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THE LATTICE VIBRATIONS OF 1,2,4,5-TETRABROMOBENZENE

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The lattice vibrations of 1,2,4,5-tetrabromobenzene in its β and γ phases have been studied using Raman and far infrared spectroscopy. The results are compared with calculations based on the atom–atom interaction model. In spite of the similar crystal structures, both the spectra and the calculated frequencies of the two phases are widely different.

In the last years, we have been interested in the problem of intermolecular forces in halogenated benzene crystals; we have studied exhaustively the lattice vibrations, intermolecular forces and related problems in chlorinated benzene crystals [1–4], and recently we have refined an intermolecular force field for brominated benzene crystals [5]. The refinement included dynamical and structural data of a series of these crystals; because of the lack of data, the lattice vibrations of 1,2,4,5-tetrabromobenzene were not taken into account, although the corresponding frequencies may be obviously calculated from the general force field obtained.

In the present work we study the lattice vibrations of 1,2,4,5-tetrabromobenzene in order to complete the experimental data on the series, and to check the accuracy and transferability of the potential parameters obtained.

1,2,4,5-tetrabromobenzene has two known phases: β, below the transition point at 319.5 K, and γ above this temperature up to the melting point. The bimolecular unit cells of both crystal phases are monoclinic, space group $P2_1/c$ (C_{2h}^5) with the molecules located at inversion centers. The unit cell parameters are:

β phase [6] : $a = 10.323$; $b = 10.705$; $c = 4.018$;
$\beta = 102°22'$.

γ phase [7] : $a = 10.00$; $b = 11.18$; $c = 4.07$;
$\beta = 103°48'$.

Not only the unit cell parameters, but also the molecular arrangements are very similar in both crystal phases [7].

For the purpose of assignment and comparison with calculated data, it is necessary to obtain polarized light data on single crystals. We have attempted to grow single crystals from the melt and from solution in different organic solvents; unfortunately, it was not possible to grow crystals large and perfect enough to allow polarized Raman, and much less infrared experiments. The crystals obtained from the melt shattered on undergoing the phase transition, and those obtained from solution which were large enough to give reasonable Raman scattered intensity showed defects – mostly twinning [6] – which prevented clear polarization results; therefore, although we have observed partial polarizations, our results refer to unpolarized spectra of essentially polycrystalline samples.

1,2,4,5-tetrabromobenzene from Eastman was repeatedly recrystallized from ethanol and further purified by zone refinement. The Raman spectra were obtained with a Jarrell–Ash 25-300 spectrophotometer, using the 4880 Å line of a Coherent Radiation CR2 Ar^+ laser as exciting source. The experiments were performed with a 90° scattering arrangement; resolution was about 1 cm^{-1}. The γ phase spectra at about 325 K were obtained simply by letting the laser source heat

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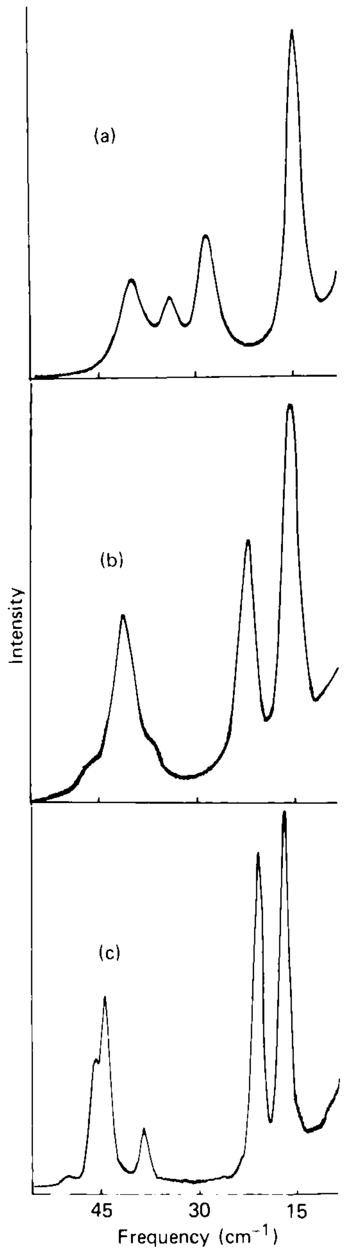

Fig. 1. Raman spectra of 1,2,4,5-tetrabromobenzene. (a) γ phase at 325 K; (b) β phase at 300 K; (c) β phase at 100 K.

up the samples; it was necessary to cool down the samples to obtain room temperature β phase spectra.

Fig. 1 shows the Raman spectra of the compound at 325 K (γ phase), and at 300 and 100 K (β phase). According to group theory, there are 6 Raman active ($3\ A_g$ and $3\ B_g$) librational modes in either phase. Of these four are found in the γ phase spectrum; five bands appear in the β phase at room temperature, and one more is resolved in the liquid nitrogen temperature spectra.

The far infrared spectra were recorded with a Grubb–Parsons modular cube interferometer, at 1 cm^{-1} resolution. Due to the weakness of the bands, their broadness at higher temperatures, and the presence of a rather large background, only the liquid nitrogen spectrum was successfully recorded, and is shown in fig. 2. Of the 3 infrared active ($2\ A_u$ and $1\ B_u$) expected translational modes, two are detected.

Table 1 shows the values of the observed frequencies of the lattice modes, and those calculated using the atom–atom model with potential parameters obtained by Burgos and Bonadeo [5]. We have placed calculated and observed values in correspondence using some indications of partial Raman polarizations and a proximity criterion; this by no means can be regarded as a definitive assignment, but only as a tentative indication. Within these limitations, the agreement between observed and calculated values is reasonable, as compared with the values found for other halogenated benzene crystals [2]. Table 1 also shows the calculated eigenvectors, i.e the normal mode composition in terms of the molecular axes translations and rotations. Here x is perpendicular to the molecular plane, y contains the

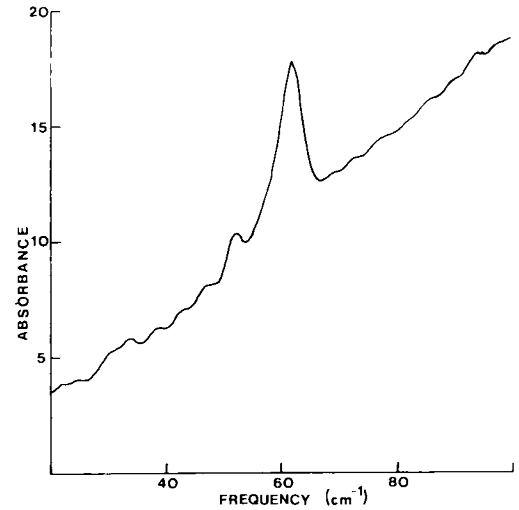

Fig. 2. Far infrared spectrum of β-1,2,4,5-tetrabromobenzene at 85 K.

Table 1
Observed and calculated lattice vibration frequencies (in cm^{-1}) of 1,2,4,5-tetrabromobenzene

Phase	$\nu_{\mathrm{exp.}}$		Sym.	$\nu_{\mathrm{calc.}}$	Eigenvectors					
	300 K	100 K			T_x	T_y	T_z	R_x	R_y	R_z
β	15.5	17.5	B_g	18.7				−0.27	0.96	0.00
	22.5	21.5	A_g	24.4				0.01	−0.68	−0.74
	37.0	38.5	A_g	29.9				0.56	−0.61	0.57
	41.0	44.5	B_g	36.7				−0.96	−0.27	−0.12
		46.0	A_g	42.3				−0.83	−0.42	0.37
	46.0	50.5	B_g	44.5				−0.12	−0.03	0.99
	–	–	A_u	33.9	−0.98	−0.20	0.07			
	–	52.0	B_u	51.8	−0.20	0.67	−0.71			
	–	62.0	A_u	52.5	0.10	−0.71	−0.70			
γ	330 K									
	14.5		A_g	18.3				−0.20	−0.87	0.45
			B_g	21.2				0.18	−0.98	0.06
	28.0		B_g	27.9				−0.93	−0.19	−0.31
			A_g	29.8				0.09	−0.48	−0.87
	34.0		B_g	35.0				−0.32	0.00	0.95
	40.0		A_g	40.7				−0.98	0.13	−0.17
	–		A_u	24.8	−0.98	0.04	−0.20			
	–		A_u	44.8	−0.17	−0.70	0.70			
	–		B_u	46.5	−0.11	0.72	0.69			

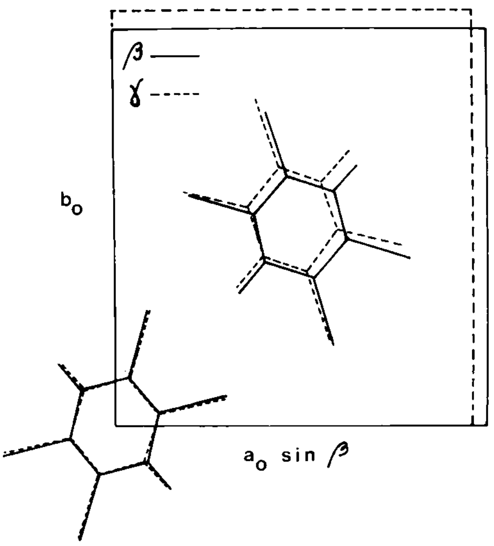

Fig. 3. Unit cells of β and γ tetrabromobenzene viewed along the c axis.

C–H bonds, and z is perpendicular to x and y. It can be seen that only the two lower lying A_g modes change substantially from one phase to the other; however, there are several crossings in the calculated frequencies. This is consistent with the fact that although the unit cells for both phases are remarkably similar, as shown in fig. 3, the Raman spectra are quite different, a fact which is correctly reflected in the calculations.

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