BRÜNGER, A. T., KURIYAN, J. & KARPLUS, M. (1987). *Science*, **235**, 458-460.
BRÜNGER, A. T., PETSKO, G. A. & KARPLUS, M. (1989). *Acta Cryst.* A**45**, 50-61.
DEISENHOFER, J., REMINGTON, S. J. & STEIGEMANN, W. (1985). *Methods Enzymol.* **115**, 303-323.
GROS, P., FUJINAGA, M., DIJKSTRA, B. W., KALK, K. H. & HOL, W. G. J. (1988). Abstr. Int. School of Crystallography, 14th Course, 'Crystallography of Molecular Biology', Erice, Italy.
HENDRICKSON, W. A. (1985). *Methods Enzymol.* **115**, 252-270.
HENDRICKSON, W. A., KLIPPENSTEIN, G. L. & WARD, K. B. (1975). *Proc. Natl Acad. Sci. USA*, **72**, 2160-2164.
HENDRICKSON, W. A. & KONNERT, J. H. (1981). In *Biomolecular Structure, Function, Conformation and Evolution*, edited by R. SRINIVASAN, Vol. 1, p. 43. Oxford: Pergamon.
HENDRICKSON, W. A. & WARD, K. B. (1975). *Biochem. Biophys. Res. Commun.* **66**, 1349-1356.
JACK, A. & LEVITT, M. (1978). *Acta Cryst.* A**34**, 931-935.
JONES, T. A. (1985). *Methods Enzymol.* **115**, 157-171.
KAPTEIN, R., ZUIDERWEG, E. R. P., SCHEEK, R. M., BOELENS, R. & VAN GUNSTEREN, W. F. (1985). *J. Mol. Biol.* **182**, 179.
KIRKPATRICK, S., GELATT, C. D. JR & VECCHI, M. P. (1983). *Science*, **220**, 671-680.
KLIPPENSTEIN, G. L., COTE, J. L. & LUDLAN, S. E. (1976). *Biochemistry*, **15**, 1128-1136.
KONNERT, J. H. & HENDRICKSON, W. A. (1980). *Acta Cryst.* A**36**, 344-349.
MCCAMMON, J. A. & HARVEY, S. C. (1987). *Dynamics of Proteins and Nucleic Acids.* Cambridge Univ. Press.
NORTHRUP, S. H. & MCCAMMON, J. A. (1980). *Biopolymers*, **19**, 1001.
PRESS, W. H., FLANNERY, B. P., TEUKOLSKY, S. A. & VETTERLING, W. T. (1986). *Numerical Recipes.* Cambridge Univ. Press.
REIHER, W. E. (1985). PhD thesis. Harvard Univ., Cambridge, MA 02138, USA.
SHERIFF, S. & HENDRICKSON, W. A. (1987). *Acta Cryst.* A**43**, 118-121.
SHERIFF, S., HENDRICKSON, W. A. & SMITH, J. L. (1987). *J. Mol. Biol.* **197**, 273-296.
SMITH, D. L., RINGE, D., FINLAYSON, W. L. & KIRSCH, J. F. (1986). *J. Mol. Biol.* **191**, 301-302.

Acta Cryst. (1989). A**45**, 409-415

The Influence of Coulombic Interactions on Thermal Parameters for Naphthalene and Anthracene: a Lattice-Dynamical Approach

BY A. CRIADO

Departamento de Fisica de la Materia Condensada, Instituto de Ciencia de los Materiales, Universidad de Sevilla, Aptdo 1065, 41080 *Sevilla, Spain*

(*Received* 8 *March* 1988; *accepted* 16 *January* 1989)

Abstract

A lattice-dynamical calculation of thermal parameters is performed for naphthalene and anthracene in the external Born-von Karman formalism using 6-exp potential functions and electrostatic interactions in the form of an atomic point-charge model. Phonon dispersion curves and density-of-states functions are calculated with and without charges. In general, the effect of the Coulombic forces is small and sensibly affects optical branches linked to the B_u mode in both compounds, improving the agreement with the experimental data. The effect on thermal parameters is roughly opposite to that of molecular non-rigidity.

Introduction

The calculation of crystallographic thermal parameters based on a knowledge of the crystal structure and the interatomic forces has been considered an interesting subject because it constitutes an independent test of the thermal parameters obtained from crystal structure analysis as well as of the proposed interatomic force model. In many cases, the hypothesis of a rigid molecule and 6-exp semiempirical potentials has been found to be successful. Most cases where such calculations have been performed concern molecules where Coulombic effects are not important (Filippini, Gramaccioli, Simonetta & Suffritti, 1973, 1976, 1978).

Recently, an extension of the method has been made by taking into account the effects of molecular non-rigidity. For a 'rigid' molecule, the contribution of intramolecular modes (though little populated) added to the external ones gives rise to a small increase of the calculated parameters (Gramaccioli, Filippini & Simonetta, 1982) especially for peripheral atoms. On the other hand, the coupling of external modes with intramolecular degrees of freedom produces a relaxation of lattice frequencies (Pawley & Cyvin, 1970); consequently, a rise of thermal parameters is observed which is comparable to the separate contribution of internal modes (Gramaccioli & Filippini, 1983). For all these cases and for others where non-rigidity is beyond question, the normal coordinates of the isolated molecule have been taken as a basis for the crystal calculations (Bonadeo & Burgos, 1982; Filippini, Simonetta & Gramaccioli, 1984; Gramaccioli & Filippini, 1985; Filippini 1985; Filippini & Gramaccioli, 1986).

0108-7673/89/060409-07$03.00

In this paper we address the question of how important Coulombic effects are in the lattice dynamics of hydrocarbons in order to study the influence of Coulombic interactions in calculated thermal parameters. Hydrocarbons are an example where a 6-exp potential model works extremely well, and therefore it may be expected that Coulombic effects be small. In fact, a recent calculation of the Coulombic contribution to the total lattice energy for a few hydrocarbons shows values less than 10% in most of them, ranging to a maximum value of 21% for benzene, whereas for a chosen set of azahydrocarbons the Coulombic contribution is substantially higher, as much as 59% (Williams & Cox, 1984). Therefore, Coulombic interactions must be crucial for describing the lattice dynamics of heteroatom molecules with strong static dipole and multipole moments due to the different electronegativities of the constituent atoms.

Lattice-dynamical calculations using Coulombic interactions have been reported, especially for small molecules (Rastogi, Anderson & Leech, 1979; Gamba & Bonadeo, 1982) where experimental dipole or quadrupole moments are known and facilitate the adoption of an electrostatic potential model. Nevertheless, for large molecules a multipolar expansion is slowly convergent and higher-order multipoles are not normally known experimentally. On the other hand, a lattice-dynamical treatment based upon a multipole expansion is rather involved (Neto, Righini, Califano & Walmsley, 1978). For these reasons a more convenient model is called for. A very practical one used previously for calculating lattice energies consists of discrete charges placed on the atomic sites (Hirshfeld & Mirsky, 1979). Although a more sophisticated model, the so-called 'distributed dipole model' (Gamba & Bonadeo, 1981), has been proposed, this is only necessary in some special cases (lone-pair atoms, for instance) and even in this case it can always be reproduced by means of two opposite charges (Williams & Cox, 1984).

The current success of the distributed charge model as opposed to the multipole expansion lies in the availability of *ab initio* and semiempirical quantum-mechanical programs which provide us with the molecular charge distribution. In fact, the so-called Mulliken charges (Mulliken, 1955) give us an idea of what charge is to be ascribed to each atom. This method of tackling Coulombic interactions has already been successfully applied in relation to lattice vibrations (Link, Grimm, Dorner, Zimmermann, Stiller & Bleckmann, 1985).

In order to study the influence of electrostatic interactions on calculated thermal parameters, two compounds were chosen, namely naphthalene and anthracene, because they have been widely used in lattice-dynamical calculations including the study of non-rigidity mentioned above, which allows results to be compared. On the other hand, naphthalene and anthracene (especially the former) have been subjected to extensive inelastic neutron experiments ranging from the determination of the phonon dispersion curves (Natkaniec *et al.*, 1980; Dorner *et al.*, 1982) and phonon eigenvectors from scattering intensities (Pawley *et al.*, 1980), to the measurement of the temperature dependence of phonon frequencies (Jindal *et al.*, 1982) together with theoretical calculations of anharmonic effects (Jindal & Kalus, 1983; Della Valle, Frascassi, Righini & Califano, 1983).

The availability of the experimental dispersion curves for these two compounds is an additional piece of information for the study of the influence of electrostatic interactions and for testing our adopted electrostatic force model.

Method of calculation

As is well known, lattice dynamics of molecular crystals can be studied within the harmonic approximation using the Born–von Karman formalism for the external molecular degrees of freedom and the corresponding frequencies and polarization vectors of the vibrational modes are obtained by solving the eigenvalue equation (Born & Huang, 1954)

$$\mathbf{D}(\mathbf{q})\mathbf{U}(\mathbf{q}) = w^2(\mathbf{q})\mathbf{U}(\mathbf{q})$$

where $\mathbf{D}(\mathbf{q})$ is the dynamical matrix. A method of partially accounting for temperature is the so-called quasi-harmonic approximation where the experimental lattice constants at a given temperature are used as a basis for calculating the dynamical matrix. In this way, the calculation remains essentially harmonic but frequencies vary with temperature *via* the changes in force constants due to thermal expansion.

In order to calculate force constants a 6-exp potential model has been used and the method of building up the dynamical matrix has been explained in detail by Pawley (1972). In principle, the electrostatic interaction can be treated in the same way but its long-range character would require brute summation over a large number of unit cells in order to attain convergence. To solve this problem, the Ewald method (Ewald, 1921; Venkataraman & Sahni, 1970) is usually used, in which the lattice sums are split into a direct- and a reciprocal-space sum that rapidly converge, allowing the use of a cut-off interaction radius.

Thermal motion of a crystal in equilibrium at a temperature T can be described as the sum of the contributions of all the independent excitations (phonons) which are present in the crystal. These excitations can be labelled with a wave vector $\mathbf{q}$ which belongs to the Brillouin zone (BZ) of the crystal. Diffraction effects of thermal motion in the rigid-body approach are governed by the $\mathbf{T}$ and $\mathbf{L}$ tensors (molecule at inversion centre) of the molecule k

(Schomaker & Trueblood, 1968) and their relation with vibrational modes is (Willis & Pryor, 1975)

$$\begin{aligned} T_{\alpha\beta}(k) &= N^{-1}M(k)^{-1}\sum_{\mathbf{q}}\sum_{j}[E_j(\mathbf{q})/w_j^2(\mathbf{q})] \\ &\quad \times e_\alpha^t(\mathbf{q}|kj)e_\beta^{t*}(\mathbf{q}|kj) \\ L_{\alpha\beta} &= N^{-1}[I_\alpha(k)I_\beta(k)]^{-1/2} \\ &\quad \times\sum_{\mathbf{q}}\sum_{j}[E_j(\mathbf{q})/w_j^2(\mathbf{q})]e_\alpha^r(\mathbf{q}|kj)e_\beta^{r*}(\mathbf{q}|kj), \end{aligned}$$

where N is the number of allowed wave vectors in the Brillouin zone, M is the molecular mass, $I_\alpha(k)$ is the principal inertia moment about the α axis, $E_j(\mathbf{q})$ is the average energy of the mode $(\mathbf{q}j)$ (k_BT for high temperatures) and $\mathbf{e}^t(\mathbf{q}|kj)$ and $\mathbf{e}^r(\mathbf{q}|kj)$ represent the translational and librational components of the polarization vectors. The sums over the BZ must be performed in practice by dividing it into a mesh (13 divisions along each reciprocal basic vector have proved to be enough) but the acoustic contribution for $\mathbf{q}=0$ needs a special treatment as it diverges. Two solutions have been proposed to overcome this problem. The first is a denser sampling near $\mathbf{q}=0$ (Filippini, Gramaccioli, Simonetta & Suffritti, 1976) and the second is an analytical evaluation of this contribution (Kroon & Vos, 1978). The latter line was followed by us. Crystal symmetry can be used to reduce the sums over the BZ to the asymmetric unit which, for monoclinic crystals, is a quarter of the whole BZ.

Naphthalene and anthracene

Naphthalene and anthracene are two representative hydrocarbons belonging to space group $P2_1/a$ with molecules ($Z=2$) placed at inversion centres. A large body of structural experimental data is available including X-ray crystal structures (Lonsdale & Milledge, 1961; Mason, 1964; Brock & Dunitz, 1982) and neutron studies (Lehmann & Pawley, 1972; Chaplot, Lehner & Pawley, 1982; Pawley & Yeats, 1969) as well as measurements of dispersion curves at different temperatures. These measurements have been made with the help of predicted neutron intensities obtained from semiempirical 6-exp models. Many different 6-exp potential sets have been proposed in the literature to account for C and H interactions but the so-called Williams IVb functions (Williams, 1967) are among the best for reproducing Raman and infrared vibration frequencies. These functions have been used in experimental work on phonon dispersion curves and, quite recently, they have proved to be a good choice for calculating temperature factors in a comparison of different potential sets (Criado & Marquez, 1988).

More recently, Williams & Starr (1977) developed a 6-exp-1 potential model placing point charges at the atomic sites. These charges and the 6-exp parameters were fitted simultaneously to reproduce the experimental crystal structures of a selected database. The resulting point-charge model consists of 0·15e charges at the H sites and opposite ones at the C atoms. These figures agree with similar electrostatic models for hydrocarbons developed by other authors (Lifson & Warshel, 1968). This 6-exp-1 parameter set was selected for this work because it includes electrostatic interactions; nevertheless, calculated thermal parameters gave a very poor agreement with experimental data. For this reason, we decided to adopt a different 6-exp-1 set combining the 6-exp potential set Williams IVb with the electrostatic part of the 6-exp-1 model of Williams & Starr (1977).

As a Williams IVb 6-exp model was obtained as the best fit to experimental data it may seem inconsistent to use it in conjunction with an added electrostatic model. Nevertheless, we must notice that only structural data were used in the derivation of Williams IVb parameters and, given that crystal packing in hydrocarbons is governed by van der Waals interactions, we can consider that these parameters are free from Coulombic effects. On the other hand, our adopted 6-exp model in these calculations is logically the Williams IVb parameter set.

C–H bond distances obtained by X-rays are shortened due to the chemical bond and following the normal use we have normalized them to 1·09 Å, getting a better agreement with experiment.

Normally, the chosen semiempirical model does not produce an energy minimum at the experimental structure and small translations and rotations are necessary to achieve the minimum. In our case a Newton–Raphson minimization procedure was used (*WMIN* program; Busing, 1972) and the shifts turn out to be small: 2·4° for the 6-exp model and 2·1° for the 6-exp-1 one in naphthalene; the corresponding values for anthracene are 1·5 and 1·1°. In order to keep to the quasi-harmonic approximation as closely as possible we have chosen as the starting point for naphthalene the structure at 92 K (Brock & Dunitz, 1982) since dispersion curves (100 K) (Sheka *et al.*, 1984) and thermal parameters at this temperature are available. For anthracene, the room-temperature structure (Lonsdale & Milledge, 1961; Mason, 1964) has been chosen to compare thermal parameters whereas the structure at 16 K (Chaplot, Lehner & Pawley, 1982) has been chosen to compare dispersion curves at 12 K (Dorner *et al.*, 1982). For all these cases an interaction cut-off radius of 8 Å was enough to ensure convergence for lattice frequencies better than 1%. For naphthalene the experimental and calculated energies are 72·4 and 92·0 kJ mol^{-1} respectively, the Coulombic contribution being 16·8%; whereas for anthracene the corresponding figures are 102·1 and 126·9 kJ mol^{-1} and the calculated electrostatic contribution represents 18·4%.

Dispersion curves

The program *DYN* developed by us was used for obtaining the phonon dispersion curves from the energy-minimized structures.

Figs. 1 and 2 show the calculated dispersion curves for naphthalene and anthracene with the 6-exp and 6-exp-1 models and the corresponding experimental ones. Calculated lattice frequencies at $\mathbf{q} = 0$ are listed in Table 1 together with the experimental values. It must be noted that whereas for naphthalene the distinction between external and internal modes is strictly valid [the frequency of the lowest internal mode is 5·09 THz (Natkaniec *et al.*, 1980)], for anthracene there are two internal modes B_u (3·13 THz) and A_u (3·59 THz) (Dorner *et al.*, 1982), which overlap with the external frequency range. It can be seen that the influence of the electrostatic terms on the lattice frequencies is generally very small. For both compounds, the most relevant difference concerns the B_u mode and its associated optical branch which raises its frequency appreciably when Coulombic forces are included, giving a frequency pattern which shows a better agreement with experiment. Other minor improvements can be noticed by careful inspection of Figs. 1 and 2. For naphthalene, the calculated lowest B_g mode shows a poorer agreement when Coulombic interactions are considered; nevertheless, for its linked optical branch, this behaviour is restricted to the vicinity of the Brillouin zone centre and the rest of the branch is not affected by this worsening. There is another calculation of dispersion curves in naphthalene including electrostatic interactions in the form of a quadrupole-quadrupole potential (Califano, Righini & Walmsley, 1979). In this instance, the main influence of electrostatic terms concerns both the B_u and the highest B_g mode in disagreement with our results. The explanation for this lies in the fact that our calculated dispersion curves with the 6-exp and 6-exp-1 models have been obtained from the corresponding energy-minimized configurations whereas Califano *et al.* (1979) proceed in both cases from the same configuration. Our equilibrium positions for the 6-exp and 6-exp-1 calculations differ by 0·74° for naphthalene and 0·70° for anthracene and we have checked that the higher frequencies are more sensitive to these shifts. We think that in order to be consistent with the lattice-dynamical hypothesis we must use the corresponding equilibrium configuration in the 6-exp and 6-exp-1 cases.

A more comprehensive picture of the influence of Coulombic interactions is delivered by the density-of-states function found with a sampling through the BZ. The results for naphthalene are shown in Fig. 3 and those of anthracene in Fig. 4. It can be seen that the influence on naphthalene is small and is localized mainly about 2 THz whereas the differences for

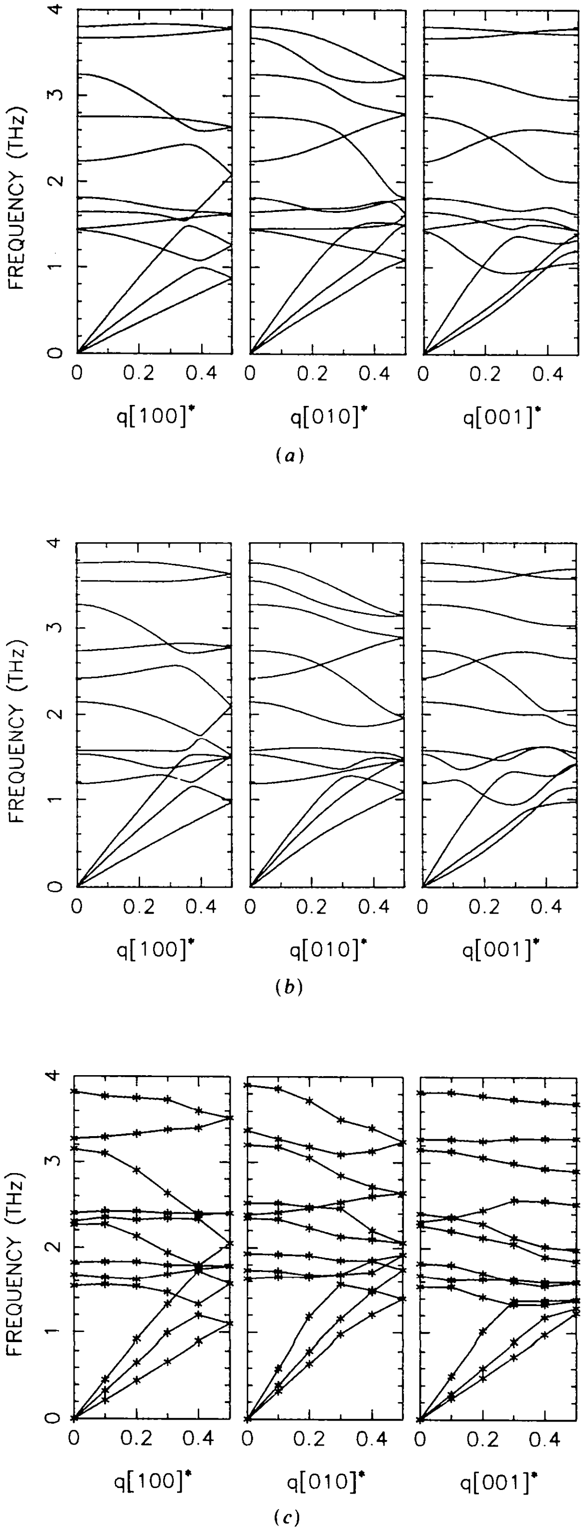

Fig. 1. (*a*) Calculated external dispersion curves for naphthalene with the 6-exp model. (*b*) Calculated external dispersion curves for naphthalene with the 6-exp-1 model. (*c*) Experimental external dispersion curves for naphthalene at 100 K (Sheka *et al.*, 1984). Data for [010]* direction (not available at 100 K) correspond to 6 K (Natkaniec *et al.*, 1980).

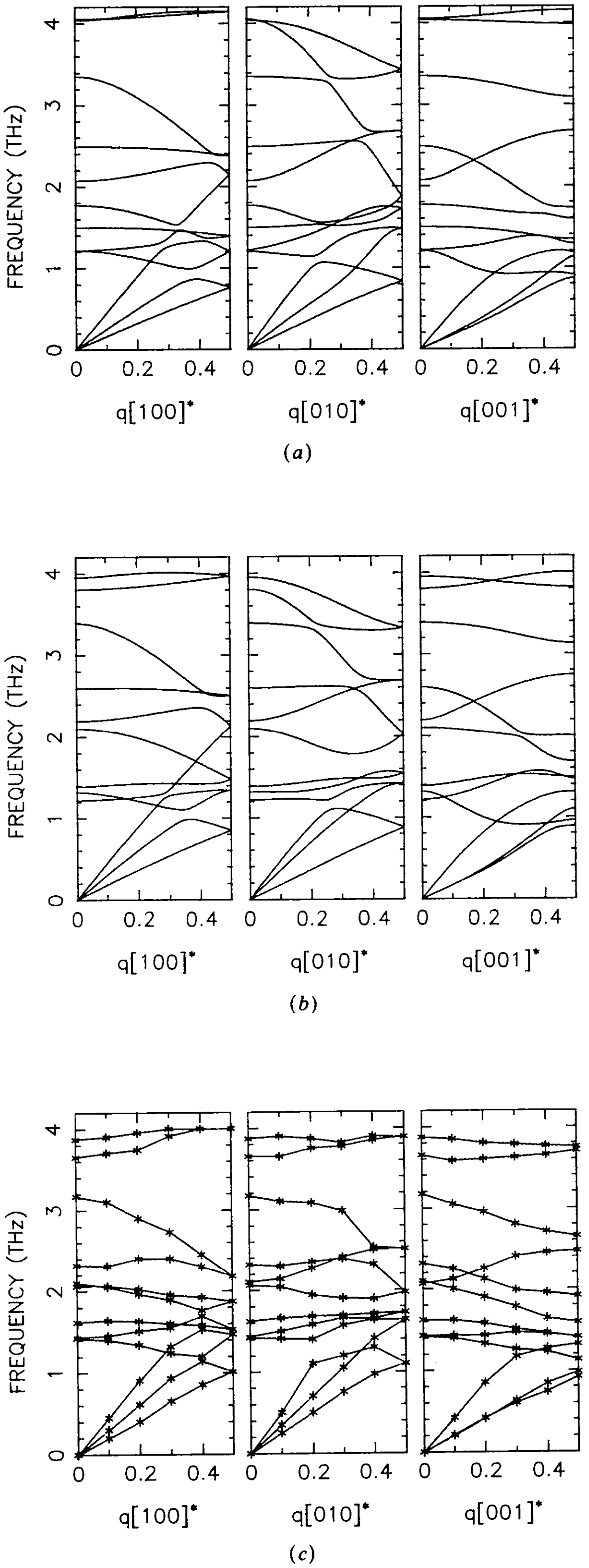

Fig. 2. (*a*) Calculated external dispersion curves for anthracene with the 6-exp model. (*b*) Calculated external dispersion curves for anthracene with the 6-exp-1 model. (*c*) Experimental external dispersion curves for anthracene at 12 K (Dorner *et al.*, 1982).

Table 1. *Calculated and experimental frequencies in* THz (1 THz = 33·37 cm^{-1})

(*a*) Without charges; (*b*) with charges; (exp.) experimental (Sheka *et al.*, 1984; Dorner *et al.*, 1982).

	(*a*)	(*b*)	(exp.)
Naphthalene (100 K)			
$B_g(\Gamma_3)$	3·78	3·77	3·82
$A_g(\Gamma_1)$	3·66	3·56	3·27
$A_u(\Gamma_2)$	3·24	3·28	3·15
$A_g(\Gamma_1)$	2·76	2·74	2·40
$B_g(\Gamma_3)$	2·24	2·42	2·30
$B_u(\Gamma_4)$	1·82	2·14	2·27*
$A_g(\Gamma_1)$	1·65	1·56	1·82
$A_u(\Gamma_2)$	1·43	1·52	1·67
$B_g(\Gamma_3)$	1·45	1·18	1·54
Anthracene (12 K)			
$B_g(\Gamma_3)$	4·04	3·95	3·87
$A_g(\Gamma_1)$	4·05	3·81	3·65
$A_u(\Gamma_2)$	3·36	3·39	3·17
$A_g(\Gamma_1)$	2·48	2·60	2·32
$B_u(\Gamma_4)$	1·77	2·10	2·10
$B_g(\Gamma_3)$	2·07	2·20	2·06
$B_g(\Gamma_3)$	1·49	1·39	1·62
$A_g(\Gamma_1)$	1·22	1·22	1·43
$A_u(\Gamma_2)$	1·21	1·32	1·42

* Extrapolated value.

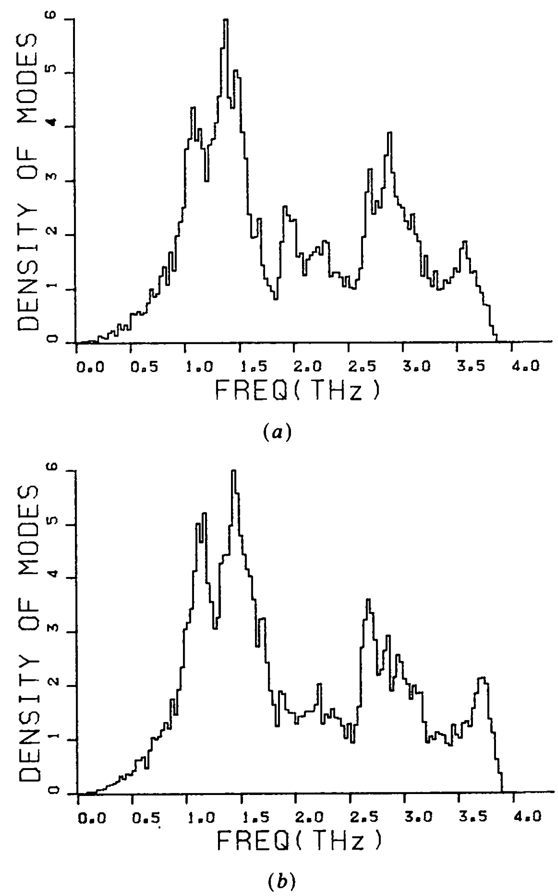

Fig. 3. (*a*) Density of states for naphthalene with charges (arbitrary units). (*b*) Density of states for naphthalene without charges (arbitrary units).

anthracene are larger and correspond to the range 1·0–1·5 THz.

Thermal motion

The calculated rigid-body thermal tensors **T** and **L** are shown in Table 2 together with the experimental ones which correspond to a Schomaker–Trueblood fit of the individual thermal parameters. We can observe that the essential disagreement between the calculated and experimental **L** tensor for anthracene obtained by other authors (Gramaccioli & Filippini, 1983) is reproduced here both for the 6-exp and 6-exp-1 models. Therefore, we can conclude that it is not an artifact due to neglecting Coulombic interactions.

The calculated and experimental atomic thermal parameters are shown in Table 3. We have defined a disagreement factor between calculated and experimental data in the form

$$R=\sum_i\sum_j |U_{ij}(\text{cal.})-U_{ij}(\text{exp.})|/\sum_i\sum_j |U_{ij}(\text{exp.})|.$$

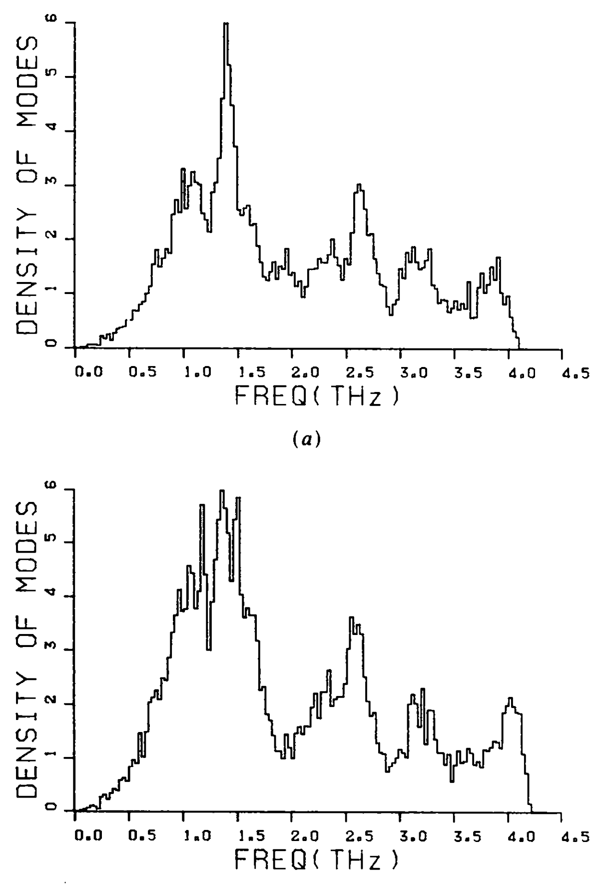

Fig. 4. (*a*) Density of states for anthracene with charges (arbitrary units). (*b*) Density of states for anthracene without charges (arbitrary units).

Table 2. *Calculated and experimental rigid-body thermal tensors* ($\times10^4$)

(exp.) Schomaker–Trueblood fit of experimental data; (*a*) without charges; (*b*) with charges.

	$\mathbf{T}$ (Å^2)			$\mathbf{L}$ (rad^2)		
Naphthalene (92 K)						
(exp.)	77	5	−6	16	0	0
		101	2		13	−3
			136			12
(*a*)	91	−3	4	16	0	−1
		112	2		12	2
			131			20
(*b*)	84	−4	2	17	0	0
		105	−1		11	2
			133			17
Anthracene (290 K)						
(exp.)	344	−24	7	29	3	3
		409	−15		25	−1
			563			11
(*a*)	353	−56	−15	44	5	8
		460	9		23	−2
			753			60
(*b*)	322	−72	19	41	8	1
		439	−5		23	−2
			666			49

This factor turns out to be 10·4 and 8·5% for the 6-exp and 6-exp-1 models in naphthalene and 22·6 and 18·8% for the corresponding values in anthracene. A better agreement is thus obtained when Coulombic interactions are included. However, some caution is necessary since thermal parameters usually suffer from large uncertainties and systematic errors. In particular, neglecting the TDS contribution to the experimental Bragg intensities produces a decrease of the experimental parameters with respect to their true value. Therefore, such an improvement is not significant because a 'harder' function tends to compensate for TDS effects in the observed counterpart.

The overall pattern is a decrease of thermal parameters when Coulombic forces are considered. This is probably due to a hardening of force constants induced by these interactions. The changes introduced are of the same order as those produced by non-rigidity (Gramaccioli & Filippini, 1983) although, at least for these compounds, they tend to oppose them.

As a conclusion, we can say that the inclusion of Coulombic interactions gives a better agreement for dispersion curves and that for naphthalene and anthracene the electrostatic effect on thermal parameters is comparable to that of non-rigidity. We must point out that the agreement with experimental curves is much better in the quadrupole model calculation mentioned before because potential parameters were adjusted to fit experimental data.

Although deriving U's from lattice-dynamical models is useful, in view of the large experimental uncertainties (and presence of systematic errors such as derive from neglecting TDS, absorption *etc.*) no attempt to derive potentials from experimental U's

Table 3. *Calculated and experimental atomic thermal tensors*

(*exp.*) Experimental (Brock & Dunitz, 1982; Mason, 1964); (*a*) without charges; (*b*) with charges.

$$T(\mathbf{H}) = \exp\left[-2\pi^2 \sum_i \sum_j U_{ij} a_i^* a_j^* H_i H_j\right],$$

$$\mathbf{H} = (hkl)(\text{Å}^2 \times 10^4).$$

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Naphthalene (92 K)						
C(1) (exp.)	165	202	140	14	94	2
(*a*)	179	211	131	13	85	−4
(*b*)	172	209	133	15	83	−4
C(2)	136	138	157	−9	85	−25
	148	151	137	−7	68	−27
	136	147	140	−7	65	−28
C(3)	100	110	144	6	79	3
	100	113	126	2	56	−3
	92	107	129	2	56	−3
C(4)	128	113	183	−1	102	15
	138	132	168	−3	84	16
	129	126	175	−1	87	18
C(5)	166	179	187	18	127	40
	169	192	162	17	101	38
	165	189	168	22	105	41
Anthracene (290 K)						
C(1)	680	820	582	13	367	−62
	682	1078	703	66	358	−12
	594	1075	640	26	331	−57
C(2)	495	585	497	−21	239	−65
	596	786	694	−2	292	−110
	505	786	644	−30	276	−138
C(3)	376	447	531	−4	239	−3
	396	557	651	2	228	−36
	346	551	599	−5	223	−51
C(4)	397	445	557	−11	252	−87
	426	504	710	−39	244	−34
	369	497	659	−36	245	−44
C(5)	361	445	540	−24	236	59
	383	550	679	−1	241	21
	342	541	623	1	239	9
C(6)	474	613	625	32	279	−87
	541	758	809	−15	347	122
	488	744	742	−6	342	102
C(7)	653	864	617	34	374	171
	643	1057	789	56	400	157
	583	1044	713	43	380	116

should be made, at least in the general case and with present-day potentials.

We acknowledge the Spanish CAICYT for financial support of this work. Thanks are due to a referee for many helpful comments.

References

Bonadeo, H. & Burgos, E. (1982). *Acta Cryst.* A**38**, 29–33.

Born, M. & Huang, K. (1954). *Dynamical Theory of Crystal Lattices.* Oxford: Clarendon Press.

Brock, C. & Dunitz, J. (1982). *Acta Cryst.* B**38**, 2218–2228.

Busing, W. R. (1972). *Acta Cryst.* A**28**, S252–S253.

Califano, S., Righini, R. & Walmsley, S. H. (1979). *Chem. Phys. Lett.* **64**, 491–494.

Chaplot, S. L., Lehner, N. & Pawley, G. S. (1982). *Acta Cryst.* B**38**, 483–487.

Criado, A. & Marquez, R. (1988). *Acta Cryst.* A**44**, 76–78.

Della Valle, R. G., Frascassi, P. F., Righini, R. & Califano, S. (1983). *Chem. Phys.* **74**, 179–195.

Dorner, B., Bokhenkov, E. L., Chaplot, S. L., Kalus, J., Natkaniec, I., Pawley, G. S., Schmelzer, U. & Sheka, E. F. (1982). *J. Phys. C*, **15**, 2353–2365.

Ewald P. P. (1921) *Ann. Phys.* (*Leipzig*), **64**, 253.

Filippini, G. (1985). *J. Mol. Struct.* **130**, 117–124.

Filippini, G. & Gramaccioli, C. M. (1986). *Acta Cryst.* B**42**, 605–609.

Filippini, G., Gramaccioli, C., Simonetta, M. & Suffritti, G. B. (1973). *J. Chem. Phys.* **59**, 5088–5101.

Filippini, G., Gramaccioli, C., Simonetta, M. & Suffritti, G. B. (1976). *Acta Cryst.* A**32**, 259–264.

Filippini, G., Gramaccioli, C., Simonetta, M. & Suffritti, G. B. (1978). *Mol. Phys.* **35**, 1659–1667.

Filippini, G., Simonetta, M. & Gramaccioli, C. M. (1984). *Mol. Phys.* **51**, 445–459.

Gamba, Z. & Bonadeo, H. (1981). *J. Chem. Phys.* **75**, 5059–5066.

Gamba, Z. & Bonadeo, H. (1982). *J. Chem. Phys.* **76**, 6215–6220.

Gramaccioli, C. M. & Filippini, G. (1983). *Acta Cryst.* A**39**, 784–791.

Gramaccioli, C. M. & Filippini, G. (1985). *Acta Cryst.* A**41**, 356–361, 361–365.

Gramaccioli, C. M., Filippini, G. & Simonetta, M. (1982). *Acta Cryst.* A**38**, 350–356.

Hirshfeld, F. L. & Mirsky, K. (1979). *Acta Cryst.* A**35**, 366–370.

Jindal, V. K. & Kalus, J. (1983). *J. Phys. C*, **16**, 3061–3080.

Jindal, V. K., Kalus, J., Bokhenkov, E. L., Chaplot, S. L., Dorner, B., Natkaniec, I., Pawley, G. S. & Sheka, E. F. (1982). *J. Phys. C*, **15**, 7283–7294.

Kroon, P. & Vos, A. (1978). *Acta Cryst.* A**34**, 823–824.

Lehmann, M. S. & Pawley, G. S. (1972). *Acta Chem. Scand.* **26**, 1996–2004.

Lifson, S. & Warshel, A. (1968). *J. Chem. Phys.* **49**, 5116–5129.

Link, K. H., Grimm, H., Dorner, B., Zimmermann, H., Stiller, H. & Bleckmann, P. (1985). *J. Phys. Chem. Solids*, **46**, 135–142.

Lonsdale, K. & Milledge, J. (1961). *Acta Cryst.* **14**, 59–61.

Mason, R. (1964). *Acta Cryst.* **17**, 547–555.

Mulliken, R. S. (1955). *J. Chem. Phys.* **23**, 1833–1840, 1841–1846.

Natkaniec, I., Bokhenkov, E. L., Dorner, B., Kalus, J., Mackenzie, G. A., Pawley, G. S., Schmelzer, U. & Sheka, E. F. (1980). *J. Phys. C*, **13**, 4265–4283.

Neto, N., Righini, R., Califano, S. & Walmsley, S. H. (1978). *Chem. Phys.* **29**, 167–179.

Pawley G. S. (1972). *Phys. Status Solidi B*, **39**, 475–487.

Pawley, G. S. & Cyvin, S. J. (1970). *J. Chem. Phys.* **52**, 4073–4077.

Pawley, G. S., Mackenzie, G. A., Bokhenkov, E. L., Sheka, E. F., Dorner, B., Kalus, J., Schmelzer, U. & Natkaniec, I. (1980). *Mol. Phys.* **39**, 251–260.

Pawley, G. S. & Yeats, E. A. (1969). *Acta Cryst.* B**25**, 2009–2013.

Rastogi, A., Anderson, A. & Leech, J. W. (1979). *Can. J. Phys.* **57**, 2120–2125.

Schomaker, V. & Trueblood, K. N. (1968). *Acta Cryst.* B**24**, 63–76.

Sheka, E. F., Bokhenkov, E. L., Dorner, B., Kalus, J., Mackenzie, G. A., Natkaniec, I., Pawley, G. S. & Schmelzer, U. (1984). *J. Phys. C*, **17**, 5893–5914.

Venkataraman, G. & Sahni, V. C. (1970). *Rev. Mod. Phys.* **42**, 409–470.

Williams, D. E. (1967). *J. Chem. Phys.* **47**, 4680–4684.

Williams, D. E. & Cox, S. R. (1984). *Acta Cryst.* B**40**, 404–417.

Williams, D. E. & Starr, T. L. (1977). *Comput. Chem.* **1**, 173–177.

Willis, B. T. M. & Pryor, A. W. (1975). *Thermal Vibrations in Crystallography.* Cambridge Univ. Press.