

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 Bonadeo 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-

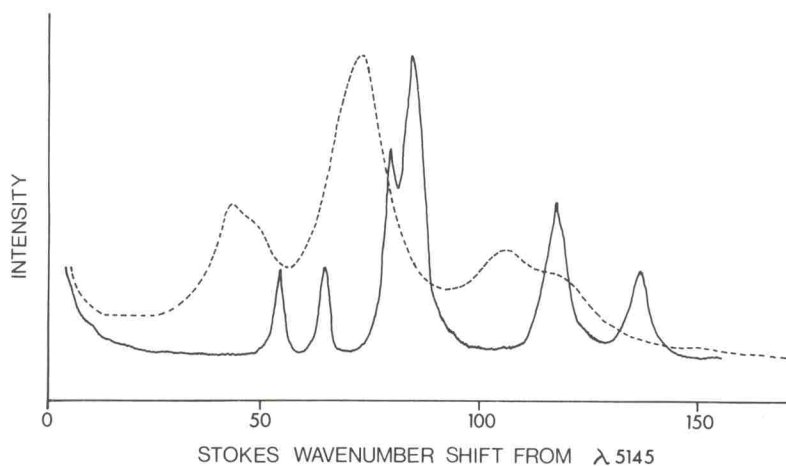


Fig. 4. Temperature dependence of the naphthalene lattice Raman spectrum. — 77°K, --- 29°K.

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.

## References

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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.