Using random laser emission to investigate the bonding energy of laser dye dimers ☆

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ABSTRACT

We report on a new method, based on random laser emission, to investigate the formation of dimers in laser dye solutions. The single peak spectrum observed at low dye concentration evolves to a double peak spectrum as the concentration increases, and a simple analysis allow us to directly investigate the dimers bonding energy. Our samples were prepared with rhodamine laser dyes dissolved in ethanol, containing TiO_2 nanoparticle scatterers. The laser dyes used in this experiment were Rhodamine 590, Rhodamine 610, Kiton Red 620, and Rhodamine 640. Our results are corroborated by theoretical and experimental data in the literature.

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1. Introduction

Since the discovery of random laser emission from dye solutions containing scattering particles [1] this subject have being extensively studied by a number of researchers [2–7]. Most of these studies are focused on the optical and laser characteristics of these systems. Some of these studies were dedicated to the analysis of the double peak emission of Rhodamine 640 laser dye solutions at high concentrations [7–9]. In the first analysis of the two peaks emission Balachandran and Lawandy [10] did not mentioned any evidence of the formation of new species, such as dimers, although the dye concentration was very high (10^{-2} M). However, they clearly found evidences that both peaks were strongly interrelated, and in their interpretation the rising of the secondary peak occurred immediately after the growth of the main short-wavelength peak, suggesting that the first was required to drive the second. John and Pang [9] have interpreted the second peak as being due to the emission of the transition from the excited level of the triplet state to its fundamental level, in a typical four level energetic scheme of organic dyes, composed by singlet and triplet fundamental and first excited states. However, the above explanations go against experimental results of Sha et al. [8], where for a neat dye solution the longer wavelength peak lasers first. Sha et al. suggested that one possible process to explain the experimental results is to consider the formation of aggregates in high-concentrated dye solutions. It was proposed that monomers are responsible for the short-wavelength emission and the aggregate complex is responsible for the long-wavelength emission.

In this Letter we have investigated the double peak emission from high-concentrated laser dye solutions containing scattering particles, and we also have found evidences that the second peak of the emission is due to the presence of dimers [11]. A simple spectral analysis allow us to measure the energy difference between the two peaks emission and investigate the interaction energy of the molecules in the dimers.

Many experiences involving the use of pure dye solutions (without nanoparticle scatterers) also relate the aggregates presence at high concentrations and that the aggregation processes depend upon the solvent type and the temperature. In a first approximation analysis we may disregard the formation of high order aggregates, and associate the emission and absorption spectra of these type of systems to the presence of monomers and dimers only. These processes of collective association of the dye molecules, in general, is negatively reflected in the fluorescence quantum yield of the laser dyes, leading to an efficiency quenching of the fluorescent emission [12]. Nevertheless, in laser dyes as Rhodamine 610 and Kiton Red, some residual fluorescence was still observable even though the molecules were almost completely dimerized. This radiation was attributed to the dimer emission species [13]. The processes of molecular aggregation was first used to explain the deviations from the Beer's law [14].

2. The exciton theory

The dipolar approach of the exciton theory [15,16] predicts that when two dye molecules come together to form a dimer unit, the original absorption peak due to the monomer splits in two peaks providing two possible absorption bands (see Fig. 1) in the so-called H band (higher energy) and J band (lower energy) [14,17]. This split in the absorption spectrum is caused by the dipole–dipole interaction between the two monomeric units in the dimer.
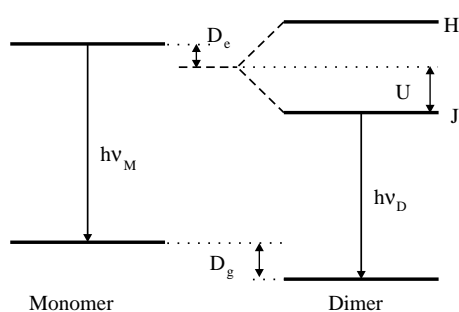
Fig. 1. Schematic representation of the energy levels for monomers and dimers according to the exciton theory. The letters H and J refer to the energy levels of the dimers, and U is the exciton interaction energy of the monomers in the dimer. D_g and D_e are the shifts of the dimer levels due to the van der Waals interaction energy of the ground and excited states respectively.

The dimer is mainly stabilized by the delocalization of the excitation energy between the two monomeric units in the dimer, the U splitting term in Fig. 1, but the van der Waals interaction in both, the ground and the excited states, D_g and D_e in Fig. 1, also contribute. The total bonding energy ΔE of the monomers in the dimer can be calculated from

$$\Delta E = U + \Delta D, \tag{1}$$

where $\Delta D = D_e - D_g$. The bonding energy not only includes the resonance splitting term U, but also the difference in the van der Waals interactions in the ground and excited states, D_g and D_e, respectively.

From the energy levels diagram, shown in Fig. 1, we can see that

$$\Delta E = hc\left(\frac{1}{\lambda_D} - \frac{1}{\lambda_M}\right) \tag{2}$$

where h is the Planck's constant, c is the light velocity, λ_M and λ_D are the emission wavelengths of the monomers and the J dimers, respectively. The h and c constants may be omitted if units of λ_D and λ_M are given in cm, and the energy unit is given in cm^{-1}.

According to the exciton theory the H dimers are non-fluorescent and the J dimers are fluorescent. This process has been verified by extensive experimental and theoretical data available in the literature [12,15,16,18]. These studies also show that, from the absorption spectra of monomers and dimers, it is possible to obtain information on the geometrical structure of the dimer, as well as, to evaluate the interaction energy between two adjacent molecules that form the dimer (U in Fig. 1) [19]. Nevertheless, there are evidences that the simplified exciton theory does not explain the complicated characteristic of the absorption curves observed in the experiments [18], mainly because it considers the molecule as point dipoles, does not take into account other types of monomer–monomer interactions and neglects the vibrational states. For these reasons, the splitting in two-levels of the dimer is not symmetric with respect to the monomer excited state.

3. The random laser spectroscopy

The splitting in the energy levels of monomers in a dimer is usually smaller than the absorption or the fluorescence linewidth, and as a consequence the spectral lines corresponding to these transitions can not be spectrally resolved. In this way, a reliable measurement of the bonding energy of the molecules in a dimer, using absorption or fluorescence spectroscopy, is not an easy task. In general it involves measurements at various temperatures and dye concentrations, and a special apparatus is needed for that purpose [20–22]. To overcome this problem we propose a new method to investigate the bonding energy between two adjacent mono-

mers within the dimer. The method consists on the use of the spectral emission of random laser systems [1,6]. In random laser systems scattering particles are added in the laser dye solution, and laser action occurs without the use of a cavity. The scattering particles are responsible for the feedback, enhancing the lifetime and pathlength of the photons inside the sample, which main effect is an increase in the amplification of the emitted light. Under this circumstance the spectral emission shows a big narrowing and the determination of the emission peaks can be done by direct inspection (see Ref. [1] for details). In this technique the maxima of emission corresponding to the monomer and dimer spectra can be easily identified, as is shown in Fig. 2.

Fig. 2 shows a comparison of fluorescence and random laser spectra for a solution of 3×10^{-3} M of Kiton Red 620 dissolved in ethanol containing TiO$_2$ nanoparticles. In the absorption and fluorescence techniques, spectra measurements are usually taken on neat ethanolic dye solutions. On the other hand, in the random laser spectra measurements, besides the dye solution, there are scattering particles in suspension. Our result, shown in Fig. 2, clearly shows that the random laser emission linewidth is at least one order of magnitude narrower than that of the fluorescence spectrum. The present method is very useful, particularly in the cases of low interaction energies, where the emission peaks are very close to each other, and the absorption or fluorescence spectra can not be resolved due to the overlapping of the spectral lines.

The observation of bichromatic emission from random lasers have been reported by many authors [1,8,10,11], but the studies in this field were mostly dedicated to the characterization of the random laser dynamics. In this Letter we explore the random laser emission to the study of the intrinsic properties of the dye solution, such as the bonding energy of the molecules in the dimer. The random laser system, besides presenting narrow spectra, does not select the laser modes, and the laser wavelengths are only determined by the gain of the dye solution, allowing multiple wavelengths to be amplified simultaneously. For these reasons, the random laser spectroscopy is a powerfull tool for the study of aggregation of laser dye molecules, and the formation of new molecular species in a solution.

To our knowledge, laser emission from dimers in samples without scatterers are not reported in the literature, and we believe that the presence of scattering particles could affect the dye aggregation. For instance, adsorption of dye molecules at the scatterers surfaces can increase the local concentration of the dye molecules, favoring the formation of the J-type dimer.
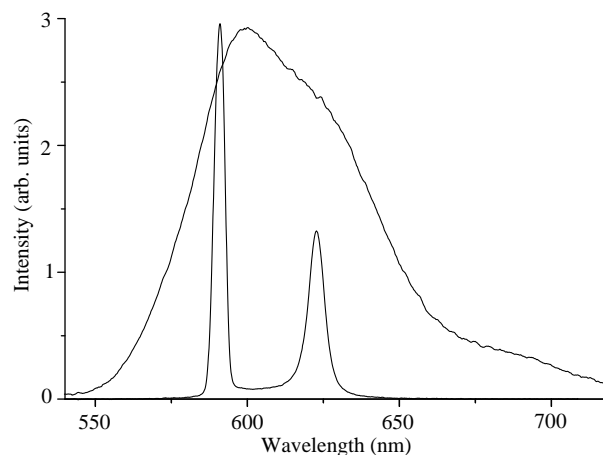

Fig. 2. Fluorescence and random laser emission spectra of a Kiton Red solution containing TiO$_2$ nanoparticle scatterers, pumped by CW and pulsed Nd:YAG lasers, respectively.

4. Experimental procedure

In our experiments the samples were optically pumped by a frequency doubled and Q-switched Nd:YAG laser operating at 532 nm. The pump laser pulse duration was 5 ns and we set its repetition rate to 10 Hz. With this repetition rate the time interval between consecutive pulses is long enough to guarantee that any residual population, eventually transferred to the triplet state, relax back to the singlet ground state before the next laser pulse arrives. In order to record the data we have used an Ocean Optics fiber spectrometer with a resolution of about 0.7 nm. The fiber used in this spectrometer had a diameter of 200 μm, and a neutral density filter (OD 2) was used in front of the fiber entrance to attenuate the random laser emission.

Our samples were prepared with several rhodamine laser dyes, supplied by Exciton, at concentrations in the range of 1×10^{-4}–1×10^{-2} M in ethanol. Nanoparticles of rutile (TiO$_2$), supplied by DuPont, were used as the scattering medium. The average size of the particles was 250 nm. The particles concentration was 10.0 g/l, corresponding to densities of the order of 6×10^{11} particles/cm^3. This concentration gives the optimal random laser efficiency.

The width of the spectral emissions depended on the pumping energy and exhibited a spectral width about 50 nm for very low pumping energies (fluorescence spectra) and about 5 nm when the pumping energies were around 4 mJ (laser spectra). The random laser threshold depends on the dye concentration, but it is below 1 mJ for most of the samples. For convenience we set the energy of the pumping laser pulse at 15 mJ for all experimental measurements.

5. Results and discussion

In Fig. 3 we present the random laser emission from four different types of the rhodamine family laser dyes. The measurements were taken in ethanolic solutions of Rhodamine 590, Rhodamine 610, Kiton Red 620, and Rhodamine 640, in concentrations of 1×10^{-4} M, 1×10^{-3} M, and 3×10^{-3} M, respectively. For all dye solutions used in the experiment the spectra show a single peak at low concentrations, and as the concentration is increased a secondary peak appears at a longer wavelength. This behavior is a strong indication that aggregation of dye molecules is taking place.

By simply measuring the position of the monomer and the dimer emission peaks it is straightforward to evaluate the bonding energy of the dye complexes, using Eq. (2). In this method the position of the peaks must be taken at a dye concentration as low as possible in order to reduce the error caused by the reabsorption effects, that usually shifts the peaks towards the longer wavelength region of the spectrum [20–22]. However, reabsorption effects on the dimer laser emission should be very low because it is redshifted with respect to the monomer emission and do not overlap with the absorption bands of both species. We measured the wavelength of the monomer from the most diluted solutions, and the wavelength of the dimers from the most concentrated solution, although the spectrum of the former one presents the two wavelengths simultaneously. Therefore, we have measured the position of the monomer peak at a concentration of 1×10^{-4} M and that of the dimer at a concentration of 3×10^{-3} M, where the dimer emission begins to appear.

Table 1 summarizes the results of the peak wavelengths and bonding energy of Rhodamine 590, Rhodamine, 610, Kiton Red 620, and Rhodamine 640, respectively. As a comparison with other results in the literature we may refer to the work of Gilani et al. [23] that reported a value of -724 cm^{-1} for the bonding energy of Rhodamine 590 in ethanol, which differs from the energy obtained in this work by less than 2% ($\Delta E = -732.9$ cm^{-1}). We may
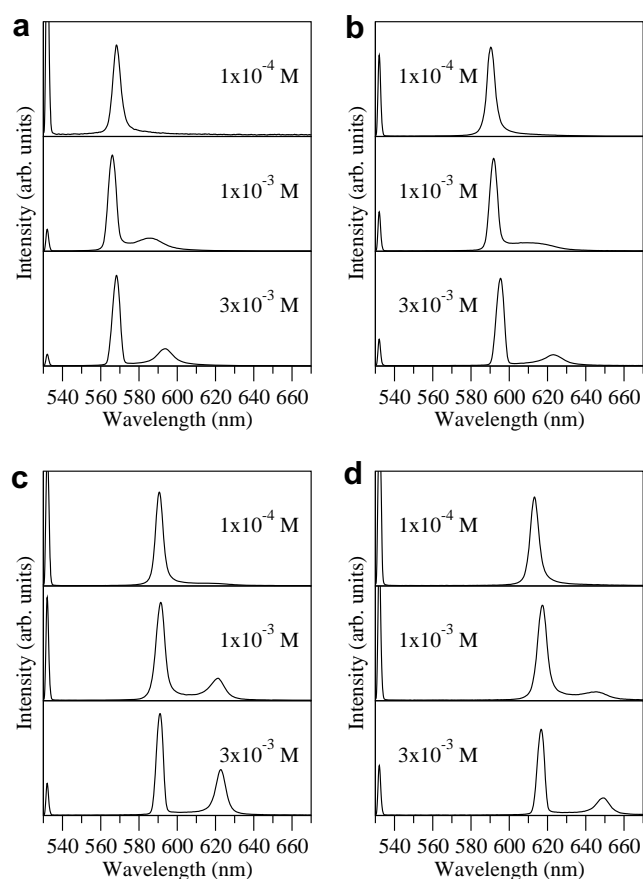

Fig. 3. Random laser emission spectra (normalized at the monomer peak) measured in ethanolic solutions of (a) Rhodamine 590, (b) Rhodamine 610, (c) Kiton Red 620 and (d) Rhodamine 640, at concentrations of 1×10^{-4} M, 1×10^{-3} M, and 3×10^{-3} M.

Table 1
Emission wavelengths and values of monomer–monomer bonding energy in dimers of Rhodamine 590, Rhodamine 610, Kiton Red 620, and Rhodamine 640 solutions

Dye	λ_M (nm)	λ_D (nm)	ΔE (cm^{-1})
Rhodamine 590	568.32	593.02	−732.9
Rhodamine 610	590.79	622.63	−865.6
Kiton Red 620	590.79	621.19	−828.4
Rhodamine 640	613.41	645.35	−806.8

also compare our experimental result of Rhodamine 590 with that calculated by Gavrilenko and Noginov [24], where a splitting in the main absorption peak of the J dimer is predicted. According to their calculation there is a strong absorption peak located at 511 nm due to the monomers and two absorption peaks located at 506 and 527 nm due to the J dimers, which corresponds to an splitting in the J band of 0.098 eV (787.5 cm^{-1}), while the energy difference between the monomer peak and the dimer longer wavelength peak is -594 cm^{-1}. Although this splitting is not experimentally observed in the absorption spectra, it is observed in emission spectra, and a possible explanation for this phenomenon is a strong energy transfer from monomers to dimers [11]. Our experimental results from high concentrated dye solutions show only two emission peaks, instead of three, as indicated by Gavrilenko and Noginov [24], that we individually associate with the monomer and the dimer emissions. But, since the calculated value for one of the absorption peaks of the J dimer almost coincides with the absorption peak of the monomer, we may not guarantee that the short-wavelength of the random laser emission spectra is exclusively due to the monomers.

Finally, we also performed experiments with Rhodamine 610 in mixed solutions of water and ethanol with the purpose of observing some residual emission due to the H dimer, since aqueous environments favor the formation of H dimers, in detriment of J dimers, favored in hydrophobic media [25]. However, the results with solutions of 2–15% of water content were negative: no additional spectral features were observed. Nevertheless, a small decrease in the magnitude of the emission spectra of the dimer and of the monomer was observed. This confirms that the formation of H dimers quenches the efficient emission from monomers.

6. Conclusion

In conclusion, we have reported on a new method to investigate the formation of dimers in high concentrated laser dye solutions. The method is based on the measurement of the random laser emission spectra of these solutions, containing TiO_2 nanoparticle scatterers, that in some circumstances may show a double peak spectrum. We have used rhodamine laser dyes, such as Rhodamine 590, Rhodamine 610, Kiton Red 620 and Rhodamine 640, dissolved in ethanol and all of them have shown indications of dimer formation at high concentrations. The results displayed in this work allow the accurate estimation of the bonding energy of the monomers in the dimer. A detailed analysis on how to determine the equilibrium constant, and other parameters are under investigation.

References

[1] N.M. Lawandy, R.M. Balachandran, A.S.L. Gomes, E. Sauvain, Nature (London) 368 (1994) 436.
[2] W.L. Sha, C.-H. Liu, R.R. Alfano, Opt. Lett. 19 (1994) 1922.
[3] R.M. Balachandran, D.P. Pacheco, N.M. Lawandy, Appl. Opt. 35 (1996) 640.
[4] B.G. Sfez, Z. Kotler, Opt. Mater. 8 (1997) 1.
[5] W. Zhang, N. Cue, K.M. Yoo, Opt. Lett. 20 (1995) 961.
[6] D.S. Wiersma, A. Lagendijk, Phys. Rev. E 54 (1996) 4256.
[7] G. Beckering, S.J. Zilker, D. Haarer, Opt. Lett. 22 (1997) 1427.
[8] W.L. Sha, C.-H. Liu, F. Liu, R.R. Alfano, Opt. Lett. 21 (1996) 1277.
[9] S. John, G. Pang, Phys. Rev. A 54 (1996) 3642.
[10] R.M. Balachandran, N.M. Lawandy, Opt. Lett. 21 (1996) 1603.
[11] P. Vaveliuk, A.M. de Brito Silva, P.C. de Oliveira, Phys. Rev. A 68 (2003) 013805.
[12] R.W. Chambers, Takashi Kajiwara, David R. Kearns, J. Phys. Chem. 78 (1974) 380.
[13] T. Kajiwara, R.W. Chambers, D.R. Kearns, Chem. Phys. Lett. 22 (1973) 37.
[14] O. Valdes-Aguilera, D.C. Neckers, Acc. Chem. Res. 22 (1989) 171.
[15] M. Kasha, Radiat. Res. 20 (1963) 55.
[16] E.G. McRae, M. Kasha, in: L. Augenstein, B. Rosenberg, S.F. Mason (Eds.), Physical Processes in Radiation Biology, Academic Press, New York, 1963.
[17] J.E. Selwyn, J.I. Steinfeld, J. Chem. Phys. 76 (1972) 762.
[18] J. Muto, J. Chem. Phys. 80 (1976) 1342.
[19] F. López Arbeloa, I. López Arbeloa, T. López Arbeloa, in: H.S. Nalwa (Ed.), Handbook of Advanced Electronic and Photonic Materials and Devices, vol. 7, Academic Press, San Diego, 2001, p. 209.
[20] I. López Arbeloa, J. Photochem. 14 (1980) 97.
[21] M. Fischer, J. Georges, Spectrochim. Acta A 53 (1997) 1419.
[22] T.P. Burghardt, J.E. Lyke, K. Ajtai, Biophys. Chem. 59 (1996) 119.
[23] A. Ghanadzadeh Gilani, R. Sariri, K. Bahrpaima, Spectrochim. Acta Part A 57 (2001) 155.
[24] V.I. Gavrilenko, M.A. Noginov, J. Chem. Phys. 124 (2006) 044301.
[25] F. López Arbeloa, P. Ruiz Ojeda, I. López Arbeloa, Chem. Phys. Lett. 148 (1988) 253.