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Lattice dynamics of orthorhombic C_2H_2

J W Leech and P J Grout

Department of Theoretical Chemistry, University of Oxford, 5 South Parks Road, Oxford OX1 3UB, UK

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Abstract. Stable lattice dynamical models of orthorhombic C_2H_2 are developed from those devised by Hirshfeld and Mirsky for the cubic phase. These satisfactorily reproduce measured phonon frequencies but cannot account for the crystal cohesive energy. Models are also identified based on the work of Nyberg and Faerman, the principal difference being bond- rather than atom-centred short-range interactions. These yield acceptable crystal energies. All models have physically realistic molecular quadrupole moments.

1. Introduction

Recently there has been much interest in the behaviour of simple molecular solids under pressure, see for example Pucci and Piccitto [1]. Our initial aim in describing the pressure dependence of the lattice modes of C_2H_2 has to some extent been achieved in [2] where a model for cubic C_2H_2 , originally derived by Hirshfeld and Mirsky [3] (hereinafter referred to as HM), was used to simulate the behaviour of its orthorhombic form. We found that the unmodified model successfully reproduced three of the five lattice frequencies observed at low temperatures (30 K) [4,5] and also gave reasonable estimates for the crystal stresses and for the observed variation of two of the Raman frequencies over the pressure range 1–3 GPa at room temperature [6]. The drawbacks of this model are (a) the calculated crystal cohesive energy is too low by about 10%, (b) the simulated crystal is not in equilibrium and (c) there is a small region of k space where one branch of the phonon dispersion curves is imaginary.

The areas of agreement between the observations and the predictions of the model were so emphatic that it was obviously worthwhile devoting effort to removing the objections mentioned above.

Before proceeding it should be emphasized that the model was constructed by bringing together transferable interaction potentials deduced by Mirsky [7] for molecular crystals containing C, H, N and O atoms together with molecular charge densities derived from Hartree–Fock wave functions calculated by McLean and Yoshimine [8]. As emphasized by HM, the process is not completely consistent since the transferable Buckingham exp-6-type potential functions were derived to explain crystal behaviour without the addition of electrostatic interactions.

Here we aim to develop physically realistic lattice dynamical models of C_2H_2 . We first devote attention to the model of HM in an effort to remove the objections mentioned above. Subsequently we focus attention on the *ab initio* work of Nyberg and Faerman (NF) [9].

Table 1. Parameter values for models based on Hirschfeld and Mirsky [3] (HM model (I)), modified HM model (II) and for three models (III-V) based on the work of Nyberg and Faerman [9]. √ denotes the same entry as in the column immediately on the left.

	I	II	III & IV Start	III	IV	V Start
$C_6/10^2$ kJ mol ⁻¹						
C-C	17.611	19.790				
C-H	4.934	2.178				
H-H	1.210	0.460		0.950	1.353	2.10
B-B			1.68	1.288	1.364	2.10
B-O			1.68	1.588	1.754	2.10
O-O			1.68			0.879
$A/10^5$ kJ mol ⁻¹						
C-C	3.000	3.685				
C-H	0.780	0.705				
H-H	0.210	0.354		2.013	2.795	3.78
B-B			3.36	2.394	3.386	2.102
B-O			3.36	3.490	4.592	3.78
O-O			3.36			4.411
$\alpha/\text{\AA}^{-1}$						
C-C	3.680	3.671				
C-H	3.940	4.019				
H-H	4.290	4.222		3.923	3.969	3.50
B-B			3.80	3.761	3.681	3.50
B-O			3.80	3.805	3.817	3.50
O-O			3.80			3.605

In section 2 we discuss the experimental information upon which the models were constructed and in section 3 we outline the calculational approach. In section 4 the various forms of the HM model are referred to and their modification described. We next turn to the construction of a model incorporating the principles of the NF work. Details of this are presented in section 5 and overall conclusions drawn in section 6.

2. Experimental and other information

2.1. The structure

Crystalline C_2H_2 has two forms: a low-temperature orthorhombic form (space group $Cmca$) [10] and a cubic form (space group $Pa3$) [11] stable between 133 K and the melting point. The orthorhombic form has two molecules in the primitive unit cell, four in the x-ray unit cell shown in figure 1, with the molecules lying in the a - c plane and making an angle θ with the a axis. The Brillouin zone for this structure is shown in figure 2 with the points and lines of high symmetry labelled using the scheme of [12].

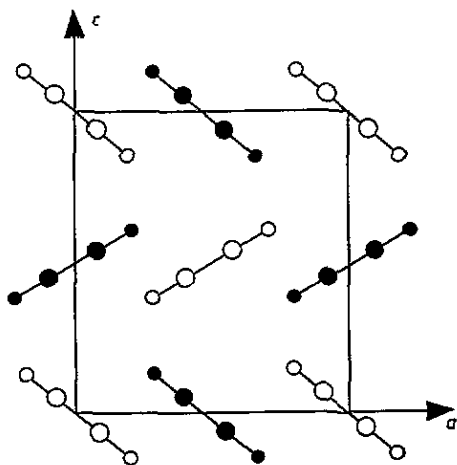


Figure 1. X-ray unit cell of orthorhombic C_2H_2 : full circles indicate molecules at $y = 0$, open circles indicate molecules at $y = b/2$.

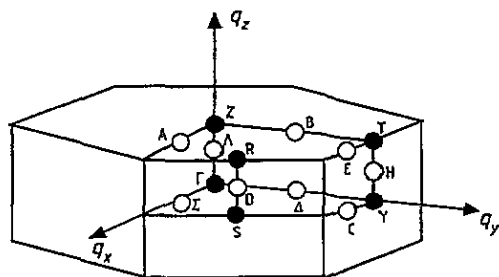


Figure 2. Brillouin zone for the one face centred orthorhombic lattice ($a < c$). Full circles indicate symmetry points and open circles symmetry lines.

Structural data from a neutron diffraction study of C_2D_2 [10] have been assumed to apply to C_2H_2 . These are given in table 1.

2.2. Crystal properties

Infrared and Raman spectroscopy have been used by a number of workers to identify the Brillouin zone centre phonon frequencies. We rely principally on the single translational and three rotational frequencies quoted by Anderson *et al* [4], supplemented by the additional translational mode at 106 cm^{-1} identified earlier by Schwartz *et al* [5]. Although the latter was not found by Anderson *et al* it is consistent

with values given by them for C_2D_2 frequencies in the same work. The experimental information is collected together in table 2.

The cohesive energy of the cubic form of C_2H_2 has been deduced as $-23.5 \text{ kJ mol}^{-1}$ at 141 K, from saturation vapour pressure measurements [13] supplemented by use of the Debye–Einstein approximation to estimate the entropic contribution [14]. Apparently unaware of the existence of saturation vapour pressure measurements in the range 100–130 K collected together in [15], Gamba and Bonadeo [14] merely estimated the cohesive energy in the orthorhombic phase as $-26.4 \text{ kJ mol}^{-1}$. However, using the data from [15] the cohesive energy can be determined, after suitable allowance for the entropic contribution, to be approximately $-25.2 \text{ kJ mol}^{-1}$. This value is also in accord with the fact that the energies of different solid phases of the same material calculated from the same potential models differ by about 7%, see, for example, [14] and [16].

3. Calculations

The physical properties of the models which were calculated are (a) the cohesive energy, (b) the extent to which the model is in static equilibrium and (c) phonon frequencies corresponding to given wave vector values.

Standard lattice dynamical techniques in the harmonic and pair potential approximation [17] were used to calculate the phonon modes. The molecules were assumed rigid and interactions between the origin molecule and its 380 nearest-neighbour molecules were included in the lattice sums. This number was to ensure that all measures of the physical properties of interest had converged to an acceptable degree. The lattice sums were all performed using a variant of the method due to Evjen [18] which in essence involved ensuring that only complete molecules were included in the summation. This is of prime importance in calculating the electrostatic energy since it is possible to obtain relatively rapid convergence of the required sums without invoking the Ewald transformation [19].

Derivatives of the free energy (which is approximated by the static lattice energy, E) with respect to crystal parameters provide measures of crystal equilibrium. These are expressed in dimensionless form as $(a_i/E)\partial E/\partial a_i$. Strictly they should be zero to ensure a physically meaningful model but it was found that for calculations involving more than 140 neighbours values in the range ± 0.01 constitute acceptable approximations to zero.

4. The Hirshfeld–Mirsky model

HM give three models for C_2H_2 whose molecules all have zero net charge and dipole moment and the same total quadrupole moment but differ in their detailed electronic structure. The most complex of these has charges, dipoles and quadrupoles at each atom site giving what is termed an ‘atomic moments’ (AM) model. In addition in the crystalline phase there are three different exp-6 functions representing the C–C, C–H and H–H interactions. Each of these models was investigated and found to echo the tendency found by others [14, 16] for the crystal to be dynamically unstable at the Y point of the Brillouin zone. Indeed there is a small region of k space surrounding the Y point in which one librational frequency is persistently imaginary. This is clearly

Table 2. Model properties for HM and NF models of table 1.

Model	Experiment	I	II	III & IV Start	III	IV	V Start	V	
$E/kJ \text{ mol}^{-1}$	-25.2(1)	-27.4	-18.0	-19.8	-19.8	-21.4	-21.1	-23.2	
R^{-6}		(✓)	(-18.0)	(-31.8)	(-21.6)	(-26.6)	(-39.7)	(-31.9)	
Exp. contribution		(✓)	(11.2)	(21.2)	(12.3)	(19.5)	(63.7)	(17.4)	
Coul.		(-15.8)	(-11.2)	(-9.2)	(-10.4)	(-14.3)	(-45.1)	(-8.7)	
$(a/E)\delta E/\delta a$	0	0.6	0.03	-0.9	0.014	0.005	-7.5	0.010	
$(b/E)\delta E/\delta b$	0	0.6	-0.02	-0.8	0.039	0.002	-9.0	-0.005	
$(c/E)\delta E/\delta c$	0	0.5	-0.03	-1.8	-0.007	-0.004	-12.0	-0.006	
$(1/E)\delta E/\delta \theta$	0	0.05	-0.01	-0.2	-0.027	-0.001	0.7	0.0003	
Frequencies/cm ⁻¹									
Trans.		75.7	81.4	126.7	91.5	88.8	197.5	89.5	
	Γ_1^-	106	105.9	107.2	100.9	101.1	220.7	100.4	
	Γ_3^-	127	131.5	128.1	129.3	130.0	313.8	131.4	
Lib.	Γ_2^-	{	84	85.1	112.3	82.0	84.9	168.5	94.1
	Γ_1^+		87.5	76.9	102.6	75.6	78.6	179.2	78.0
	Γ_3^+	222.4	241.1	220.9	169.3	174.3	313.8	170.7	
	Γ_4^+	174.5	173.8	274.5	208.3	185.4	425.2	183.0	
	Γ_2^+	real	65.8i	17.1	77.9i	17.7i	13.3	126.4i	13.0
Y_8									
No of imaginary frequencies (2)	0	196/	0/	NC	21/	0/	NC	0/	
		20000	160000	160000	160000	160000	160000	160000	
$Q_2/e \text{ \AA}^2$ (3)	1.13	1.5	1.18	1.13	1.31	1.26	0.95	1.15	
Θ/B (4)	(5.42)	(7.19)	(5.65)	(5.44)	(6.30)	(6.06)	(4.56)	(5.52)	
$Q_4/e \text{ \AA}^4$ (3)	---	5.60	4.93	3.67	6.59	4.25	4.65	4.15	
$Q_6/e \text{ \AA}^6$ (3)	---	21.08	25.80	9.75	27.47	13.33	26.1	11.15	

(1) See text.

(2) Expressed as (No of frequencies)/(No of frequencies sampled).

(3) Moment values assume linear distribution of charge and are calculated as $Q_n = \sum g_i z_i^n$.(4) Quadrupole moments calculated as $\Theta_{zz} = \sum g_i z_i^2 = \sum g_i (3z_i^2 - r_i^2)/2$ (off-axis components ignored).

NC: not calculated.

satisfactory agreement with the above constraints. For each path of variation it was observed that frequency and energy values tended to stabilize before the equilibrium measures.

Considerable computational effort was saved by first applying the simplex method to models with a small number of neighbours (42) and then in the final stages extending the number to 380. In the final stage of refinement charges and quadrupoles were introduced at the molecule centre as well as at C and H sites. Details of one such model are given in column II of tables 1 and 2.

The allowable extent of differences between calculated and constraining values is, to some extent, a matter of opinion. In our view an acceptable model would involve not more than 2% difference in frequencies, lattice energy within 10% of the 'experimental value' and equilibrium values (expressed as $(a/E)\partial E/\partial a$ etc) within the range ± 0.05 . These values to some extent reflect the reliability of the experimental data and the accuracy of determination of the model properties but also allow for the comparative crudeness of the model. Our best model (see column II of tables 1 and 2) achieves the requirement for the four equilibrium conditions but two of three rotational frequencies are in only fair agreement with experimental values and energy agreement is far from satisfactory.

In our calculations the 16 potential parameters were varied to produce a best fit of 12 experimental quantities. We therefore cannot regard the models as being unique; however it was found, from a variety of initial potential parameter values and initially assumed variations, that the final calculated values were often sufficiently close to give overall confidence in the broad details of the models.

It must also be noted that in the minimization procedure the moments of the charge distribution were unconstrained yet the final value of the quadrupole moment is in reasonable agreement with that given in [21]. There are as yet no experimental data with which to compare Q_4 and Q_6 .

In an attempt to improve the model further non-axis components of dipoles and quadrupoles compatible with crystal symmetry were introduced. This was an attempt to allow for the effect of polarization in the crystal environment. Cell parameters and molecule lengths were also varied. Resulting changes in the parameters and magnitudes of 'off-axis' components were sufficiently small to be classified as allowable perturbations on the original values. However there resulted some worsening of agreement with measured frequency values and the energy discrepancy was unresolved. Since this model represented no essential advance no details are given here.

4.2. *k*-dependent frequencies

Phonon frequencies were determined at each of 16 000 points, uniformly distributed over the irreducible octant of the first Brillouin zone. All frequencies were real in contrast to the situation with the unmodified HM models each of which showed many imaginary frequencies. The resulting frequency distribution is shown as curve (a) in figure 4.

4.3. Summary

Minor changes of the HM AM model produced a stable model of orthorhombic C_2H_2 in reasonable agreement with observed phonon frequencies and with measured molecular quadrupole moment. The major defect was poor agreement (-28%) with

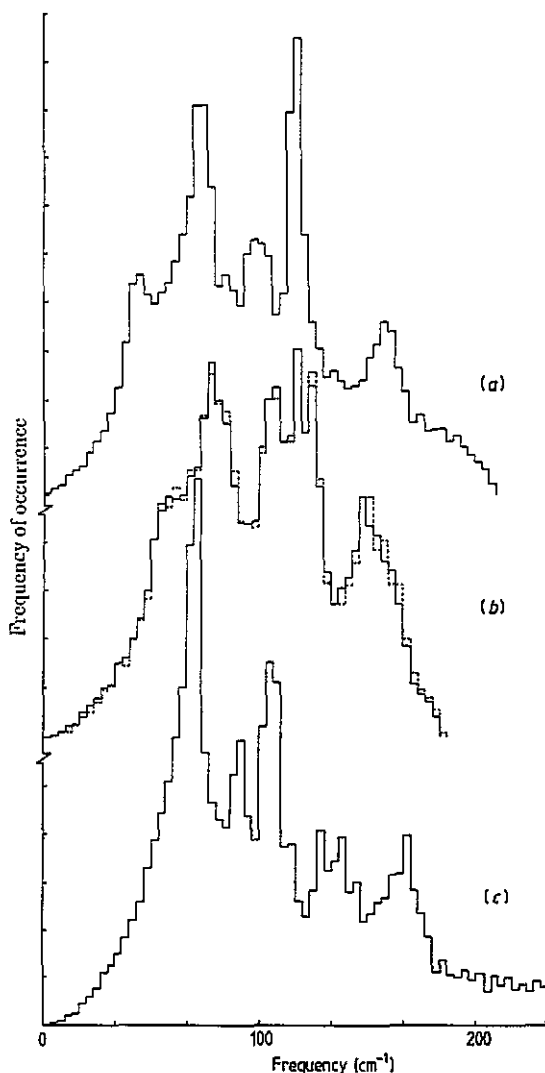


Figure 4. Phonon density of states for (a) modified HM model; (b) NF model V; (c) NF model III. For 380 neighbours shown with solid curve; and (in b only) for 42 neighbours shown with broken curves.

lattice energy. An attempted simulation of polarization effects produced no effective improvement.

5. The Nyberg–Faerman model

Nyberg and Faerman (NF) [9] have calculated the lattice energy of both cubic and orthorhombic C_2H_2 using Gaussian atomic orbitals. They write the lattice energy as the sum of exchange (E_{ex}), coulombic (E_{es}), inductive (E_{ind}) and dispersion (E_{disp}) contributions:

$$E_{latt} = E_{ex} + E_{es} + E_{ind} + E_{disp}$$

The sum of the exchange, coulombic and inductive terms, E_{HFSCF} , was determined by an SCF-MO calculation at the Hartree-Fock level and the dispersion term found using a modified London approach in which localized MOs were centred on the C and H atoms and at positions on the C-H and C≡C bonds.

For the orthorhombic form NF obtained a value of $-23.5 \text{ kJ mol}^{-1}$ for the lattice energy, differing by 7% from the value of $-25.2 \text{ kJ mol}^{-1}$ which we estimated from experiment in section 2. Of this amount $-13.2 \text{ kJ mol}^{-1}$ was attributed by them to E_{HFSCF} and the remainder to E_{disp} . Bond-bond interactions dominated E_{disp} with only 0.5% being associated with interactions involving atomic centres.

This result suggests developing a lattice dynamical model for C_2H_2 in which short-range and coulombic interactions occur between bond sites in addition to coulombic ones between atomic sites. It should be emphasized that the work of NF provides no direct evidence for centering the short-range interactions wholly at bond sites but this is clearly a simple extension of their conclusions.

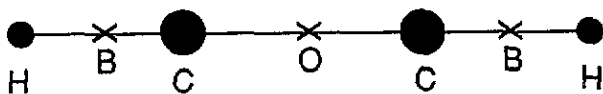


Figure 5. C_2H_2 molecule showing positions of bond centres, B and O.

The positions of the interaction sites (O, B, C, H) on the C_2H_2 molecule are shown in figure 5. ℓ_B is given in [9] as 1.28 \AA . Since the NF results are expressed only in terms of the total contributions to the lattice energy there is choice in the form of the interactions and the magnitudes of the parameters involved.

In this work we assume Buckingham potentials between bond sites. The coulombic interactions are generated by monopoles, dipoles and quadrupoles situated on both atom and bond sites. Allowing for overall charge neutrality and for molecular symmetry such a model has 19 parameters to be determined. These were found using the simplex method [20]. As when considering HM based models some complication of procedure was required because determination of model properties (principally librational frequency values) to an acceptable precision requires consideration of at least 248 neighbours. In order to minimize computational effort the initial stages of the minimization used 42 neighbours and this was extended to 380 neighbours in the final stages. The experimental parameters to which the model is fitted remain, as previously, at 12 thus giving a non-unique potential.

5.1. Computational details

In table 1 the final potential parameters of three of our models are given and, in the corresponding columns in table 2, the resulting calculated quantities. These models were all more or less successful in reproducing the experimental data but differed considerably in the details of their assumed interactions.

The starting point for the first model is given in tables 1 and 2. The parameters of all three Buckingham potentials were initially assumed identical. The charges at the four sites were $q_C = +4$, $q_H = +1$, $q_B = -2$ and $q_O = -6$ units in accordance with what one might expect from naive notions of bonding. The unit (approx $0.05e$) was determined by comparing with the details of the HM model. The other dominant coulombic feature of the HM model is large dipoles at C and H sites. A similar

dominance was assumed here by placing dipoles of strength $0.95D$ at the bond sites B. The starting values of the quadrupoles were all zero.

Initially all the 19 potential parameters were allowed to vary within the simplex procedure [20]; this resulted in a relatively poor model and in order to improve the fit the molecular interaction site distance, ℓ_B , was also allowed to vary. The resulting model III of tables 1 and 2 had zone centre frequencies that were in only fair agreement with experiment but lattice energy was much improved over that of the HM model. Static equilibrium indicator values were acceptable though they slightly exceeded the range of variation found when neighbour numbers were increased beyond 248. A small number (21) of imaginary frequencies were found in sampling 16000 k points within an irreducible octant of the Brillouin zone indicating a mild departure from dynamical equilibrium.

In an attempt to remove these deficiencies the same starting model was used and the same parameters varied. However the molecular bond interaction site distance from the molecule centre, ℓ_B , was now varied from the beginning. This resulted (model IV) in improvements in both energy and centre zone frequencies; static equilibrium measures were completely satisfactory and dynamical equilibrium was indicated by finding no imaginary frequencies among the 160000 sampled.

As with the modified HM model polarization effects were allowed for by introducing variable off-axis components of the dipoles and quadrupoles. Since this did not produce appreciable improvements in the models details are not given here.

In view of the overdetermined nature of the models (variable parameter numbers exceed numbers of experimental quantities to which fitted) it seemed desirable to test the sensitivity of the final model with respect to the starting point. To this end a third model (V) was introduced in which the initial parameters were appreciably different from those of III and IV. These are given in table 1. The effect was a noticeable change in the details of the final model accompanied by a slight worsening of the agreement with experimentally determined frequencies but a further marked improvement in crystal energy. Static and dynamical equilibrium were still satisfactory.

The sampling of large numbers of points of the Brillouin zone as a test for dynamical stability has been emphasized. This process also provides data for constructing frequency distributions for the various models and hence the free energy and the thermodynamic properties of the crystal. It was found that histograms for models IV-V were similar. The differences between these two sets and that for model III were significantly smaller than between them and those for the improved HM model of model II. In figure 4 these histograms are shown. The similarities between the various histograms is emphasized further in figure 4(b) where we show those resulting from the same model V taking account of both 42 and 380 neighbours, and this in spite of the fact that the dispersion curves for these models showed rather large variations.

The dispersion curves were similar for all 380-neighbour models based on NF, the main difference being in the details of the highest-frequency branches. In figure 6 we show the dispersion curves for model V labelled with the irreducible multiplier representations of the point group of the wavevector using the tables in [12].

5.2. Discussion

Three lattice dynamical models of C_2H_2 have been identified based on the findings of NF that the dispersion forces in C_2H_2 can be bond centred. These are broadly similarly successful in reproducing the experimentally observed lattice frequencies.

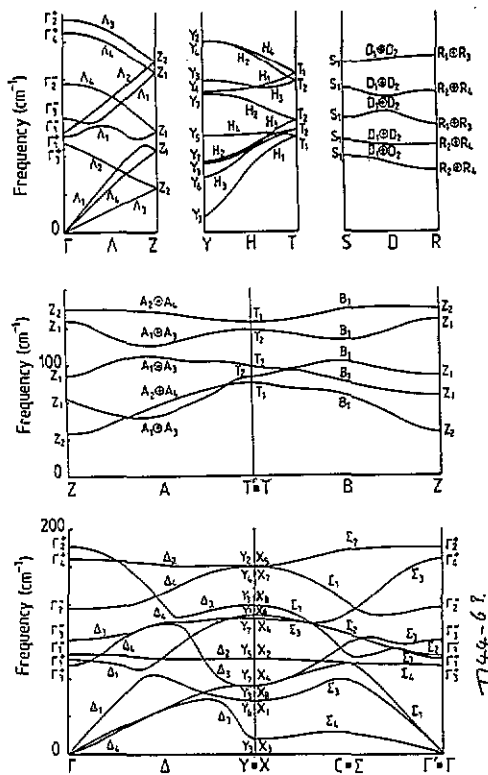


Figure 6. Phonon dispersion curves for NF model V, labelled with the irreducible multiplier representations of the point group of the wavevector [12].

Two of the models exhibited excellent static equilibrium, the other is not quite as good in this respect though still acceptable. With minor exception in III the models were dynamically stable, in the sense that all the phonon modes were real at each of the 16000 sampled points in the Brillouin zone.

There is considerable variation in the details of the interactions of the various models. This is such that it was impossible to infer any uniqueness about the individual interactions between centres. In this situation the question arises concerning the utility of the models. This can be established by showing they are capable of predicting satisfactory values for observable quantities not taken into account in their construction. One such quantity is the net molecular quadrupole moment that is derived from the various monopoles, dipoles and quadrupoles placed at four types of interaction site. As seen in table 2 the range of calculated values is from 5.52 to 6.30 which is essentially the same as that of the values deduced in [21] from experiment. This agreement together with the fact the lattice energy is, in contrast to that of model II, in fair agreement with experiment suggests that all the models were indeed realistic. The calculated values of higher moments show a much greater variability but there are, to the authors' knowledge, no experimental values with which to compare them. They should thus provide a sensitive test of the models when such

measurements become available.

A second predicted property, albeit a less sensitive one, is the phonon density of states. Generally these values are very similar and any one would provide a reasonable description of the thermodynamics of the crystal. Thus calculations of the thermodynamic properties would not distinguish between models. There are differences of detail but these are such as to require comparison with direct measurements of the phonon density of states in order to differentiate between models.

All three models predict essentially the same value ($\sim 90 \text{ cm}^{-1}$) for the out-of-plane translational frequency which is not optically active. Again the small range of variation suggests a general property of the NF model. Values for the fourth (thus far unobserved) rotational frequency do not agree in this way. This together with the higher charge moments and details of dispersion curves when they are observed will provide further information with which to decide between the merits of the various models.

A noticeable feature of all three models is a tendency for calculated values of the largest translational frequency (experimental value 127 m^{-1}) to be 2–4% too large and for the 106 cm^{-1} translation to be 5–6% too small. This points to a common deficiency of the models. Since the original HM model fitted the frequencies but not the equilibrium conditions this emphasizes the need to be wary of any model that fits the optical modes and ignores equilibrium conditions. Such a model means, of course, that the Taylor series expansion used in deriving the equations of motion of the system [22] is made about non-equilibrium positions and hence is invalid.

In model V the total lattice energy ($-23.2 \text{ kJ mol}^{-1}$) agrees with NFS computed value of $-23.5 \text{ kJ mol}^{-1}$ although it is partitioned in a rather different way: in model V E_{disp} is $-30.9 \text{ kJ mol}^{-1}$, and thus E_{HFSCF} is $+7.7 \text{ kJ mol}^{-1}$, compared with NFS $-10.33 \text{ kJ mol}^{-1}$ and $-13.18 \text{ kJ mol}^{-1}$ respectively. It should, however, be noted that in both cases total energy is about 7% greater than the experimental value.

6. Conclusions

The various Hirshfeld and Mirsky (HM) models for orthorhombic C_2H_2 have been investigated and a modified stable form developed of the 'atomic moments' AM one. The chief objection to this is its poor agreement (-28%) with the measured lattice energy. Its properties are compared with those of other models based on the *ab initio* work of Nyberg and Faerman (NF) in which the dispersion force interactions are bond-based rather than atom-centred. It is found that the position of this bond-centred interaction must be shifted appreciably from that suggested by NF and partition of lattice energy between the various forms of interaction is rather different.

The NF models are superior to the modified HM one in possessing a more realistic lattice energy. All models predict values for the net molecular quadrupole moment in good agreement with experiment, all are highly stable in both a static and dynamic sense. There is some variation in the details of predicted dispersion curves, particularly at higher frequencies. The models display such a variety of parameter values that it is difficult to deduce anything but the broadest details of the molecular interactions.

A note of caution is sounded about using thermodynamic properties calculated from phonon density of states to validate the microscopic details of models and

attention is drawn to the importance of ensuring that the lattice is in static equilibrium. In connection with the latter point it should be emphasized that there would have been no difficulty in identifying an otherwise completely satisfactory HM type of model if no attention had been paid to static equilibrium. This should be borne in mind in assessing the merits of lattice dynamical models which ignore this fact!

Acknowledgments

One of the computer programs used in this work is a significant development of that supplied to one of us (JWL) many years ago by Professor G S Pawley, to whom we express our thanks.

References

- [1] Pucci R and Piccitto G (ed) 1991 *Molecular Systems under High Pressure; Proc. 2nd Archimedes Workshop on Molecular Solids Under Pressure* (Amsterdam: Elsevier)
- [2] Leech J W and Grout P J 1991 *Proc. 2nd Archimedes Workshop on Molecular Solids Under Pressure* ed R Pucci and G Piccitto (Amsterdam: Elsevier) pp 337-40
- [3] Hirshfeld F L and Mirsky K 1979 *Acta Crystallogr. A* **35** 366-70
- [4] Anderson A, Andrews B and Torrie B H 1985 *J. Raman Spectrosc.* **16** 202-7
- [5] Schwartz Y A, Ron A and Kimmel S 1971 *J. Chem. Phys.* **54** 99-105
- [6] Aoki K, Kakudate Y, Yoshida M, Usuba S, Tanaka K and Fujiwera S 1987 *Solid State Commun.* **64** 1329-31
- [7] Mirsky K 1978 *Computing in Crystallography; Proc. Int. Summer School on Crystallography Computing* (Delft: Delft University Press)
- [8] McLean A D and Yoshimine M 1967 *Tables of Linear Molecular Wave Functions* (San Jose, CA: IBM)
- [9] Nyberg S C and Faerman C H 1989 *Mol. Phys.* **67** 447-54
- [10] Koski H K and Sandor E 1975 *Acta Crystallogr. B* **31** 350-3
Koski H K 1975 *Acta Crystallogr. B* **31** 933-5
- [11] Van Nes G H J 1978 *Doctoral Thesis* University of Groningen
- [12] Grout P J, English P S and Leech J W 1975 *J. Phys. C: Solid State Phys.* **8** 1620-32
- [13] Jones A H 1960 *J. Chem. Eng. Data* **5** 197
- [14] Gamba Z and Bonadeo H 1982 *J. Chem. Phys.* **76** 6215-9
- [15] Landolt-Börnstein *New Series* 1961 *Zahlenwerte und Funktionen* 6th edn, vol II, part 2 (Berlin: Springer) p 151
- [16] Filippini G, Gramaccioli C M and Simonetta M 1980 *J. Chem. Phys.* **73** 1376-80
- [17] Walmsley S H 1967 *J. Chem. Phys.* **48** 1438-44
- [18] Evjen H M 1933 *Phys. Rev.* **39** 675-87
- [19] Ewald P P 1921 *Ann. Phys., Lpz.* **64** 253-87
- [20] See, for example,
Press W H, Flannery B P, Teukolsky S A and Vetterling W T 1986 *Numerical Recipes* (Cambridge: Cambridge University Press) pp 289-93
- [21] Dagg I R, Anderson A, Smith W, Missio M, Joslin C G and Read L A A 1988 *Can. J. Phys.* **66** 453-9
- [22] Boru M and Huang K 1957 *The Dynamical Theory of Crystals* (Oxford: Clarendon)