

**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<sup>+</sup> 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 °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,  $\gamma_i = -d \log \nu_i / d \log V$ , 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.

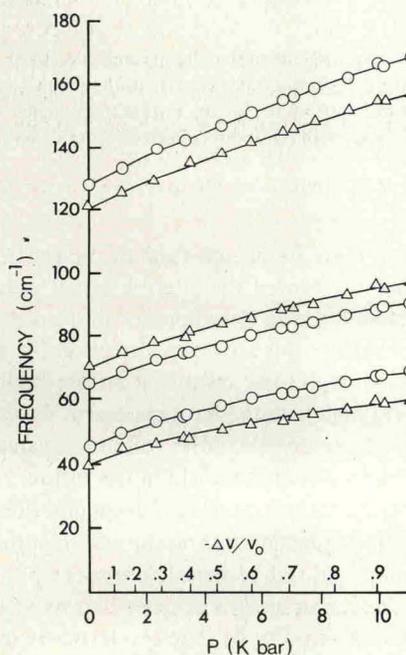


Fig. 1. Pressure and volume dependence of anthracene Raman-active lattice frequencies. Circles represent B<sub>g</sub> frequencies, triangles A<sub>g</sub>.

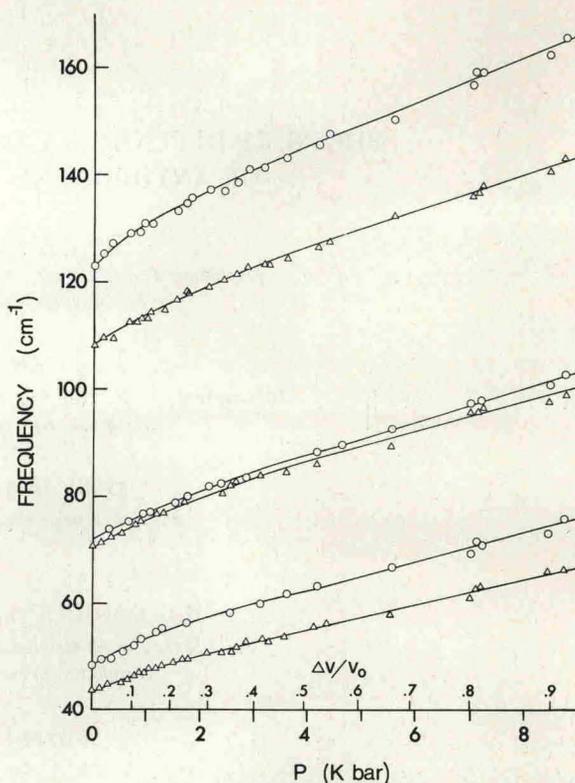


Fig. 2. Pressure and volume dependence of naphthalene Raman-active lattice frequencies. Circles represent B<sub>g</sub> frequencies, triangles A<sub>g</sub>.

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<sub>1</sub>/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<sub>g</sub> 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].

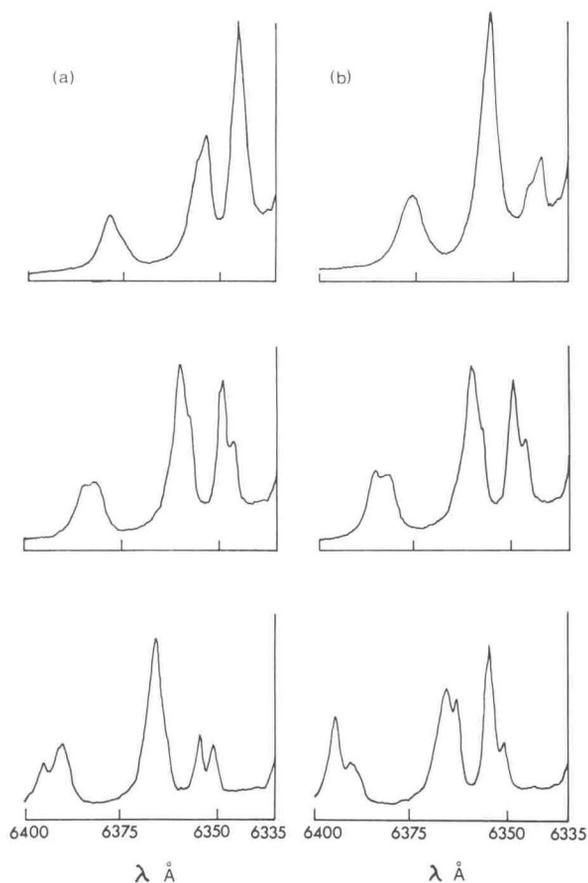


Fig. 3. Pressure dependence of anthracene lattice Raman spectra. (a)  $c(bc)b$  polarization, (b)  $c(ac)b$  polarization. Due to scattering in the sample polarization data are not quantitative.

The elastic constants of anthracene [10] and naphthalene [11] have been measured by acoustic methods. We have calculated the dispersion curves using the methods of Bouadeo and Taddei [12] and from the limiting slopes of the acoustic frequency versus wave vector have obtained the sound velocities. The sound velocities and dispersion curves obtained here are in reasonable agreement with those obtained by Pawley [8], allowing for the differences in potential energy parameters used. The elastic constants, derived directly from the velocities, will not be compared with experiment since a certain amount of arbitrariness is involved in deriving the non-major constants from the velocities. Sufficient indication of the agreement with the direct experimental sound velocities is shown in table 2.

Instead of maintaining a purely theoretical approach and using our derived elastic constants to compute the effect of pressure on structure, we have chosen to use the constants taken from experiment [10,11]. A pressure is assumed (1000–2000 atmospheres) and the strains calculated. The compressions did not agree very closely with the pressure–volume data [4], but any attempts to scale the calculations would not affect the values of the Grüneisen parameters derived. With the compressed unit cell parameters, the lattice frequencies were again calculated, and values of  $\gamma_i$  obtained. The values of  $\gamma_i$ , calculated and observed, are given in table 3 for anthracene, and the agreement shown there is reasonable cause to accept the model potential as representing the intermo-

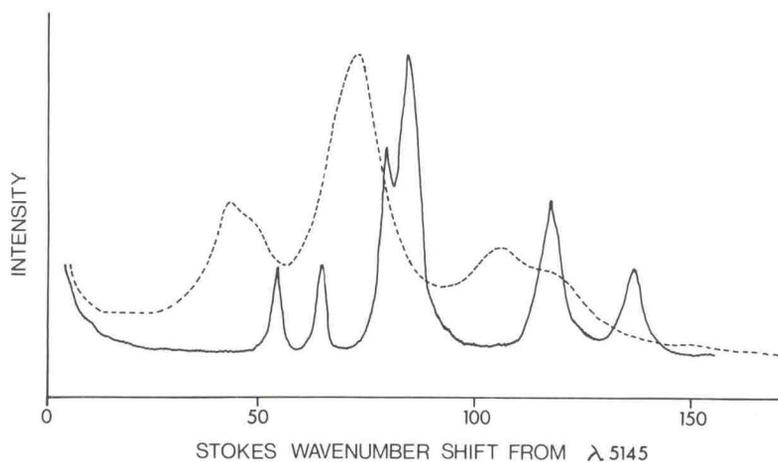


Fig. 4. Temperature dependence of the naphthalene lattice Raman spectrum. — 77°K, --- 29°K.

Table 1  
Lattice frequencies of naphthalene and anthracene, observed and calculated

	Naphthalene		Anthracene	
	$\nu_{\text{obs}}^{\text{a)}$	$\nu_{\text{calc}}$	$\nu_{\text{obs}}^{\text{a)}$	$\nu_{\text{calc}}$
$A_g$	109	106	121	120
	74	79	70	76
	51	52	39	40
$B_g$	125	101	125	109
	71	73	65	67
	46	47	45	49
$A_u$	102	97	101	101
	49	50	44	39
$B_u$	65	65	60	62

a) Raman data ( $A_g$ ,  $B_g$ ) from this work and ref. [2]. Infrared ( $A_u$ ,  $B_u$ ) from ref. [13].

Table 2  
Sound velocities (in  $10^5$  cm/sec) observed and calculated for anthracene and naphthalene at 298°K

Propa- gation	Displace- ment	Anthracene		Naphthalene	
		$\nu_{\text{obs}}^{\text{a)}$	$\nu_{\text{calc}}$	$\nu_{\text{obs}}^{\text{b)}$	$\nu_{\text{calc}}$
100	100	2.81	2.54	2.64 (2.62)	2.47
	010	1.59	1.77	1.91 (1.94)	1.79
	004	1.32	1.58	1.34	1.45
010	010	3.32	2.72	2.95 (2.93)	2.79
	001	1.15	1.09	1.65	1.51
	100	1.75	1.96	1.96	2.23
001	001	3.75	3.80	3.35 (3.36)	3.82
	100	1.35	1.47	1.07 (1.16)	1.25
	010	1.39	1.53	1.71 (1.71)	2.10

a) Ref. [9]. b) Ref. [14]; in parentheses ref. [10].

molecular situation adequately. We must note that the calculation whose results are presented here did not include all possible refinements. For example, the molecular orientations may change on compression; we have tried allowing the orientations to relax to equilibrium\* at the new density and have found changes

Table 3  
Grüneisen parameters,  $\gamma_i = -d \log \nu_i / d \log V$ , for anthracene

	$\nu_{\text{obs}}$	$\gamma_{\text{obs}}$	$\gamma_{\text{calc}}$
$A_g$	109	3.7	3.2
	74	4.9	4.1
	51	6.2	5.1
$B_g$	125	3.6	3.7
	71	5.0	4.7
	46	6.3	5.4

in the calculated frequencies. Also, the elastic constants may depend on pressure; we have calculated sound velocities as a function of pressure (density) and have found these changes to be predicted. The results quoted above in table 3 are thus not to be taken as the best that theory can do; they are, however, representative of the results obtained with various reasonable variations on the calculations.

The values of the Grüneisen parameters, averaging about 5, are higher than those typically obtained for ionic crystals, and the implication is that a very distance-sensitive potential is associated with the frequencies being observed. Such a steep potential can only arise from the close-range intermolecular repulsions, and these are an important feature of the atom-atom potential at distances corresponding to molecular contacts in crystals.

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\* Using the computer program PACK3, kindly provided by D.E. Williams, with the same intermolecular potential used in the lattice frequency calculations.

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