الفيزياء الضوئية لصبغة الكومارين 460 : تأثير درجة الحرارة على زمن عمر التألق ومعدل الانتقال اللاإشعاعي

علي عبد الكريم حسين
قسم الفيزياء -كلية العلوم، جامعة بغداد - جادرية
بغداد - العراق

الملخص:
يتضمن البحث دراسة تأثير درجات الحرارة على كل زمن عمر التألق، الناتج الكمي ومعدل الانتقال اللاشعاعي لصبغة الكومارين 460 مذابة في الميثانول ضمن مدى درجات الحرارة (160-300 K). استخدمت تقنية الفوتون المفرد لقياس أطياف انحلال التألق. تم ملاحظة النقصان في زمن عمر التألق مع زيادة درجة الحرارة، كما تم حساب طاقة التنشيط لهذه الصبغة كانت $10.57 KJ.mole^{-1}$ وذلك بالاستفادة من منحني ارينوس.

Photophysics of Coumarin 460: Temperature Effect upon Fluorescence Lifetime and Non-Radiative Rate Parameter

Ali A-K. Hussain
Physics Department-College o Science, University of Baghdad –Jadriya
Baghdad-Iraq

Abstract:
The temperature in luence on the luorescence li etime, quantum yields and non-radiative rate parameter or coumarin 460 dye dissolved in methanol was investigated in the temperature range (160-300 k). A single photon counting technique was used or measuring the luorescence decay curves. A noticeable decrease o the luorescence li etime with increasing the temperature was observed. The non-radiative activation energy o 10.57 K.J. $mole^{-1}$ was measured by the help o Arrhenius plot.

INTRODUCTION:

A group of widely used laser dyes emitting in the blue-green region of the spectrum is derived from coumarin by substitution with amine group in the 7-position [4]. The lasing performance and stability of 7-amino-4-methyl coumarin was examined [7], and demonstrated that the main problem of this group of dyes seems to be oxidation of the 4-methyl group, leading to carboxylic acid compound, absorbing at the lasing wavelength. The influence of the molecular structure and the nature of the solvent on the properties of coumarin 460 dye (for other common names see [5]) was studied [2] and large Stokes shift was observed.

The absorption maximum of coumarin 460 dye in ethanol occurs at 373 nm, while it loses at 460 nm depending on the type of solvent [4]. Coumarin 460 (C460) dye can be operate in a pulse and CW modes (Maeda, 1984). It was one of the most efficient laser dyes [4, 6]. The aim of this study is concentrated on measuring and investigating some photo-physical parameters, i.e., fluorescence lifetime, quantum yield, and non- radiative parameter, all as a function of temperature.

EXPERIMENTAL:

Spectrograde C460 was supplied by Lambda Physic and used without further purifications. High purity methanol was supplied by BDH. Two samples of C460 dissolved in methanol were prepared with concentrations 10^{-2} and $5\ \chi 10^{-5}$ M using freeze-pump-thaw method to achieve free oxygen samples. Fluorescence decay curves were measured by using a spectrometer based on a single photon counting method. This spectrometer consists of the following units: a nitrogen flash lamp, two monochromators, two photo multipliers (for start and stop signals), two discriminators, a time to amplitude converter, a time calibrator, and a multi-channel analyzer connected with a personal computer. The block diagram of the setup is shown in fig.(1).

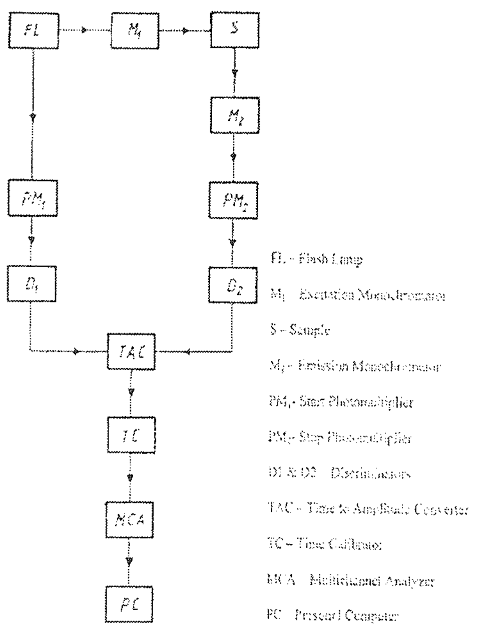

Fig.(1): The Block diagram of the spectrometer based on a single photon counting method.

The emission beam was detected in the front-face mode (reflection) in order to minimize re-absorption and reemission effects. The samples were subjected in a home made cryostat and cooled by a liquid nitrogen poured into the cryostat. All the decay curves were analyzed using an iterative least-squared de-convolution method [7]. The accuracy of fit was controlled the reduced chi-square χ^2.

RESULTS &DISCUSSLON:

The fluorescence decay curves of C460 in menthol in the temperature range (160-300 K) were analyzed as single-exponential curves with $0.8<x^2 < 1.2$, in which a total of about 2000 counts was collected in the peak of each source and decay curves. Fig.(2) illustrate the fitted decay curves of C460 10^{-2} M at 300 K.

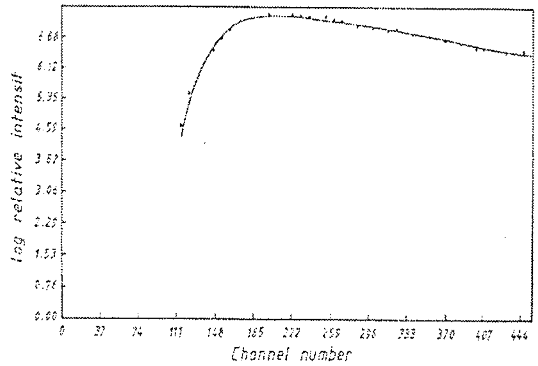

Fig.(2): The fitted decay curve of coumarin 460 dye dissolved in methanol (10^{-2} M) at 300 K.

The temperature dependence of fluorescence lifetime τ of coumarin (C460) dissolved in methanol for the concentration 10^{-2} and $5x10^{-5}$ μ is shown in fig. 3. A clear decrease of the fluorescence lifetime of the dye with increasing temperature can be observed for both concentrations. Since the radiative lifetime τ_0 is almost constant (Arbeloa, 1994), the decrease in τ may be attributed to an increase in the non-radiative rate K_{nr} as the temperature increases [3]. Similar behavior was previously observed by Arbeloa, 1991 [1] for rhadomine dyes. Fig.(3) shows also some fluctuation in the lifetime values below 180 K, which is nearly the freezing point of methanol. These fluctuations can be referred to the high variation of solvent viscosity below this temperature.

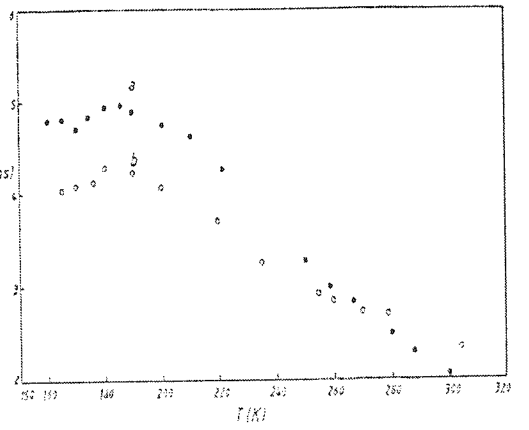

Fig.(3): τ values of C 460 versus the temperature, a) 10^{-2} M and b) $5x10^{-5}$M

The radiative lifetime τ_0 of C460 was measured as 5.59 ±0.07 ns (deduced from the value of τ at very dilute solution). A ccording to the equation (Birks, 1970):

$$\emptyset = \frac{\tau}{\tau_0} \quad \text{and} \quad K_{nr} = \frac{1-\phi}{\tau}$$

The quantum yield ϕ and non-radiative rate parameter K_{nr} were determined. Fig. 4 depicts a plot of in K_{nr} versus the inverse of the absolute temperature. A relatively good linear Arrhenius plot was obtained from which the non-radiative activation energy E_{nr} can be obtained. The value of E_{nr} is equal to the slope of the straight line in fig.4 multiplied by Boltzman constant, hence, a value of 0.11 eV (=10.57 $KJ.mloe^{-1}$) was resulted for C460 dye. This value lies between the two values 3 and 13 $KJ.mole^{-1}$ obtained previously by Arbeloa, 1994 [2], for C460 dye dissolved in ethanol and water respectively. As the coumarin dyes family is solvent dependent [4], and sine methanol is of higher polarity than methanol and lesser than water according to their dielectric constants (Weast,1988), 24.3, 32.6, 80.2 for ethanol, methanol and water respectively, then the present value of E_{nr} seems to reasonable.

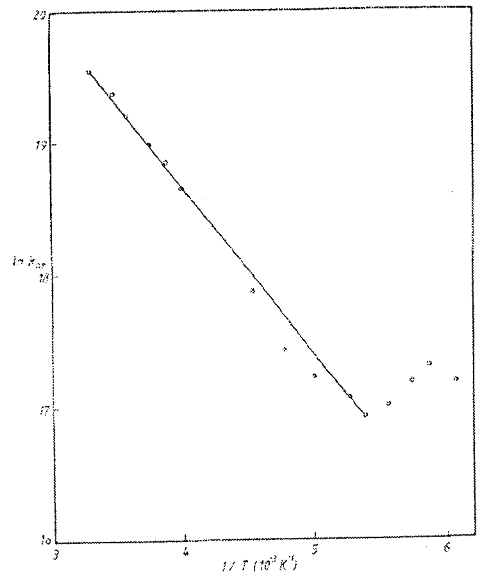

Fig.(4): In K_{nr} values against 1/T for C460 dye.

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