

1603 cm^{-1}) and aliphatic (2951 cm^{-1}) and aromatic carbon-hydrogen stretch (3006 to 3078 cm^{-1})

When the dianthracene crystals were compressed and illuminated, for example at 514.5 nm and 296 K, a weak but broad luminescence background appeared around 10 kbar (fig. 5) and grew in intensity until at pressures higher than 25 kbar, the intensity was competitive to the Raman process. Fig. 9 shows the structureless excimer-like luminescence excited with laser radiation at 457.9, 488.0, 514.5 and 632.8 nm. At 32 kbar the emission is more intense than the dianthracene Raman spectra; however, some of the stronger Raman peaks excited at 514.5 nm could still be followed. The intensity of the emission band induced by pressure and irradiation decreased with decreasing excitation energy. An interesting observation is that both pressure and irradiation appear to be required in creating high photoreactivity in dianthracene. The luminescence lifetime was determined to be approximately 10 ns at 25 kbar and 296 K when excited by 448.5 nm radiation.

DISCUSSION

The most significant conclusion of this study relates to the apparent *stability* of dianthracene. The Raman spectra demonstrate that the dimer is quite stable under compression to 20 kbar and higher pressures, contrary to other reports. No significant intensity of bands associated with the monomer and no obvious mode-instability or "softening" were observed. One difference between these and other studies of the stability under compression was that crystals and compacted powder were used here whereas others have studied powder highly dispersed in compacted KBr matrices.^{5, 7} The shearing and exposure of a large surface area in preparation of KBr pellets may induce decomposition of the dimer, although this was not detected in the infrared spectra of dianthracene-KBr pellet shown in fig. 2.

The pressure dependences of the spectra of the lattice modes and many internal modes of dianthracene are qualitatively similar to those observed for benzene, naphthalene and anthracene.^{2,3-25} However, the shifts of the internal mode frequencies are especially large, by factors of 2 to 6. It is especially interesting that the modes whose frequencies are most sensitive to pressure are the very low-frequency lattice modes and the very high-frequency aromatic C-H stretch modes. This suggests that the predominant factor is the density dependence of the intermolecular H-H distances between atoms on the periphery of the molecules and the associated change of the intermolecular repulsive potentials. Changes of intermolecular C-H distances also may contribute to this effect. The relatively large magnitudes of these shifts suggests that the compressibility of dianthracene may be even larger than that of anthracene which, combined with the higher density of dianthracene at atmospheric pressure, implies that the relative stability of dianthracene is even greater at high pressures.²¹ This is consistent with the reported pressure-induced dimerization and polymerization of similar aromatic molecules.^{26, 27}

The structureless and anomalous high pressure emission bands are a most puzzling feature of this work on dianthracene, and it is difficult to identify the emitting levels. The shape of each high pressure emission spectrum is very similar to one of the three reported excimer fluorescence spectra of dianthracene, namely the red-emitting or the "stable" and "unstable" green emitting sandwich dimers.^{8, 28} The high pressure emission band excited with the He-Ne laser (fig. 9), for example, is similar to the isolated red excimer fluorescence in crystalline dianthracene, while the spectra excited with the Ar ion laser (fig. 9) may be related to the green emitting sandwich dimer. The measured fluorescence lifetime of 10 ns at 296 K and 25 kbar and excited by 448.5 nm radiation is not easily compared with the 77 K sandwich excimer lifetimes

of 215 and 10 ns for the "unstable" and "stable" green emitting and finally 110 ns for the red emitting sandwich dimers.²⁸⁻³⁰ The fluorescence lifetime of the compressed dianthracene, however, is not inconsistent with the lifetimes of the excimer emissions at 77 K, since the latter are expected to be considerably shorter at ambient temperatures. It can be seen from the above discussion that the luminescence spectra of compressed dianthracene may arise from a distribution of close coupled sandwich-like defects that were created and trapped in the crystal under pressure. An alternate explanation is the occurrence of a high pressure phase transition in which another crystalline modification is formed.³¹

Further Raman and infrared studies of large single crystals of dianthracene would be desirable to explain the stability of the dimer. Polarization studies would be especially useful to establish the assignments of many of the Raman active peaks. The problem lies, however, in locating an appropriate solvent for dianthracene from which a large crystal could be grown.

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