

## FLUORESCENCE-BASED INVESTIGATION OF THE JÁNOSSY EFFECT ANOMALOUS WAVELENGTH DEPENDENCE

---

*Carlo Manzo, Domenico Paparo, Stefano Lettieri,  
and Lorenzo Marrucci\**

*INFN “COHERENTIA” and Università di Napoli “Federico II”,  
Dipartimento di Scienze Fisiche, Complesso di Monte S. Angelo,  
via Cintia, 80126 Napoli, Italy*

*In order to explain the wavelength dependence of the “Jánossy effect” observed in certain dye-doped liquid crystals, we investigated the fluorescence emitted by 1,8-diamino 4,5-dihydroxy 3,6-diisopentyl anthraquinone dye dissolved in different hosts. We measured the lifetime  $\tau_e$ , rotational time  $\tau_r$ , initial anisotropy  $r_0$  and fluorescence quantum yield  $\Phi$  of photo-excited dye molecules versus excitation-light wavelength  $\lambda$ . The only significant  $\lambda$ -dependence observed was that of the quantum yield  $\Phi$ , which showed a marked increase with  $\lambda$ .  $\Phi(\lambda)$  appears to be well correlated with the Jánossy effect. These results rule out several proposed explanations for the Jánossy effect wavelength dependence and suggest a simple alternative explanation.*

*Keywords:* amino-anthraquinone; dye; fluorescence; photosensitive materials; quantum yield

### INTRODUCTION

Since the early 90's it has been found that small amounts of certain dyes dissolved in nematic liquid crystals may strongly enhance the orientational optical nonlinearity of the host [1]. This enhancement is sometimes called “Jánossy effect”, from the name of its discoverer. This effect is actually not even limited to the liquid crystalline phase, as closely related phenomena have been observed also in dye-doped isotropic liquids [2,3].

We thank R. Eidenschink of Nematel for providing HK271, the Servizio Elettronico e Rivelatori of INFN and Dipartimento di Scienze Fisiche di Napoli for technical assistance, and G. Baldacchini of ENEA – Frascati and Marirosa Tenore of Università “Federico II” di Napoli for help with the steady-state fluorescence measurements.

\*Corresponding author. Tel.: +39-081-676124, Fax: +39-081-676346. E-mail: lorenzo.marrucci@na.infn.it

A model proposed few years ago seems capable of explaining most features of this phenomenon [4,5]. This model is based on the following two processes: (a) light absorption excites preferentially dye molecules oriented parallel to the electric field, thus generating an anisotropy in the dye population; (b) the guest-host intermolecular interactions are modified by this electronic excitation, so that the dye anisotropy is reflected into an anisotropic mean-field acting on the host molecules. The resulting effect is a dye-induced optical torque that is superimposed to the usual dielectric-anisotropy one and enhances the nonlinear orientational response of the host. This model has been recently confirmed by several quantitative tests [6–9].

Nevertheless, some features of the Jánossy effect remain still obscure. One of them is the peculiar wavelength dependence exhibited by certain dyes [10,11]. Based on the model above, one would expect a dye-induced torque scaling just as the dye absorption spectrum. What one finds instead in these dyes is that an excess photon energy reduces the torque, in some cases even leading to its sign-inversion (reorientation perpendicular to the electric field) [11]. Different possible explanations have been proposed for this phenomenon [6,11], but this issue remains unsettled.

In order to test these proposals, we investigated the excitation-light wavelength dependence of the dye fluorescence. In this paper we report the results of this study and discuss their implications on the Jánossy effect wavelength dependence.

## FLUORESCENCE EXPERIMENTS

We used the 1,8-dihydroxy 4,5-diamino 2,7-diisopentyl anthraquinone dye (HK271, provided by Nematel, Mainz, Germany), which shows a significant wavelength dependence of the Jánossy effect [10]. The  $S_1 \rightarrow S_0$  transition dipole of HK271 is along the longest molecular axis [12]. We used also a deuterated form of HK271, where the hydrogens in the amino and hydroxyl groups have been replaced with deuterium by means of the procedure described in Ref. [7]. Moreover, we made some control measurements on Rhodamine 6G and Rhodamine B (respectively Rh6G and RhB, Lambda Physik). As liquid-crystalline host, we used 4'-n-pentyl-4-cyanobiphenyl (5CB). Although 5CB is a liquid crystalline material having a nematic phase between 297 K and 308 K, in order to avoid the complications associated with an anisotropic host, our study was limited to the temperature range 311–368 K in which 5CB is in its ordinary isotropic liquid phase. In order to investigate the dependence of fluorescence on the host molecular structure, certain measurements have been performed in ethyl alcohol and in a liquid paraffin (a mixtures of alkanes, melting point  $-18^\circ\text{C}$ ).

The solutions were prepared at several concentrations ranging from  $10^{-6}$  to  $10^{-3}$  mol/L. In all measurements, we identified the concentration below which nonlinear effects were negligible, and in our discussion we consider only results obtained in this range.

We made separate experiments of time-resolved and steady-state fluorescence. Let us first describe the time-resolved fluorescence set-up. 20-ps pulses from an optical parametric generator pumped by a frequency-tripled Nd:YAG laser were used as excitation-light tunable in the whole HK271 absorption range ( $500 \div 670$  nm). The sample cell of thickness  $1.0 \pm 0.1$  mm was placed into an oven allowing temperature control to within 0.1 K. The transient fluorescence emitted after the excitation pulse absorption was detected by means of a fast photodiode (about 100 ps rise-time) and sampled by 2 GHz analog bandwidth electronics; a polarizer placed on a rotating holder was used to select parallel ( $\parallel$ ), perpendicular ( $\perp$ ), and magic ( $54.7^\circ$ ) linear polarizations of the detected fluorescence light with respect to that of the excitation one. As the detection apparatus has a finite response time, the signal  $S(t)$  we measure is actually the convolution of the fluorescence intensity with the instrumental response function  $R(t)$  [13]. To measure this response function, we replaced the sample with an opaque plate and collected the scattered light, which has essentially the same time-duration as the laser pulse and therefore can be considered as a delta-function input to the detection system. We measured the response function at wavelengths ranging within the whole fluorescence spectrum of HK271. The response function shape and temporal parameters (rise time, FWHM) remained approximately constant in the region of interest. In the analysis, the parallel and perpendicular signals,  $S_{\parallel}(t)$  and  $S_{\perp}(t)$ , were first combined into  $S_e(t) = S_{\parallel} + 2S_{\perp}$  and  $S_d(t) = S_{\parallel} - S_{\perp}$ . Each of these combinations was then fitted by a single exponential decay convoluted with the measured response function  $R(t)$ . The fit parameters are the decay times, corresponding respectively to the excited-state lifetime  $\tau_e$  and the effective time  $\tau_d = (\tau_e^{-1} + \tau_r^{-1})^{-1}$ , where  $\tau_r$  is the rotational time [13], and two preexponential factors  $c_e$  and  $c_d$ . The ratio  $r_0 = c_d/c_e$ , called initial degree of anisotropy, gauges the degree of excited-state dye orientational anisotropy immediately after the laser pulse.

By verifying that  $S_e(t) = 3S_{magic}(t)$ , we made sure that the detection efficiency of our apparatus was independent of light polarization [13]. We tested the set-up and the analysis procedure by measuring the fluorescence lifetime  $\tau_e$  of Rh6G at  $10^{-4}$  mol/L in ethylene glycol and in ethanol, finding in both cases  $\tau_e = 3.6 \pm 0.1$  ns, in agreement with values reported in the literature for the case of negligible energy transfer [14,15]. This ensured that energy transfer effects could be neglected for our experimental geometry [15]. As a further test, we verified that the fluorescence lifetime

of HK271 was independent of dye concentration in the range  $10^{-4} \div 10^{-3}$  mol/L and that the value of  $r_0$  is independent of dye-concentration and laser intensity.

For the steady-state fluorescence measurements we used a VARIAN Cary Eclipse fluorescence spectrophotometer; this allowed us to obtain both excitation spectra, collecting at several emission wavelengths, and emission spectra induced by several excitation wavelengths. These spectra have been measured in the right-angle geometry in a standard fused-quartz cuvette.

Finally, absorption spectra of all samples have been measured with a JASCO's V-series UV-Visible spectrometer.

## RESULTS AND DISCUSSION

In Reference [5] the following approximate expression of the dye-induced optical nonlinearity is obtained, expressed in terms of the molecular merit-figure  $\mu$  defined in Reference [6]:

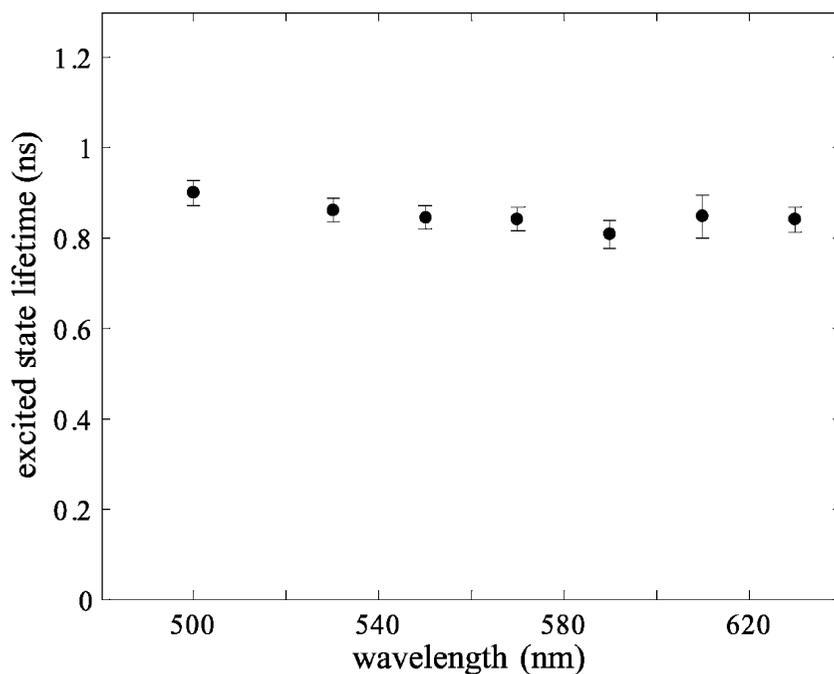
$$\mu = \frac{2}{15h} \left( \frac{\tau_e D_e}{1 + 6\tau_e D_e} \right) \left( \frac{u_e}{D_e} - \frac{u_g}{D_g} \right). \quad (1)$$

In this expression,  $\tau_e$  is the dye excited state lifetime,  $D_e(D_g)$  the diffusional rotational constant for the excited (ground) state,  $h$  the Planck constant, and  $u_e(u_g)$  the mean field intermolecular interaction potential for the excited (ground) state. The diffusional rotational constant is related to the rotational time  $\tau_r$  by means of the relationship  $D_e = 1/(6\tau_r)$ . Equation (1) is based on the assumption that there is a single relevant excited state (presumably the first-excited singlet state  $S_1$ ). Based on Eq. (1) and assuming that the excited-state presents no kind of polymorphism, no excitation-wavelength dependence of  $\mu$  is expected. This in turn implies that the dye-induced torque magnitude is simply proportional to the absorption coefficient [6]. Therefore, to explain the  $\mu$  wavelength dependence observed in many dyes, we have to go beyond this simple model.

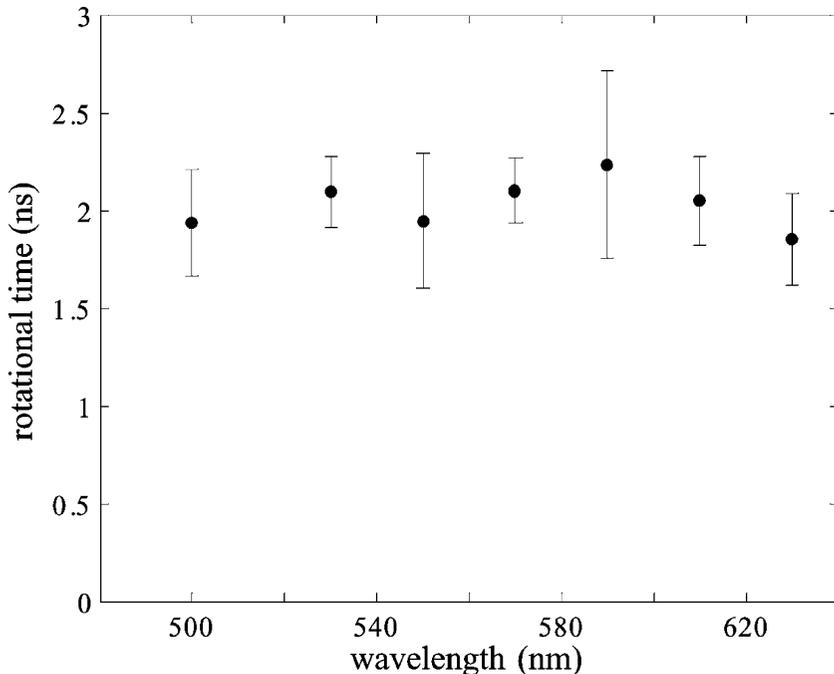
Perhaps the simplest possible extension of the model is that the excited state changes somehow its nature when it is excited with an excess-energy photon. Possible modifications are long-lived internal vibrations excited by the photon extra-energy, or variations in the intramolecular or intermolecular hydrogen-bond or other physical interactions (e.g., an excess photon energy may lead to breaking a hydrogen bond) [6]. Another possibility could be that there are actually more than one close-lying excited electronic states (although it is uncommon that any electronic excited state higher in energy than  $S_1$  is long-lived). All these forms of polymorphism of the excited state of the dye could lead to an excitation-wavelength

variation of some of the molecular parameters appearing in Eq. (1). By time-resolved fluorescence, we could directly check if either  $\tau_e$  and/or  $\tau_r = 1/(6D_e)$  depend on the excitation-light wavelength. The measured values of excited-state lifetime  $\tau_e$  and the rotational time  $\tau_r$  of HK271 in 5CB at  $T = 323$  K versus excitation wavelength  $\lambda$  are plotted in Figures 1 and 2, respectively. Within the experimental uncertainties, no significant variation of these parameters with  $\lambda$  is observed. Similar results have been found at different temperatures and on several samples, including deuterated ones. The temperature dependence and the effect of deuteration for a fixed excitation wavelength have been investigated in detail and the results have been reported elsewhere [16].

In the wavelength range 570–590 nm, besides the usual fluorescence, we observed a fast-decaying isotropic additional signal (decay time smaller than 100 ps), so that a double-exponential fit was necessary to analyze our data (this explains why in this region we have larger error-bars; the



**FIGURE 1** Excitation-wavelength dependence of the HK271 excited-state lifetime  $\tau_e$  in 5CB at 323 K. The error bars are calculated for a statistical confidence level of 99%, not taking into account the uncertainties associated with the instrumental response function.



**FIGURE 2** Excitation-wavelength dependence of the HK271 rotational time  $\tau_r$  dissolved in 5CB at 323 K. The error bars are calculated as in Figure 1.

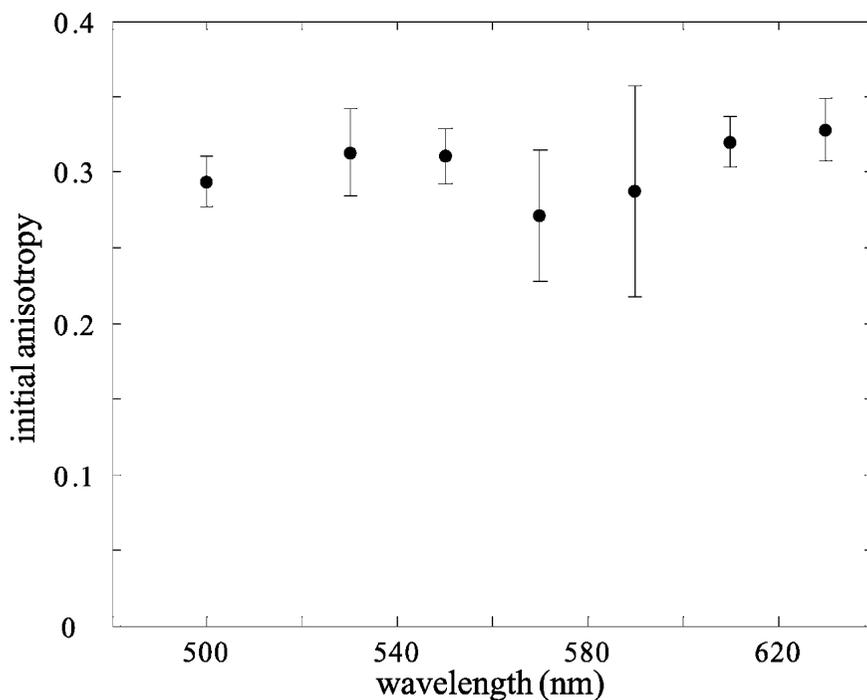
data in the figure refer only to the normal “slow” decay term). We do not know whether such fast signal is due to HK271 or to unknown impurities.

We cannot exclude by means of our measurements that the excited-state parameters  $u_e$  depend somehow on  $\lambda$ , but this possibility is extremely unlikely, as changes of  $u_e$  would be probably correlated with changes of  $\tau_r$ . More generally, the possibility of a long-lived polymorphism of the excited state is further excluded by our observation that the shape of the steady-state fluorescence emission spectra does not change for a varying excitation light wavelength (data not shown). All ground-state parameters cannot of course depend on  $\lambda$ . Therefore, any explanation of the wavelength-dependence of the Jánossy effect based on a long-lived polymorphism of the excited-state is ruled out by our results.

A second possibility, first proposed in Reference [11], is that the fast vibrational relaxation immediately following the photon absorption, whose magnitude depend on the photon excess energy, could lead to a significant random reorientation of the excited dye molecules. This in turn would naturally lead to a wavelength dependence of the Jánossy effect, as the diminished anisotropy of the excited dye population is reflected into a

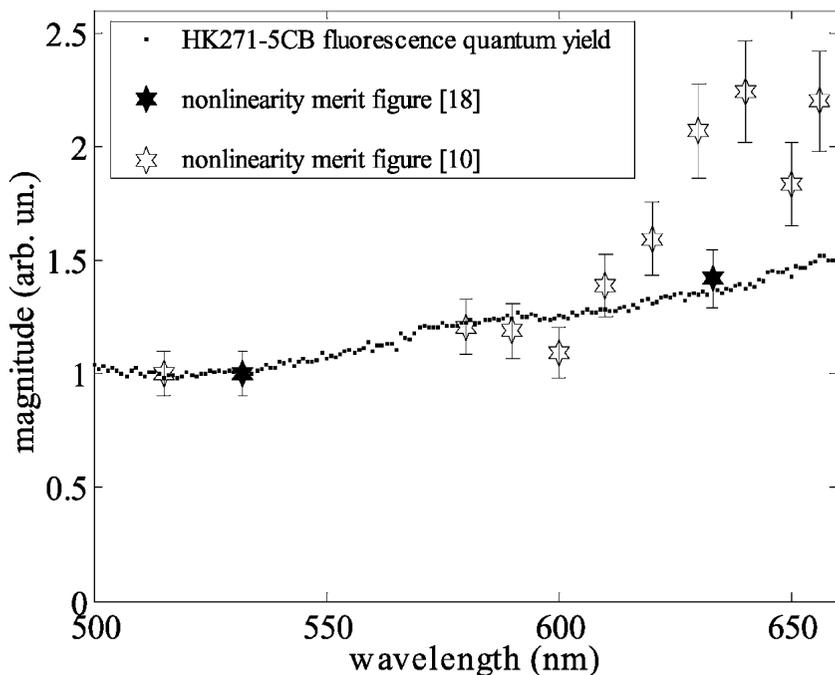
smaller orientational mean-field acting on the host. This hypothesis is also related to the old but still debated question of the possible influence of nonradiative decay of energy on molecular orientation, e.g., by way of a strong local heating or other mechanisms. In Reference [17], Pantke and Labhart demonstrated for a specific system that excitation with excess energy does not produce any change in the reorientation of dye molecules. However, this effect cannot be ruled out *a priori* for different systems.

A rapid loss of orientational order after excitation would be reflected into a reduced initial degree of anisotropy  $r_0$  in the time-resolved fluorescence data. Therefore, if this effect is significant, we should see an excitation-light wavelength dependence of  $r_0$ . In Figure 3, we report our results in the case of HK271 in 5CB at 323 K. Within uncertainties, no significant wavelength dependence is observed. It must be mentioned that the average measured value of  $r_0 \approx 0.32$  is somewhat smaller than the value  $r_0 = 0.4$  predicted by an ideal rod-like molecule theory [13]. This however is typical of this sort of measurements and has several possible causes [12,16].



**FIGURE 3** Excitation-wavelength dependence of the HK271 initial degree of anisotropy  $r_0$  at 323 K. The error bars are calculated as in Figure 1.

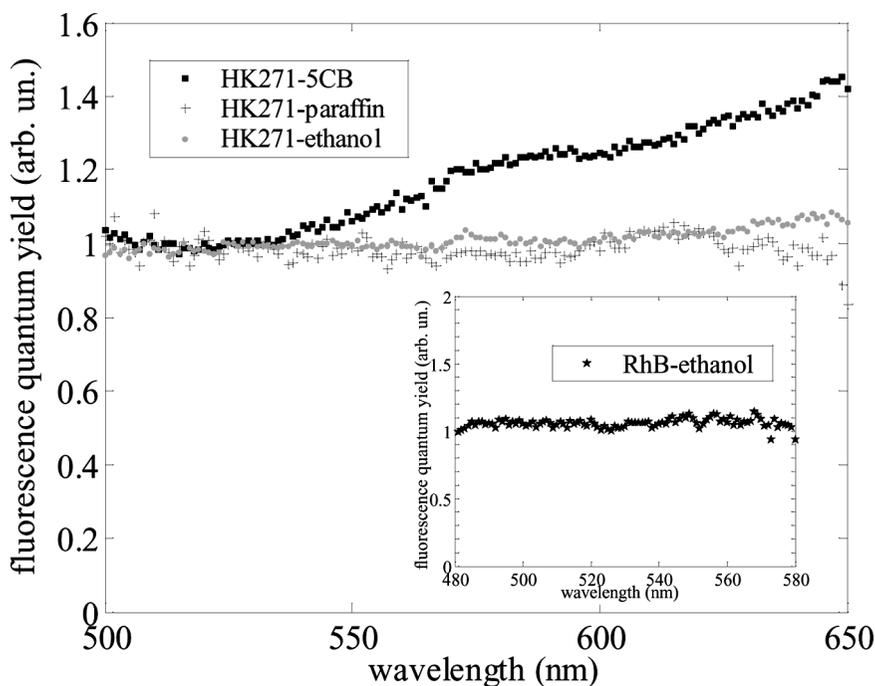
A third possible explanation of the wavelength dependence of the non-linearity merit figure  $\mu$  is that a  $\lambda$ -dependent fraction of the excitations is “wasted”, for example because they are followed by an immediate nonradiative relaxation back to the ground state or because they are immediately followed by an intersystem-crossing to an ineffective triplet state. If it occurs, this effect is usually more likely at higher photon energies (lower  $\lambda$ 's), where more decay channels are present. This effect should be however reflected also into a  $\lambda$ -dependence of the fluorescence quantum yield  $\Phi$ , that monitors the  $S_1$ -fluorescent state population induced by absorption. The quantum yield  $\Phi(\lambda)$  can be obtained by taking the ratio of the number of fluorescence photons as deduced from the excitation steady-state fluorescence spectrum (i.e., fluorescence intensity at a fixed emission wavelength for a varying excitation wavelength) to the number of absorbed photons as deduced from the absorption spectrum. Figure 4 illustrates our results in the case of HK271 in 5CB at  $10^{-4}$  mol/L, showing a



**FIGURE 4** Excitation-wavelength dependence  $\Phi(\lambda)$  of the fluorescence quantum yield in HK271-5CB compared with the wavelength dependence  $\mu(\lambda)$  of the dye-induced optical nonlinearity merit figure in HK271-E63 (E63 is a mixture of cyanophenyls), as reported in Refs. [18] (filled stars) and [10] (open stars). The  $\mu(\lambda)$  data are rescaled so as to be superimposed to the  $\Phi(\lambda)$  data at the lowest wavelengths.

significant increase of  $\Phi$  with  $\lambda$ . As a check, we measured also the  $\Phi(\lambda)$  of RhB, known to be a good quantum counter [19]. Our results in RhB dissolved in ethanol (at  $10^{-6}$  mol/L) are reported in the inset of Figure 5 and show the expected  $\lambda$ -independent behavior of  $\Phi$ .

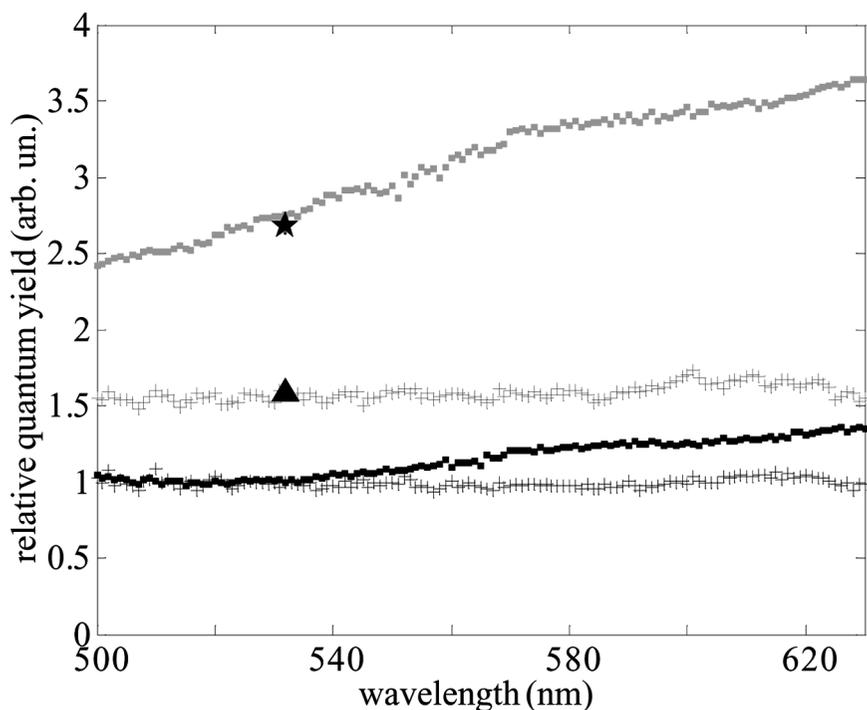
In Figure 4, we also compare  $\Phi(\lambda)$  with the  $\mu(\lambda)$  of HK271 in E63 (a cyanophenyl mixture) reported in two different works (Refs. [10] and [18]). We find a good quantitative correlation with the data of Ref. [18] and a qualitative correlation with the data of Ref. [10] (the discrepancy between the two sets of  $\mu$  data has not been explained). This correlation supports the validity of this last explanation. As a further test, we investigated the dependence of the  $\Phi(\lambda)$  behavior on the host. In Figure 5, we show the measured  $\Phi(\lambda)$  for HK271 in 5CB (at  $10^{-4}$  mol/L), paraffin (at  $3 \times 10^{-6}$  mol/L) and ethanol (at  $10^{-4}$  mol/L). It is seen that the  $\Phi(\lambda)$  is significantly



**FIGURE 5** Effect of the host on the fluorescence quantum yield excitation-wavelength dependence  $\Phi(\lambda)$  of HK271. The hosts are 5CB (black squares), paraffin (crosses) and ethanol (gray circles). The three  $\Phi(\lambda)$  curves have been rescaled so as to be superimposed at  $\lambda = 532$  nm. Inset: fluorescence quantum yield excitation-wavelength dependence of RhB, known to be a good quantum counter, dissolved in ethanol.

nonconstant only in 5CB. A very small increase is perhaps present in ethanol, while  $\Phi(\lambda)$  is constant in the nonpolar paraffin. This solvent effect may be related to the presence of host-dependent nonradiative decay channels, in connection with intermolecular hydrogen bonds between HK271 and 5CB (see Ref. [16] and references therein).

Finally, we investigated the effect of deuteration on the  $\Phi(\lambda)$  behavior for HK271 in 5CB and in paraffin. The results are shown in Figure 6, where it is seen that deuterated samples exhibit the same  $\Phi(\lambda)$  as protonated ones except for a  $\lambda$ -independent overall multiplicative enhancement. This enhancement is in excellent agreement with the corresponding increase



**FIGURE 6** Effect of hydrogen-deuterium substitution on the fluorescence quantum yield  $\Phi(\lambda)$ . Shown are the quantum yield for protonated (black squares) and deuterated (gray squares) HK271-5CB and for protonated (black crosses) and deuterated (gray crosses) HK271-paraffin. The quantum yields of the protonated solutions have been rescaled so as to be superimposed at the lowest wavelengths. The data for the deuterated compounds have been kept in scale with the corresponding protonated ones, so as to show the increased yield associated with deuteration. At  $\lambda = 532$  nm, the deuterated-protonated lifetime-ratio is also shown for HK271-5CB (star) and HK271-paraffin (triangle).

of the excited-state lifetime  $\tau_e$  measured at  $\lambda = 532$  nm, as shown in the same figure. Since the quantum yield can be written as  $\Phi = k_R\tau_e$ , where  $k_R$  is the radiative decay probability per unit time, this result implies that deuteration affects only the nonradiative decay channels, as expected.

## CONCLUSIONS

Studying the steady-state and time-resolved fluorescence at varying excitation-light wavelength, we have investigated different possible explanations for the peculiar wavelength dependence of the dye-induced optical nonlinearity observed for an amino-anthraquinone dye. Our results rule out several possible models that have been proposed in the literature and support a simple picture of decreasing population of the dye first-excited singlet state with increasing photon energy, as revealed by a decreasing quantum yield. The effect of the solvent and of deuteration has been also investigated.

## REFERENCES

- [1] Jánossy, I., Lloyd, A. D., & Wherrett, B. S. (1990). *Mol. Cryst. Liq. Cryst.*, 179, 1.
- [2] Paparo, D. *et al.* (1997). *Phys. Rev. Lett.*, 78, 38.
- [3] Muenster, R., Jarasch, M., Zhuang, X., & Shen, Y. R. (1997). *Phys. Rev. Lett.*, 78, 42.
- [4] Jánossy, I. (1994). *Phys. Rev. E*, 49, 2957.
- [5] Marrucci, L. & Paparo, D. (1997). *Phys. Rev. E*, 56, 1765.
- [6] Marrucci, L. *et al.* (1997). *J. Chem. Phys.*, 107, 9783.
- [7] Kreuzer, M., Hanisch, F., Eidenschink, R., Paparo, D., & Marrucci, L. (2002). *Phys. Rev. Lett.*, 88, 013902.
- [8] Kreuzer, M., Benkler, E., Paparo, D., Casillo, G., & Marrucci, L. (2003). *Phys. Rev. E*, 68, 011701.
- [9] Truong, T. V., Xu, L., & Shen, Y. R. (2003). *Phys. Rev. Lett.*, 90, 193902.
- [10] Paparo, D. *et al.* (1994). *Mol. Cryst. Liq. Cryst.*, 251, 73.
- [11] Kósa, T. & Jánossy I. (1995). *Opt. Lett.*, 20, 1230.
- [12] Myrvold, B. O., Spanget-Larsen, J., & Thulstrup, E. W. (1986). *Chem. Phys.*, 104, 305.
- [13] O'Connor, D. V. & Phillips, D. (1984). *Time-correlated single photon counting*. Academic Press: London, UK.
- [14] Philips, L. A., Webb, S. P., & Clark, J. H. (1985). *J. Chem. Phys.*, 83, 5810.
- [15] Scully, A. D., Matsumoto, A., & Hirayama, S. (1991). *Chem. Phys.*, 157, 253.
- [16] Paparo, D., Manzo, C., Marrucci, L., & Kreuzer, M. (2002). *J. Chem. Phys.*, 117, 2187.
- [17] Pantke, E. R. & Labhart, H. (1973). *Chem. Phys. Lett.*, 23.
- [18] Marrucci, L., Paparo, D., Vetrano, M. R., Colicchio, M., & Santamato, E. (2000). *J. Chem. Phys.*, 113, 10361.
- [19] Taylor, D. G. & Demas, L. N. (1979). *An. Chem.*, 51, 717.