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► To cite this version:

J. Tocho, M. Murphy, E. Rodríguez, F. Cussó. Simultaneous photoacoustic and luminescence multiple wavelength experiments. Journal de Physique IV Proceedings, 1994, 04 (C7), pp.C7-405-C7-408. 10.1051/jp4:1994795 . jpa-00253326

HAL Id: jpa-00253326

<https://hal.science/jpa-00253326>

Submitted on 1 Jan 1994

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Simultaneous photoacoustic and luminescence multiple wavelength experiments

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Abstract: Fluorescence quantum efficiencies in solid and liquid materials were determined by simultaneous photoacoustic and luminescence experiments after excitation at several wavelengths, with at least one of them connecting a relaxation of known quantum efficiency. Results for Eu^{2+} in alkaline halide, Cr^{3+} in LiNbO_3 , and a cyanine in ethanol solutions, are given.

1. INTRODUCTION

The fluorescence quantum efficiency (ϕ) of a luminescent material is obviously one of its most relevant parameters. Photoacoustic methods have been extensively used in the quantum efficiency determination of gases and liquid materials by comparing photoacoustic signals of the sample with that of a standard material with known quantum efficiency.¹ For most solid state materials this procedure is not adequate because of the fact that changing the sample may affect the acoustic coupling.

An alternative method based on the simultaneous detection of photoacoustic and luminescent signals, after excitation at different wavelengths, was recently proposed.² The comparison of the different photoacoustic (PAS) and luminescence (LUM) signals generated after excitation at two different wavelengths provides a method for absolute quantum efficiency determination.

2. THEORY

Fig. 1 represents a schematic energy diagram for materials used in this work. Different

contributions to prompt heat and luminescence are indicated. The relaxation from the bottom of the lower excited state gives two thermal contributions: q_2 with efficiency $(1 - \phi)$ and q_3 associated with the nonradiative relaxation within the ground state with efficiency ϕ . A thermal contribution within excited state (q_1) must be added. After excitation to a higher excited state.

Fig. 1. Energy diagram indicating different contributions to PAS and LUM.

Fig. 2. Basic experimental setup used for simultaneous measurements of PAS and LUM.

the nonradiative relaxation to the bottom of lower state produces a thermal contribution q_4 that must be added to the others. A fraction of this higher excited population might not be able to decay immediately to the lower states. This fraction will be designated with α and no contribution to prompt heat will be considered. Taken into account this loss, the photoacoustic and the luminescence signals after excitations with λ_L or λ_H photons can be written as:

$$\text{PAS}(\lambda_L) = K_p [q_1 + (1-\phi).q_2 + \phi.q_3].N_a(\lambda_L), \quad (1)$$

$$\text{PAS}(\lambda_H) = K_p.(1 - \alpha).[q_4 + (1-\phi).q_2 + \phi.q_3].N_a(\lambda_H), \quad (2)$$

$$\text{LUM}(\lambda_L) = K_L . \phi . N_a(\lambda_L), \quad (3)$$

$$\text{LUM}(\lambda_H) = K_L . (1 - \alpha) . \phi . N_a(\lambda_H), \quad (4)$$

where $N_a(\lambda_L, \lambda_H)$ indicates the number of photons absorbed at each wavelength and K_p and K_L are

instrumental constants for acoustic and luminescence detection. After some rearrangement of eq. [1-4], it can be demonstrated that the quantum efficiency is given by:

$$\phi = \frac{\lambda_E}{\lambda_L} \frac{\Lambda - \lambda_L / \lambda_H}{\Lambda - 1}, \quad (5)$$

where λ_E is the emission wavelength and Λ , which is the quantity to be experimentally determined, is given by the ratio between of slopes of the photoacoustic (PAS) signal in terms of the amount of detected luminescence (LUM) signal excited at different flux densities of high (λ_H) or low (λ_L) energies:

$$\Lambda = \frac{\partial \text{PAS}(\lambda_H) / \partial \text{LUM}(\lambda_H)}{\partial \text{PAS}(\lambda_L) / \partial \text{LUM}(\lambda_L)} \quad (6)$$

3. EXPERIMENTAL

The method described above is applied in the present work to different materials, Eu^{+2} ions in KCl, Cr^{+3} in ferroelectric LiNbO_3 , and to a well known liquid material as it is a solution of dimethyloxidicarbocyanine iodide (DODCI). Photoacoustic and luminescent signals were simultaneously detected by using a resonant PZT, and a photomultiplier-monochromator combination. Solid samples were cut in the form of rectangular slabs of 10 x 5 x 1 mm. Liquid samples were contained in 10 x 10 x 40 mm quartz cells. Fluorescence was collected with an optical fiber in both cases. Pump flux was changed with a variable density wedge (visible) or a half wave - polarizer combination (UV).

Absorption bands of Eu^{+2} ions in alkali halide crystals were excited with the third and fourth harmonics of Nd:YAG laser at $\lambda = 355 \text{ nm}$ and $\lambda = 266 \text{ nm}$ respectively. Two wavelengths (500 nm and 660 nm) of a nitrogen pumped dye-laser were used to excite the absorption bands of Cr^{+3} in LiNbO_3 . The fundamental wavelength ($\lambda = 600 \text{ nm}$) and second harmonic ($\lambda = 300 \text{ nm}$) of a flash lamp pumped dye-laser (Rh 6G) were used to measure a solution of DODCI in ethanol. The experimental set-up can be seen in Fig. 2.

4. RESULTS AND DISCUSSION

From the results shown in figures 3 for solid materials, fluorescence quantum yields were calculated as: $\phi(\text{Eu}:\text{KCl}) = 1.04 \pm 0.06$, $\phi(\text{Cr}:\text{LiNbO}_3) = 0.05 \pm 0.02$. For the liquid sample, a prior experiment was performed in order to check the validity of the model described by eq. [1-4]. Luminescence excited by 295 nm and by 590 nm was plotted in terms of exciting energy. A factor of 2 relating the two slopes of Fig. 4 confirmed that almost all molecules excited to

the high energy level relax through the radiative state S_1 . From Fig. 3 and by using eq. 5, $\phi(\text{DODCI})$ can be calculated as 0.52 ± 0.06 . As is well known, the photophysics of DODCI is more complicated and isomerization channels starting at S_1 can accumulate energy in the metastable species.³ This fact will slightly reduce the value calculated for ϕ .

Fig. 3. Experimental results from which Λ and ϕ can be calculated.

Fig. 4. Luminescence intensity for DODCI excited at two wavelengths.

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