/2$ and $E_\sigma < E_\alpha + \hbar\omega$ the sign of the leading correction will be positive, signifying that the probe beam produces fluorescence *enhancement*, as is also the case for $\omega > \omega'/2$ and $E_\sigma > E_\alpha + \hbar\omega$. In contrast, the sign is negative for $\omega < \omega'/2$, $E_\sigma > E_\alpha + \hbar\omega$ and for $\omega > \omega'/2$, $E_\sigma < E_\alpha + \hbar\omega$, each representing fluorescence *suppression*. On insertion of eq 4 into eq 1, typical values of $I'(\Omega')$ may be calculated for various probe laser intensities. Setting $\omega = 2\omega'/3$, and adopting typical values $|\boldsymbol{\mu}^{0\alpha}| = 16 \times 10^{-30}$ C m, $\Delta E = 10^{-20}$ J, and $\hbar\omega = 10^{-19}$ J, it is determined that fluorescence is enhanced by $\sim$10% for an irradiance of 10^{15} W m^{-2}, and by $\sim$54% for $I = 5 \times 10^{15}$ W m^{-2}. The linear scaling with I will eventually fail in the nonperturbative regime at higher intensities.

Next, we consider polarization effects. On the application of a polarized beam to an absorbing system, the photoselection of excited-state populations is usually the origin of polarized, anisotropic emission. The anisotropy, r, is determined from the general expression $r = (I'_{\parallel} - I'_{\perp})/(I'_{\parallel} + 2I'_{\perp})$, where $I'_{\parallel}$ and $I'_{\perp}$ are fluorescence intensities measured through polarizers oriented parallel and perpendicular, respectively, to the excitation beam (polarized in the z-direction and represented by $\mathbf{e}_0$). On the inclusion within eq 1 of $(\mathbf{e}_0 \cdot \boldsymbol{\mu}^{\alpha0})$, i.e., a factor denoting initial excitation by the polarized beam, and following a rotational-average, these intensities are defined as

$$I'_{\|}(\Omega') = \left(\frac{|\boldsymbol{\mu}^{0\alpha}|^2|\boldsymbol{\mu}^{\alpha 0}|^2 ck'^4}{40\pi^2\varepsilon_0}\right)\left[\frac{2\cos^2\beta+1}{3} + \frac{KI(\cos^2\beta+2)}{21c\varepsilon_0}\right] \tag{5}$$

and

$$I'_{\perp}(\Omega') = \left(\frac{|\boldsymbol{\mu}^{0\alpha}|^2|\boldsymbol{\mu}^{\alpha 0}|^2 ck'^4}{40\pi^2\varepsilon_0}\right)\left[\frac{2-\cos^2\beta}{3} + \frac{KI(3-2\cos^2\beta)}{7c\varepsilon_0}\right] \tag{6}$$

where **e** is oriented in the x-direction, and the fluorescence is resolved for polarizations $\mathbf{e}'$ in the z- and x-directions, respectively. Here, β is the angle between the absorption and emission transition moments, the former photoselected by the excitation laser. For the following illustrative purposes, in the construction of eqs 5 and 6 the susceptibilities are simplified to $K|\boldsymbol{\mu}^{0\alpha}|^3$ and the final term of eq 1 (quadratically dependent on probe laser intensity) is assumed to be negligible. On insertion of eqs 5 and 6 into the general anisotropy equation, we find

$$r = \frac{3\cos^2\beta - 1 + (KI/c\varepsilon_0)(\cos^2\beta - 1)}{5 + (KI/7c\varepsilon_0)(20 - 11\cos^2\beta)} \tag{7}$$

In the limiting case $I = 0$, the well-known expression[14] $r = (1/5)(3\cos^2\beta - 1)$ is recovered. Generally, however, a change in fluorescence anisotropy can be seen to result from the interaction with the probe beam, although it is to be re-emphasized that the state of the latter beam is unaffected. Further analysis of eq 7 shows that, under the specified conditions (**e** oriented in the x-direction), the anisotropy r will decrease when the probe effects an increase in fluorescence intensity, whereas when the probe suppresses the emission, r increases in value. The same conclusion can be drawn for spectra that are recorded from samples in vitrified solution to obviate rotational relaxation. In contrast, fluorophores that undergo full rotational relaxation prior to emission normally emit isotropic fluorescence; setting $\langle\cos^2\beta\rangle = {}^1/_3$, this is again confirmed by eq 7 in the case where $I = 0$. However, in the presence of the probe laser, anisotropy will persist. Experiment should be able to confirm the presence of this residual anisotropy.

For detailed experimental determination and characterization of the described mechanism, a relatively straightforward adaptation of standard laser fluorescence spectroscopy should be practicable. Fluorescence decay is commonly followed over an ultrashort time interval immediately following pulsed laser excitation. For detection of the fluorescence intensity enhancement or diminution when pulses of a probe beam are present, time-correlated photon detection may prove the system of choice. The fundamental mode of a titanium:sapphire laser appears to represent an expedient choice for the probe, combining the features of relatively low but tunable optical frequency and high power beam delivery. To clearly observe laser-controlled fluorescence, competing processes should obviously be minimized. The most potentially significant process involves multiphoton absorption from $|\alpha\rangle$ to an ionization (or dissociation) continuum state, enhanced through near-resonance with $|\sigma\rangle$ following one-photon absorption. The selection of a long-wavelength fluorophore will exclude two-photon absorption of this type, provided that "accidental" resonances with higher level states are avoided. Three-photon absorption will be much less efficient, by a factor that may be estimated as $\hbar c\omega/IV \simeq 30$ for $I = 10^{15}$ W m^{-2} (V denotes a typical fluorophore volume); therefore three or more photon absorption will prove negligible.

In conclusion, we observe a broader context for the result presented here. It is already known that a strong local static field may significantly modify the rate of fluorescent decay as, for example, through the influence of subwavelength apertures,[15] surface fields,[16] and surface plasmons.[17−19] Fluorescence can also be controllably influenced by the engagement of resonance energy transfer.[20] Our results show that such modifications to spontaneous fluorescent emission may also occur without the presence of surfaces, through direct interaction with the electric field of off-resonant electromagnetic radiation.

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