J. Phys. Chem. A **1997,** *101,* 5753−5757

High-Pressure Tuning of One- and Two-Photon-Induced Fluorescence of an Organic Crystal NDPB†

Z. A. Dreger, G. Yang, J. O. White, and H. G. Drickamer*

*School of Chemical Sciences, Department of Physics and The Frederick Seitz Materials Research Laboratory,
University of Illinois, 600 S. Mathews Avenue, Urbana, Illinois 61801-3792*

Received: April 28, 1997; In Final Form: June 4, 1997⊗

We report strongly pressure-dependent up-conversion fluorescence from an organic crystal, 4-(*p*-nitrophenyl)-3,4-dihydropyrazo[*c*]-benzo[*b*]morpholine (NDPB). The fluorescence has a similar pressure dependence following both one- and two-photon excitation. In both cases, we observe a significant shift of the emission spectrum to lower energies and decrease of emission intensity in a relatively narrow pressure range (0−20 kbar). Time-resolved measurements of fluorescence decay yield two lifetimes corresponding to the local and charge-transfer state, which decrease with pressure. Similar pressure dependence of the emission energies and lifetimes in one- and two-photon-induced fluorescence indicate that in both cases the same excited states participate in the fluorescence. The same decrease of fluorescence intensity in both cases indicates that the one- and two-photon absorption spectra have similar pressure dependence.

1. Introduction

High-pressure tuning (HPT) of the electronic properties of various organic molecular systems by means of one-photon absorption (OPA) has been a subject of numerous investigations in the past (see e.g. refs 1−4). It has been demonstrated that high pressure as a perturbing variable can be a very useful tool in the study of electronic processes by altering the interaction between molecules in a continuous and controlled fashion. From the practical point of view, pressure can be used to tune the emission from a lasing medium. Moreover, pressure dependence of the emission efficiency is a valuable probe of the interaction between an excited molecule and its surroundings. Up to now, to our knowledge, all high-pressure luminescence experiments have been done with one-photon excitation. In this paper we present the first comparison of the pressure dependence of one- and two-photon-induced fluorescence (O-TPIF).

Multiphoton processes have become widely accessible since the advent of pulsed high-power lasers. In practice, two-photon absorption (TPA) spectroscopy has many advantages over the conventional OPA due to its higher spatial resolution, better background rejection, deeper penetration depth, and reduced photobleaching. In addition, the different selection rules followed by two-photon excitation allow one to populate electronic states that are not accessible with one-photon excitation. In molecular systems, TPA occurs at a chromophore in which transitions to states of the same parity are allowed, a reversal of the parity rule of OPA.[5−9] The excitation rate for TPA is proportional to the square of the incident intensity.

One probe of two-photon processes is two-photon-induced fluorescence (TPIF) called also up-conversion fluorescence. In general, the theory of TPIF presupposes the existence in the excited system of intermediate states, which may be of various natures. They may be real; i.e., they may have a finite, rather long lifetime. In this case, the excitation of the emitting states can be realized as a result of a consecutive (stepwise) absorption of two photons on the same molecule. However, in most organic molecules, the intermediate states are virtual and the two photons are absorbed simultaneously. In this case, the electronic transition is induced when two photons combine via the imaginary portion of the third-order susceptibility, which is the higher-order term of nonlinear susceptibility capable of producing frequency combinations corresponding to molecular transitions.[10] This two-photon absorption has a cross section that is typically on the order of 10^{-50} (cm^4 s)/(photon molecule). For many years, due to the relatively small TPA cross sections of most materials, two-photon processes found limited applications. Lately, progress in the synthesis of molecules with large TPA cross sections has opened up numerous practical applications of TPA.[11,12] These applications include up-conversion lasers,[13] two-photon laser scanning fluorescence microscopy,[14,15] three-dimensional optical data storage,[16,17] and photodynamic therapy.[18]

In this paper we use high pressure to modify the molecular electronic states and thus the fluorescence in an organic compound that exhibits strong one- and two-photon-induced fluorescence. The experiments presented here serve three purposes: (i) they demonstrate that a two-photon absorption phenomenon occurs and can be successfully measured under high-pressure conditions; (ii) they show that pressure can be used to tune up-conversion fluorescence; (iii) they compare the pressure tunability of one- and two-photon-induced emission in a case where the intermediate state is virtual. For our study we chose 4-(*p*-nitrophenyl)-3,4-dihydropyrazo[*c*]-benzo[*b*]morpholine (NDPB), a recently synthesized organic compound with intramolecular charge transfer, which shows efficient up-conversion.[19,20]

2. Experiment

A schematic diagram of the experimental setup for the generation of one- and two-photon induced emission using a diamond anvil cell (DAC) is shown in Figure 1. A mode-locked Nd:YLF (neodymium yttrium lithium fluoride) laser with a 76 MHz train of 50 ps pulses at 1053 nm was the source of two-photon excitation. The peak power in the pulse train is ∼4.5 kW. In the case of one-photon excitation, we use either a CW He-Cd laser at 441.6 nm or the second harmonic from the Nd:

---

† This work was supported in part by the Basic Energy Sciences Division of the Department of Energy under Contract DEFG02-91R45439.

* To whom correspondence should be sent.

⊗ Abstract published in *Advance ACS Abstracts,* July 15, 1997.

S1089-5639(97)01435-7 CCC: $14.00

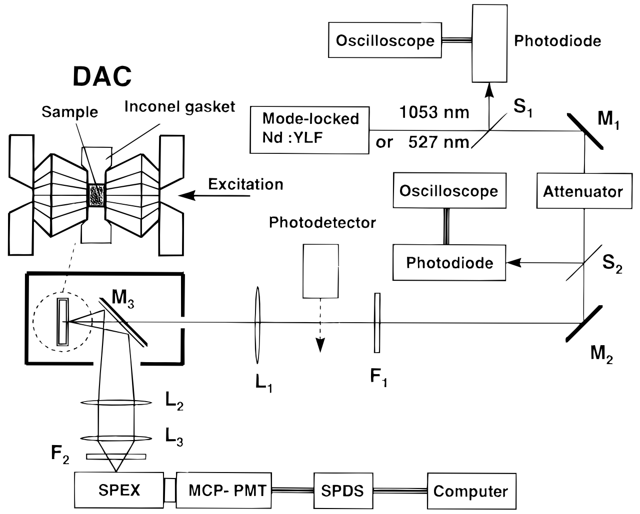

Figure 1. Schematic diagram of the experimental setup. DAC, diamond anvil cell; M_1, M_2, M_3, mirrors; L_1, L_2, L_3, lenses; S_1, S_2, beam splitters; F_1, long-wavelength band-pass filter; F_2, short-wavelength band-pass filter; SPEX, spectrometer; MCP-PMT, microchannel plate-photomultiplier; SPDS, single-photon detection system.

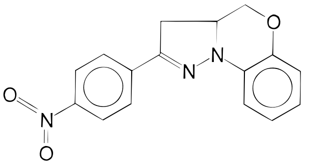

Figure 2. Molecular structure of 4-(*p*-nitrophenyl)-3,4-dihydro-pyrazo-[*c*]-benzo[*b*]morpholine (NDPB).

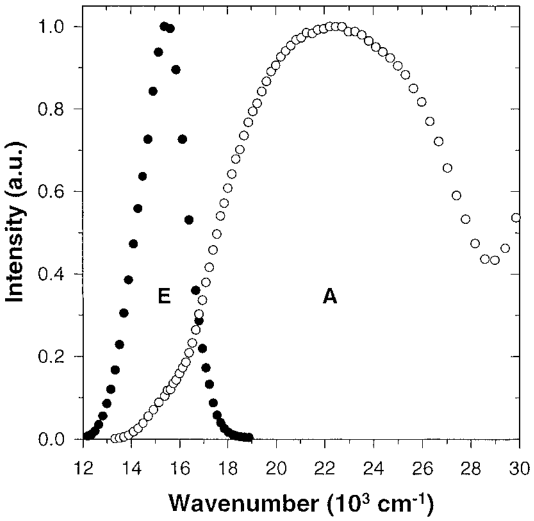

Figure 3. Absorption and emission spectra of NDPB upon one-photon excitation.

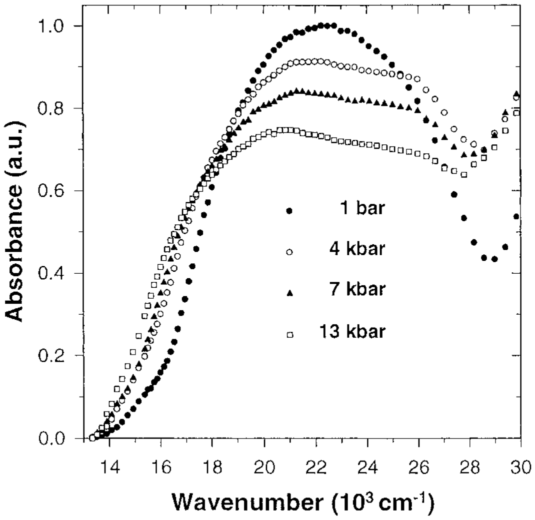

Figure 4. Effect of pressure on the one-photon absorption spectrum of NDPB.

YLF laser at 526.5 nm. In the TPA experiments the typical pump intensity in the sample is ~0.8 MW/cm^2 and can be varied in the range 0.15−2.5 MW/cm^2 by an attenuator. In the case of two-photon excitation, a long-wavelength pass filter (F_1) is inserted before the sample to eliminate any light from the laser at 526.5 nm. A colored glass filter (F_2) was placed in front of the entrance slit of the spectrometer to block the scattered pump light. The one- and two-photon-induced fluorescence spectra are dispersed with an 0.25 m spectrometer and detected by a microchannel plate photomultiplier tube (MCP-PMT) coupled to a single-photon detection system (SPDS) and computer. The SPDS consisted of a constant fraction differential discriminator, a time-to-amplitude converter, and a pulse height analyzer. All spectra are corrected for the sensitivity of the spectrometer and PMT and transmission of the filters. The experimental setup for the UV−vis absorption measurements under pressure has been described elsewhere.[21]

High pressure is generated in a gasketed Merrill-Bassett type DAC at room temperature, utilizing low-fluorescence UV-transmitting diamonds. Microcrystals of NDPB are suspended on a thin polymeric film (poly(vinyl alcohol)) and placed in a 0.3 mm hole in an Inconel gasket. Glycerol serves as a pressurizing medium. Pressure is determined by monitoring the shift of the R_1 fluorescence from a small ruby chip in the same chamber. The shift is linear (0.0365 nm/kbar) up to 200 kbar.[22] A CW He-Cd laser line at 441.6 nm is used to pump the ruby.

NDPB, a derivative of pyrazoline, is synthesized according to the method described in ref 23. The microcystals are approximately (0.01 × 0.01 × 0.06) mm^3 in size.

3. Results

The NDPB crystal (see Figure 2) shows a strong OPA in a wide spectral range extending from UV to vis above a low-energy threshold at 13.3×10^3 cm^{-1} ≡ 750 nm (Figure 3). Below 750 nm NDPB is highly transparent, and the absorption at 1053 nm is negligible. One-photon excitation of the sample within the main absorption band induces strong fluorescence with a spectral maximum located at 15.5×10^3 cm^{-1} (645 nm). This emission peak is significantly shifted to lower energy with respect to the main absorption band. Although the absorption spectrum has a complex shape (perhaps several overlapped transitions are involved), one can easily see that the Stokes shift exceeds 5×10^3 cm^{-1}. This large Stokes shift can be attributed to the intramolecular charge redistribution that takes place between absorption and emission. With increasing pressure, the absorption and emission intensity decrease and shift to lower energy. The absorption spectrum of NDPB broadens with pressure and then splits into two bands (Figure 4). A gradual decrease of the absorption also occurs.

Illuminating the NDPB crystal with an intense infrared beam produces the same red emission as is normally caused by visible light. Intensity of this emission depends quadratically (exponent 2 ± 0.1) on the peak intensity of the pump laser, indicating two-photon absorption. The exponent is almost pressure independent. In Figure 5 we show one- and two-photon fluorescence spectra of NDPB as a function of pressure. A comparison of the upper and lower graphs reveals that (i) in both cases the fluorescence peak is located at 645 nm (at 1 bar), (ii) spectral shapes are similar, but the fluorescence bandwidth

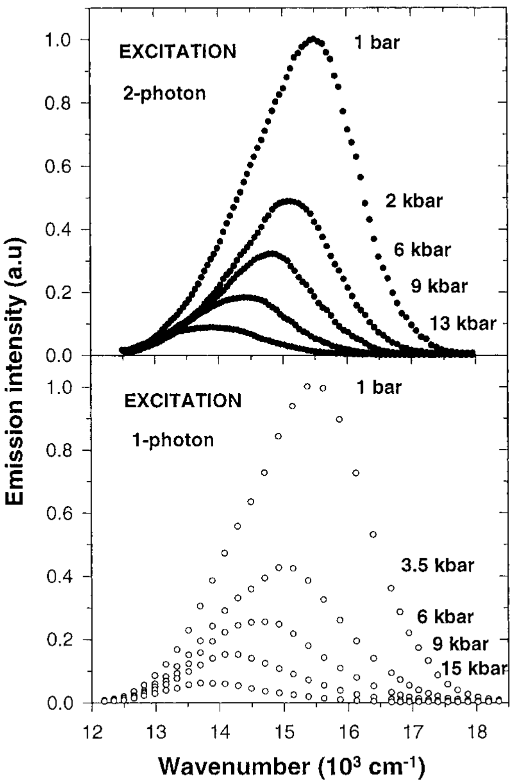

Figure 5. Fluorescence spectrum of NDPB at several pressures upon one- and two-photon excitation.

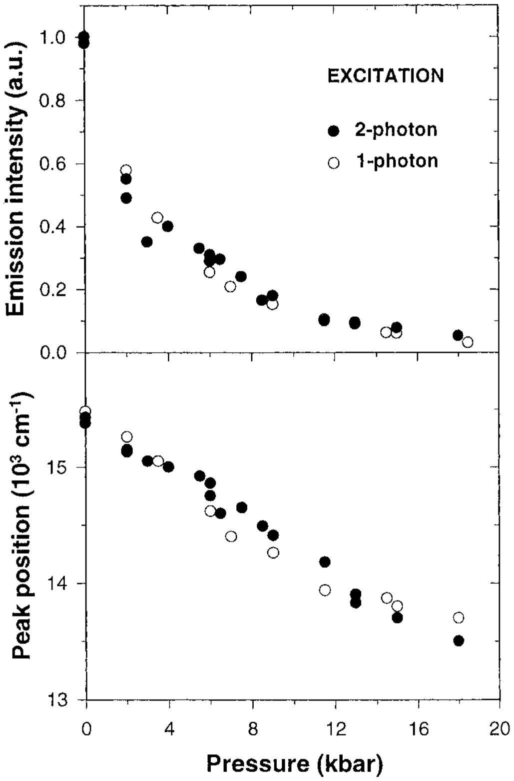

Figure 6. Pressure tuning of the intensity and energy of the emission spectra of TPIF (●) and OPIF (○) of NDPB.

(fwhm) is a few hundreds of cm^{-1} narrower in the case of TPA than OPA, and (iii) under pressure both spectra shift to lower energy in a similar way. The changes under pressure are displayed in Figure 6. The effect of pressure is spectacular because over the relatively narrow pressure range (15 kbar) the emission peak shifts ~2 × 10^3 cm^{-1} (100 nm) to lower energies. A significant decrease of the emission intensity is associated with this shift. This effect is reversible. It is also striking that the changes in emission intensity and peak position with pressure are almost identical for OPA and TPA.

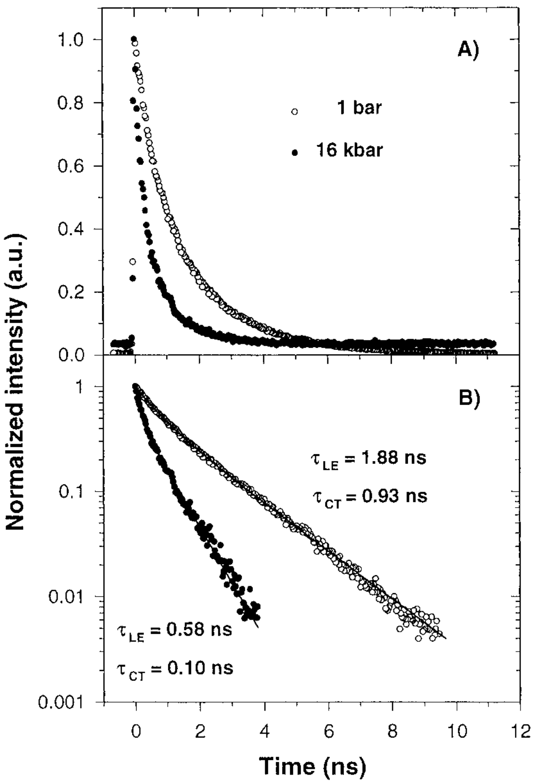

Figure 7. (A) Decay of TPIF intensity of NDPB at 1 bar (atmospheric pressure) and 16 kbar. (B) Log plot and double exponential fit to the above results.

To characterize the emitting state induced by OPA and TPA, a decay of OPIF and TPIF was measured under high-pressure conditions. In Figure 7A, for example, typical decays of TPIF at two different pressures are presented. From these results, one notices that decays are not single exponential, and with increasing pressure the decay becomes faster. A double-exponential function fits the results reasonably well (see Figure 7B). The results from decay of OPIF and TPIF under different pressures are combined in Figure 8. In the entire pressure range, the decay exhibits two components and both decrease with pressure. The character and magnitude of the changes under pressure are very similar for OPA and TPA.

4. Discussion

A similarity of the one- and two-photon fluorescence spectra implies that the emission of NDPB in both cases takes place from the same excited state. Furthermore, the double-exponential decay of OPIF and TPIF and the large Stokes shift indicate that two excited states are involved and that the fluorescence originates in a state that is distinct from the local excited state. Thus, we propose that absorption of one or two photons by the molecule takes place to the same local excited state (LE) from which the molecule may relax to the ground state (G) or transform to a charge-transfer (CT) state. The CT state can then decay radiatively or nonradiatively to the ground state. Because the shape of the emission spectrum is essentially independent of pressure, the observed fluorescence, which is significantly shifted with respect to the absorption band, is considered to originate essentially from the CT state. The processes mentioned above are schematically represented in Figure 9. In the case of pulsed illumination, this model yields

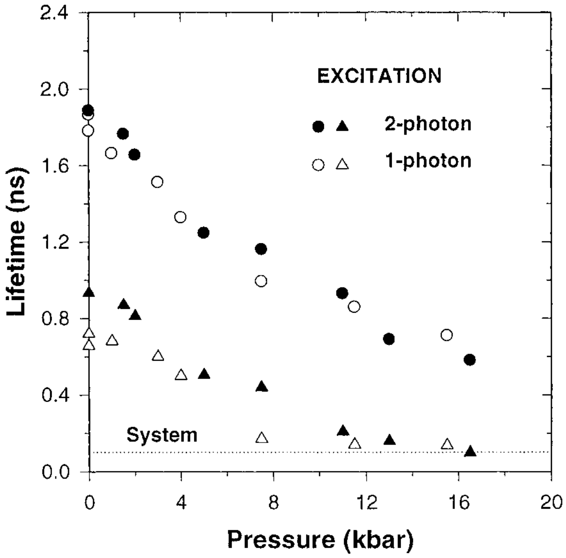

Figure 8. Pressure effect on the fluorescence decay induced by one- and two-photon excitation: ○, ●, local excited state (LE); △, ▲, charge-transfer state (CT). Dashed line indicates the time response of the detection system.

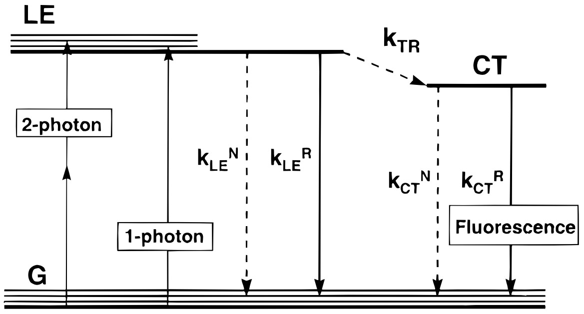

Figure 9. Kinetic model: G, ground state; LE, local excited state; CT, charge transfer state; bold lines, lowest ground and excited state. The meaning of the various rate constants is explained in the text.

the following expressions for time-averaged and instantaneous fluorescence intensity:

$$I_{\mathrm{FL}} = A_{\mathrm{abs}}(1 + k_{\mathrm{LE}}{}^{\mathrm{N}}/k_{\mathrm{TR}})^{-1}\,(1 + k_{\mathrm{CT}}{}^{\mathrm{N}}/k_{\mathrm{CT}}{}^{\mathrm{R}})^{-1} \quad (1)$$

$$I_{\mathrm{FL}}(t) = B\exp[-(k_{\mathrm{LE}} + k_{\mathrm{TR}})t] + (1 - B)\exp[-k_{\mathrm{CT}}t] \quad (2)$$

$$\text{with} \quad B = N_{\mathrm{LE}}(0)k_{\mathrm{TR}}/N_{\mathrm{CT}}(0)[k_{\mathrm{CT}} - k_{\mathrm{LE}} - k_{\mathrm{TR}}] \quad (3)$$

$$\text{and} \quad k_{\mathrm{LE}} = k_{\mathrm{LE}}{}^{\mathrm{N}} + k_{\mathrm{LE}}{}^{\mathrm{R}}, \quad k_{\mathrm{CT}} = k_{\mathrm{CT}}{}^{\mathrm{N}} + k_{\mathrm{CT}}{}^{\mathrm{R}} \quad (4)$$

where A_{abs} is replaced by αI_{ex} for OPA or $\delta I_{\mathrm{ex}}{}^2$ for TPA; α and δ are absorption coefficients, respectively for OPA and TPA; symbols $k_{\mathrm{LE}}{}^{\mathrm{N}}$, $k_{\mathrm{LE}}{}^{\mathrm{R}}$ and $k_{\mathrm{CT}}{}^{\mathrm{N}}$, $k_{\mathrm{CT}}{}^{\mathrm{R}}$ stand for nonradiative (N) and radiative (R) rates, respectively, for the LE and CT states; k_{TR} stands for the transformation rate constant; $N_{\mathrm{LE}}(0)$ and $N_{\mathrm{CT}}(0)$ are the populations, respectively, of the LE and CT state at the time of excitation ($t = 0$).

Equation 2 fits successfully the fluorescence decay curves obtained at all pressures and for either one or two-photon excitation (Figure 7B). The changes in the decay curves under pressure are shown in Figure 8. It should be mentioned that the preexponential factor B (eq 3) changed under pressure from 0.62 at 1 bar to 0.52 at 16 kbar.

To analyze the effect of pressure on fluorescence intensity, it is convenient to consider its relative changes with pressure. Therefore, eq 1 is rewritten to the following form

$$\frac{I_{\mathrm{FL}}(p)}{I_{\mathrm{FL}}(0)} = \frac{\tilde{a}(\mathrm{p})\,\tau_{\mathrm{CT}}(p)\,\tau_{\mathrm{LE}}(p)\,k_{\mathrm{CT}}^{\mathrm{R}}(p)\,k_{\mathrm{TR}}(p)}{\tilde{a}(0)\,\tau_{\mathrm{CT}}(0)\,\tau_{\mathrm{LE}}(0)\,k_{\mathrm{CT}}^{\mathrm{R}}(0)\,k_{\mathrm{TR}}(0)} \quad (5)$$

where here "p" and "0" stand, respectively, for high and atmospheric pressure (1 bar); $\tau_{\mathrm{LE}} = (k_{\mathrm{LE}} + k_{\mathrm{TR}})^{-1}$ and $\tau_{\mathrm{CT}} = k_{\mathrm{CT}}{}^{-1}$ are lifetimes, respectively for the LE and CT state, and $\tilde{a}(p)$ is an absorption coefficient that is equal to $\alpha(p)$ or $\delta(p)$, respectively, for OPA and TPA.

From independent lifetime and one-photon absorption experiments, we know the pressure dependences of $\tau_{\mathrm{CT}}(p)$, $\tau_{\mathrm{LE}}(p)$, and $\alpha(p)$. Thus, in the first approximation we assume that the remaining parameters in eq 5 are pressure independent. With this assumption eq 5 reduces to

$$\frac{I_{\mathrm{FL}}(p)}{I_{\mathrm{FL}}(0)} \approx \frac{\alpha(p)\,\tau_{\mathrm{CT}}(p)\,\tau_{\mathrm{LE}}(p)}{\alpha(0)\,\tau_{\mathrm{CT}}(0)\,\tau_{\mathrm{LE}}(0)} \quad (6)$$

A comparison of eq 6 with experimental results is shown in Figure 10. For the case of both OPIF (dashed line) and TPIF (solid line), eq 6 follows the experimental points reasonably well. Thus our assumption about the pressure independence of $k_{\mathrm{CT}}{}^{\mathrm{R}}$ and k_{TR} may be correct. Because the fluorescence of NDPB shifts to lower energies with increasing pressure, a decrease of the emission intensity could be caused by enhanced nonradiative relaxation. According to the energy gap law, nonradiative relaxation is enhanced when the excited and ground states are in closer proximity.[24,25]

As can be seen in Figure 10 the intensity changes in OPIF (dashed line) and TPIF (solid line) are more or less the same. A small difference between these curves results from slightly different excited state lifetimes. Similarities between one- and two-photon *fluorescence*, indicated by experimental results and the model, imply that the pressure change in one- and two-photon *absorption* is also comparable. Thus in the case of the NDPB crystal, the one-photon behavior is a good measure of the pressure changes in TPA. This result suggests that the same excited states are reached regardless of the difference in excitation modes for TPA and OPA. Because the parity restrictions may be relaxed in the case of molecules with no center of symmetry, the similarity between TPA and OPA is not surprising.[26,27] In fact, for molecules having no center of symmetry, it has been predicted that one-photon-allowed transitions are likely to show nonnegligible two-photon absorption if the excitation changes the dipole moment.[28] Thus, two-photon transitions may proceed via a mechanism involving the intermediate states, which include the virtual states as well as the initial and final absorbing states. One consequence of the above consideration is that one observes here the same pressure dependence of the one- and two-photon-induced fluorescence.

5. Summary

We have shown that the fluorescence from crystalline NDPB exhibits a remarkable shift of 100 nm over a 20 kbar pressure range. Moreover, with increasing pressure there is also a significant decrease of the emission intensity and the excited state lifetimes. These effects are very similar for both one- and two-photon excitation. We show that the fluorescence properties of NDPB are governed by two forms of the molecule with different intramolecular charge separation that are reached in the excited state. Similarities in pressure dependence of one- and two-photon-induced *fluorescence* are caused by two factors: (i) the changes in one- and two-photon *absorption* are comparable, and (ii) *emission* comes from the same excited state in both cases.

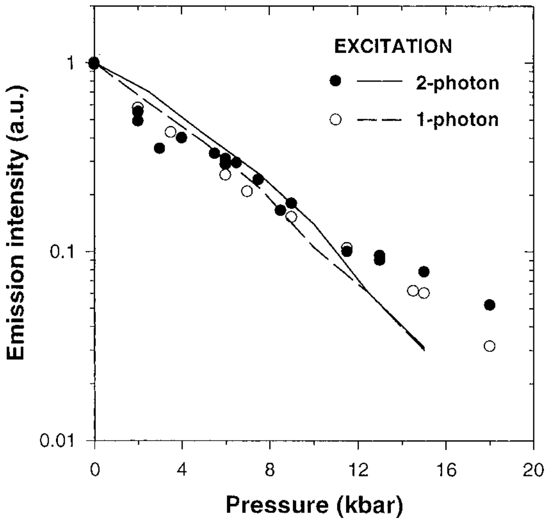

Figure 10. Comparison of the experimental changes of OPIF and TPIF intensity under pressure with the pressure dependence of the product of OPA coefficient and fluorescence lifetimes. Lines represent data obtained from eq 5.

Acknowledgment. The authors acknowledge support from the Division of Materials Science of the Department of Energy under Contract DEFG02-91R45439.

References and Notes

(1) Offen, H. In *Organic Molecular Photophysics*; Birks, J. B., Ed.; Wiley-Interscience Publishers: New York, 1973; Vol. 1, Chapter 3.

(2) Drickamer, H. G. *Annu. Rev. Phys. Chem.* **1982**, *33*, 25.

(3) Drickamer, H. G. In *Photochemistry and Photophysics*; Rabek, J. F., Ed.; CRC Press: Boca Raton, FL, 1989; Vol. 1, p 137.

(4) Drickamer, H. G.; Dreger, Z. A.; Lang, J. M. In *High Pressure Chemistry, Biochemistry and Materials Science*; Winter, R., Jonas, J., Eds.; Kluwer Academic Publishers: Dordrecht, 1993; p 43.

(5) Peticolas, W. L. *Annu. Rev. Phys. Chem.* **1967**, *18*, 233.

(6) McClain, W. M. *Acc. Chem. Res.* **1974**, *7*, 129.

(7) McClain, W. M.; Harris, R. A. In *Excited States*; Lim, E. C., Ed.; Academic Press: New York, 1977; p 1.

(8) Birge, R. R. In *Ultrasensitive Laser Spectroscopy*; Kliger, D. S., Ed.; Academic Press: New York, 1983; p 109.

(9) Goodman, L.; Rava, R. P. *Acc. Chem. Res.* **1984**, *17*, 250.

(10) Beljonne, D.; Brédas, J. L.; Cha, M.; Torruellas, W. E.; Stegeman, G. I.; Hofstraat, J. W.; Horsthuls, W. H. G.; Möhlmann, G. R. *J. Chem. Phys.* **1995**, *103*, 7834.

(11) Bhawalkar, J. D.; He, G. S.; Prasad, P. N. *Rep. Prog. Phys.* **1996**, *59*, 1041.

(12) Prasad, P. N.; He, G. S. In *Nonlinear Optical Materials, Theory and Modeling*; Karna, S. P., Yeats, A. T., Eds.; ACS Symposium Series 628; American Chemical Society: Washington DC, 1996; p 225.

(13) Zhao, C. F.; He, G. S.; Bhawalkar, J. D.; Park, C. K.; Prasad, P. N. *Chem. Mater.* **1995**, *7*, 1979.

(14) Denk, W.; Strickler, J. H.; Webb, W. W. *Science* **1990**, *248*, 73.

(15) Denk, W.; Piston, D. W.; Webb, W. W. In *Handbook of Biological Confocal Microscopy*; Pawley, J., Ed.; Plenum Publishers: New York, 1995; p 445.

(16) Parthenopoulos, D. A.; Rentzepis, P. M. *Science* **1989**, *245*, 843.

(17) Strickler, J. H.; Webb, W. W. *Opt. Lett.* **1991**, *16*, 1780.

(18) Lenz, P. *J. Phys. IV* **1994**, *4*, 237.

(19) Wang, H. Z.; Zheng, X. G.; Mao, W. D.; Yu, Z. X.; Gao, Z. L.; Yang, G. Q.; Wang, P. F.; Wu, S. K. *Appl. Phys. Lett.* **1995**, *66*, 2777.

(20) Dreger, Z. A.; Yang, G.; White, J. O.; Drickamer, H. G. *Bull. Am. Phys. Soc.* **1997**, *42*, 596.

(21) Dreger, Z. A.; Drickamer, H. G. *Chem. Phys. Lett.* **1991**, *179*, 199.

(22) Barnett, J. D.; Block, S.; Piermarini, G. *Rev. Sci. Instrum.* **1973**, *44*, 1.

(23) Shimizu, T.; Hayashi, Y.; Miki, M.; Teramura, K. *J. Heterocycl. Chem.* **1990**, *27*, 1669.

(24) Englman, R.; Jortner, J. *Mol. Phys.* **1970**, *18*, 145.

(25) Dreger, Z. A.; Lang, J. M.; Drickamer, H. G. *Z. Phys. Chem.* **1994**, *184*, 173.

(26) Xu, C.; Webb, W. W. *J. Opt. Soc. Am. B* **1996**, *13*, 481.

(27) Fischer, A.; Cremer, C.; Stelzer, E. H. K. *Appl. Opt.* **1995**, *34*, 1989.

(28) Dick, B.; Hohlneicher, G. *J. Chem. Phys.* **1982**, *76*, 5755.