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Two Examples of Pressure Tuning Spectroscopy in Solid Polymeric Media

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Pressure tuning spectroscopy has proved to be a powerful tool for characterizing electronic excitations, testing theories, and inducing electronic transitions of both scientific and technological significance. In this brief paper we outline two studies involving luminescence of molecules dissolved in solid polymers: (1) Two-photon excitation is a process of importance in the operation of many useful lasers. From our pressure study of Rhodamine B in poly(acrylic acid), we characterize the differences between the paths for one- and two-photon excitation. (2) Some molecules can assume two different geometries in the excited state and have potential as switching devices. We test a model for the processes involved by showing that the change of the steady-state emission intensity as a function of pressure can be predicted from time-dependent data.

Introduction

Organic molecules provide the possibility for diversity and control of optical properties in many cases not available from inorganics. Organic crystals are, however, generally quite unstable for long-term practical devices and mechanically difficult to handle. In relatively dilute solution in unreactive polymeric media, both the stability and the mechanical problems can be largely overcome.

In this paper we demonstrate the use of pressure tuning spectroscopy to analyze two different luminescent phenomena for organic molecules dissolved in solid polymeric media. The first of these, two-photon excitation, is important in the operation of a number of useful lasers. The second, excited-state isomerization, has potential as a switching device.

Both sets of experiments were carried out in a Merrill–Bassett diamond anvil cell (DAC). The details of the absorption and emission measuring techniques are described in the literature^{1–5} and need not be repeated here.

Two-Photon Excitation

The usual fluorescence process involves excitation from a ground state, S_0 , to an excited vibrational level of the S_1 electronic state, followed by rapid thermal relaxation to the lowest vibrational level of S_1 and emission of fluorescence or thermal decay to S_0 . The fluorescence maximum is thus lower in energy than the absorption maximum by an amount known as the Stokes' shift.

For some molecules which have nonlinear optical properties, it is possible to excite emission in the visible region at higher energy than the laser excitation in the near-infrared, utilizing a two-photon process. Some applications of this phenomenon are given, e.g., in refs 6–15.

In our laboratory we have made a number of studies of the effect of pressure on two-photon processes^{13–15}

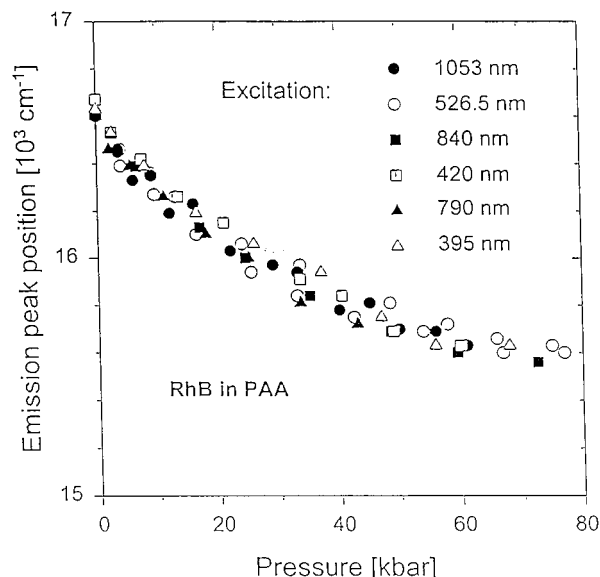


Figure 1. Pressure dependence of the energy of the emitting state of RhB in PAA following various one- and two-photon excitations. Reprinted with permission from ref 15. Copyright 1998 American Chemical Society.

which help to explain the similarities to and differences from one-photon events. Here we present one such study involving Rhodamine B (RhB) in solid poly(acrylic acid) (PAA).

The first absorption peak ($S_0 \rightarrow S_1$) in RhB is at $17.9 \times 10^3 \text{ cm}^{-1}$ (559 nm). It was excited using the 1053 nm line of a Nd:YLF laser for the two-photon process and its second harmonic at 526.5 nm for the one-photon process. There are higher absorption maxima at $23.8 \times 10^3 \text{ cm}^{-1}$ (420 nm) and $25.3 \times 10^3 \text{ cm}^{-1}$ (395 nm) assigned to the S_2 and S_3 excited states. These were excited using a Ti-sapphire laser with the 840 and 790 nm lines for the two-photon process and their second harmonics for the one-photon excitation.

In Figure 1 we present the emission peak location as a function of pressure for the three one-photon excitations and the three two-photon excitations. Figure 2

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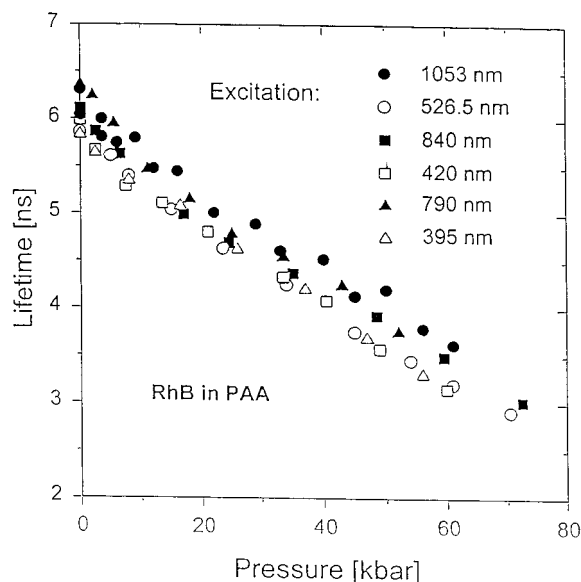


Figure 2. Pressure dependence of the lifetime of the emitting state of RhB in PAA following various one- and two-photon excitations. Reprinted with permission from ref 15. Copyright 1998 American Chemical Society.

shows the lifetime data similarly plotted. It is clear that although three different excited states are involved and there are two different excitation paths to each, in all cases the observed emission is $S_1 \rightarrow S_0$.

The change in emission efficiency with pressure for both the one- and two-photon processes is shown in Figure 3. For all three different wavelengths involved, the decrease in efficiency is distinctly greater for the two-photon excitation than for the corresponding one-photon process.

The relative efficiency as a function of pressure for the one- and two-photon processes is exhibited in eqs 1 and 2.

$$I_1 = \frac{I_1(p)}{I_1(0)} = \frac{k_1^r(p) \tau_1(p) \sigma(p)}{k_1^r(0) \tau_1(0) \sigma(0)} \quad (1)$$

$$I_2 = \frac{I_2(p)}{I_2(0)} = \frac{k_2^r(p) \tau_2(p) \delta(p)}{k_2^r(0) \tau_2(0) \delta(0)} \quad (2)$$

The variables involved are the radiative rates (k^r), the lifetimes (τ), and the absorption cross sections (σ for the one-photon process and δ for the two-photon excitation). From Figure 2 it is clear that the lifetimes, τ , are independent of the excitation process. It has been shown¹⁶ that radiative rates for organic molecules in polymeric media are relatively pressure independent. Thus, to a high degree of accuracy, we can write

$$\delta'/\sigma' \cong I_2/I_1 \quad (3)$$

As can be seen from Figure 4, the ratio decreases by a factor of about 2 in 60 kbar and the changes are similar for the three excitations.

The RhB molecule in the ground state has relatively low symmetry. It can be shown that the ground state of the π electrons has A_1 symmetry, while S_1 has B_2 symmetry and S_2 and S_3 are considered to have A_1 symmetry. Both transitions to A_1 and B_2 are symmetry allowed for two-photon absorption. Evidently, the two-

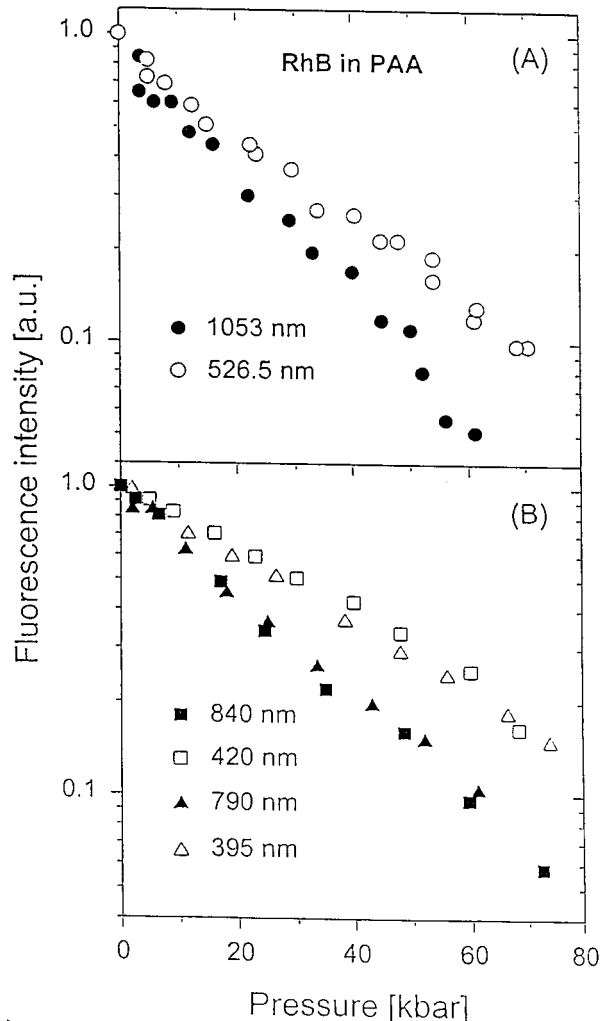


Figure 3. Pressure-induced fluorescence intensity change for RhB in PAA following one- and two-photon excitation: (A) Nd:YLF; (B) Ti-Al₂O₃ laser. Reprinted with permission from ref 15. Copyright 1998 American Chemical Society.

photon processes involve states other than those relevant to one-photon processes and the transfer from these states to S_1 (the emitting state) is inhibited by pressure to a greater extent than the $S_2 \rightarrow S_1$ or $S_3 \rightarrow S_1$ transitions or than the internal conversion from S_2 , S_3 , or S_1 to S_0 .

Intermolecular Twist in the Excited State

A large class of molecules, frequently benzene derivatives with donor and acceptor side groups, have a planar ground state with an excited state which is, in general, also planar, but when excited, it can isomerize by twisting one or more of the side groups. This process is accompanied by charge transfer. These molecules (labeled TICT) have been widely studied because of their potential scientific or practical applications.^{17–26} A number of high-pressure studies have been made.^{27–31} We present here results for *p*-(*N,N*-dimethylamino)-benzylidenemalononitrile (DMABMN) in dilute solution in poly(vinyl acetate) (PVA) and poly(vinyl chloride) (PVC). We show that the rather large change in steady-state emission intensity can be predicted from the time-dependent data.

The structure of DMABMN is shown in Figure 5. Figure 6 exhibits the model used to describe the process.

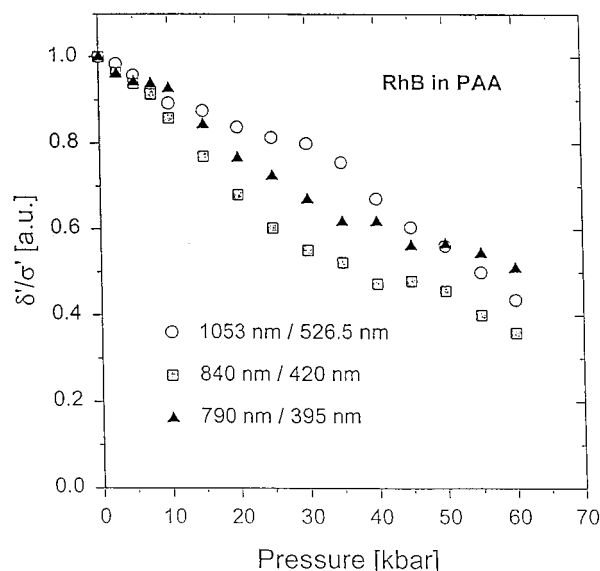


Figure 4. Pressure effect on ratio of the relative absorption cross section for two-photon excitation δ' to relative absorption cross section for one-photon excitation σ' for various excitations. Reprinted with permission from ref 15. Copyright 1998 American Chemical Society.

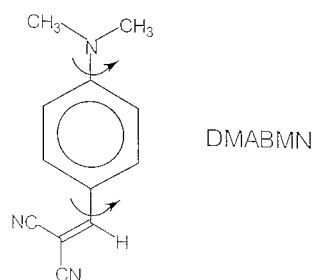


Figure 5. Structure of DMABMN. Reprinted with permission from ref 31. Copyright 2000 Elsevier Press Ltd.

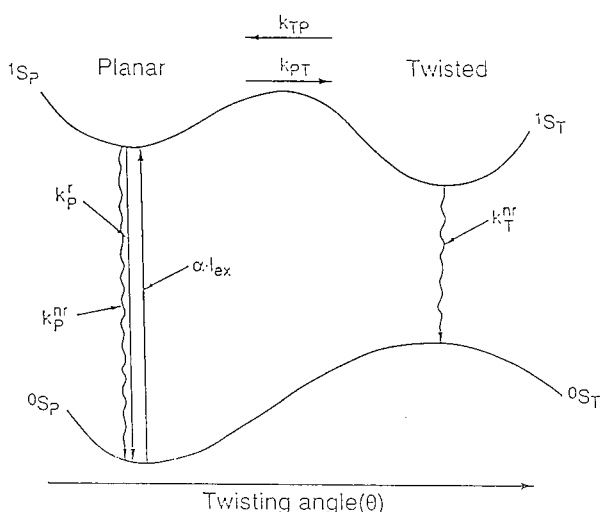


Figure 6. Model for the processes involved in the ground and planar and twisted excited state. Reprinted with permission from ref 31. Copyright 2000 Elsevier Press Ltd.

Because there is only one emission peak with a modest Stokes' shift, we assume that only nonradiative decay occurs from the twisted excited state.

The following series of equations describe the time-dependent observations. The time dependence can be

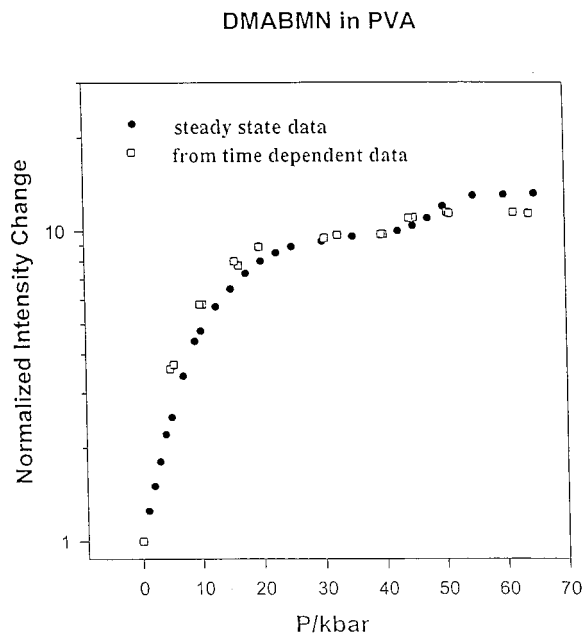


Figure 7. Effect of pressure on the emission efficiency of DMABMN in PVA: (●) from steady-state measurement and (□) predicted from time dependent data. Reprinted with permission from ref 31. Copyright 2000 Elsevier Press Ltd.

fit accurately by the sum of two exponential decays:

$$\frac{I(t)}{I(0)} = \gamma[\exp(-\beta_1 t)] + (1 - \gamma)[\exp(-\beta_2 t)] \quad (4)$$

Then, by straightforward algebra, one can obtain combinations of the constants defined in Figure 6:

$$k_P^r + k_P^{nr} + k_{PT} = k_P + k_{PT} = \gamma\beta_1 + (1 - \gamma)\beta_2 \quad (5)$$

(total dissipation of excitation from the excited planar state)

$$k_T + k_{TP} = (1 - \gamma)\beta_1 + \gamma\beta_2 \quad (6)$$

(total dissipation of energy from the twisted excited state)

$$k_{PT}k_{TP} = \gamma[(1 - \gamma)(\beta_1 - \beta_2)^2] \quad (7)$$

The steady-state intensity change with pressure is given by

$$\frac{I(p)}{I(0)} = \frac{\alpha(p) k_T(p)}{\alpha(0) k_T(0)} \times \frac{\left[(k_P + k_{PT})(0) - \left(\frac{k_{PT}k_{TP}}{k_T + k_{TP}} \right)(0) \right]}{\left[(k_P + k_{PT})(p) - \left(\frac{k_{PT}k_{TP}}{k_T + k_{TP}} \right)(p) \right]} \quad (8)$$

As indicated in the previous section, there is considerable evidence that the radiative rates have minimal pressure dependence. The absorption at the excitation wavelength 441.6 nm shows very little pressure dependence. Thus, the term in square brackets which involves only the results from eqs 5–7 should predict $I(p)/I(0)$.

The comparisons are made in Figures 7 and 8. The experimental steady-state results are given by the solid circles and are the average of five separate loads with very little scatter $\pm 2.5\%$. The squares are the predicted results (average of three loads). Both steady-state and

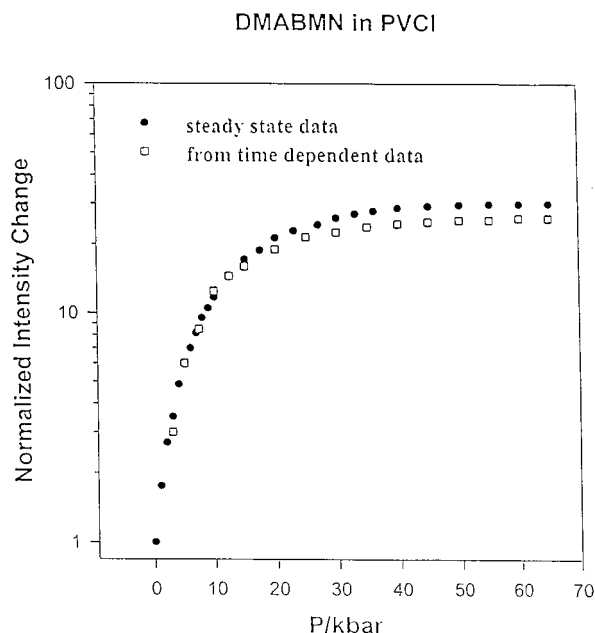


Figure 8. Effect of pressure on the emission efficiency of DMABMN in PVCl: (●) from steady-state measurements and (□) predicted from time-dependent data. Reprinted with permission from ref 31. Copyright 2000 Elsevier Press Ltd.

time-dependent results are reversible upon release of pressure. In PVA the intensity increases by a factor of ~11 in the first 20 kbar, and then it levels with a reproducible rise of 10–15% to near 45–50 kbar. For PVCl the intensity increases by a factor of ~30 in the first 25 kbar and then levels. Note that the increase near 45–50 kbar in PVA is reproduced by the time-dependent data; at present we have no definite cause for this second rise. For PVA the glass transition T_g is ~35 °C, while for PVCl, it is about 110–120 °C. Evidently, the PVA is sufficiently pliable to present less resistance to the twist.

It should be mentioned that at 1 atm the change in time dependence in PVCl was very rapid, and we could not deconvolute the instrument response accurately. At 3 kbar or above, the fit could be made satisfactorily.

Summary

These two recent examples, selected from a much more extensive set of studies, illustrate how pressure tuning spectroscopy can help characterize complex excitations and test models for processes of potential technological importance.

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