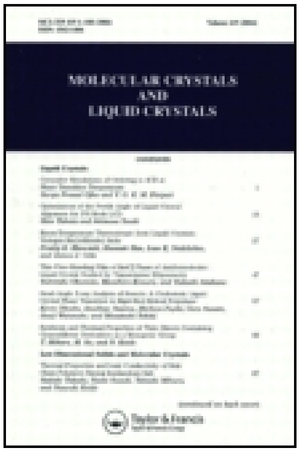

Molecular Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl15

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To cite this article: David E. Hein & Henry W. Offen (1969): Fluorescence Spectra in Frozen Heptane at High Pressures, Molecular Crystals, 5:3, 217-227

To link to this article: http://dx.doi.org/10.1080/15421406908083457

Molecular Crystals. 1969. Vol. 5, pp. 217–227

Printed in Great Britain

Fluorescence Spectra in Frozen Heptane at High Pressures‡

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Received July 31, 1968

Abstract—The fluorescence spectra of coronene and 1,12-benzoperylene have been studied in frozen heptane as a function of pressure (0–30 kbar). The fluorescence red shifts at 77°K are 5 cm^{-1}/kbar and 8.3 cm^{-1}/kbar, respectively. High pressures broaden vibronic bands and increase background intensity. The 0, 0 band becomes more pronounced under pressure. The intensity pattern of the 1,12-benzoperylene fluorescence is altered considerably by compression of the heptane matrix. Permanent changes in the spectra after pressure treatment are very slight compared to the reversible effects of high pressures on the spectral characteristics of these two aromatic hydrocarbons.

Introduction

Impurities embedded in frozen *n*-paraffin solutions can give rise to multiple and extremely narrow vibronic lines in electronic transitions. For example, the 0,0 fluorescence band of 1,12-benzoperylene in hexane has a linewidth of 1 cm^{-1} at 4°K.[1] This is the Shpolskii effect of quasilinear multiplet spectra,[2,3] observed when large π-electron systems are monomolecularly dispersed in molecular crystals of *n*-paraffin solvents. The aim of much work is the determination of the causes for these essentially phononless transitions, i.e. the nature of the impurity (or solute) center in the crystalline environment of long-chain zigzag host molecules. A theoretical model, developed in analogy with the Mössbauer effect,[4] can explain many features of quasilinear spectra, but some theoretical predictions are not confirmed by temperature-dependent studies of linewidth.[1,5] It is known that the nonideality or

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‡ This work is supported by the U.S. Office of Naval Research.

heterogeneity of the host crystal contributes substantially to the observed linewidth. The present work employs very high pressures to explore the effects of matrix compression on impurity fluorescence.

The systems chosen for this study are coronene and 1,12-benzoperylene in frozen heptane. The quasiline fluorescence spectrum of coronene in heptane at 77°K has frequently been studied at atmospheric pressure.[6–9] The highly symmetrical coronene molecule is suspected to be very sensitive to geometrical distortion and is therefore a good candidate for high pressure studies. Bowen and Brocklehurst[6] first pointed out that 1,12-benzoperylene impurities are common in coronene and can lead to misinterpretations of the superposed spectra. Hence 1,12-benzoperylene was also studied in the same solvent to be sure of its absence in the pressure effects on the coronene spectrum. This was the case (*vide infra*) and, additionally, the pressure study of these two molecules led to interesting comparisons.

Experimental

The final step in purifying coronene and 1,12-benzoperylene (Aldrich Chemicals) was microsublimation.[10] Extensive column chromatography and recrystallization did not appear to remove the 1,12-benzoperylene impurities, but triple microsublimation yielded a sufficiently pure product which showed at 77°K negligible intensity above 425 nm when excited at 365 nm, where benzoperylene absorbs strongly.[4] The heptane (MCB Spectroquality Grade) solutions were prepared by twofold dilution of saturated solutions at room temperature, followed by nitrogen bubbling.

The high pressure optical cell and pressure calibration at low temperatures has been described.[11] The optical system consisted of a 100 W mercury lamp (PEK Labs), a 10 cm water filter and Corning # 7-54 filter for excitation and a 0.5 m Jarrell-Ash spectrometer with RCA 1 P 28 or 1 P 21 photomultiplier for DC detection of the filtered (Corning # 3-73) front-surface fluorescence 90° from the excitation axis. Slit widths of 400 μ were necessary to register the spectrum on a Speedomax W recorder.

Heptane solutions were placed into sealed plastic capsules to fit cylindrical holes drilled centrally in the salt filling the sample chamber or placed directly into the cylindrical salt cavity. No adverse effects from contact with NaCl were noted. It was frequently difficult to get sufficient intensity for spectra after cooling to 77°K and before any pressure was applied. The 1 atm spectra could be obtained after compaction to 20 kbar at 77°K followed by melting and refreezing of the heptane solvent. The cooling rate was roughly 20 degrees per minute near the melting point of heptane. There was generally an increase in intensity with pressure for heptane samples which was assumed to be largely due to varying transmission of the heptane solvent and the salt–heptane interface rather than enhanced radiative properties of the solute.

Coronene Fluorescence

Some of the observed pressure effects on the coronene fluorescence in frozen heptane are illustrated in the first three figures. The multiplet structure of the 444 and 472 nm lines at 77°K, which is a doublet for coronene[6–8] under moderate resolution, is faintly noticeable in Fig. 1. Comparison of the spectra before and after pressure treatment shows that the multiplet lines become less distinct and the total intensity increases considerably, largely due to the transmission properties of the crystalline solvent in the high-pressure optical cell. In addition to some broadening one pressure cycle (0, 10, 20, 30, and again 0 kbar) results in a 3–5 Å red shift of the entire 1 atm fluorescence spectrum. Subsequent pressure cycles do not appear to produce further irreversible effects at liquid nitrogen temperatures within the present resolving power of the optical system. These features demonstrate that heptane does not relax entirely to its conformation prior to pressure treatment. But these effects are small compared to the reversible pressure-induced red shift of 5 cm^{-1}/kbar and the considerable

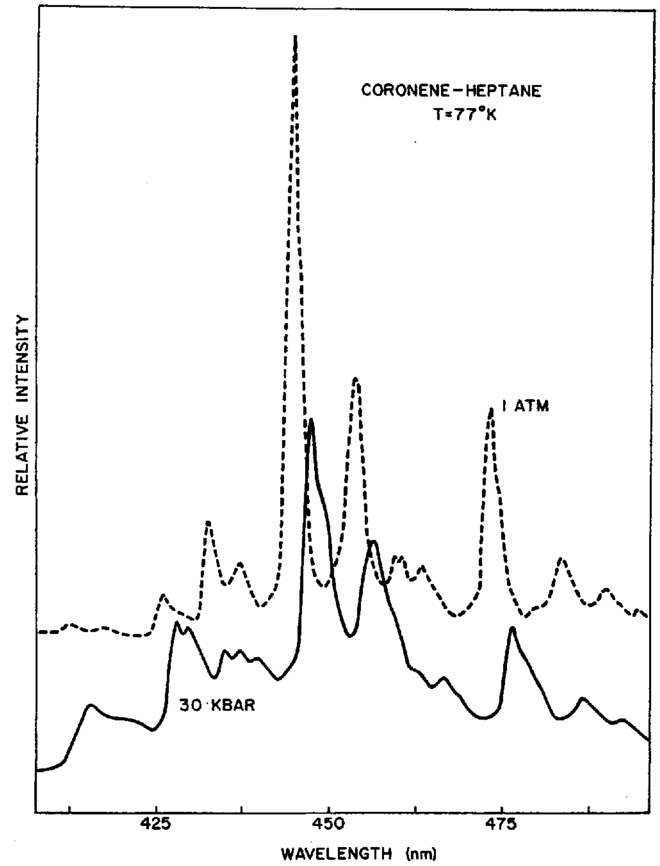

Figure 1. Fluorescence spectra of coronene in heptane at 77°K for the 1 atm and 30 kbar isobars.

broadening of the quasilinear spectra (Fig. 1). The increase in bandwidth, always measured at half-height, is shown in Fig. 2 for the strongest vibronic transition (444 nm) as a function of pressure. The fractional frequency displacement $\Delta\nu/\nu$ is 0.6% at 30 kbar compared to a 140% fractional change in bandwidth at the same pressure. The band contour shades toward longer wavelengths at higher pressures. Figure 1 also illustrates that much of the total intensity at 30 kbar forms part of the background continuum.

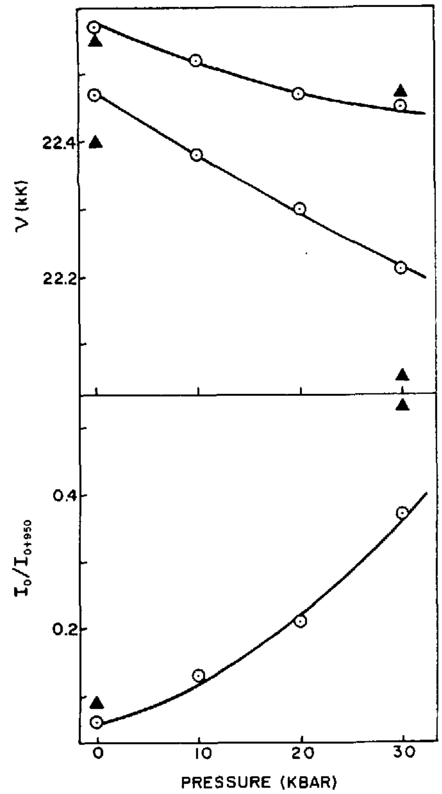

Figure 2. Bandwidths at half-height of the 0,0 + 950 cm^{-1} band and intensity ratio I_0/I_{0+950} as a function of pressure at 77°K (○) and 177°K (▲). The points in the upper portion of the figure locate each side of the 444 nm band at half-intensities.

The $^1L_b \rightarrow {}^1A_1$ transition in coronene is considered to be forbidden by symmetry.[12,13] This assignment is confirmed by the enhancement of the 0–0 band (426 nm) relative to the vibrationally induced transitions at higher pressures. This can be seen by comparing the 0 and 30 kbar spectra in Fig. 1. The pressure-induced changes in the intensity of the 0–0 band and 0–0 + 950 cm^{-1} band (444 nm), as illustrated in Fig. 2, clearly demonstrate how increased solvent perturbations enhance radiation from forbidden electronic transitions. One novel feature observed at high pressure is an apparent 90 cm^{-1} split of the 0–0 band at 30 kbar. Unfortunately, the signal-to-noise ratio is too small at lower pressures to be sure about the splitting. Similar splitting can be noticed also in the next 0–0 + 650 cm^{-1} band system. The origin of distinct multiplet structure at high pressures is unclear. There is another unusual feature in the 30 kbar fluorescence of coronene in heptane at 77°K (Fig. 1). This is the considerable intensity located *above* the band origin. The band located about 770 cm^{-1} toward the blue of the 0–0 band shows a pressure shift similar to the remainder of the band. The molecule benzoperylene is not responsible for the short wavelength emission (*vide infra*). Further studies at higher resolution are clearly desirable to understand these novel pressure-induced effects.

The coronene-heptane system was also studied at −96°C, which is just below the melting point of the solvent. Figure 3 illustrates

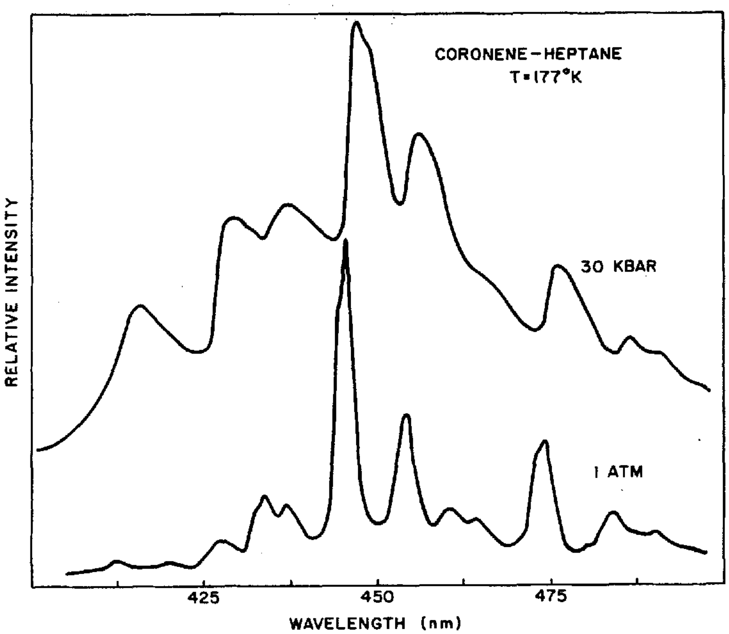

Figure 3. Fluorescence spectra of coronene in heptane at 177°K for the 1 atm and 30 kbar isobars.

the spectra at two isobars. Since it was difficult to regulate temperatures at 177°K over long periods, the spectra were studied at only two pressures (0 and 30 kbar). The 1 atm " quasilinear " spectral bands have broadened about 50% by this temperature increase, but the relative intensity distribution among the various vibronic bands and the background continuum is very similar to the 1 atm spectrum observed at 77°K. The only difference is an intensity redistribution among the doublets (cf. Figs. 1 and 3) which is promptly changed by pressure to yield again band shading toward longer wavelengths. Figure 2 illustrates that pressure broadening and 0–0 band intensity enhancement are more pronounced at higher temperatures. In fact, the half-height of the 444 nm band maximum at 30 kbar is already located in the background continuum. The increase in temperature has produced a red shift[5] of $\sim 50\text{cm}^{-1}$ in the 0–0 band and a $\sim 30\,\text{cm}^{-1}$ red shift of the band center of the 444 nm band. The pressure-induced red shift is about the same at both temperatures. It can be seen from Fig. 3 that a pronounced emission above the 0–0 band develops at 30 kbar. The intensity distribution in this unidentified band is different from that observed at 77°K and 30 kbar. It is emphasized that the pressure effects on the high-energy fluorescence are reversible. The distinct band splitting observed in the coronene fluorescence at high pressures and lower temperatures is now absent.

1,12-Benzoperylene Fluorescence

This molecule was originally studied to eliminate the possibility that it was responsible for emission above 425 nm in the coronene spectra. A comparison of band locations in the observed spectra (see Figs. 1 and 4) confirms the absence of this source of contamination in the coronene emission. The 1 atm spectrum of benzoperylene in heptane at 77°K clearly shows the Shpolskii effect (Fig. 4). The spectral location is identical and the intensity distribution appears similar to the published spectrum[6] in hexane solvent. According to Bowen and Brocklehurst[7] the quasilinear spectra are much sharper in hexane and pentane than in heptane, so that heptane is generally not chosen for studying the Shpolskii effect in benzoperylene.[1] The nonideal inclusion of the solute in the heptane crystal structure is evident from the considerable background continuum in the 1 atm spectrum, illustrated in Fig. 4.

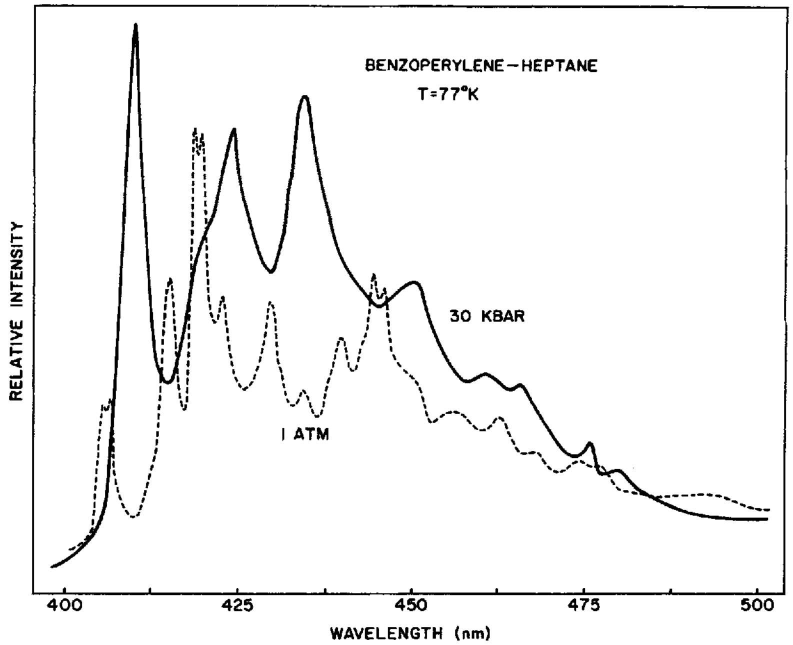

Figure 4. Fluorescence spectra of benzoperylene in heptane at 77°K for the 1 atm and 30 kbar isobars.

The influence of pressure on this solute, as in the case of coronene, leads to small irreversible effects after pressure treatment and to a red shift and band broadening at higher pressures. In contrast to coronene the 30 kbar spectrum does not possess band splittings or intensity above the 406 nm band origin. The new feature found for benzoperylene is the significant pressure-induced intensity redistribution, as illustrated for 30 kbar in Fig. 4. A band located ~ 1000 cm^{-1} from the origin (434 nm at 30 kbar) becomes prominent in the spectrum. The energy interval is suggestive of the totally symmetric breathing vibration found in other aromatic hydrocarbons such as benzene and coronene. In this case, where benzoperylene is nonideally packed into heptane, matrix compression has profound consequences on the sources of fluorescence intensity. Another demonstration of specific solvent perturbations is the intensity of the 0–0 band relative to the 419 and 445 nm bands, which is very sensitive to experimental conditions. The complicated 1 atm spectrum, which to our knowledge has not been assigned and which does not have a strong 0–0 + 1000 cm^{-1} transition, is replaced at high pressure by a simple spectrum, reminiscent of room temperature spectra, consisting of the band origin and vibronic bands based on 800 and 1000 cm^{-1} frequencies. The 0–0 band red shift of 8.3 cm^{-1}/kbar is larger than the pressure dependence of the coronene fluorescence, as would be expected for a more " allowed " transition. Judging by the magnitude of the red shift the net increase in interaction is not far different from that observed for pyrene ($^1L_b \rightarrow {}^1A_1$) in plastics at room temperature.[14]

Discussion

The pressure study of the coronene and benzoperylene fluorescence in frozen heptane has revealed details in the influence of high pressures which are generally masked at room temperatures. While these studies at high pressures are marked by relatively low optical resolution, permanent pressure effects and by uncertainties in applied pressure and intensities, interesting features are nevertheless gleaned from these high-pressure spectroscopic studies at low temperatures. Improved optical resolution and greater control over temperature and crystallization rates of several frozen aliphatic hydrocarbon media will probably bring forth additional details and understanding of molecular interactions in inert environments and their influence on electronic processes in interstitial impurity centers.

This first study in highly compressed frozen heptane illustrates the magnitude of spectral shifts, band broadening, and intensity redistributions among the different vibronic components as well as betwen vibronic bands and background continuum. The latter partitioning process is always in favor of the background at higher pressures, especially at higher temperatures (compare Figs. 1 and 3). This can probably be attributed to pressure-induced heterogeneities in the solvent crystal structure. Another source of pressure broadening is greater interactions of the solutes[1] transition moment with lattice phonons. This would cause the observed pressure-enchanced 0,0 band intensities of both compounds, irrespective of symmetry and the " degree of forbiddenness " of the electronic transition. It also means that site differences, leading to multiplet spectra from two or more sets of molecules, are diminished under pressure. In this respect it is interesting to note that pressure apparently changed the population ratio between the two predominant sites in the paraffin crystal lattice at 177°K (Fig. 3), in order to give shading toward lower energies at higher pressures. The force field around the impurity center must be modified by pressure in order to explain the considerable intensity redistribution witnessed in the fluorescence band of benzoperylene. In this case the crystal packing at high pressure may strongly influence the intramolecular H · · · H steric repulsion at the position in the molecule where one additional ring fusion gives coronene. The changes with pressure appear smooth and no evidence for polymorphic transformations in the solvent is found.

An intriguing observation is the coronene fluorescence intensity which is found above the band origin and becomes more pronounced at higher pressures and at higher temperatures. A similar intensity appearance has been observed in the coronene fluorescence in liquid hexane,[7] and also in the phosphorescence spectra of coronene in polymethylmethacrylate[15] and in perhydrocoronene.[16] Zander[16] suggests that the bands above 5250 Å are due to transitions from vibrationally excited states of the triplet level. The high-energy fluorescence may also be assignable to transitions from higher vibrational levels of the ^1L_b state.[7] These transitions must then become more probable under compression. The possibility cannot be excluded that pressure enhances emission from or the formation of photochemical isomers of coronene. The high pressure experiments have emphasized the presence of this unusual radiative process, in addition to establishing the nature and magnitude of environmental effects on fluorescence spectra in frozen, well-defined solvents.

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