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PRESSURE DEPENDENCE OF THE LATTICE FREQUENCIES OF ANTHRACENE AND NAPHTHALENE*

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The pressure dependence of the Raman lattice modes of anthracene and naphthalene molecular crystals has been studied in the range 0–10 kbar, using hydrostatic pressure and laser excitation. Grüneisen parameters in the range 3–6 have been observed. Calculations of the elastic constants and the pressure dependence of the lattice frequencies have been carried out using an intermolecular potential of the atom–atom type, with parameters derived from other crystalline properties. Agreement with experimental data is good.

The temperature variation of the vibrational frequencies of crystal lattices involves a mixed dependence on both temperature and volume, whereas the effects of pressure involve the volume dependence only (to a good first approximation), and allow a useful separation of the two dependences [1]. We report here a study of the pressure dependence of the Raman-active lattice vibrations of the molecular crystals anthracene and naphthalene, and the results of a calculation of these frequencies and of the elastic constants. We used a form of the intermolecular potential which has proved useful elsewhere for molecular crystals. Studies such as this are a new direction for molecular crystals, though some results on intramolecular frequencies at high pressure have appeared. We expect that pressure-dependence studies will play a valuable role in the molecular crystal field in the future.

The experimental methods have been described elsewhere [2]. Crystals of anthracene and naphthalene were subjected to hydrostatic pressure up to 10 kbar, and the Raman spectra were excited by a He–Ne laser (50 mW at 6328 Å). The crystals were oriented, and the spectra partially polarized, but the experimental conditions made polarization data unreliable. Polarized spectra are also taken at one atmosphere

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pressure using an Ar^+ laser and a single crystal sample cut parallel to the optic axes to confirm the assignments of Suzuki et al. [3]. Spectra of polycrystalline samples were obtained from room temperature to 77 $^\circ$K to record the line frequency and width dependence.

Figs. 1 and 2 show the observed frequencies as a function of pressure and volume, which was calculated from the pressure using the data of Vaidya and Kennedy [4]. All six allowed frequencies increase with pressure; the observed Grüneisen parameters, $\gamma_i = -\mathrm{d} \log \nu_i / \mathrm{d} \log V$, vary from about 3 for the highest to about 6 for the lowest frequency. Intramolecular vibration frequencies are uniformly much less pressure-sensitive.

Fig. 3, showing the spectra of anthracene at 1 atm, 3.2 kbar and 9.3 kbar, illustrates the data obtained. Some polarization effects are noticeable, and agree with the Suzuki [3] assignments. Fig. 4 shows the characteristic effects of temperature; frequency shifts and linewidth changes, but no change in qualitative pattern. The linewidths do not change with pressure. There are no known phase changes in these systems.

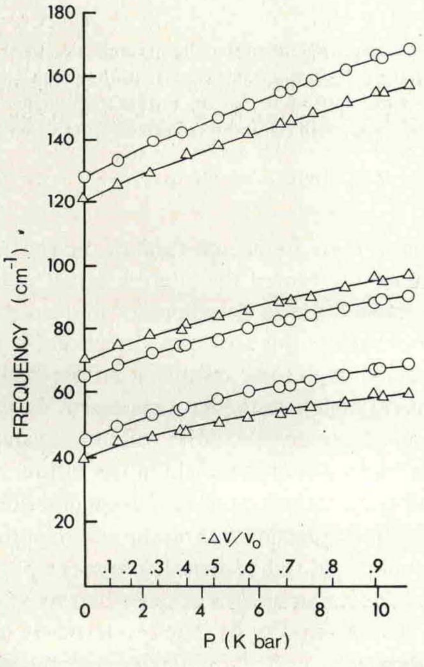

Fig. 1. Pressure and volume dependence of anthracene Raman-active lattice frequencies. Circles represent B_g frequencies, triangles A_g.

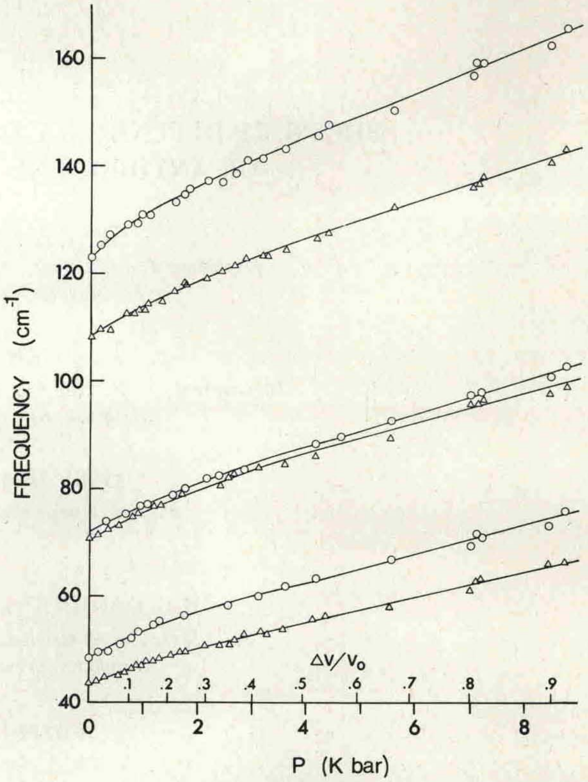

Fig. 2. Pressure and volume dependence of naphthalene Raman-active lattice frequencies. Circles represent B_g frequencies, triangles A_g.

We calculated the lattice frequencies using the methods of Taddei et al. [5], using an intermolecular potential of the atom–atom type, involving interactions between all pairs of atoms on neighboring molecules. The parameters for this potential were taken from the work of Williams [6] (potential set number IV from combined data on aliphatic and aromatic molecules). The crystal structures (both are $P2_1/a$ with two molecules per unit cell) were from Cruickshank [7]. We confirmed that the observed crystal structures and sublimation energies were closely in accord with those calculated using the potential. Table 1 gives the observed and calculated one-atmosphere-pressure frequencies, showing close agreement except for the highest B_g frequency. This frequency has invariably been calculated to be too low in our work on both these compounds, a discrepancy which also appeared in the pattern of the earlier calculations by Pawley [8] and Weulersse [9].