Time resolved area normalized emission spectroscopy (TRANES) of DMABN confirms emission from two states

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Abstract—4-*N*,*N*-Dimethylaminobenzonitrile (DMABN) is a simple molecule which is extensively studied to understand the excited state kinetics and the origin of time dependent fluorescence in several organic solvents. We use a recently described method, time resolved area normalized emission spectroscopy (TRANES), for the analysis of wavelength dependent fluorescence of DMABN in acetonitrile and 1,4-dioxane. An isoemissive point was observed in the TRANES spectra, which confirms that there are only two emissive species A* and B*: A → A* ⇔ B*.

Keywords: TRES; TRANES; DMABN; fluorescence; isoemissive point.

INTRODUCTION

The dual fluorescence of 4-*N*,*N*-dimethylaminobenzonitrile (DMABN) was first reported by Ernst Lippert *et al.* [1, 2] and subsequent model compound studies were reported by Grabowski and coworkers [3–5]. The dual fluorescence of DMABN and its model compounds has been extensively studied in organic solvents [6–9] and there are reports of studies in solid phase also [10–12]. The main interest in DMABN and its model compounds is the origin of the so-called anomalous red-shifted fluorescence emission in polar solvents and the underlying photophysics [13, 14]. It was originally proposed to be a charge transfer (CT) state [1]. The CT state was proposed to be a twisted intramolecular charge transfer (TICT) state, which is formed from the initial excited state (or local excited state, LE) [3–5]. Further detailed experimental and theoretical studies of DMABN and other DMABN-like molecules have led to a sustained debate on the structure of the CT state and the mechanism and time scale of its formation. The necessity of invoking a twisted geometry in the excited state was questioned and other models, in particular,

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wagged-ICT (WICT) [15], Pseudo-Jahn-Teller ICT (PICT) [16], and rehybridized-ICT (RICT) [17] were proposed as alternative photophysical models for TICT. A basic question that has been addressed is whether charge transfer precedes or follows a geometry change. It is conceivable also that there may be a continuum of emissive species (*a la* solvation dynamics) between the initial excited state and the final one if the activation barrier is low or zero. Different models of excited state kinetics will be discriminated better if one were able to determine unambiguously the number of emissive species in the sample of interest. Interestingly, the number of 'distinct' emissive species in the excited state has never been determined for DMABN or other DMABN-like molecules in a model-independent manner.

Recently, we reported a novel and model-free method called time resolved area normalized emission spectroscopy (TRANES) for the analysis of wavelength dependent luminescence decays [18]. TRANES method is a one-step extension of the frequently used TRES (time resolved emission spectra) method. Interpretation of TRANES spectra is relatively simple. For example, observation of identical TRANES spectra confirms emission from a single species and an isoemissive point in the TRANES spectra confirms emission from two species, and so on. It was shown [18] by mathematical analysis that an isoemissive point in the TRANES spectra is the necessary and sufficient condition to confirm the presence two emissive species irrespective of their origin. Isoemissive point occurs at a wavelength (or frequency) at which the ratio of the radiative rates at that wavelength (or frequency) is equal to the ratio of the total radiative rates of the two emissive species. The isoemissive point is the equivalent of the classical isosbestic point in time dependent absorption spectroscopy. A continuous distribution of excited state species (e.g. solvation dynamics) is also easily detected in the TRANES spectra [18]. Also, TRANES spectra of complex systems may be analyzed to identify the existence of three or four emissive species [19].

In this paper, we report that the TRANES spectra of DMABN in acetonitrile and 1,4-dioxane confirm that there are only two emissive species.

METHODS AND MATERIALS

4-*N*,*N*-Dimethylaminobenzonitrile (DMABN) purified by recrystallization was gifted by Prof. A. Samanta (University of Hyderabad, Hyderabad, India). Acetonitrile (HPLC grade from S.D. Fine Chemicals, Mumbai) and 1,4-dioxane (Qualigens fine Chemicals, Mumbai) were used as received. Steady state fluorescence spectra were recorded using a spectrofluorimeter (Fluorolog FL111 T-format spectrometer) and corrected for the spectral sensitivity of the photomultiplier (Hamamatsu R928A). Time resolved fluorescence decays were obtained by time-correlated single photon counting (TCSPC) method [20, 21]. The sample was excited in the absorption band by 'vertically' polarized, 295 nm picosecond laser pulses (4 MHz) derived from Ti-sapphire laser (Tsunami, Spectra Physics Inc., USA). Fluorescence emission at magic angle ($54.7°$) was dispersed in a monochromator (f1, spectral width 2.5 nm)

and detected ($3-4 \times 10^3$ s^{-1}) by a MCP PMT (R2809). The laser pulse was detected by a fast photodiode. The pulses from the PMT and photodiode are processed through preamplifier (IBH), CFD (Tennelec), TAC (Canberra) and MCA (Tracor Northern) and stored in a personal computer. The instrument response function is ~40 ps. The fluorescence decays were collected at a resolution of 21.5 ps/channel. The peak height of the decay is typically 10 000 counts. The wavelength dependent fluorescence decays were analyzed by TRANES program developed in house (available on request).

RESULTS AND DISCUSSION

Fluorescence decays of DMABN obtained in 5 nm intervals were analyzed by the model-free method of TRANES described earlier [18]. The four steps involved in the construction of TRANES spectra are as follows:

(I) Fluorescence intensity decays are collected at all emission wavelengths in 5 nm intervals.

(II) Each fluorescence intensity decay, $I(\nu, t)$, is fitted to a four exponential function (equation (1)) solely for the purpose of deconvolution and removal of noise. The criteria of good fit are random distribution of weighted residuals and chi-square value close to unity [21]. The value of the lifetimes and sign and value of the pre-exponential factors are not given any physical significance. The average lifetime, τ_{av}, is calculated as defined in equation (2). It may be noted that the sum in the denominator of equation (2) must contain only positive values of pre-exponential factors.

$$I(\nu, t) = \sum_{i=1}^{4} \alpha_i(\nu) e^{\frac{-t}{\tau_i(\nu)}}, \tag{1}$$

$$\tau_{av}(\nu) = \frac{\sum_{i=1}^{4} \alpha_i(\nu)\tau_i(\nu)}{\sum_{i=1}^{4} \alpha_i(\nu)}, \tag{2}$$

τ_{av} is proportional to the area under the fluorescence decay and thus proportional to the quantum yield. If the steady state spectrum is broad, τ_{av} is expected to vary smoothly (multiple species) or be unchanged (single species) with the emission wavelength.

(III) Time resolved emission spectra (TRES) are calculated at different times (t_k) using equation (3).

$$I(\nu, t_k) = I_{ss}(\nu) \frac{\sum_{i=1}^{4} \alpha_i(\nu) e^{\frac{-t_k}{\tau_i(\nu)}}}{\sum_{i=1}^{4} \alpha_i(\nu)\tau_i(\nu)}. \tag{3}$$

In equation (3), $I_{ss}(\nu)$ is the steady state fluorescence intensity taken from the spectrum that was corrected for the quantum efficiency of the photomultiplier.
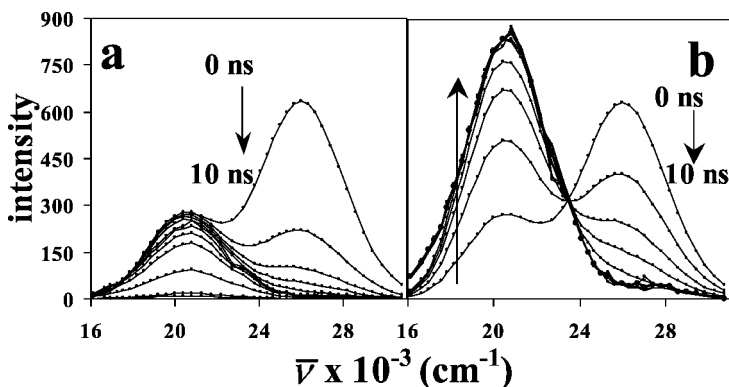
Figure 1. (a) Time resolved emission spectra (TRES) and (b) time resolved area normalized emission spectra (TRANES) for DMABN in acetonitrile. Excitation wavelength = 295 nm. [DMABN] = 20 μM. The spectra are shown for t = 0, 0.01, 0.02, 0.03, 0.04, 0.05, 0.1, 0.2, 0.5, 1, 3, 8 and 10 ns.
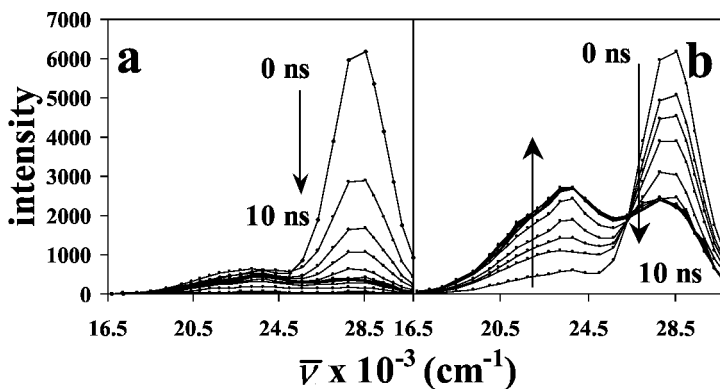

Figure 2. (a) Time resolved emission spectra (TRES) and (b) time resolved area normalized emission spectra (TRANES) for DMABN in 1,4-dioxane. Excitation wavelength = 295 nm. [DMABN] = 20 μM. The spectra are shown for t = 0, 0.01, 0.02, 0.03, 0.05, 0.1, 0.2, 0.5, 1, 3, 7 and 10 ns.

(IV) TRANES spectra are calculated by equating the area of each spectrum in TRES to a constant value; e.g. the area at time, $t = 0$.

Fluorescence decays of DMABN were obtained as described in Methods section. Figures 1 and 2 show the time resolved emission spectra (TRES) and time resolved area normalized emission spectra (TRANES) for DMABN in acetonitrile and 1,4-dioxane. The TRES and TRANES spectra are distinctly different for times, $t = 0$, 0.01, 0.02, 0.03, 0.04, and 0.05 ns. The TRANES spectra for $t > 0.1$ ns are identical. The presence of an isoemissive point is unambiguously indicated in the TRANES spectra of DMABN in acetonitrile and 1,4-dioxane. As shown in reference [18], an isoemissive point in TRANES spectra is equivalent to isosbestic point in time dependent absorption spectra. We conclude therefore that there are only two emissive species in the sample. In previous studies, the dual emission of DMABN in organic solvents has been attributed to emission from two species

based on an assumed model of excited state kinetics [10, 15]. On the other hand, the conclusion based on TRANES spectra is not based on any *a priori* model of excited state kinetics!

The observation of isoemissive point in TRANES spectra effectively rules out all models that predict three or more emissive species in the sample. Now we consider only those specific models that give rise to two emissive species. The two important models in this context are ground state heterogeneity (A and B species in ground state are excited to A* and B*) and excited state kinetics (Species A is excited to A* which populates B*). These two models can now be distinguished by analysis of the fluorescence decays for consistency with the decay equation appropriate for these models. In the first case, the fluorescence decay will be a single or bi-exponential but the pre-exponential factor is never negative at any wavelength. In the latter case, the fluorescence decay will be single or bi-exponential but at long emission wavelength it is always bi-exponential with one negative pre-exponential factor. The fluorescence decays of DMABN in acetonitrile and 1,4-dioxane are found to be consistent with the second model: A → A* ⇔ B*. The fluorescence decays at wavelengths greater than 500 nm fitted well to biexponential function with a negative pre-exponential factor. The lifetime of A* and B* were determined to be 10 ± 5 ps and 3.00 ± 0.05 ns in acetonitrile, and 20 ± 7 ps and 3.75 ± 0.03 ns in 1,4-dioxane, respectively. The observation of negative pre-exponential factor and the values of lifetimes are in good agreement with those reported in the literature [15, 22, 23].

The photophysics of DMABN and similar dipolar molecules with *N,N*-dialkyl group continue to attract considerable discussion in literature [24–27]. Analysis of fluorescence decays and spectra based on TRANES on molecules similar to DMABN may or may not reveal an isoemissive point. The molecules that do not show an isoemissive point in the TRANES spectra of a DMABN-like molecule will be the most interesting ones indicating intermediate states between A* and B*. Therefore, they are useful in the context of the ongoing discussion of TICT vs PICT vs other models of intramolecular excited state dynamics of floppy molecules [28].

CONCLUSION

The analysis of wavelength dependent fluorescence of DMABN in acetonitrile and 1,4-dioxane by the time resolved area normalization emission spectroscopy (TRANES) reveals the presence of an isoemissive point and hence there are only two emissive species.

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