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Excimer Delayed Fluorescence of Compressed Naphthalene Crystals*

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The compression of naphthalene crystals (to 30 kbar) at 77°K creates, irreversibly, defects in the lattice. These defects capture singlet and triplet excitons, leading exclusively to excimer and delayer excimer fluorescence. Triplet trap depths of $\sim$600 cm^{-1} at 1 atm and $\sim$700 cm^{-1} at 30 kbar are estimated from the temperature dependence of the delayed excimer fluorescence. A wide distribution of singlet trap depths and excimer conformations is indicated by the pressure modifications of the excimer fluorescence band.

INTRODUCTION

Electronic processes in molecular crystals at low temperatures are frequently determined by trapping phenomena. Triplet excitons which migrate further than singlet excitons are more sensitive to the presence of traps in the crystalline lattice. Doping with chemical impurities has been one important method for introducing traps of known depth and concentration and has illuminated energy migration in mixed crystals of aromatic molecules. Even in the absence (or near absence) of chemical impurities, various types of structural defects in the crystal can lead to trapping of electronic energy which may alter the exciton properties significantly. The present work is concerned with the role of physical defects in the luminescence phenomena of crystalline naphthalene.

Naphthalene has received frequent attention in the spectroscopic study of organic crystals.[1–4] The fluorescence,[5–7] phosphorescence,[8] and delayed fluorescence[9,10] of chemically "pure" naphthalene crystals has been characterized. The triplet lifetime of 130 msec in the crystal[8] ($T \geq 77$°K) is considerably shorter than 2.6 sec for $C_{10}H_8$ in a durene matrix.[11] The faster electronic relaxation in the pure crystal may be attributed to quenching by any remaining chemical impurities or, more probably, physical defects. Traps arising from disordered regions in the crystal have long been suspected to scatter excitons,[12] but their concentration and other characteristics are established only with extreme difficulty. Fluorescence attributed to physical defects has been reported for naphthalene crystals at 4.2°K.[13] Schnaithmann and Wolf[14] have deliberately introduced physical defects into the naphthalene crystal through plastic deformation produced by application of $\sim$10 kbar pressure. They observed two types of shallow traps ($\epsilon \lesssim 200$ cm^{-1}), observable below 20 and 100°K, respectively, and another type of defect, observable up to room temperature, which was characterized by excimer fluorescence. Such traps capable of excimer formation and emission have also been identified by Jones and Nicol[15,16] in naphthalene crystals at high pressures and room temperature. The present work further characterizes these emitting traps and demonstrates that triplet–triplet annihilation can be observed at these "excimer-forming" defect sites below 180°K.

EXPERIMENTAL

Naphthalene (J. B. Hinton, zone refined) was either repeatedly zone refined or subjected to potassium fusion[17] followed by vertical zone melting. Both preparations gave the same results in the present experiments. Crystal phosphorescence was not detected. Single crystals were grown from the melt in a 3-mm Pyrex tube. These crystals were cleaved to dimensions of 1 mm×1 mm×0.5 mm in order to fit the NaCl sample chamber of the optical high-pressure cell.[18] The cell can be used over the range 77–400°K and 1 atm–30 kbar. The cleavage plane of the crystal is oriented $\sim$30° with respect to the excitation beam and 60° with respect to the analyzing beam. Samples are loaded at room temperature and cooled to 77°K at a rate of 7°C/min. For measurements as a function of temperature, the cell was warmed at a rate of 2–4°C/min.

Excitation was accomplished by light from a 100-W Hg lamp passed through 0.25-m Jarrell–Ash monochromator (1–2-mm slits, $\lambda_{ex} = 313$ nm) for fluorescence measurements or through No. 7-54 filter for delayed fluorescence measurements with out-of-phase rotating sectors. Spectra were taken with an 0.5-m Jarrell–Ash monochromator (400-μ slits), a 1P 21 photomultiplier tube, and a photon-counting system (SSR Instruments, Model 1100). The dark count was 5–8 counts/sec while the signals were 5–5000 times this rate.

RESULTS AND DISCUSSION

Excimer Fluorescence at 77°K

Exciton trapping by physical defects introduced by squeezing naphthalene crystals is illustrated in Fig. 1. The typical naphthalene fluorescence at 1 atm is markedly quenched by $P \sim 1$–5 kbar and is replaced by excimer fluorescence which is the only fluorescence observable at 30 kbar, shown in Fig. 1. The identification of the pressure-induced crystal fluorescence as excimer fluorescence is based on spectral comparisons with concentrated solutions[19,20] and implies a similar conformation (but not necessarily identical geometry) at the defect site as in the excited state aggregate in solutions.[4] The defect sites introduced by squeezing the naphthalene crystal (both in the presence and absence

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of ultraviolet illumination) remain after removing the pressure on the crystal at 77°K and monomer fluorescence I_M is permanently quenched by squeezing (Fig. 1). The excimer intensities I_E near 400 nm are generally 2–3 times as great as the initial monomer fluorescence near 339 nm. Comparison of the initial I_M with the I_E of the squeezed crystal leads to the conclusion that the luminescence process at the excimer-forming defect sites is as efficient as in ethanol solution, for which a quantum yield ratio $\phi_E/\phi_M=3$ has been reported.[21] Exact intensity ratios in naphthalene crystals are not easily established because the trap concentration and distribution is not reproducible from run to run. However, subsequent pressure cycles (1 atm–30 kbar–1 atm, etc.) give reproducible $I_E(P)$, where the ratio $I_E(30)/I_E(0)$ varies between 0.5 and 1.5. Most frequently the excimer fluorescence is quenched with increasing pressure (Fig. 1), although increases in I_E of 50% have also been observed in a few samples. In any event, high pressures have introduced traps of sufficient concentration to capture all singlet excitons, i.e., $I_E/I_M>1000$.

Excimer Delayed Fluorescence at 77°K

Long-lived emission was absent in our crystalline naphthalene samples at 77°K. However, a pressure of 0.5 kbar on the sample is sufficient to produce the broad emission shown in Fig. 2. The intensity decay of this broad emission is nonexponential, yielding an approximate lifetime of 200 msec, similar to the value reported by Benz, Hacker, and Wolf[10] for "pure' naphthalene crystals. The lifetime is shortened 30%–50% at 30 kbar which is the typical response of lifetimes to high pressures.[22] The intensity of this emission at 30 kbar is about 0.05% of I_E. As noted in Fig. 2 the release of pressure enhances this emission severalfold. Subsequent pressure cycles give reproducible results for a given sample as in the case of excimer fluorescence, but the intensity is more pressure sensitive and yields intensity ratios of 3 to 7 for $P=1$ atm relative to $P=30$ kbar.

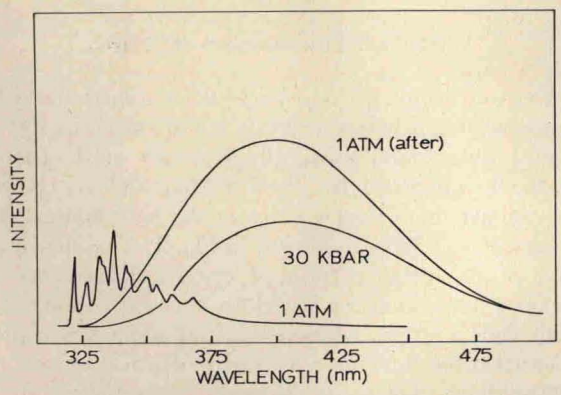

FIG. 1. Fluorescence spectra of naphthalene crystals at 77°K before squeezing (1 atm), at 30 kbar, and after pressure release (1 atm).

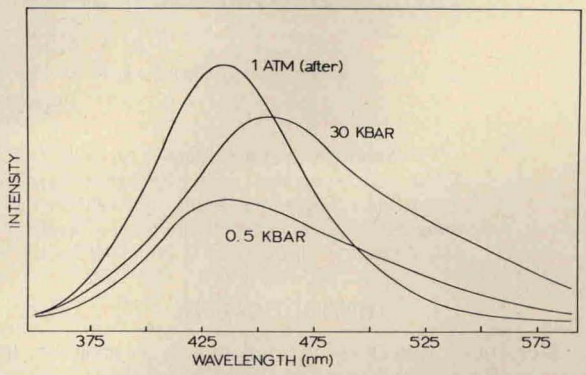

FIG. 2. Delayed fluorescence spectra of naphthalene crystal at 77°K at 0.5 kbar (gain × 5), 30 kbar (gain × 5), and after pressure release (gain × 1).

This pressure-induced long-lived emission is assigned to excimer delayed fluorescence on the basis of the following observations. The spectral location and large bandwidth is similar to that for the excimer fluorescence. The intensity varied quadratically with the exciting light intensity at low light levels. The square law implies a bimolecular process, in this case triplet–triplet annihilation at the excimer-forming defect sites. It should be noted that the analogous process of excimer delayed emission from naphthalene in ethanol glass has a lifetime of 11 msec at 77°K,[23] while the τ value in the crystal more nearly corresponds to expectations for a triplet–triplet annihilation process.[8,10] The excimer delayed fluorescence I_{DE} arises from the bulk of the crystal and is not a surface effect because crushing the crystal or surrounding the sample in the cell with cellulose acetate or Lucite films only modifies the intensity but does not influence the other characteristics of I_{DE}. The delayed excimer emission is only observed when prompt I_E is also present. Jones and Nicol[15,16] previously established that light catalysis is required during squeezing at room temperature in order to observe excimer fluorescence after pressure release at 298°K. Thus, squeezing the crystal in the dark at room temperature leads to very little excimer emission and no I_{DE} upon cooling to 77°K at 1 atm. But squeezing the crystal under ultraviolet illumination at room temperature results in both prompt and delayed excimer fluorescence at 77°K and 1 atm. Therefore all the experimental information supports the view that triplet–triplet annihilation at excimer-forming defects is responsible for the long-lived emission.

The Nature of Triplet Traps

The present work has established that pressure can introduce lattice defects into naphthalene crystals which trap singlet and triplet excitons, form excimers,

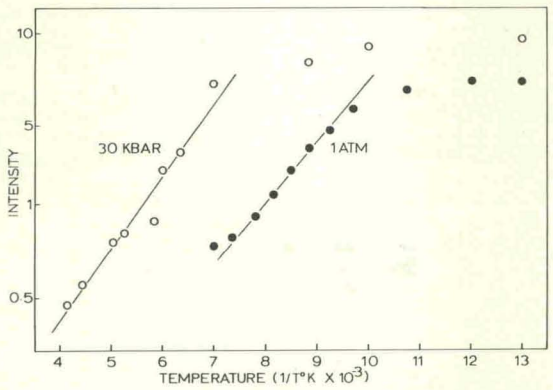

FIG. 3. Excimer delayed fluorescence intensities as a function of temperature at 1 atm and at 30 kbar. The intensity scales are arbitrary.

and are responsible for all observed luminescence of the squeezed crystals at 77°K. The pressure-induced traps must be of sufficient depth to be important at temperatures above ~50°K, i.e., $\epsilon \sim 500$ cm^{-1} according to the empirical relation $T_{max} \sim 0.1\ \epsilon$ obeyed in mixed crystals.[24–26] This implies that the properties of pressure-induced traps are similar to traps produced by chemical doping.[10,24–27] In the absence of phosphorescence the trap depth, ϵ, can only be estimated from the temperature dependence of I_{DE}. The plot in Fig. 3 leads to an activation energy of ~600 cm^{-1} at 1 atm. At pressures of 30 kbar, I_{DE} does not drop off until higher temperatures and with an activation energy of ~700 cm^{-1}. In analogy to mixed crystals, the higher dropoff temperature at 30 kbar is consistent with a deeper trap. Accurate trap depths cannot be determined because the plots (Fig. 1) are curved and not completely reproducible. This is not surprising because there is undoubtedly a distribution of trap depths about the mean value and other quenching processes contributing to the loss of I_{DE} at higher temperatures.

Comparison of Figs. 1 and 2 show that the prompt and delayed fluorescence are not superimposable at 1 atm, i.e., the band in the DE spectrum is narrower and located at longer wavelengths ($\lambda_{max} = 435$ nm) compared to the E spectrum. A difference in the prompt and delayed fluorescence of naphthalene crystals has been reported below 50°K and attributed to the superposition of subspectra in the delayed emission.[10] An analogous explanation can be applied in the present case by postulating that the mean trap depth differs for singlet and triplet excitons. Due to the longer diffusion lengths of triplet excitons annihilation will occur predominantly at the deepest traps. Not only do the E and DE band peaks differ at 1 atm but also in their pressure response. Delayed excimer fluorescence shows a red shift of ~1000 cm^{-1} at 30 kbar which may be identified with the effects of solvation and stronger specific interactions at the defect sites.[28] In contrast the prompt fluorescence does not show a red shift. The shift is very dependent on sample treatment and varies from a negligible shift to a 1600-cm^{-1} blue shift at 30 kbar. In this case reorientation rather than a solvation effect seems to determine the pressure response. Further work is required to establish the complicated behavior of singlet traps.

CONCLUSION

Squeezing naphthalene crystals introduces defects into the lattice. These defects can trap singlet and triplet excitons ($\epsilon \lesssim 700$ cm^{-1}), resulting in excimer fluorescence. The geometry of the emitting species appears very similar to that attained in solution, although there appears to be a range of trap depths and a corresponding distribution of excimer geometries, leading to a variable P, T response. Both the spectral and intensity variations from sample to sample are to be expected for pressure-induced defects, because the concentration and distribution of traps are not easily reproduced under quasihydrostatic conditions (especially at low pressures). Limitations of the experimental techniques make it very difficult to control concentrations.

The pressure-induced defects are probably dislocations which control plastic deformation. Information on the detailed nature of these structural defects is not available, in fact high-pressure spectroscopic measurements may become an important method for their characterization. The pressure parameter can be utilized to give the distance dependence of the various interactions and the volume requirements of the excimer-forming process at defects. Physical defects anneal and hence a temperature dependence of the excimer fluorescence at high temperatures may provide significant information about the mechanical properties of organic crystals. It is surprising that the spectral differences between the prompt and delayed excimer fluorescence are so large. One suggestion is that there are actually two classes of defects. For example, the excimer formation process between translationally equivalent and inequivalent naphthalene molecules in the imperfect crystal may lead to different trap depths.

The trap depth of ~600 cm^{-1} measured by triplet exciton–trap annihilation in naphthalene is not very different from the trap depth of ~1000 cm^{-1} for pressure-induced defects in benzophenone crystals, as deduced from the pressure effect on the phosphorescence spectrum.[29] Similar traps may be present in both organic crystals, although the work to date is but the first step in characterizing imperfect crystals possessing deep traps induced by compression.

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