Calculation of thermal expansion and implicit phonon frequency shift in deuterated anthracene

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Rajiv Bhandari and V K Jindal

Department of Physics, Panjab University, Chandigarh-160014, India

Abstract. The calculation of implicit shift to the phonon energies for phonons in deuterated anthracene $C_{14}D_{10}$ at $q = 0$ is presented, the explicit shift having been already described. This implicit shift is then compared with the shift obtained by neutron scattering experiments and Raman measurements. The calculation of thermal expansion, compressibility and Grüneisen constants, which occur in the calculation of implicit shift, is also presented and a comparison with the measurements is made. All these results are in rough agreement with their measured counterparts, which therefore strengthens faith in the general approach adopted but at the same time indicates the necessity of improvement in the model for the molecular crystal of deuterated anthracene.

1. Introduction

In the recent past, extensive theoretical and experimental work has been done to investigate the harmonic and anharmonic properties of molecular crystals such as naphthalene and anthracene. As a result, a reasonable amount of data on the temperature and pressure dependence of the phonon frequencies for these crystals is available (Bokhenkov *et al* 1976, 1977, 1978, Mackenzie *et al* 1977, Natkaniec *et al* 1980, Schmelzer *et al* 1981, Jindal *et al* 1982, Dorner *et al* 1982, Häfner and Kiefer 1987, Jordan *et al* 1989). Although the calculation of the anharmonic frequencies and band widths of molecular crystals is quite involved, mainly owing to the complexities of the theoretical procedure, nevertheless theoretical results have been reported for some cases. The anharmonic phonon frequencies differ from harmonic phonon frequencies by a shift from their harmonic low-temperature frequencies. This shift, normally described as the phonon frequency shift depends upon the temperature and consists of two parts from the calculation point of view. The part arising from the explicit anharmonic terms in the crystal potential energy has been termed the explicit shift. The other part arises because of the implicit temperature dependence of the phonon frequencies and is obtained from the volume dependence of the phonon frequencies. The latter contribution has been termed the implicit shift. For deuterated naphthalene both the explicit and the implicit shifts have been calculated already (Jindal and Kalus 1983, 1986).

Deuterated anthracene is a much larger molecule and, owing to non-rigidity of the molecule–molecule motions, there is a mixing of internal and external modes for this crystal. This crystal has also been studied from a theoretical viewpoint, by calculating the anharmonic phonon frequencies and linewidths in a similar manner to that of

naphthalene. The results for explicit anharmonic shift are available (Jordan *et al* 1989); these have to be added to the implicit anharmonic frequency shift in order to make a comparison with the measured phonon frequency shift. This paper presents the calculation of the implicit anharmonic phonon frequency shift, thereby completing the calculation of anharmonic phonon frequency shift in deuterated anthracene. We calculate the implicit anharmonic phonon frequency shift at all Γ points for deuterated anthracene and compare these with experimental results of anharmonic phonon frequency shift obtained by neutron inelastic coherent scattering results (Jindal *et al* 1982) or Raman measurements (Häfner and Kiefer 1987). This paper also simultaneously calculates thermal expansion, compressibility and Grüneisen constants which are then compared with the available experimental data. The procedure and assumptions regarding the model of our molecular crystal are similar to those of Jindal and Kalus (1986).

This paper is organized as follows. The theoretical procedure for the calculation of the implicit phonon frequency shift is given in section 2. An expression for thermal expansion for subsequent use is also obtained in this section. In section 3, the numerical calculations for anharmonic phonon frequency, compressibility, thermal expansion, implicit shift, etc, are described and results presented. Comparison of the calculated and experimental results is made and discussed in section 4. Concluding remarks are presented in section 5.

2. Theoretical procedure

The temperature dependence of phonon frequencies which is an explicit function of temperature and volume can be expressed as,

$$\omega_{qj} = \omega_{qj}(T, V(T)). \tag{1}$$

Therefore, the shift due to the temperature in the phonon frequencies consists of two parts:

$$d\omega_{qj}/dT = (\partial\omega_{qj}/\partial T)_V + (\partial\omega_{qj}/\partial V)_T(\partial V/\partial T). \tag{2}$$

The first part is the explicit contribution and arises owing to the explicit anharmonic terms in the crystal potential. The second term which is due to the volume dependence of the phonon frequencies is an implicit function of temperature. The explicit contribution for deuterated anthracene has already been calculated by Jordan *et al* (1989). The implicit contribution can further be written as

$$(\partial\omega_{qj}/\partial T)_{im} = (\partial\omega_{qj}/\partial V)_T(\partial V/\partial T) = -\gamma_{qj}\omega_{qj}\beta \tag{3}$$

where γ_{qj} is the Grüneisen constant and is defined as

$$\gamma_{qj} = -\partial(\ln\omega_{qj})/\partial(\ln V) \tag{4}$$

and β is the volume thermal expansion coefficient and is given by

$$\beta = (1/V)(\partial V/\partial T). \tag{5}$$

Rewriting equation (3) as

$$\partial\omega_{qj}/\omega_{qj} = -\gamma_{qi}\beta\,\partial T \tag{6}$$

assuming γ_{qj} to be independent of temperature and integrating it from $T = 0$ to $T = T$, we obtain the expression for the fractional implicit shift as

$$(\Delta\omega_{qj}/\omega_{qj})_{im} = \exp[-\gamma_{qj}\varepsilon(T)] - 1 \tag{7}$$

where $\varepsilon(T) = \int_0^T \beta\,dT$, which is the volume thermal expansion. It is evident that the

Table 1. The Williams potential parameters.

Atom pair	A (kcal mol^{-1} Å^{-1})	B (kcal mol^{-1} Å^{-1})	α (Å^{-1})
C–C	568	83 630	3.60
C–D	125	8766	3.67
D–D	27.3	2654	3.74

calculation of the implicit phonon frequency shift (equation (7)) requires a calculation of the Grüneisen constants γ_{qj} and volume thermal expansion $\varepsilon(T)$.

To calculate the thermal expansion, we follow the procedure and details described by Jindal and Kalus (1986). The expression for lowest-order thermal expansion is given by

$$\varepsilon_0 = \frac{1}{2V_0 B} \sum_{qj} \gamma_{qj} \hbar \omega_{qj} \coth\left(\frac{\hbar \omega_{qj}}{2kT}\right) \tag{8}$$

and the next-highest-order thermal expansion is given by

$$\varepsilon = \varepsilon_0 \left(1 - \varepsilon_0 \tfrac{1}{2} \frac{V_0^3 (\partial^3 \Phi/\partial V^3)_0}{V_0 B} + \frac{kT}{V_0 B} \sum_{qj} \bar{\gamma}_{qj}^2 (k_0^2 \operatorname{cosech}^2 k_0 - k_0 \coth k_0)\right) \tag{9}$$

where $V_0 = V(0)$ is the unstrained volume and B is the bulk modulus which is defined as

$$B = V_0 (\partial^2 \Phi/\partial V^2)_{V_0}. \tag{10}$$

In equations (8)–(10), ω_{qj} is the harmonic phonon frequency at $V = V_0$, $k_0 = \hbar \omega_{qj}/2kT$ and $\bar{\gamma}_{qj}$ is the renormalized Grüneisen constant (Jindal and Kalus 1986).

3. Numerical calculations

For the calculation of thermal expansion (equation (8)) and implicit phonon frequency shift (equation (7)), we need to calculate

(i) the phonon frequencies,
(ii) the Grüneisen constants and
(iii) the bulk modulus.

For this, we now describe the numerical procedure followed for the calculation of these quantities.

3.1. Phonon frequencies

To calculate the phonon frequencies we assume a rigid-molecule approximation and a 6-exponential potential of the form

$$V(r) = -A/r^6 + B \exp(-\alpha r) \tag{11}$$

where A, B and α are constants depending upon the nature of the atoms involved. Of the three sets of constants A, B and α which are commonly in use, we have chosen those provided by Williams (1967) as has been done for the case of naphthalene. These constants are given in table 1.

R Bhandari and V K Jindal

Table 2. Calculated and measured phonon frequencies.

		ω_{qj} (THz)	
Branch	Character	Neutron scattering experiments	Calculated
4	Γ_3	1.618 ± 0.007	1.242
5	Γ_4	—	1.397
6	Γ_2	1.424 ± 0.005	1.446
7	Γ_1	1.409 ± 0.004	1.613
8	Γ_1	2.33 ± 0.018	1.910
9	Γ_3	2.053 ± 0.007	2.501
10	Γ_2	3.1 ± 0.024	3.327
11	Γ_3	3.84 ± 0.009	4.097
12	Γ_1	3.54 ± 0.098	4.259

The harmonic phonon frequencies ω_{qj} for the value of q in the Brillouin zone can be obtained by diagonalizing the dynamical matrix of our molecular crystal:

$$M_{\mu_1\mu_2}(k, k', q) = \frac{1}{[m_{\mu_1}(k)m_{\mu_2}(k')]^{1/2}} \sum_{l'} \Phi_{\mu_1\mu_2}(lk, l'k')$$
$$\times \exp\{iq \cdot [R(l'k') - R(lk)]\}. \tag{12}$$

The details of the procedure are similar to those used by Pawley (1967, 1972). In the lattice summation of the potential, atom contacts up to 5.5 Å from the 12 surrounding molecules were taken into account. The contribution to the potential beyond 5.5 Å was assumed to be governed by the attractive part of the potential only and was obtained approximately. The crystal structure parameters a, b, c, β and the orientation of the molecule were varied until the total crystal potential energy was a minimum. The dynamical matrix was then diagonalized to obtain the phonon frequencies ω_{qj}. The phonon frequencies using the Williams potential parameter sets at Γ points are given in table 2.

3.2. Grüneisen constants

To calculate the Grüneisen constants (equation (4)), we need the volume dependence of the phonon frequencies. This is obtained by computing the 'new volume' of the crystal under a hydrostatic pressure p. For this, one minimizes the potential energy function

$$\Phi_T = \Phi(V) + p \, \Delta V \tag{13}$$

by varying the crystal structure parameters (Schmelzer *et al* 1981). This new structure gives the new volume, and the dynamical matrix is again diagonalized corresponding to this structure. From these changes in the phonon frequency, the Grüneisen constants are easily calculated. We present the results for the Grüneisen constants thus calculated for various phonon modes at Γ points in table 3.

3.3. Bulk modulus

To calculate the bulk modulus (equation (10)), we require the potential energy as a function of volume. The total potential energy of the crystal of N molecules is given by

Table 3. Calculated and measured Grüneisen Raman parameters. The measured results were obtained at room temperature.

Phonon branch	γ_{qj}	
	Raman measurements	Calculated
4	4.39	3.052
5	a	5.030
6	a	3.136
7	4.37	2.841
8	3.59	4.897
9	3.51	4.388
10	2.91	3.375
11	2.96	4.048
12	a	2.630

a These modes are not Raman active.

$$\Phi = \tfrac{1}{2}N \sum_{l'k'}{}' \varphi(lk, l'k') \tag{14}$$

where the prime implies that $lk \neq l'k'$. Rewriting the intermolecular potential energy $\varphi(lk, l'k')$ in terms of the atom–atom potential, equation (14) becomes

$$\Phi = \tfrac{1}{2}N \sum_{l'k'}{}' \sum_{ij} V(r_{ij}^{lk,l'k'}) \tag{15}$$

where i and j run through the number of atoms in a molecule and $r_{ij}^{lk,l'k'}$ represents the atom–atom distance between atom i of molecule lk and atom j of molecule $l'k'$. One part of the summation in equation (15) is calculated exactly for atoms within a radius R of 5.5 Å. The remaining 'distant-potential' part Φ_{dist} can be approximated by neglecting the short-range repulsive part and assuming the molecules to be uniformly distributed outside a sphere of radius R. So, we obtain

$$\Phi_{dist} \simeq -\tfrac{1}{2}N\left(\sum_{ij} A_{ij}\right)n \int_0^\infty \frac{4\pi r^2}{r^6}\, dr \tag{16}$$

where n is the number of molecules per unit volume. For our case, $n = 2/V_C$, where V_C is the volume of a unit cell. Therefore,

$$\Phi_{dist} \simeq -(4\pi/3)N(A_T/V_C R^3) \tag{17}$$

$$A_T = \sum_{ij} A_{ij} = N_C^2 A_{CC} + 2N_C N_D A_{CD} + N_D^2 A_{DD} \tag{18}$$

where N_C and N_D are the numbers of C and D atoms per molecule. Then the total potential energy of the crystal was obtained from these two contributions (i.e. equations (15) and (17)).

In order to obtain the potential energy at various volumes, a new volume corresponding to an applied pressure was obtained by minimizing $\Phi + p\,\Delta V$ with respect to the crystal structure parameters. The procedure is identical with that used by Jindal and Kalus (1986). From these data, Φ at various volumes was obtained and has been

Table 4. The total potential energy at various unit-cell volumes and pressures.

p (kbar)	V (Å^3)	Φ (kcal mol^{-1})
−2	475.207	−23.559
0	468.178	−23.712
−2	459.948	−23.617
4	453.381	−23.318

Table 5. Coefficients of the potential energy Φ and volume relationship and compressibility. The experimental results are from the work of Vaidya and Kennedy (1971). These results are for protonated anthracene.

				K (bar^{-1})	
a	b	c	d	Calculated	Experimental
987.3297	−5.4728	9.5268×10^{-3}	-5.2328×10^{-6}	3.549×10^{-11}	14.736×10^{-11}

tabulated in table 4. A plot of Φ for various cell volumes is given in figure 1. We have fitted this curve to the equation

$$\Phi = a + bV_0 + CV_0^2 + dV_0^3 \tag{19}$$

where Φ is in kilocalories per mole and V_0 is the volume of a unit cell in cubic ångströms. This equation facilitates the evaluation of the bulk modulus B, or the compressibility $K = 1/B$. The calculated result is presented in table 5. The coefficients a, b, c and d are also presented in table 5.

3.4. Thermal expansion

Once the phonon frequencies, Grüneisen constants and bulk modulus have been calculated as discussed earlier, the thermal expansion can now be easily calculated using equations (8) and (9) for lowest-order ε_0 and next-highest-order ε, respectively. The Brillouin zone summation encountered in equation (8) has been carried out using a mesh size of 4 for the q-vector. The calculated results for ε_0 are plotted in figure 2.

To calculate the next-highest-order thermal expansion, we require firstly $(\partial^3\Phi/\partial V^3)_0$, which can be immediately obtained from equation (19), and secondly γ_{qj}, the renormalized Grüneisen constants. Since the third term in equation (9) was found to be negligibly small for naphthalene, we assume that this holds for anthracene also. The results for ε are also plotted in figure 2.

3.5. Implicit shift

Using the various ingredients as obtained above, we now calculate the implicit shift from equation (5). This implicit shift is plotted in figure 3.

4. Discussion

We now discuss the numerical results obtained in the previous section for the Grüneisen constants, compressibility, thermal expansion and implicit phonon frequency shifts. The
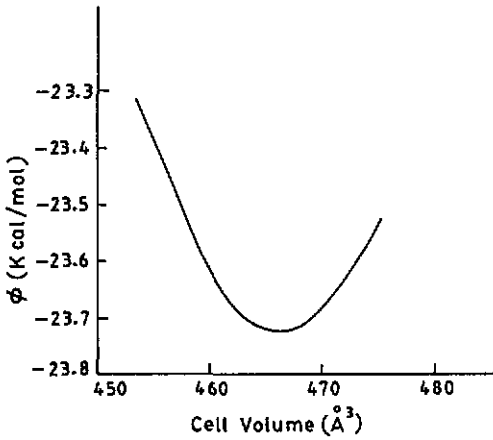
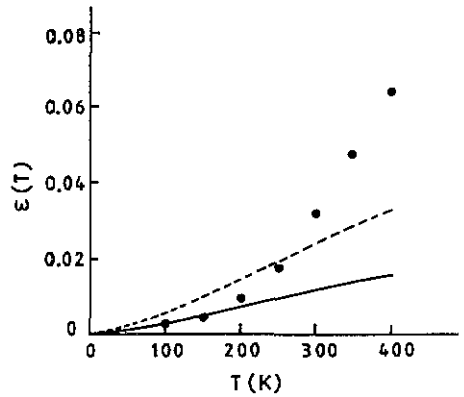Figure 1. The total crystal potential energy plotted as a function of cell volume.

Figure 2. Volume thermal expansion $\varepsilon(T)$ as a function of temperature: ——, lowest-order thermal expansion; – – –, higher-order thermal expansion; ●, experimental data obtained from the data collected by Häfner and Kiefer.
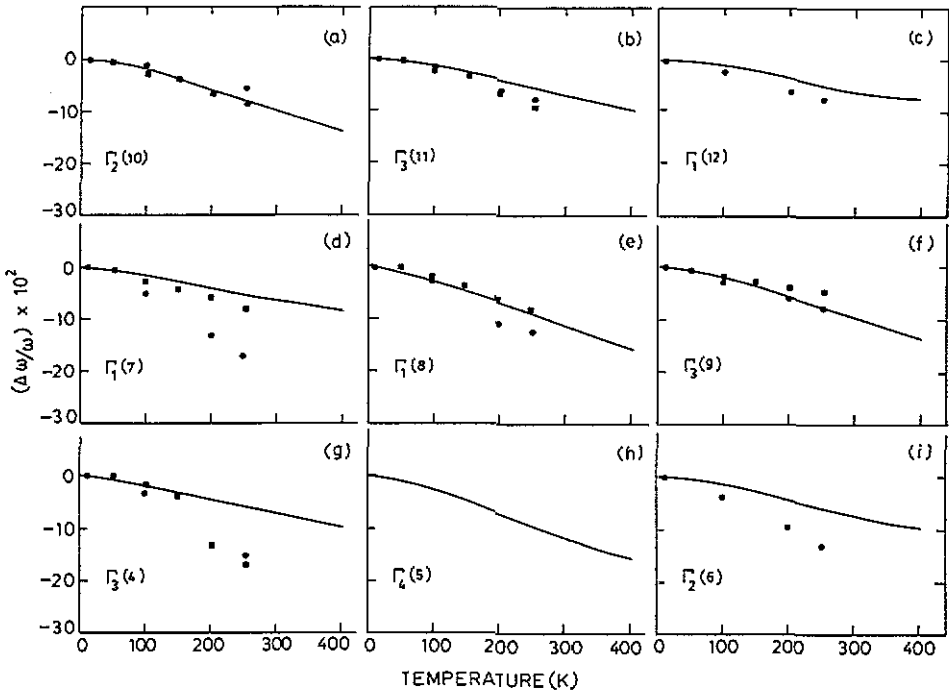

Figure 3. Calculated and experimental results of the relative shift in the phonon frequencies of the nine optic translational and liberational modes at Γ points as a function of temperature: ——, calculated implicit shift; ●, measured total relative shift obtained from neutron scattering experiments; ■, measured total relative shift obtained from Raman scattering experiments.

calculation has been carried out assuming a rigid-molecule model, which for anthracene molecules is not a good approximation. The inclusion of some of the internal modes is useful in this case. A comparison of these quantities with available experimental data from neutron scattering or Raman measurements has also been made.

In table 2, the phonon frequencies measured from neutron inelastic scattering experiments (Jindal *et al* 1982) at 14 K are compared with our calculated results. The model calculation reproduces the phonon frequencies only approximately. In table 3, we also present the measured value of the Grüneisen constants (Häfner and Kiefer 1987). The comparison of the calculated Grüneisen constants with the measured Grüneisen constants of Raman-active modes shows that the calculated Grüneisen constants are different from the measured values by up to 30%. For comparison of compressibility calculated here, we also present in table 5 its measured value at 0 K. In the absence of any good data for the measurement of the compressibility for deuterated anthracene, a comparison has been made with the data for protonated anthracene (Vaidya and Kennedy 1971) measured at room temperature. The value of compressibility is expected to decrease at 0 K and thus a significant improvement is expected in the agreement between the calculated and measured values.

The results of thermal expansion (figure 2) are in reasonably good agreement with the measured results up to around room temperature. The measured values shown in figure 2 for thermal expansion have been obtained from the data given by Häfner and Kiefer. However, at high temperatures, the measured thermal expansion shows a very rapid increase with increasing temperature. In figure 3, the measured total relative shifts using neutron inelastic scattering experiments (Jindal *et al* 1982) and Raman scattering experiments (Häfner and Kiefer 1987) are also shown. The implicit phonon frequency shifts (figure 3) thus calculated account for the major part of the total measured shifts for various modes. Keeping in view that the explicit anharmonic shifts are expected to be positive, our estimate of the implicit shifts here is somewhat higher. In fact, if the experimental value of thermal expansion is used to calculate the implicit shift, the total shift thus calculated by adding to it the explicit shift (Jordan *et al* 1989) will be in good agreement with the measured shift. Obviously, our model for the calculation of phonon frequencies in deuterated anthracene is rather simplified. Firstly, we assume a rigid-molecule model which is not true for the molecule of deuterated anthracene. Secondly, while calculating the harmonic lattice dynamics, no attempt has been made to improve the phonon dispersion curves by modifying the atom–atom potential. We shall take the potential parameters accepted already as valid for all C–C, C–D or D–D interactions.

5. Concluding remarks

In this paper, we have calculated the implicit shift to the phonon frequencies for deuterated anthracene for all the phonons at Γ points. The results for the calculation of the explicit shift have recently been reported for these phonons (Jordan *et al* 1989). In fact a similar exercise has already been done for deuterated naphthalene. With the completion of this work, the calculation of shifts to the phonon frequencies in deuterated anthracene also becomes complete. This work therefore helps us to understand in a better way the harmonic and the anharmonic potentials used for these systems. Whereas for deuterated naphthalene the results of various quantities such as the Grüneisen constants, thermal expansion, compressibility and phonon frequency shift agreed more closely with the measured values, for deuterated anthracene the agreement is poorer

for all these quantities. The reasons probably lie in the approximate model which is used for the determination of phonon frequencies. However, the results, although not in quantitative agreement, still suggest that improved potentials for larger molecules such as anthracene can lead to better agreement with the measured results. Since the use of atom–atom interactions valid for all C–C-, C–D- and D–D-type interactions, coupled with simple rigid-molecule approximation, has yielded fairly acceptable results for various physical quantities, the hypothesis of the use of atom–atom potentials to form a molecule–molecule potential can be considered to be widely acceptable.

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