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Lattice dynamics and phase transition of acetylene[a]

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The statical properties and lattice dynamics of the two known phases of crystalline acetylene have been studied, using a model which takes account of electrostatical intermolecular as well as atom–atom interactions. Good agreement with observed statical and dynamical properties of both phases has been achieved. The calculated phonon dispersion curves and group symmetry considerations led us to the identification of the phonons in both phases which are possibly associated with the structural phase transition.

INTRODUCTION

Crystalline acetylene has two known phases: a high temperature cubic phase (CP), stable between 133 K and the melting point (191 K) and a low temperature orthorhombic phase (OP), stable under 133 K.

The cubic crystal structure belongs to the $Pa3$ (T_h^6) space group,[1] isomorphic to CO_2, with four molecules in the unit cell; the orthorhombic crystal belongs to the $Cmca$ (D_{2h}^{18}) space group,[2] with two molecules in the primitive unit cell.

In a recent paper, Filippini *et al.*[3] have made a thorough study of the statical and dynamical properties of both crystal phases of acetylene. Using a number of existing semiempirical potentials of the atom–atom type, including the "6 – exp," "6 – exp – 1," and "9 – 6 – 1" forms they found that in all cases: (a) the calculated heats of sublimation are too low; (b) the heat of sublimation of the CP is larger than that of the OP; (c) The Raman frequencies of the cubic phase are calculated much too high; and (d) there are imaginary frequencies at $k=0$ or $k\neq 0$ for the OP. They also performed a refinement of potential parameters in various forms, with and without the addition of electric charges, but although the Raman frequencies and crystal structure of the cubic phase could be adequately reproduced, the corresponding heat of sublimation was still about 30% too low, and, even worse, the OP structure and frequencies cannot be adjusted. They speculate on the possibility that the problems are due to inaccuracies in the determination of the OP structure from powder data, and the heat of sublimation, of which only old measurements are available.

Klein and McDonald[4] have performed a molecular dynamics calculation in which they also encounter problems in connection with the intermolecular potentials (the same ones used by Filippini *et al.*), although they conclude that there is no reason to doubt the presently available values of the heat of sublimation and molecular electrical multipoles.

In our recent calculation of statical and dynamical properties of a series of azabenzene crystals,[5] we came across quite similar problems; they could be overcome by adding to the atom–atom model an adequate electrostatic interaction. We found that a very simple distributed dipole model, consisting in placing dipoles on the C–H bonds and near the N atoms of the molecules reproduced very well the charge distributions of the various molecules, and also allowed a good fit of the observed crystals properties. The model automatically includes the high-order multipole moments which are usually neglected in molecule centered multipole expansions. On the other hand, the formalism (and computer program) is flexible in the sense that it also allows to simulate a charge distribution with practically any desired values, including zero, of the molecular multipole moments, without the cumbersomeness of the expressions for the calculation of the higher multipole interactions.

It is well known that since the intermolecular distances in molecular crystals are short, molecule centered multipole expansions must be taken with care; however it was striking to observe that, at least for the azabenzenes, high order multipole interactions are extremely important, and in some cases give the main contribution to calculated normal modes.

In the present work we have studied the lattice dynamics of the orthorhombic and cubic phases of crystalline acetylene, using the atom–atom model plus electrostatic interactions represented by point dipoles distributed on the molecules. Although some of the problems encountered by Filippini *et al.*[3] appear in our calculations, they may be overcome by taking account of the high-order electrostatic interactions.

CALCULATION METHOD

The calculation method used in the present work is described in detail in Refs. 5–7 and will only be briefly sketched here. The crystal data taken into account in the refinement are the following: (a) frequencies at $k=0$; (b) the heat of sublimation, obtained from the packing energy and entropic effects, as described in Refs. 5 and 8; (c) crystal equilibrium conditions,[5-7] which take into account the rigid body molecular motions necessary to attain the minimum energy structure, starting from the observed structure at which all the calculations are performed. These quantities are calculated using atom–atom interactions of the Buckingham form: $V_{ij}=-A\,r_{ij}^{-6}+B\exp(-C\,r_{ij})$, where r_{ij} is the dis-

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TABLE I. 2^l permanent multipolar moments (Q_l) in eA^l.

	Q_2	Q_4	Q_6
Two dipole model with $\mu = \pm 0.3138$ eA and $d = \pm 1.218$ A	1.53	4.54	10.10
Hirshfeld and Mirsky model (Ref. 10) with charges $q = \pm 0.312e$ localized at the atomic nuclei	1.50	4.68	13.15
Hirshfeld and Mirsky model (Ref. 10) with charges, dipoles, and quadrupoles localized at the atomic nuclei	1.50	5.60	21.15

tance between atoms i, j belonging to different molecules, plus electrostatic interactions calculated using a distributed dipole model. Parameters A and B corresponding to different interactions and a factor ϵ^2 which multiplies the electrostatic interaction as a whole are refined using an iterative mean squares procedure.

PRELIMINARY CALCULATIONS AND ELECTROSTATIC INTERACTIONS

The most simple form of the distributed dipole model is, in this case, to place two symmetrically opposed dipoles on the C–H bonds of acetylene. Amos and Williams[9] have performed an *ab initio* calculation of the first two nonzero electric multipole moments, i.e., the quadrupole and the hexadecapole; due to the molecular symmetry, only one term of each moment is independent. With these two data, the magnitude and distance to the molecular center of the dipole are uniquely determined, giving $\mu = 0.3138$ eA and $d = 1.218$ A.

The attempts to refine with this model failed completely, and results similar to those reported by Filippini *et al.*[3] were observed: some frequencies tend to be imaginary, the heat of sublimation of the OP is calculated lower than that of the CP and, in addition, some parameters tend to be negative.

At this point, either the experimental data are unreliable, as hypothesized by Filippini *et al.*,[3] or the interaction model, and more specifically the electrostatic part of it, must be wrong or incomplete.

Hirshfeld and Mirsky[10] have calculated electrostatic interactions in crystalline C_2H_2 using a model proposed by Hirshfeld.[11] They represent the molecular charge distribution by charges, dipoles, and quadrupoles localized at the atomic nuclei. Table I shows the values for the first three nonzero multipole distributions obtained from our two dipole model, Hirshfeld and Mirsky's model,[10] and a simple point charge distribution localized at the atomic nuclei proposed by Hirshfeld and Mirsky[10] to give the same value of the quadrupole as their complete model; it should be noted that due to the fact that the charge distributions are linear, only one element of the 2^6 pole is independent, instead of the two required by symmetry. Filippini *et al.*[3] used the point charge model with several different values for the charges; however, the relative values of the successive multipoles remain unchanged on varying the magnitudes of the charges. Since the point charge model and our two-dipole model give practically identical values for the three multipoles, it is little wonder that we met very similar difficulties. It can be seen, however, that the magnitude of the 2^6 pole obtained with the Hirshfeld and Mirsky model[10] is about twice that of the two other models. This led us to investigate the influence of this term on the crystal properties of C_2H_2; we have verified that the next nonvanishing multipole 2^8 has no appreciable influence on the calculated properties.

The Hirshfeld and Mirsky model,[10] with its distributed quadrupoles, leads to rather cumbersome expressions for the dynamical calculations. In fact, it is possible to construct other reasonable models which give the same results for the quadrupole and hexadecapole, but differ in the higher order multipoles. One possible way to do this is to place four (two independent) dipoles along the molecular axes, and to vary their magnitude and position.

RESULTS AND DISCUSSION

We have performed a number of refinements with this electrostatic model, varying the dipole positions and magnitudes so as to obtain values for the 2^6 pole from 10 to 24 eA^6 (see Table I). As the 2^6 pole becomes larger, all problems connected with the refinement tend to disappear: the agreement with experimental data gets better, and the atom–atom parameters which were initially negative, get lower in magnitude, until getting positive. With the 2^6 pole equal to 24 eA^6, the refinement is apparently quite satisfactory; however, when we used the refined parameters to calculate frequencies throughout the Brillouin zones(BZ), we found that some acoustic branches near the Γ point of the CP were imaginary.

The appearance of these imaginary frequencies may well be connected with the phase transition, as will be discussed later. However, the crystal structures used for the calculations were determined at temperatures which are sufficiently far away from the transition temperature to expect real frequencies for all normal modes. Therefore we expanded our refinement program to take account of this situation: the frequencies at some previously determined relevant points of the BZ are calculated; if they are real, they are disregarded in the refinement; if they are imaginary, their Jacobian with respect to the potential parameters is calculated and they are conditioned to take real values in the corresponding refinement cycle. In order to maintain the calculation within reasonable size, only a few BZ points must be chosen in each case on the basis of preliminary calculations. In our case, we included a point near Γ in the Σ direction for the CP, and point Y (following the notation of Zak[12]) for the OP. During the refinement it was observed that the conditions for real frequencies at these points are to some degree contradictory, again a fact which probably is connected with the phase transition. In any case, it is possible to obtain a set of potential parameters which gives reasonable agreement with experiment (the mean square deviation is only about 10% larger when the additional conditions are imposed) and real frequencies for both crystal

TABLE II. Experimental and calculated statical and dynamical properties of acetylene crystals. Units: ΔH_{sub} and E_{pack} in kcal/mol; ν in cm^{-1}; equilibrium condition R in degrees, molecular rotation around C_2 site axis. For definitions of Q_2, Q_4, Q_6 see the text.

	Expt.	Calc.	Atom–atom	Q_2	Q_4	Q_6
Cubic phase at 141 K[a]						
ΔH_{sub}	5.3[b]					
E_{pack}	−5.6[c]	−6.0	0.81	0.28	−0.09	0.00
Lattice frequency A_u	···	67	0.58	0.61	−0.28	0.09
E_u	···	65	1.05	−0.04	−0.05	0.04
F_u	···	90	0.98	−0.06	0.05	0.03
	···	62	1.16	−0.09	0.04	−0.11
E_g	22[d]	20	5.76	8.46	−6.83	−6.39
F_g	67[d]	61	−1.17	3.41	−1.76	0.52
	33[d]	38	−0.22	6.24	−4.27	−0.75
Orthorhombic phase at 4.2 K[e]						
E_{pack}	−6.3[f]	−6.3	0.78	0.24	−0.08	0.06
Lattice frequency A_u	···	87	0.74	0.25	−0.05	0.06
B_{3u}	106[g]	96	1.02	−0.18	0.10	0.06
B_{2u}	127[g]	132	1.10	−0.01	−0.03	−0.06
A_g	88[h]	88	0.40	0.81	−0.94	0.73
B_{1g}	(122)[h]	133	−0.28	0.91	−0.47	0.84
B_{3g}	86[h]	85	0.33	0.71	−1.12	1.08
B_{2g}	86[h]	86	−0.55	2.10	−0.95	0.40
Equilibrium condition $R(°)$[i]	···	4.0	0.52	0.52	−0.60	0.56

[a]Crystal structure of Ref. 1; molecular structure of Ref. 2.
[b]References 24 and 25.
[c]Estimated as in Ref. 5, using the Debye–Einstein approximation for the calculation of the entropic contribution (Ref. 8).
[d]Raman frequencies at 173 K, Ref. 14.
[e]Reference 2.
[f]Estimated as in footnote c from an approximate upper limit of ΔH_{sub}, ignoring the heat of transition, which has not been measured.
[g]Infrared frequencies at 40 K, Ref. 26.
[h]Raman frequencies at 4.2 K, Ref. 14.
[i]Calculated as $[(\partial V/\partial R)/(\partial^2 V/\partial R^2)]_{obs}$; see the text and Ref. 7.

phases throughout the Brillouin zones.

Table II shows the calculated and observed values of the crystal properties under consideration, and the contribution of the different interactions to each of them, calculated as explained in Ref. 5. In this case, the column labeled Q_2 contains the quadrupole–quadrupole interactions, the one labeled Q_4 quadrupole–hexadecapole and hexadecapole–hexadecapole interactions, and the one labeled Q_6 includes 2^6-pole–quadrupole plus remaining interactions terms, i.e., they correspond to the inclusion of succesively higher order terms in the molecular multipole expansion (not in the Hamiltonian). It can be seen that as in the case of the azabenzene crystals,[5] the high-order multipole terms affect very little the heat of sublimation, moderately the equilibrium conditions, but very considerably some frequencies.

The refined potential parameters are shown in Table III. As for the azabenzene crystals,[5] the factor ϵ^2, which multiplies the electrostatic interactions, is less than one. This fact can be partly explained, as in Ref. 5, in terms of a reduction of the effective interaction due to the fact that polarization effects have not been included explicitly in the calculation. However, an estimation of this effects based on a value of the dielectric constant of about 2, obtained from the Claussius–Mossotti equation and a molecular polarizability of 3.4 A^3,[9] leads to a factor ϵ of only about 0.7. In any case it is well possible that the molecular multipoles are reduced in the crystal, since the molecules themselves appear to be smaller, specially in the OP, where at 4.2 K there is a 10% reduction in the effective volume occupied by the molecules with respect to the volume at 141 K.

TABLE III. Refined parameters for the intermolecular potential.

Contact	A (kcal A^6/mol)	B (kcal/mol)	C (A^{-1})
C–C	485 ± 35	437100 ± 7600	3.909
C–H	100 ± 15	5600 ± 280	3.703
H–H	330 ± 15	7330 ± 430	3.746
Multiplicative factor for the multipolar moments ϵ		0.544 ± 0.005	
Electrostatic multipolar moments:		ϵQ_2 = (0.832 ± 0.008) eA^2	
		ϵQ_4 = (2.470 ± 0.030) eA^4	
		ϵQ_6 = (13.060 ± 0.150) eA^6	
Equivalent distributed dipole model:			
	d_1 = 0.528 A	μ_1 = (0.2667 ± 0.0024) eA	
	d_2 = 2.0 A	μ_2 = (0.0337 ± 0.0003) eA	

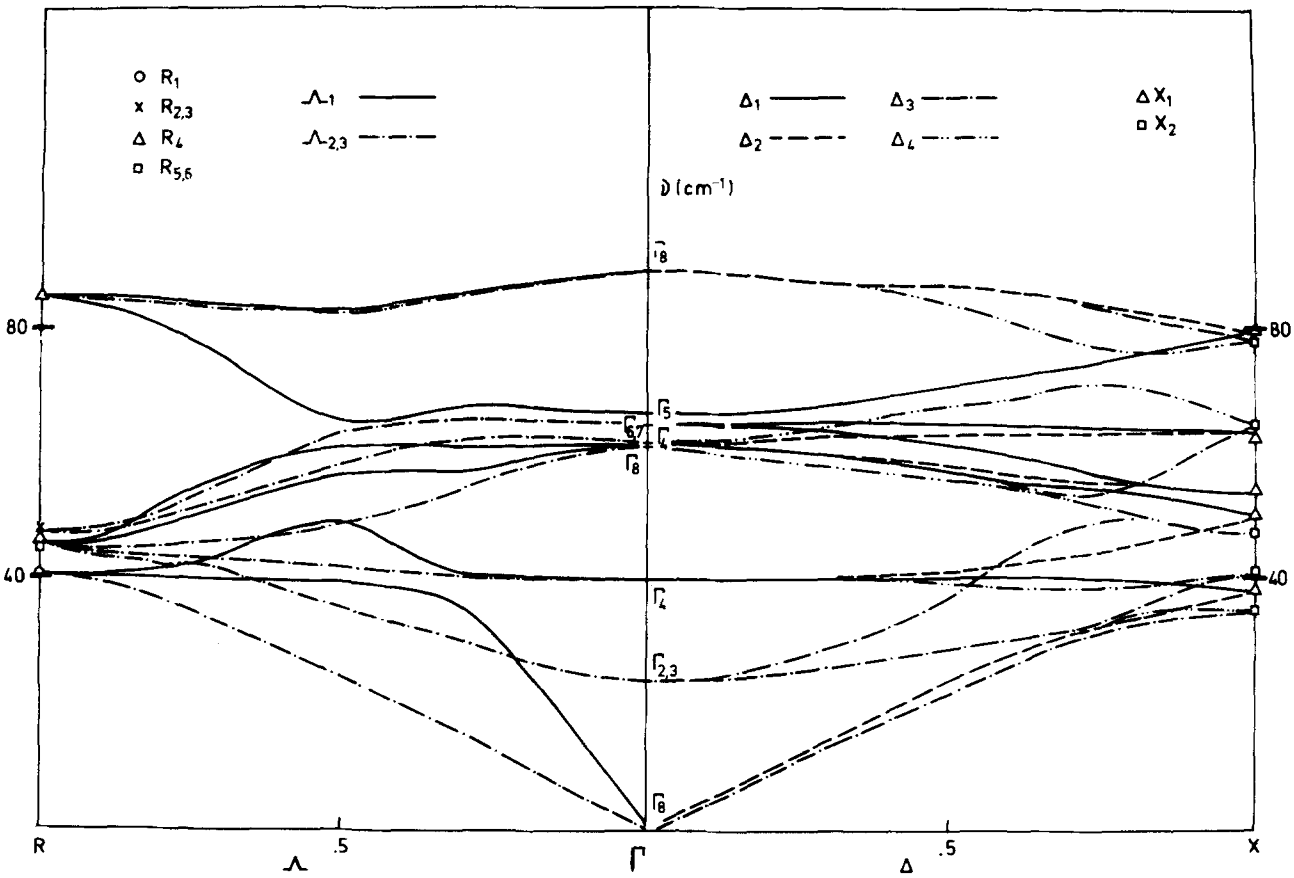

FIG. 1. Phonon dispersion curves for cubic acetylene at 141 K, in the $\Gamma - X(\xi, 0, 0)$ and $\Gamma - R(\xi, \xi, \xi)$ directions. Branch labels following Zak (Ref. 12).

DISPERSION CURVES AND PHASE TRANSITION

Figures 1 and 2 show the calculated dispersion curves for some relevant directions in the BZ of the two phases of crystalline C_2H_2. It can be seen that the modes which tended to become imaginary, i.e., the $\Gamma_{2,3}$ mode and the acoustic branches of the CP and the Y_4 mode of the OP, have quite low frequencies. We will try to associate this fact with the phase transition.

In the CP, the molecular axes are oriented in the directions of the cube diagonals; the centers of mass are located at the positions of an fcc lattice. In the OP, the molecules are stacked in parallel layers which are perpendicular to the short axis of the one face centered unit cell; the lengths of the three lattice vectors are quite similar[2] ($a = 5.547$ A, $b = 6.002$ A, $c = 6.188$ A), and close to the CP crystal value[1] ($a = 6.091$ A). It has already been suggested that the main effect of the phase transition is a rotation between the two molecular orientations.[13,14]

According to Koski and Sándor,[15] the CP–OP transition in acetylene is most probably of the first order; if this is so, the ideas presented by Boyle *et al.*[16] regarding the symmetry properties of such transitions may be applied. We may then find an intermediate symmetry group of real or virtual existence, with whose aid it is possible to determine which motions are responsible for the phase transition; it is implicitly assumed that the phase transition is due to the softening of lattice modes, and that there exists a continuity between the lattice vibrations in both phases and through the intermediate space groups.

Using tables of the "zellengleich" supergroups of the space groups[17] and the "klassengleich" supergroup—subgroup relationships between the space groups[18] of Boyle and Lawrenson, it can be found that one possible route for the phase transition is

$$T_h^6(Pa3) \rightarrow D_{2h}^{15}(Pbca) \rightarrow D_{2h}^{18}(Cmca) .$$

From the CP(T_h^6) it is possible to reach the orthorhombic intermediate group through a symmetry reduction of the zellengleich (cell-preserving) type, which affects only the point symmetry elements of the unit cell, but not the associated translations, without change in the unit cell volume. In our case, with a small deformation which makes the three lattice vector lengths different, the four threefold axes disappear; the associated modes are the acoustic ones near $k = 0$ of the CP.

Starting from the OP, the D_{2h}^{18}–D_{2h}^{15} transition corresponds to a symmetry reduction of the klassengleich (crystal class-preserving) type, with doubling of the unit cell volume and a reduction of the molecular site symmetry. Associated with this transition is a rotation of the molecules at the BZ boundary; in fact, Y_4, the lowest lying mode at point Y (see Fig. 2), is a pure

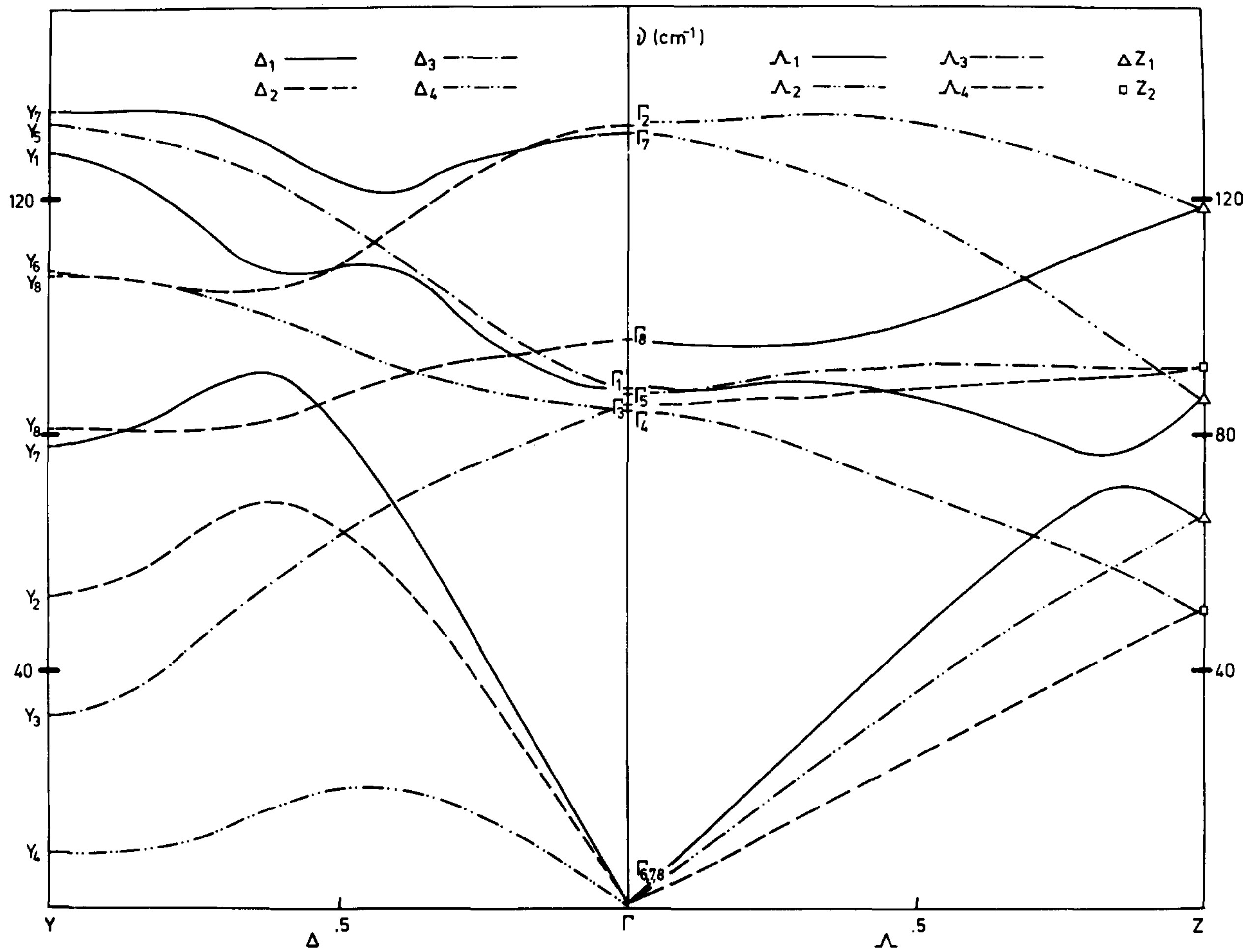

FIG. 2. Phonon dispersion curves for orthorhombic acetylene at 4.2 K, in the $\Gamma - Y(0, \xi, 0)$ and $\Gamma - Z(0, 0, \xi)$ directions. Branch labels following Zak (Ref. 12).

rotation which doubles the OP unit cell in the appropriate direction to reach the D_{2h}^{15} symmetry. Observing the calculated eigenvectors, it is found that this rotation approximately leads from the high symmetry basal plane position to the direction of the parallelopiped diagonals. On the other hand, the Y_4 mode is closely related to the lowest-lying rotational $\Gamma_{2,3}$ mode of the CP. Since in order to apply the symmetry arguments it is necessary to assume that the distortions are infinitesimal, in the real case the description of the motions provided by the calculated eigenvectors will be only approximate. With this limitation, the description of the phase transition in terms of lattice dynamical results and group symmetry considerations is astonishingly accurate and complete.

CONCLUSIONS

In the present work, we have shown that it is possible to fit with one set of intermolecular potentials the crystal properties of both phases of crystalline acetylene, if electrostatic interactions up to the 2^6 pole are taken into account; it is worthwhile to discuss this interaction further. It is clear that the molecular charge distribution may be represented reasonably well with quite different models, for instance, Hirshfeld and Mirsky[10] and the distributed dipoles model; furthermore, due to the parametrization involved in the fitting, the exact physical meaning of the interaction is somewhat obscured. If one takes the Hirshfeld and Mirsky picture, in which charges, dipoles and quadrupoles are localized at the nuclei, it can be immediately seen that the electrostatic interaction is mathematically equivalent to an anisotropic atom–atom interaction, since it can be expressed as a nuclei based cosine expansion. The difference, of course, is that the order of magnitude and the relative values of the expansion coefficients are fixed by the molecular charge distribution.

It is well known that atom–atom plus quadrupole–quadrupole interactions cannot account for the observed crystal structure of the halogens Cl_2, Br_2, and I_2, which are isostructural with the OP of acetylene. The T_h^6 structure, to which the CP of acetylene belongs, is calculated more stable for these compounds. There is quite some controversy in the literature with respect to the causes of this, and various explanations, including short range intermolecular valence forces,[9] charge transfer,[20] dipolar molecules[21] and anisotropic interactions,[22,23] have been offered. In the case of acetylene, we have found that only including the 2^6 pole we could find a lower packing energy for the CP than for the OP. In view of the discussion above, there seems to be a close connection between this fact and the results of Nyburg and Wong-Ng,[23] who have found that anisotropic atom–atom forces stabilize the D_{2h}^{18} (*Cmca*) structure of solid chlorine.

During our potential parameter refinement, we found a set which reproduced well optically active frequencies, but gave imaginary frequencies at $k=0$; this is more or less frequent, but emphasizes once more the need for a check of the intermolecular potential throughout the BZ. The tendency of the frequencies of some normal modes to get imaginary is many times regarded as a nuisance, and attributed to defects in the interaction potential. Although this may be so in some cases, in the present one it is associated with clear physical reasons; these normal modes, in fact, provide a very clear mechanism for the structural phase transition of acetylene.

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