High-Pressure Effects on Fluorescence of Anthracene Crystals

Z. A. Dreger,* H. Lucas, and Y. M. Gupta

Institute for Shock Physics and Department of Physics, Washington State University, Pullman, Washington 99164-2816

Pressure-induced changes on the fluorescence spectra of anthracene crystals were examined up to 5 GPa. Changes in the spectra are demonstrated to be sensitive both to the sample morphology and to the compression conditions (e.g., hydrostaticity). Under hydrostatic pressure, there was no excimer fluorescence from anthracene single crystals. This result is in sharp contrast to previously published data. Because the normal fluorescence was not obscured by the excimer emission, pressure-induced energy shifts for vibronic bands could be determined. These shifts cannot be described adequately by available theoretical descriptions. Strong excimer fluorescence from anthracene crystals was observed only under nonhydrostatic conditions. This fluorescence is attributed to the emission from structural defects formed at the onset of plastic deformation in the crystals. The fluorescence spectra of polycrystalline samples exhibit a new weak band, identified as defect-related excimer emission. The intensity of this emission can be enhanced by pressure, mainly because of the increasing concentration of defects.

I. Introduction

The application of high pressure to solids is a powerful method for changing their physical and chemical properties. Various approaches are used to understand the response of compressed solids at the atomic and/or molecular level.[1−3] In particular, high-pressure optical spectroscopy provides a useful tool to examine the changes in intermolecular interactions and dynamics in molecular solids. Pressure is a well-suited parameter for the study of molecular solids, because of the relative weakness of their intermolecular forces. Thus, modest pressures can produce large changes in the electronic, vibrational, and crystal structure of these solids. Apparently, the occurrence of these changes is dependent not only on the molecular and crystal structure of the solid, but also, to some degree, on the crystal quality and pressure conditions that are imposed on the crystal.

In this paper, we present results of fluorescence studies on anthracene crystals to demonstrate the effects of sample morphology and hydrostaticity on the electronic structure of this model molecular crystal. Examination of these effects has the potential for providing new data and, thus, improving the understanding of pressure-induced changes in molecular crystals.

Anthracene was chosen for this study, as a representative of the large class of polycyclic hydrocarbons that have served for a long time as model compounds for organic molecular crystals. Although anthracene has been studied extensively under high-pressure compression in the past,[4−8] the results reported from different laboratories vary significantly. Unresolved questions concern two issues: a possible second-order phase transition at ∼2.4 GPa,[9−11] and the occurrence of pressure-induced excimer fluorescence.[12−18] Here, we focus on pressure-induced changes in fluorescence, to clarify the origin of the excimer emission.

Under ambient conditions, the fluorescence spectrum of anthracene crystals displays a profound vibrational progression from the first excited state—the ^1L_a band. Under high pressure,

significant changes in the spectrum have been observed.[12−21] The main feature is a loss of normal fluorescence intensity and an almost simultaneous appearance of a broad, featureless band at much lower energies than the normal fluorescence (between ∼3×10^3 and 6×10^3 cm^{-1}). Previously, the new band was observed at pressures as low as 0.7 GPa; at 1.5 GPa, virtually all the fluorescence occurred at the new spectral location.[12−14] This emission was assigned to the fluorescence from excimer states[22] that were formed because of optical excitation of the crystal under high pressure. It was proposed[16] that, at high pressure, a pre-dimer configuration (the association of two closely interacting molecules) could be formed in defected regions of the crystal, resulting in the creation of deep trapping centers of an excimer nature. An alternative explanation for the new band was proposed based on an exciton self-trapping phenomenon.[19−21] This process was considered to be inherent to neat anthracene. In this model, the excitation was assumed to be trapped in lattice distortions that were produced by excitons themselves. As a result, a new potential energy minimum is formed, which leads to self-trapping of the exciton and finally to the new fluorescence band.

The new band in the fluorescence spectrum persists, even upon pressure release,[12−16] indicating irreversible changes to the crystal. This observation has not attracted enough attention in previous studies. The occurrence of irreversible changes raises an important question: what is the role of pressure in the excimer emission? To clarify this issue, the experiments reported here were performed under well-controlled pressure conditions and with single crystals of good quality. Using this approach, we can mitigate the problems that have been encountered in previous measurements.[12−18] To characterize the factors that are responsible for the occurrence of the excimer emission, single-crystal results are compared to results obtained with polycrystalline samples. Also, the single-crystal emission was examined under nonhydrostatic conditions.

The remainder of this paper is organized as follows. Sample preparation and experimental techniques are described in the next section (Section II). Section III includes experimental results

* Author to whom correspondence should be addressed. E-mail: dreger@wsu.edu.

High-Pressure Effects on Fluorescence of Anthracene

J. Phys. Chem. B, Vol. 107, No. 35, 2003 **9269**

and discussion and is divided into two parts. In Part A, the effects of pressure on the normal fluorescence are presented and the single-crystal fluorescence is characterized; this part also includes a comparison between the fluorescence of single crystals and that of polycrystals. Part B describes the excimer fluorescence; the occurrence of this emission in single crystals under nonhydrostatic conditions and in polycrystalline samples is examined. The main findings are summarized in Section IV.

II. Experimental Method

Experiments were performed on two different sample types: single crystals and polycrystals. Single crystals were grown either from the solution or the vapor phase. Zone-refined anthracene with 99.9% purity (from Aldrich) was used to grow single crystals from dichloroethane (99.8%, high-performance liquid chromatography (HPLC) grade) solvent.[23] The vapor-grown crystals were obtained from Prof. N. Karl (University of Stuttgart) and Prof. D. Cleary (Gonzaga University). In all cases, the crystals were of a high quality. Examination under a stereoscope (at a magnification of $160\times$) of small single crystals typically used in our experiments did not reveal any microscopic imperfections. Polycrystalline samples were prepared from single crystals. The grain size in the powder particles was estimated to be few micrometers.

High pressure was generated in a diamond-anvil cell (DAC), with a modified Merrill−Bassett design, utilizing low-fluorescence type II diamonds. Brilliant-cut diamonds with 16 facets and a culet size of 0.5 mm were used. The sample was confined in the space between the diamonds and an Inconel gasket. The gasket was pre-indented to 0.1 mm and had an aperture of 0.2 mm. Crystals loaded into the cell had a platelet shape, with lateral dimensions of $\sim$0.1 mm in the (001) plane, and were 0.03 mm thick. For polycrystalline samples, the gasket aperture was either half or completely full of polycrystals. In the latter case, the sample itself served as a pressure medium. In all other experiments, glycerol (Aldrich, 99.5+%, spectrophotometric grade) was used as a pressure-transmitting medium. Glycerol provides hydrostatic conditions to a pressure of at least 7 GPa at room temperature and does not react with anthracene. Pressure in the cell was determined by monitoring the shift of fluorescence of R-lines from a ruby chip.[24,25] A 532-nm line from a continuous-wave (CW) diode-pumped laser (CrystaLaser) was used to excite the ruby. The hydrostaticity of the environment in the DAC was determined by recording changes in the separation between the R_1 and R_2 lines and their spectral broadening.

Anthracene samples were excited using the 337-nm line from a nitrogen laser (model VSL-337ND-S with a DUO-220-dye laser module, Laser Science). An average power of $\sim$1 mW at 30 Hz was employed. Occasionally, different excitation lines, such as 365 and 425 nm, were used. Laser plasma lines were removed from the laser output, using a narrow band interference filter. The laser beam, with a size of 5 mm^2, went through a lens assembly and was weakly focused onto the (001) plane of the crystal. The fluorescence signal from the sample collected in a backward-scattering geometry was directed through a 385-nm-long band-pass filter and another lens assembly into an optical fiber. It was then delivered to the 0.1-mm entrance slit of a spectrometer (model SpectraPro 150, ARC) equipped with a 300 grooves/mm grating that was blazed at 500 nm. The recorded spectral range extended from 380 nm to 800 nm, corresponding to the energy range of 26.3×10^3 to 12.5×10^3 cm^{-1}. The detector used was a liquid-nitrogen-cooled charge-coupled device (CCD) (1024×256 back-illuminated chip,

Roper Scientific). All recorded spectra were corrected for any spectral variation of the detection system. For this purpose, the spectral sensitivity of the entire system (collection, dispersion, and acquisition combined) was calibrated using a tungsten-filament quartz halogen lamp (model EN-101, Eppley) as a standard light source.

III. Results and Discussion

III.A. Normal Fluorescence. Fluorescence spectra of anthracene single crystals and polycrystals were measured up to pressures of 5 GPa at room temperature. Above pressures of 5−6 GPa, cracks appeared on single-crystal surfaces, causing irreversible changes in the spectra. For this reason, all experiments were performed at pressures of ≤5 GPa. Figure 1 illustrates representative, pressure-induced changes in the spectra of single crystals and polycrystals. For polycrystals, the results presented are from experiments with (Figure 1B) or without (Figure 1C) the pressure-transmitting medium. For the latter, the abbreviated term "no medium" will be used hereafter.

III.A.1. Single-Crystal Emission Spectra. At 1 atm, a typical single-crystal fluorescence spectrum shows five vibronic transitions (denoted as 0-n, where $n = 0-4$) from the lowest excited singlet state to the ground state; ^1L_a-electronic transition. Because the emission of the 0-0 transition is partially reabsorbed, its energy cannot be determined accurately. The energy of this transition is estimated to be $\sim$24.6 $\times$ 10^3 cm^{-1}. Energies of the remaining transitions are listed in Table 1. They are obtained by fitting the fluorescence spectrum with Gaussian peaks. In the fitting procedure, the widths of the 0-2, 0-3, and 0-4 vibronic bands for a given pressure are fixed at the same value. However, the 0-0 and 0-1 bands assume variable widths, as a result of the reabsorption effect. With increasing pressure, as can be observed in Figure 1, the fluorescence spectrum shifts strongly to lower energies while preserving the entire vibrational structure. This result is in sharp contrast to the previously published data,[12−19] where a new band appeared at $\sim$20 $\times$ 10^3 cm^{-1} at pressures as low as 1 GPa. There is no such band in our data, and the pressure-induced changes (Figure 1A) are totally reversible. The observed changes also include gradual broadening and decreasing intensity of the vibronic bands.

To ensure that the observed effects are reproducible, experiments were performed on single crystals grown by two different methods (see section II). Regardless of the crystal source, the same behavior was observed. All single crystals studied showed no additional band in the spectrum associated with excimer emission, indicating that the excimer emission is not formed in anthracene single crystals that have been subjected to hydrostatic compression.

We attribute the differences between our results and previously published results[12−18] to two factors: (i) the presence of defects and (ii) nonhydrostaticity. These are further examined in experiments that have been performed on single crystals under nonhydrostatic conditions and on polycrystalline samples. The results of these experiments are presented in Section III.B.

The absence of excimer emission from hydrostatically compressed anthracene single crystals has important implications. It permits the examination of pressure effects on the normal fluorescence of anthracene and, thus, on its electronic structure. This information could not be obtained previously, because the normal fluorescence was obscured or entirely replaced by the broad excimer band. Consequently, previous analysis of the effects of pressure on the electronic structure of anthracene was based only on the absorption data and was, therefore, very limited.
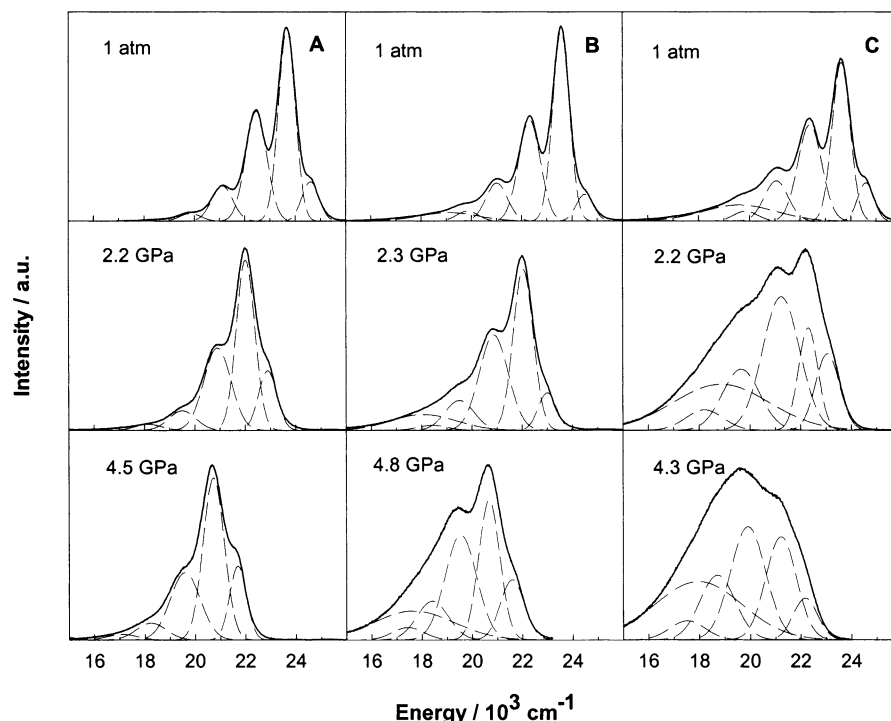
Figure 1. Fluorescence spectra of anthracene at different pressures: column (A) single crystal, column (B) polycrystal, column (C) polycrystal (no medium). The spectra are arbitrarily scaled. Dashed lines depict Gaussian peaks fitted to the spectra.

TABLE 1: Energy of Fluorescence Bands of Anthracene Crystals at Ambient and Elevated Pressure

band	$E_i(0),^a$ 10^3 cm^{-1}	$a_i,^b$ 10^3 cm^{-1} GPa^{-1}	$b_i,^c$ 10^3 cm^{-1} GPa^{-2}
	Single Crystal		
0-1	23.62	0.72	0.024
0-2	22.37	0.73	0.03
0-3	21.06	0.73	0.03
0-4	19.77	0.72	0.035
	Polycrystal		
0-1	23.63	0.75	0.033
0-2	22.38	0.73	0.03
0-3	21.07	0.74	0.03
excimer	19.3 ± 0.1	0.65	0.025
	Polycrystal (No Medium)		
0-1	23.6	0.62	0.028
0-2	22.38	0.59	0.031
0-3	21.07	0.64	0.03
excimer	19.6 ± 0.1	0.57	0.028

^{a} Standard deviation = ±0.04 × 10^3 cm^{-1}. ^{b} Standard deviation = ±0.02 × 10^3 cm^{-1} GPa^{-1}. ^{c} Standard deviation = ±0.005 × 10^3 cm^{-1} GPa^{-2}.

III.A.2. Single-Crystal Energy Shifts. Our fluorescence spectra provide direct information regarding the electronic structure of anthracene (energies, bandwidths, and intensities) under pressure. This information is new and is useful for understanding the intermolecular interactions in anthracene crystals.

The effects of pressure on energies of the vibronic bands in single crystals are presented in Figure 2. As the pressure increases, all vibronic bands shift to lower energies (red shift). The energy changes are nonlinear, with the departure from linearity being measurable at >1 GPa. The experimental data can be fitted well to a second-order polynomial of the following form: $E_i(P) = E_i(0) - a_i P + b_i P^2$. The calculated values of a_i, b_i, and $E_i(0)$ are listed in Table 1. The separation between the vibronic components is 1230, 1310, and 1260 cm^{-1} between the 0-n and 0-($n + 1$) transitions, where n = 1, 2, and 3, respectively. This separation reflects the contribution of several,
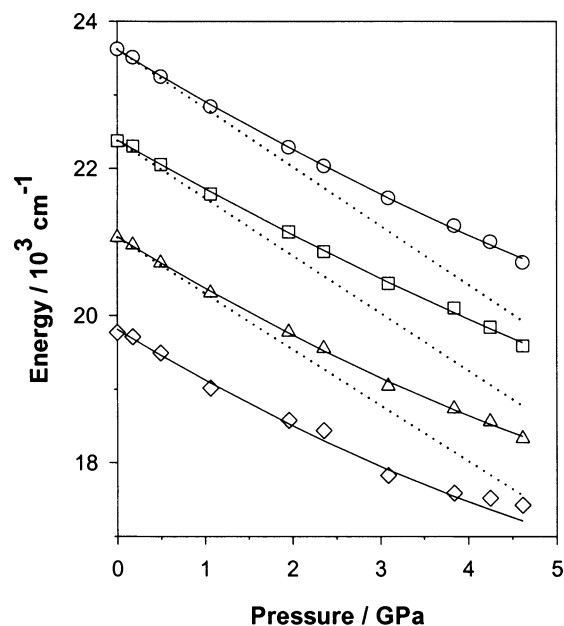

Figure 2. Effect of pressure on the energies of the vibronic bands in anthracene single crystals: (○) 0-1 transition, (□) 0-2 transition, (△) 0-3 transition, and (◇) 0-4 transition. Lines represent least-squares fit to the data, with parameters listed in Table 1. Dotted lines display results of theoretical calculations from ref 27.

totally symmetric C−C stretching modes of anthracene that are located between 1250 and 1630 cm^{-1}; these modes have been observed in Raman measurements.[11,17] At pressures of >5 GPa range, the energies of the vibronic bands decrease by 3000 (0-1), 2900 (0-2 and 0-3), and 2700 cm^{-1} (0-4), while their separations decrease by ~100 cm^{-1}. The total energy shift of the vibronic bands is higher than shifts that have been reported previously, on the basis of absorption measurements in polycrystalline samples.[26]

Energy shifts of electronic states in compressed molecular crystals have been studied theoretically using molecular exciton

theory.[6,27] Schipper has presented the most complete calculations to date,[27] and we compare his calculations to our experimental data to evaluate the applicability of this description for anthracene. According to the exciton theory,[28–30] the energy change of the singlet excited state (S) can be described by changes in the dispersion and resonance interactions in the crystal. For compressed anthracene crystals, the shift in energy of the excited states is expressed as follows:[27]

$$\Delta E_{\pm}^{S}(\vec{k}) = [\Delta D^{S} + \Delta I_{11}^{S}(\vec{k})] \pm \Delta I_{12}^{S}(\vec{k}) \qquad (1)$$

where ΔD^{S} is the change in the dispersion interaction between the excited molecule and the surrounding molecules; $\Delta I_{11}^{S}(\vec{k})$ and $\Delta I_{12}^{S}(\vec{k})$ are the changes in the resonance interactions (exciton transfer) between translationally equivalent and non-equivalent molecules, respectively; $\vec{k}$ is the exciton wave vector, and the symbol "$\pm$" represents the two bands of the excited state, corresponding to each molecular term (two molecules in a unit cell). The separation between the two bands (Davydov splitting) is ~ 100 cm^{-1} and is rarely observed in experiments at room temperature.

The dispersion and resonance terms exhibit different dependences on the intermolecular distance (R_{mn}) and are often presented as being proportional to $1/R_{mn}^{6}$ and $1/R_{mn}^{3}$, respectively. These dependencies are the main contributors to lattice compression effects on the excited states in the crystal.

To relate energy shift to lattice compression, the interaction expressions are expanded in terms of the displacement (strain) from the uncompressed value. In the limit of small displacements (according to ref 27, this approximation should be valid at pressures up to 4 GPa for anthracene), the mean energy shift for the ν vibronic transition can be presented as follows:

$$\Delta E_{S}^{s\nu} = \frac{1}{2}[E_{+}'(s\nu,u_i) + E_{-}'(s\nu,u_i)]\delta u_i \qquad (2)$$

where $E_{\pm}'(s\nu,u_i)$ are numerically calculated strain derivatives of the interaction energy and δu_i is the strain, expressed in the unit-cell coordinates.

Calculations of the energy shift as a function of pressure can be derived directly from the knowledge of strains that result from hydrostatic pressure. Using the experimentally determined elastic constants for anthracene,[31] the energy shifts that correspond to the ν vibronic band under pressure P were calculated:[27]

$$\Delta E_{S}^{s\nu}(P) = -k_{S}^{\nu}P \qquad (3)$$

with $k_{S}^{\nu} = 0.8 \times 10^{3}$, 0.8×10^{3}, 0.78×10^{3}, and 0.76×10^{3} cm^{-1} GPa^{-1}, for $\nu = 0$, 1, 2, and 3, respectively.

Some comments are merited when one compares eq 3 with the experimental data in Table 1 and Figure 2. The calculated energy shifts are in good agreement with the linear coefficients obtained from fluorescence measurements (see Table 1). However, eq 3 predicts a linear dependence, which does not match the experimental data as shown in Figure 2. Deviations of theoretical predictions from the measurements are large and total >30% (~ 1000 cm^{-1}) of the total energy shift measured at 4.5 GPa, indicating that the theoretical treatment inadequately describes the experimental data. Equation 3 seems to be applicable only for pressures below ~ 1 GPa, when strains are sufficiently small. Anthracene is a highly compressible solid; therefore, the nonlinear terms would be required both in the strain calculations and in the expansion of the interaction operator. This can be achieved by including the third-order
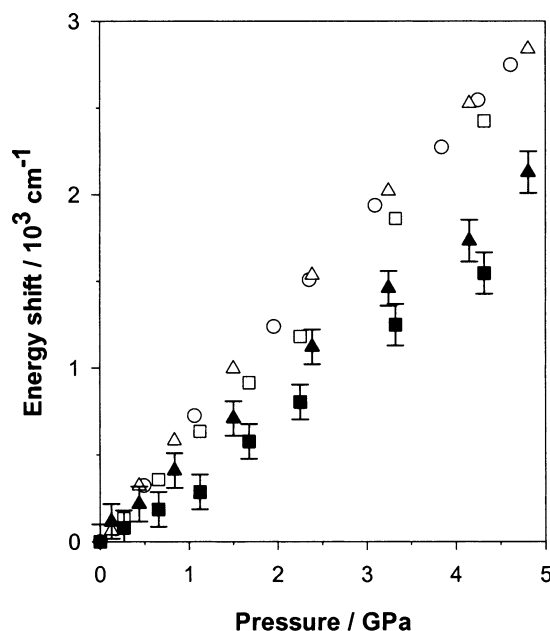

Figure 3. Energy shifts for the 0-1 vibronic band: (○) single crystal, (△) polycrystal, and (□) polycrystal (no medium). Corresponding solid symbols represent the energy change for the excimer band in polycrystalline samples. Symbols of the same shape correspond to the same sample type.

elastic constants or by incorporating into the calculation the experimental data from X-ray studies under high pressure in the calculations. However, the required information is not presently available for anthracene single crystals.

III.A.3. Single-Crystal Versus Polycrystal Response. The response of single crystals is compared with that of polycrystalline samples, to examine the role of sample morphology on fluorescence under pressure. This comparison may also help to understand previously published results that have been obtained for polycrystals. As shown in Figure 1, the fluorescence spectra of single crystals and polycrystals are slightly different, even at 1 atm. A low-energy band is clearly observed in the spectra of polycrystalline samples. The spectral differences between single crystals and polycrystals become more pronounced under pressure. This is discussed in more detail in the next subsection. Although the spectral changes in polycrystalline samples are significant, the normal fluorescence is still discernible in the spectrum. Here, the pressure effects on the normal fluorescence of polycrystals are compared to that of single crystals, in terms of energy shifts, vibronic band broadening, and fluorescence intensities.

The energy shifts for polycrystalline samples are very similar in character to those for single crystals (see Table 1). However, the shift values are somewhat smaller for polycrystalline samples that have been compressed directly, without a medium. Differences between single crystals and polycrystals for the 0-1 vibronic bands are illustrated in Figure 3. It is observed that the energy shift is not very sensitive to the sample morphology.

Pressure-induced spectral shifts are invariably accompanied by an increase in vibronic bandwidths. The latter is illustrated in Figure 4, where the 0-2 vibronic bands are compared. We chose to present the 0-2 data because this band is not affected by reabsorption. The width of the band was determined as a full width at half-maximum (fwhm) of the Gaussian peak. At 1 atm, the widths of the band are 0.98×10^{3}, 1.01×10^{3}, and 1.1×10^{3} cm^{-1} for single crystals, polycrystals, and polycrystals (no medium), respectively. As the pressure increases, the vibronic bands have a tendency to broaden. In the case of a
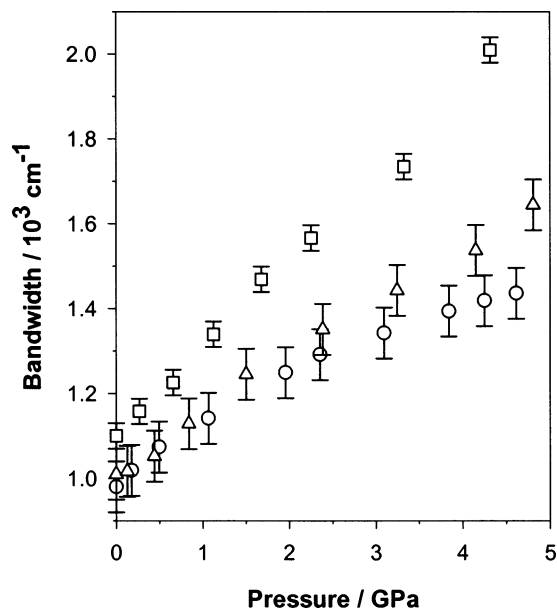
Figure 4. Vibronic band broadening for the 0-2 transition: (○) single crystal, (△) polycrystal, and (□) polycrystal (no medium).

Figure 5. Effects of pressure on the fluorescence intensity. Open symbols denote the normal fluorescence, normalized to the intensity at 1 atm: (○) single crystal, (△) polycrystal, and (□) polycrystal (no medium). Solid symbols denote the excimer fluorescence, relative to the total fluorescence at 1 atm: (▲) polycrystal and (■) polycrystal (no medium). Plotted lines represent the relative excimer fluorescence, normalized to the intensity of normal fluorescence: (···) polycrystal and (− − −) polycrystal (no medium).

single crystal, the vibronic bandwidth increases by ∼40% at 5 GPa. The rate of broadening decreases gradually as the pressure increases. Polycrystalline samples show much larger broadening, particularly in the experiment with no medium.

So far, no theory has been applied successfully to the analysis of pressure-induced broadening, specifically, for electronic spectra of pure molecular crystals. Presumably, the broadening should occur because of fluctuations in the interactions that produce the energy shifts.[4,32] This phenomenological idea would imply that the greater the energy shift, the greater the spectral broadening. However, this is not consistent with our data. For instance, the polycrystalline sample with no medium shows the smallest energy shift but the largest broadening. The large broadening in this case may arise from an increase in inhomogeneous deformation at the grain boundaries, defect formation, and enhancement of exciton scattering at crystal defects.

The intensity of the normal fluorescence (integrated over all vibronic bands) decreases under pressure in all cases studied. However, the relative intensities of the individual vibronic bands are not affected by pressure, indicating no change in intramolecular conformation. As can be observed in Figure 5, the fluorescence intensity of single crystals decreases gradually by a factor of ∼3 over the 5 GPa range. Several factors may contribute to the intensity decrease: (i) a decrease in the absorption coefficient, (ii) an increase in the intersystem crossing rate, and (iii) an increase in the rate of nonradiative transition to the ground state. It is worth noting that both the emission intensity (Figure 5) and the energy of the vibronic bands (Figure 2) change in a similar nonlinear fashion (see Figures 2 and 5). This similarity may indicate that the decrease of fluorescence intensity is controlled mainly by an increase in the rate of the nonradiative transition between the excited state and the ground state (energy-gap law).[33,34] To further examine this conjecture, fluorescence lifetime measurements will be necessary. In polycrystalline samples, the normal fluorescence intensity decreases faster than in the single crystals. However, in polycrystals a new band accompanies the normal fluorescence.

III.B. Excimer Fluorescence. *III.B.1. New Band−Polycrystals.* In addition to the normal fluorescence, the spectra of polycrystalline samples show a long tail at low energies, corresponding to a new broad band (see Figure 1B,C). This band is more
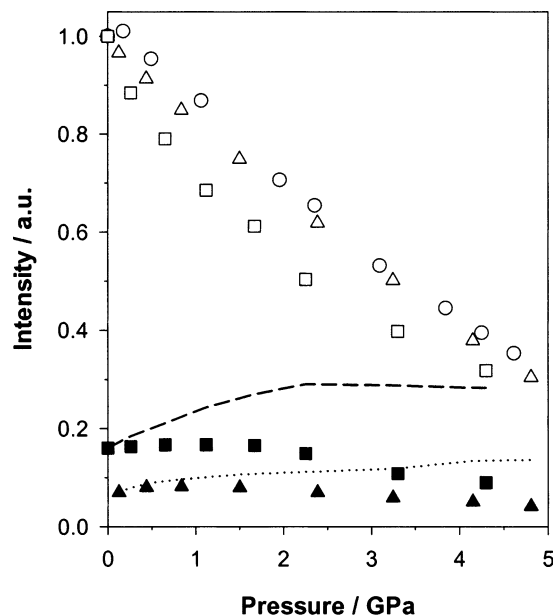
intense when polycrystals are tightly compacted into the aperture of the gasket (Figure 1C). With increasing pressure, a red shift and an intensity enhancement of this band occur. Upon release of pressure, its intensity is higher than before the application of pressure. Because of the limited amount of data, the exact origin of this emission could not be identified precisely. However, its dependence on the sample loading conditions and history (irreversibility) suggests a defect-related emission. The emitting centers are most likely located near the surface of microcrystals where dislocations may assist the anthracene molecules to assume suitable orientation for the formation of excimers.[35−37] The excimer nature of defects is suggested because of the broad (fwhm ≈ 3000−4000 cm^{-1}), red-shifted (∼5000 cm^{-1} below the exciton band), and structureless character of the observed emission.[12−16,38,39]

The excimer band was observed when the excitation energy was within the absorption of the exciton band. This result implies that the defect is excited by the migrating exciton rather than directly by the light. In this case, after the exciton is generated, it migrates through the crystal and, during its lifetime, may become localized at a defect. If the molecular spacing and configuration are appropriate, the localized exciton may interact with an unexcited molecule to form an excimer. Our data are consistent with this scenario. Figure 5 shows that the decrease of normal emission intensity of polycrystalline samples is larger than that for single crystals. This suggests an additional channel of deactivation in polycrystalline samples. A greater decrease in normal emission in polycrystals is accompanied by an increase of the excimer emission intensity. The absolute increase in the excimer intensity is not large. However, its contribution to the total emission grows with pressure, because the normal fluorescence decreases with pressure (see dotted and dashed lines in Figure 5). This effect is more pronounced for samples with no medium; the lack of a medium leads to greater nonhydrostaticity.

High-Pressure Effects on Fluorescence of Anthracene

J. Phys. Chem. B, Vol. 107, No. 35, 2003 **9273**

Pressure enhancement of the excimer emission could be attributed to the increase in both the exciton-defect interaction and the concentration of defects. This conclusion is supported by the following observations. As already mentioned, under pressure, the decrease in the normal fluorescence intensity in polycrystals is larger than that in single crystals. This may imply a reduction in the exciton lifetime in polycrystalline samples, presumably because of an increase in the exciton-defect interaction. The increase in the concentration of defects is supported by the observation of irreversible changes in the spectra upon pressure release. These changes include an apparent increase of excimer-band intensity, relative to the uncompressed sample.

As can be observed in Table 1 and Figure 3, the energy of the excimer band decreases with pressure less than the corresponding exciton band. Consequently, the rate of nonradiative energy deactivation from the excimer state should change less than the rate from the molecular exciton state. This process could further increase the relative contribution of the excimer emission to the total fluorescence.

III.B.2. Nonhydrostatic Compression. Although polycrystalline samples behave differently than single crystals, the pressure-induced changes observed in this work do not resemble those reported by others.[12−19] The normal fluorescence is still discernible in the polycrystalline sample spectrum and the contribution of excimer emission to the total fluorescence is low, even at 5 GPa. However, the increase in the excimer emission is larger for samples with no medium. In this case, plastic deformation can occur at the microcrystal boundaries, because of an inability to accommodate deformation variations in neighboring grains. The plastic deformation can, in turn, lead to defect formation and, consequently, stronger excimer emission.

It seems likely that the nonhydrostatic conditions in the high-pressure cell can lead to processes that are similar to those resulting from shear stresses in the sample. These stresses conditions may have caused the results that were obtained earlier.[12−19] To examine this conjecture, we performed an experiment with a single crystal that was subjected to nonhydrostatic loading conditions. In this experiment, a single crystal of anthracene was directly compressed, along the normal to the (001) plane, between two diamond anvils without a gasket. There was no lateral confinement; therefore, the crystal was subjected to uniaxial stress. Because of the crystal softness, the applied stress caused large irreversible deformation and plastic flow. The change in the thickness of the crystal was estimated by measuring the distance between the two bases of the cell.

Representative results from this experiment are shown in Figure 6. The changes in the fluorescence spectrum under these conditions are very pronounced. When the crystal is compressed (∼30% change in thickness; panel B), a broad, intense, and structureless band appears to the red side of the normal fluorescence. As the deformation increased, the intensity of the normal fluorescence decreased and the low-energy band became dominant in the spectrum. The changes in the spectrum closely resemble those attributed previously to the pressure-induced excimer emission.[12−18] As can be observed in Table 2, the excimer emission occurs at very low stresses. When excimer emission dominates the spectrum almost entirely (∼56% change in thickness; panel C), the stress in the sample, estimated from the normal fluorescence shift, is <0.4 GPa.

This experiment shows that strong excimer emission can be observed at very low stresses but under nonhydrostatic conditions, indicating that pressure is not the primary variable that causes excimer emission in anthracene crystals. This emission can occur under nonhydrostatic conditions at the onset of plastic
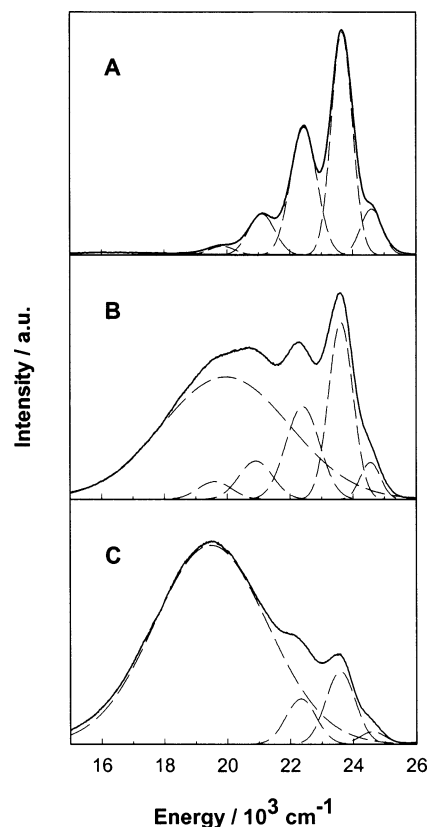

Figure 6. Fluorescence spectra of anthracene single crystals (initial thickness of ∼0.08 mm) under uniaxial compression: (A) 1 atm, (B) 31% change in thickness, and (C) 56% change in thickness (also see Table 2). Dashed lines represent Gaussian peaks fitted to the spectra.

TABLE 2: Changes in Fluorescence of Anthracene Single Crystal under Uniaxial Compression

estimated change in thickness,[a] %	I_E/I_T[b]	E_E,[c] 10^3 cm^{-1}	E_{0-2},[d] 10^3 cm^{-1}	estimated stress, GPa
0	0.00		22.38	0.0
20	0.17	19.42	22.29	0.1
31	0.45	19.49	22.14	0.3
56	0.84	19.53	22.10	0.4
68	0.91	19.58	n/m[e]	n/m[e]

[a] Standard deviation = ±5%. [b] Contribution of the excimer emission to the total fluorescence. [c] Excimer band energy. Standard deviation = ±0.04 × 10^3 cm^{-1}. [d] Energy of the 0-2 vibronic band of normal fluorescence. Standard deviation = ±0.04 × 10^3 cm^{-1}. [e] Not measurable.

deformation in the crystal. Given this finding, the occurrence of excimer emission in the earlier experiments could be attributed to uncontrolled nonhydrostaticity in the high-pressure cell.

IV. Summary

The effect of pressure on the fluorescence of anthracene crystals has been examined up to a pressure of 5 GPa. We have demonstrated that pressure-induced changes in the fluorescence spectra are sensitive both to the morphology of the sample (single crystal versus polycrystal) and to the loading conditions in the cell (hydrostaticity). It was found that, under hydrostatic loading, there was no excimer emission from single crystals. This result is in sharp contrast to the previously published data, where strong excimer emission was observed. We attribute this discrepancy to the presence of nonhydrostaticity in the cell and resulting defects in the crystals in previous experiments.

Because of the absence of excimer emission, pressure-induced changes in the normal fluorescence have been examined. These changes included strong red-shifting of the vibronic bands, band broadening, and a gradual loss of intensity. The energy of the vibronic bands is found to decrease nonlinearly with pressure. This decrease is not described adequately by available theoretical treatments.

In contrast to single crystals, the spectra of polycrystalline samples exhibit an additional emission band. We attributed this band to the defect-related excimer emission. The intensity of this emission increased with pressure. However, even at 5 GPa (the highest pressures applied), the spectrum of polycrystalline samples was still dominated by the normal fluorescence.

Strong changes are introduced in the fluorescence spectrum under nonhydrostatic loading conditions. In this case, even at stresses of <0.4 GPa, the single crystal fluorescence is dominated entirely by excimer emission. Therefore, we concluded that excimer emission in anthracene crystals is not caused by high-pressure itself. Instead, the occurrence of excimer emission is proposed to originate from the structural defects introduced by plastic deformation in the crystal.

References and Notes

(1) Holzapfel, W., Isaacs, N. S., Eds. *High-Pressure Techniques in Chemistry and Physics: A Practical Approach*; Oxford University Press: Oxford and New York, 1997.

(2) Drickamer, H. G.; Frank, C. W. *Electronic Transitions and the High Pressure Chemistry and Physics of Solids*; Chapman and Hall: London, 1973.

(3) Ferraro, J. R. *Vibrational Spectroscopy at High External Pressures*; Academic Press: New York, 1984.

(4) Offen, H. W. In *Organic Molecular Photophysics*; Birks, J. B., Ed.; Wiley: London, New York, Toronto, and Sydney, 1973; Vol. 1, Chapter 3.

(5) Silinsh, E. A. *Organic Molecular Crystals, Their Electronic States*; Springer–Verlag: Berlin, Heidelberg, and New York, 1980; Chapter 4.

(6) Rice, S. A.; Jortner, J. In *Physics of Solids at High Pressure*; Academic Press: New York and London, 1965; pp 63–168.

(7) Okamoto, B. Y.; Drickamer, H. G. *J. Chem. Phys.* **1974**, *61*, 2870.

(8) Léger, J. M.; Aloualiti, H. *Solid State Commun.* **1991**, *79*, 901.

(9) Adams, D. M.; Tan, T. K. *J. Chem. Soc., Faraday Trans. 2* **1981**, *77*, 1711.

(10) Hamann, S. D. *High Temp.–High Pressures* **1978**, *10*, 503.

(11) Zhao, L.; Baer, B. J.; Chronister, E. L. *J. Phys. Chem. A* **1999**, *103*, 1728.

(12) Jones, P. F.; Nicol, M. *J. Chem. Phys.* **1965**, *43*, 3759.

(13) Tanaka, J.; Koda, S.; Shionoya, S.; Minomura, S. *Bull. Chem. Soc. Jpn.* **1965**, *38*, 1559.

(14) Offen, H. W. *J. Chem. Phys.* **1966**, *44*, 699.

(15) Ohigashi, H.; Shirotani, I.; Inokuchi, H.; Minomura, S. *Mol. Cryst.* **1966**, *1*, 463.

(16) Jones, P. F.; Nicol, M. *J. Chem. Phys.* **1968**, *48*, 5440.

(17) Nicol, M.; Vernon, M.; Woo, J. T. *J. Chem. Phys.* **1975**, *63*, 1992.

(18) Politov, A. A.; Phursenko, B. A.; Boldyrev, B. B. *Dokl. Acad. Nauk* **2000**, *371*, 59.

(19) Mizuno, K.; Matsui, A. *J. Phys. Soc. Jpn.* **1986**, *55*, 2427.

(20) Kobayashi, M.; Mizuno, K.; Matsui, A. *J. Phys. Soc. Jpn.* **1989**, *85*, 809.

(21) Matsui, A. *J. Opt. Soc. Am. B* **1990**, 1615.

(22) The word "excimer" is commonly used to denote the formation of a dimeric species that has a definite binding energy in the excited state and radiates to a repulsive ground state.

(23) Karl, N. In *Crystals: Growth, Properties, and Applications*; Freyhardt, H. C., Ed.; Springer–Verlag: Berlin, Heidelberg, and New York, 1980; Chapter 1, and references therein.

(24) Piermarini, G. J.; Block, S.; Barnett, J. D.: Forman, R. A. *J. Appl. Phys.* **1975**, *46*, 2774.

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

(26) Wiederhorn, S.; Drickamer, H. G. *J. Phys. Chem. Solids* **1959**, *9*, 330.

(27) Schipper, P. E. *Mol. Cryst. Liq. Cryst.* **1974**, 28, 401.

(28) Davydov, A. S. *Theory of Molecular Excitons*; Plenum Press: New York and London, 1971.

(29) Craig, D. P.; Walmsley, S. H. *Excitons in Molecular Crystals*; W. A. Benjamin, Inc.: New York, 1968.

(30) Rice, S. A.; Jortner, J. In *Physics and Chemistry of Organic Solid State*; Labes, M., Fox, M., Weissberger, D., Ed.; Wiley: New York, 1967; Volume III, pp 199–497.

(31) Afanas'eva, G. K.; Myasnikova, R. M. *Sov. Phys.–Cryst.* **1970**, *15*, 156.

(32) Jones, P. F. *J. Chem. Phys.* **1968**, *48*, 5448.

(33) Englman, R.; Jortner, J. *Mol. Phys.* **1970**, *18*, 145 and references therein.

(34) Freed, K. F.; Jortner, J. *J. Chem. Phys.* **1970**, *52*, 6272.

(35) Seko, T.; Ogura, K.; Kawakami, Y.; Sugino, H.; Toyotama, H.; Tanaka, J. *Chem. Phys. Lett.* **1998**, *291*, 438.

(36) Silinsh, E. A.; Capek, V. *Organic Molecular Crystals: Interaction, Localization, and Transport Phenomena*; Springer–Verlag: Berlin, Heidelberg, and New York, 2000.

(37) Ostapenko, N. I.; Sugakov, V. I.; Shpak, M. T. *Spectroscopy of Defects in Organic Crystals*; Kluwer Academic Press: Dordrecht, Boston, and London, 1993.

(38) Birks, J. B. *Photophysics of Organic Molecules*; Wiley–Interscience: London, New York, Sydney, and Toronto, 1970.

(39) Pope, M.; Swenberg, Ch. E. *Electronic Processes in Organic Crystals and Polymers*; Oxford University Press: New York, 1999.