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Fluorescence line-narrowing difference spectra: Dependence of Huang–Rhys factor on excitation wavelength

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ABSTRACT

It is well known that fluorescence line narrowed (FLN) difference spectra (ΔFLN spectra) reduce to single-site fluorescence line shape function in the low-fluence limit. This finding is confirmed by the observation of different line shapes of FLN and ΔFLN spectra obtained for pyrene (Py) in ethanol glass at various excitation wavelengths using time-resolved fluorescence measurements. A peculiar dependence of the Huang–Rhys factor (S) on excitation wavelength was discovered, and discussed in terms of the solute–solvent, intermolecular Lennard–Jones potential. A V-shaped frequency dependence of the S-factor suggests that the repulsive–dispersive potential is not sufficient to account for a complex 'color effect'.

1. Introduction

A delta fluorescence line-narrowed (ΔFLN) spectrum is the difference between two consecutive FLN measurements separated by a certain period of spectral hole-burning (SHB) [1–4]. In many cases [5–13], the localized exciton model introduced by Hayes et al. [14] was used to analyze the experimental fluorescence line-narrowing spectra. In this model, FLN and ΔFLN spectra can be expressed with a common formula, i.e. the spectra are taken to be proportional to the following infinite sum:

$$\mathrm{FLN}(\omega) \propto \Delta\mathrm{FLN}(\omega) \propto \sum_{R=0}^{\infty}\sum_{P=0}^{\infty}\left(S^R\frac{e^{-S}}{R!}\right)\left(S^P\frac{e^{-S}}{P!}\right) \times \int_{-\infty}^{\infty} d\omega_{\mathrm{ZPL}} N(\omega_{\mathrm{ZPL}}-\omega_c) l_R(\omega-\omega_{\mathrm{ZPL}}+R\omega_m) l_P(\omega_{\mathrm{exc}}-\omega_{\mathrm{ZPL}}-P\omega_m) \quad (1)$$

In the above equation, S is the Huang–Rhys factor measuring linear electron–phonon (el–ph) coupling strength; $N(\omega_{\mathrm{ZPL}}-\omega_c)$ stands for the inhomogeneous site-distribution function (IDF) of zero-phonon line (ZPL) frequencies; $l_0(\omega)$ is a Lorentzian function representing the ZPL, while $l_{R(P)}(\omega)$ is the R- (P-) phonon profile for R, $P > 0$.

The ΔFLN signal corresponds to FLN spectra of pigments burned away during the hole-burning (HB) process. Therefore, the authors argued [5–13] that Eq. (1), introduced for FLN spectra [14] can also be applied to ΔFLN measurement. However, this could be questioned when comparing Eq. (1) to the theory developed by Fünfschilling et al. [4]. According to Fünschilling's analysis, the contribution from pseudo- and multi-PSB (terms with $R > 0$ in Eq. (1)) should be negligible at low-burn fluence (hole depth less than 10% of ZPL absorbance; burn fluence measures light dose for HB per unit area in J cm^{-2}). On the other hand, Eq. (1) clearly indicates that the terms with $R > 0$ are significant at any burn fluence.

To better understand this contradiction, Reppert et al. [15] derived the lineshape function of ΔFLN spectra. Under the assumption that the system is excited by a laser with an infinitely narrow line width, a ΔFLN spectrum can be described as:

$$\Delta\mathrm{FLNS}(\omega) \propto F * [A_B \cdot (N - N_0 - N_1)] \propto F * \left(k \cdot N \cdot A_B^2 - N_1 \cdot A_B\right) \quad (2)$$

In this formula, F stands for a single-site fluorescence spectrum; $*$ means convolution; N is the IDF of pigments before burning as above; N_1 and N_0 are the IDFs of burned and unburned pigments after HB has taken place, respectively; A_B is the reflection of the single-site absorption line shape function around burn frequency ω_B; k is a constant that depends on the properties of the system, burn fluence, and average HB quantum yield. (For detailed derivation of Eq. (2), see Ref. [15].) Numerical calculations in Ref. [15] demonstrated

Abbreviations: ΔFLN (ΔFLNS), delta/difference fluorescence line-narrowed (spectrum); BChl, bacteriochlorophyll; fwhm, full-width at half-maximum; el–ph, electron–phonon; EtOH, ethanol; IDF, inhomogeneous distribution function; L-J, Lennard–Jones; PSB, phonon side band; Py, pyrene; S, Huang–Rhys factor; (S) HB, (spectral) hole-burning; ZPL, zero phonon line.

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that the term inside the brackets in Eq. (2) resembles delta function, resulting in a ΔFLN spectrum similar to the fluorescence line shape function, with ZPL centered at the excitation wavelength, as shown by Eq. (3):

$$\Delta\mathrm{FLNS}(\omega) \approx F(\omega) * \delta(\omega - \omega_B) = F(\omega - \omega_B) \quad (3)$$

.In this equation, $\delta(\omega - \omega_B)$ is delta function equal to one at $\omega = \omega_B$. Fitting the ΔFLN spectrum with formula (1) will underestimate the contribution of real PSB, as well as the value of the Huang–Rhys factor.

In order to determine the real shape of resonant FLN spectra, one has to eliminate a strong background of scattered exciting light, which overlaps with ZPL. For systems with long luminescence lifetimes, a continuous-wave (CW) laser with a chopper, or a pulsed laser, can be used, along with a time-gated detection, which can collect emission signals after termination of the excitation pulse. If the fluorescence lifetime is short (e.g., for many photosynthetic complexes, the fluorescence lifetime of chlorophylls is in the order of a few nanoseconds), the time-delay measurement using a 10-ns pulse laser is not applicable. In this case, ΔFLN measurement is necessary to remove the scattered light (which is extremely difficult) for correct determination of ZPLs, e.g. as shown in [5–13,16]. This method requires the fluctuation of laser intensity in FLN measurements be negligible compared to the ΔFLN signal, i.e., the scattering contribution must be much smaller than the real signal in the total spectrum. In addition, for better determination of system parameters in ΔFLN measurement, burn fraction should be less than 10% [15].

In order to experimentally test the conclusions drawn from Eq. (3) [15], ΔFLN spectra were measured for a selected system (Py molecules in ethanol glass) with a large fluorescence quantum yield (ϕ_{fl} = 0.65–0.92) and relatively long fluorescence lifetime (τ_{fl} = 515 ns) [17]. In this case, time-resolved detection is possible and ΔFLN spectra can be easily measured without light-scattering contributions at ZPLs. Moreover, we show that *S* varies across the inhomogeneously broadened absorption band. The frequency-dependent *S*-factor is discussed in terms of the Lennard–Jones (L–J) model of intermolecular, repulsive–dispersive potential [16,18–20]. The observed color effect behaves differently, as compared to predictions [16,20]. Electrostatic interactions between the polar solvent and the chromophore could lead to enhanced electron phonon coupling strength at the edges of IDF.

2. Experimental

For FLN measurements, a Lambda Physik Lextra 100 XeCl excimer laser was used as a pump source for a Lambda Physik FL 2002 Scanmate tunable dye laser system (10 Hz, line width 5 GHz). A 1-m McPherson monochromator (model 2601, slit width 50 μm) with 2400/mm grating and a Princeton Instruments photodiode array were used for dispersion and detection of fluorescence. The corresponding accuracy in frequencies for FLN measurements was about ±2 cm^{-1}. In order to minimize scattered light from the laser, a Princeton Instruments FG-100 pulse generator was used for time-resolved spectroscopy, with a detector delay time of 40 ns and a gate width of 200 ns. For all spectroscopic measurements, 30 μL of Py in ethanol (concentration ~10^{-5} M, O.D. at 334 nm ~0.86 and <0.1 at 0–0 transition) was placed in a quartz capillary tube with ~2.5 mm inner diameter and immersed in a helium cryostat with quartz optical windows. All fluorescence spectra were collected with 30 s acquisition time with laser power of ~4 mW. For ΔFLN measurement, two consecutive FLN signals are collected with no separate HB process, as HB takes place during the acquisition of FLN spectra. Therefore, ΔFLN signal, which is the difference between the two consecutive FLN measurements, has burn fluence of about 12 J cm^{-2}.

3. Results

Results of the experiment are shown in Figures 1 and 2. The fluorescence origin band (thick gray line) and FLN spectra (colored curves) of Py in ethanol glass at temperature *T* = 5 K were obtained for five excitation wavelengths within the 0–0 origin band (see figure caption for details). To ensure that scattered-light intensity does not contribute to resonant ZPLs, the spectra were obtained using time-resolved measurements. The FLN spectra shown in the main frame of Figure 1 show the same trend as the calculation in Fig. 3 of Ref. [15]. That is, FLN spectra have significant contributions from non-resonant excitation as broad and intense 'wings', particularly at the high-energy side of the IDF. The inset shows pre-burn (black), and post-burn (blue) FLN spectra, and the resulted ΔFLN spectrum, which is obtained as a difference.

The corresponding ΔFLN spectra are displayed in Figure 2. Frequency-dependent *S* factors (see Table 1) are plotted as a function of excitation wavelength (diamonds in the insert of Figure 2). It is obvious that the line shape of ΔFLN spectra significantly differ from the corresponding FLN spectra, i.e. the FLN and ΔFLN signals collected under identical conditions are not proportional to each other. This strongly suggests that formula (1) is not applicable to ΔFLN signals. Therefore, the collected ΔFLN spectra are close to the single-site emission line shapes, according to Ref. [15]. The apparent values of *S* factors calculated from ΔFLN spectra in Figure 2 are shown in Table 1. The *S* factor reaches a minimum value (0.49) close to the band maximum at λ_{ex} = 371.58 nm, and increases when the excitation wavelength is shifted towards the edges of IDF. The *S* values are reproducible, and a similar dependence on wavelength was collected when repeating the measurement (data not shown). The ΔFLN signal is usually much weaker than the corresponding FLN spectrum, due to the subtraction process. In particular, the ΔFLN signal recorded on the red edge at 372.58 nm is very weak with a low signal-to-noise ratio, leading

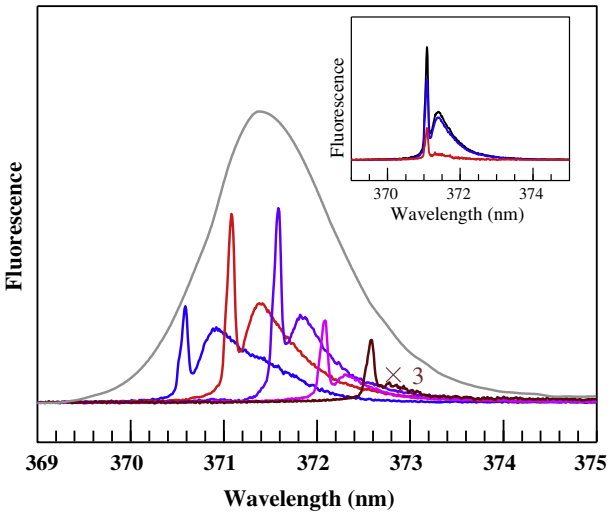

Figure 1. FLN spectra of Py in ethanol glass at *T* = 5 K. Colored lines are spectra collected with excitation wavelengths at 370.58, 371.08, 371.58, 372.08, and 372.58 nm, respectively. The thick gray curve is fluorescence origin, excited non-selectively at λ_{ex} of 308 nm. In the inset, black line stands for the pre-burn FLN spectrum, and the blue curve is the post-burn FLN measurement. The red curve is the difference between the two. The gate width is 200 ns, and delay time is 40 ns. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)