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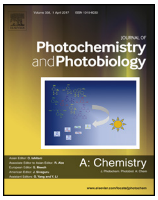

High precision energy measurements from the analysis of wide spectral features. Application to the fluorescence of YAG:Ce^{3+}

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ABSTRACT

Advantage is taken of a complete and precise experimental study of the luminescent properties of yttrium aluminium garnet doped with Ce^{3+}, previously accomplished by other authors, to confirm the accuracy of the invoked theoretical methods for dealing with the realistic calculation of the electromagnetic spectra of condensed phases. The fluorescent spectra at $T = 0$ and $T = 250\,\mathrm{K}$ of YAG:Ce^{3+} were calculated with no adjustable parameter, giving complete agreement with experiment. The energy released by the electronic transitions was determined with precision better than 5% the full width at half maximum of the spectral features. It is shown that fitting the experimental features with a lineshape function well grounded in the physics of the emission process can greatly improve the accuracy of the analysis of the spectra. Thermal quenching of the fluorescent yield is discussed and calculated in a less accurate way, but anyway showing good agreement with experiment. The same theoretical framework can be extended to infrared and Raman spectroscopies to improve the accuracy of these analytic techniques.

1. Introduction

Fluorescence is generally associated to transitions of a local electronic orbital causing a significant structural variation, and hence a strong perturbation of the dynamics of nuclear degrees of freedom. The absent, or very weak [1], zero-phonon line in the observed spectra proves in empirical way that few-phonon processes are infrequent. The wide frequency spectra of the exchanged photons, the large Stokes shifts and peak asymmetries, and the marked dependence of the spectral features on the local and long-range properties of the hosting medium, have all them a common explanation: the large amount of energy spent in exciting acoustic traveling waves in the medium hosting the fluorescent molecule [2,3]. From a thermodynamic standpoint, the electronic and electromagnetic radiation fields are two weakly coupled systems going through a transformation between two well defined states, in thermal equilibrium with the energy reservoir constituted by the acoustic vibrational modes of the extended material medium. By the entropy law, the thermal bath always takes a positive amount of energy in the average. In photon absorption processes the radiation field statistically provides the energy delivered to the thermal bath, and the electron field does in the emission events. Then the Stokes shift is a direct consequence of the second law of thermodynamics. Peak asymmetries have a similar general explanation, since photons carrying an energy excess, or defect, are more probable in absorption, or emission, processes.

The technology of fluorescence has advanced at an accelerating pace in a variety of applications [4–6]. Many of them follow from the sensitivity of the optical properties of the fluorophores to the physical attributes of the embedding medium [7–13]. Despite these advances, there are still some aspects which deserve deeper understanding. Recent papers report a theoretical framework able to reproduce with high numerical precision the temperature dependent lineshapes [2] and quenching [3] of the fluorescent spectra of molecules in a condensed environment. The purpose of this communication is to take advantage of a thorough and complete study of the optical properties of YAG, previously published by other authors [1], to briefly show the power of the methods for the analysis of fluorescent spectra put forward in these papers [2,3], and the convenience of having at hand a good theoretical tool for analyzing the empirical facts.

Yttrium aluminum garnet ($Y_3Al_5O_{12}$ or YAG) doped with Ce^{3+} is a phosphor widely applied in white LEDs for converting blue to yellow light, among many other technical applications. Fed by the

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violet and blue lines of the commonly employed halophosphate phosphor, YAG:Ce^{3+} produces a broad emission band shifted to yellow which combines with the white light of the LED phosphor to make it warmer. The experimental study of Bachmann et al. is particularly useful because exhibits spectra taken at temperatures from near $T = 0$ up to $T = 600$ K [1]. However, what makes this experiment special is that the resolution was large enough to clearly observe at 489 nm the zero-phonon line of one of the two partially superimposed emission bands. This quite unusual observation in fluorescent spectra gives not only the absolute energy released in the main electronic transition, $^2d \rightarrow {}^2F_{5/2}$, as $E = 2.535$ eV [1,14], but also the probability of a zero-phonon event. A shoulder in the spectral maximum suggests the contribution of a competing secondary transition, interpreted as $^2d \rightarrow {}^2F_{7/2}$ [1,14]. The relative intensity of the zero-phonon line at a temperature $T = 4$ K is 0.27% of the total intensity of the main emission band.

2. Theory and calculations

2.1. The equation for the line shape of an octahedrally symmetric emitter

In general, the lineshape function is given by the function [2,3,15,16]

$$\begin{aligned} F(\hbar ck;T) = {} & \frac{a}{\pi\hbar v_s}\int_{-\infty}^{\infty} d\tau \quad \exp\{-\alpha[J(\tau;T) - J(\infty;T)]\} \\ & \times \quad \exp\left\{i\left[\alpha I(\tau) - \frac{2a}{\hbar v_s}(\hbar ck - E)\tau\right]\right\} \\ & + \quad \exp[-\alpha J(\infty;T)]\,\delta(\hbar ck - E), \end{aligned} \tag{1}$$

where $\hbar ck$ is the photon energy, E the energy difference of the two electronic states involved in the transition, a is essentially the bond length, and v_s the mean speed of sound of the acoustic modes of vibration of the medium. The general form of the auxiliary functions $J(\tau;T)$ and $I(\tau)$ depends on the symmetry of the surroundings of the optically sensitive orbital [16]. For the simplest case of octahedral symmetry they read

$$J(\tau;T) = \int_0^{aq_D} \frac{dx}{x}\left(1 - \frac{\sin x}{x}\right) \coth(\beta x) \sin^2(\tau x), \tag{2}$$

$$I(\tau) = \frac{1}{2}\int_0^{aq_D} \frac{dx}{x}\left(1 - \frac{\sin x}{x}\right) \sin(2\tau x), \tag{3}$$

with q_D being the cutoff for the wavenumber of acoustic waves, and the adimensional magnitudes appearing in the lineshape function $F(\hbar ck;T)$ are given by [2]

$$\alpha = \frac{3(\Delta F)^2}{\pi^2\hbar\rho v_s^3} \quad \beta = \frac{\hbar v_s}{2ak_BT} \quad \tau = \frac{v_s}{2a}t, \tag{4}$$

where k_B is the Boltzmann constant, T the temperature, α an electron–phonon coupling constant, and

$$J(\infty;T) = \frac{1}{2}\int_0^{aq_D} \frac{dx}{x}\left(1 - \frac{\sin x}{x}\right) \coth(\beta x). \tag{5}$$

The second term in the right hand side of Eq. (1) for $F(\hbar ck;T)$, containing the delta-function is the zero-phonon line, and the first one the phonon broadened distribution. The lineshape function $F(\hbar ck;T)$ is normalized as [2,15,16]

$$\int_{-\infty}^{\infty} d(\hbar ck)\, F(\hbar ck;T) = 1 \tag{6}$$

and hence the relative contribution of zero-phonon processes to the total fluorescent yield is

$$I_{ZPL} = \exp[-\alpha J(\infty;T)]. \tag{7}$$

Bauchmann et al. measured $I_{ZPL} = 0.0027$ at $T = 4$ K. At $T \approx 0$, Eq. (5) does not depend on the constant β because the hyperbolic function goes rapidly to unity as β grows. With practically no precision loss, one can replace $J(\infty;4\,\mathrm{K})$ by $J(\infty;0\,\mathrm{K}) = 0.5817$. This way, the low temperature data allows to determine the constant α

$$0.0027 = \exp(-\alpha \times 0.5817) \Rightarrow \alpha = 10.17. \tag{8}$$

It is assumed here that $aq_D = (12\pi^2)^{1/3}$, corresponding to octahedral symmetry.

On the other hand, the maximum of the main peak of the $T = 4$ K spectrum is at $\lambda = 523$ nm (2.370 eV). As the zero phonon line is at $\lambda = 489$ nm (2.535 eV) the contribution to the Stokes shift of emission is the difference 0.165 eV. This result is useful to determine the energy scale factor in Eq. (1) that puts the maximum of the distribution in the right place. This gives

$$\frac{\hbar v_s}{2a} = 8.8121 \times 10^{-22}\,\mathrm{J} = 0.00550\,\mathrm{eV}. \tag{9}$$

The mean speed of sound in YAG is $v_s = 5.47 \times 10^3$ m/s [17]. Replacing in Eq. (9), one obtains that $a = 0.327$ nm, which is a very reasonable value. The calculated distance of substitutional Ce^{3+} in YAG to the nearest oxygen neighbors is 0.23–0.24 nm [18]. The figure for a is closer to the six Al^{3+} neighbors with coordination quasioctahedral, whose distances to the Ce^{3+} ion are 0.300 and 0.336 nm [18]. Hence the assumption of octahedral symmetry for aq_D is consistent with the predominance of the bonding of the Ce^{3+} ions with their Al^{3+} next-neighbors.

2.2. Results for band shapes

Knowing the two constants α and $\hbar v_s/(2a)$ the lineshape function (1) can be evaluated for $T = 0$. The resulting curve is shown in Fig. 1, together with the experimental data of Bauchmann et al. for $T = 4$ K. The coincidence between theory and the main feature of the experimental spectrum (attributed to the $5d^1 \rightarrow {}^2F_{5/2}$ transition [14]) is remarkable, particularly because the theoretical curve has no adjustable parameter.

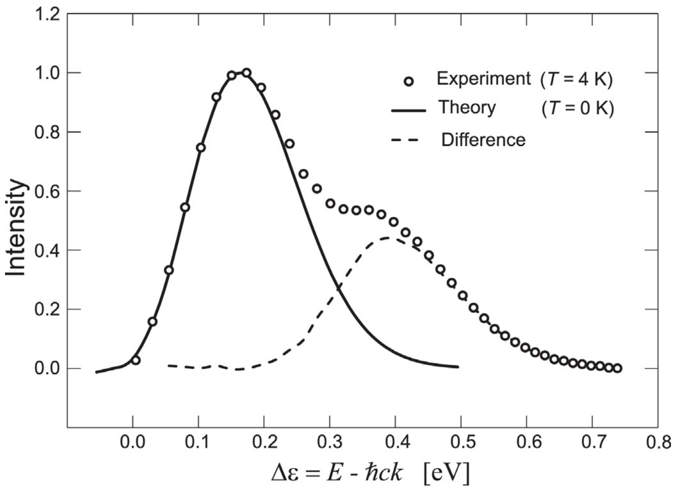

Fig. 1. Open circles represent the fluorescent emission spectrum of YAG:Ce^{3+} at $T = 4$ K, as measured by Bauchmann et al. [1]. The solid line represents Eq. (1) with constants determined from the experiment and no fitting parameter. The origin of $\Delta\varepsilon$ is in the energy of the zero-phonon line of the transition $^2d \rightarrow {}^2F_{5/2}$. The broken line is the difference, evidencing the existence of a competing transition, presumably $^2d \rightarrow {}^2F_{7/2}$. Intensities are in units of the maximum of the distribution.