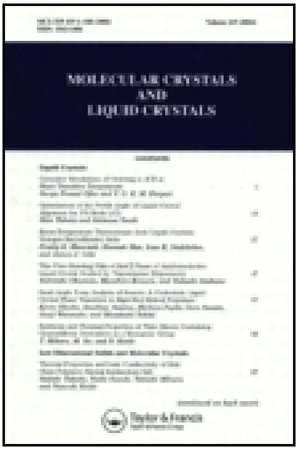

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Phonon Frequencies Calculations in Molecular Crystals from Atomic Interaction Potential: III Study of a SEMI RIGID Molecular Model: Durene

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Phonon Frequencies Calculations in Molecular Crystals from Atomic Interaction Potential.

III STUDY OF A SEMI RIGID MOLECULAR MODEL: DURENE.

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Calculations of some internal and external zero-wave vector phonon frequencies have been carried out using interaction potential functions between nonbonded atoms. It is shown that potential functions obtained from crystal data can also be used to predict some internal properties of molecules. Experimental data and calculated results are compared for Durene crystal.

INTRODUCTION

In a recent work, Sanquer and Messager[1] have shown that intermolecular calculations could explain various properties of molecular crystals. Semi-empirical functions were used to describe Van der Waals interactions between nonbonded atoms.

It was shown that good results may be obtained with atom–atom functions of the form $-A/R^{-6} + B\exp(-CR)R^{D}$ where A, B, C, D are semi empirical constants, R is the distance between the two atoms. It is well known that methyl reorientation barrier height may be calculated from interaction potentials[2] but no librational internal frequencies have been deduced from these parameters. The constants were taken from the literature. It is often argued that potential constants which are refined to reproduce crystal properties cannot be used to predict internal ones (for example molecular conformation) because in molecules, distances between atoms are shorter than those occuring in a crystal. It is not our opinion: in durene for example the shortest H–H intermolecular distance is 2.70 Å and the shortest intra-molecular distance effective in fixing the position of the CH_3 group is about

2.4 Å. Thus, we think that a good interaction function should give good results in both problems, at least qualitatively. In fact Sanquer and Messager[1] found that the best agreement between calculated and experimental properties in benzene crystal was obtained using functions first obtained by Bartell[3] to predict internal configuration of molecules. Durene is a good example because there is an amount of interesting experimental data which can be used for testing any potential functions for both internal and crystal properties:

1) very detailed crystallographic structures have been recently published.[4,5]

2) there exist very detailed studies on low frequencies spectra. In particular the eigenvectors of the low frequencies Raman spectrum are known with a great accuracy.[6] There exist also good low frequency I. R. spectra on single crystal.[7]

3) data are reported on the particular properties of CH_3 groups. A barrier height of internal reorientation of about 2 kcal/mole is found from N.M.R., thermodynamic or neutron data.[10]

4) there is experimental evidence of low frequency librations modes of methyl groups.[8–10]

As the barrier height, the low methyl libration frequency modes are determined primarily by Van der Waals interactions between atoms in the molecule.[2]

METHODS

Molecular model

The molecular model is that of rigid tops which are allowed to have different orientations (Figure 1). We consider only Van der Waals interactions between atoms in the molecule and the configuration which corresponds to the internal potential minimum will be called "free molecular configuration." The configuration of the molecule in the crystal is obtained by minimising the sum of the internal and external potentials. We obtain the "Crystalline molecular configuration." It is possible to take into account other possibilities of deformation of the molecule but only if the internal field is well known.[11] This is not the case in durene because essentially there is no complete experimental interpretation of the low internal frequencies (see however the work of Kovner[12]).

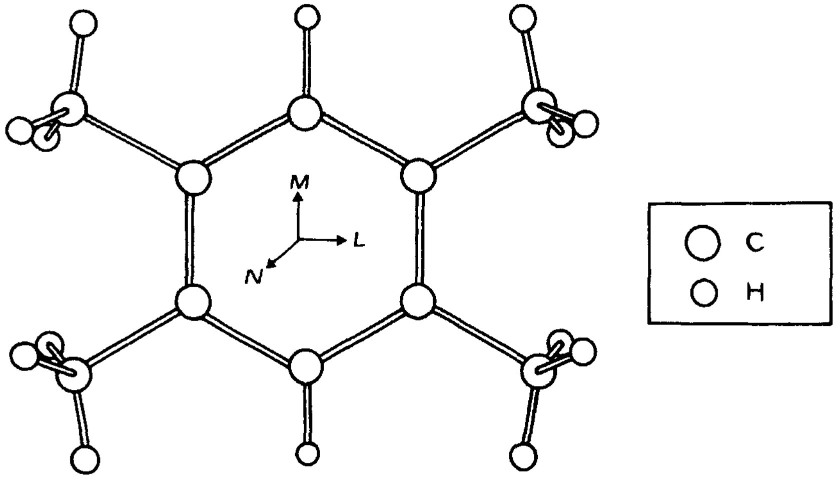

FIGURE 1 Molecular configuration of Durene.

Frequency calculations

The method of calculation of phonon frequencies within the framework of rigid-body motion was described in a preceding article.[1] However, for reason of computing time it is best to use analytical derivatives[11] in place of pure numerical derivatives when calculating the elements of the dynamical matrix. Of course, the result is the same as the approximations involved are identical. The method of introducing internal degrees of freedom was given by Messager[13] in a recent paper and applied to the special case of biphenyl. In durene, however, we have a little more complex situation because we have four methyl groups. We suppose that, in the free molecule, the libration modes of the methyl groups belong to some species of the molecular symmetry group (Figure 2). These modes are then subject to coupling with all the modes

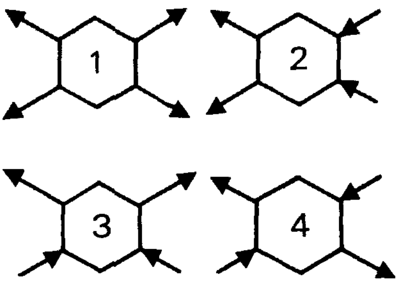

FIGURE 2 Internal methyl librational modes in Durene: the arrows show the direction of the angular momentum for each methyl group.

in other molecules of the crystal. We thus obtain the internal modes of the crystal.

Potential parameters refinement

We will limit ourselves to the Buckingham type potential

$$-\frac{A}{R^6} + B\exp(-CR)$$

but the method is applicable to any analytical definition of the interatomic potential function.[14,15]

The least-squares equation is:

$$\Delta X = (J^+WJ + CE)^{-1}J^+W\,\Delta P$$

with the following definitions

J = Jacobian matrix (J^+ is the transposed matrix),
W = diagonal weight matrix,
ΔX = variation on the coefficients which correspond to variations on the physical properties ΔP,
C = coefficient proportional to the parameter of fitting quality[16]
E = unit matrix.

An element J_{lm} of the Jacobian matrix is defined as $\partial P_l/\partial X_m$, P_l some calculated property, X_m one of the potential function coefficient.

P is a column matrix consisting of 13 elements in the special case of durene which are:

1) the calculated energy of formation of the crystal. There is no experimentally determined value for Durene crystal: we have supposed that the value of 16 kcal/mole was correct. (Energy calculated with Williams or Liquori parameters[20,17]).

2) the calculated first derivatives over any displacement of the molecule (3 rotations in a centrosymmetric crystal). These derivatives must be zero for the observed positions.

3) the calculated zero wave vector phonon frequencies. These are equivalent to conditions on the second order derivatives of the potential over displacements of the molecules (nine frequencies in durene).

Then, we have 13 physical properties to determine 9 coefficients of the Buckingham potential function used in durene. Crystallographic parameters were not included because no low temperature crystallographic data are available on durene which is a very anharmonic crystal.

As the potential constants are related to the internal properties of atoms some combinations between pairs have been proposed, thus reducing the number of unknown variables. If A_1, B_1, C_1 and A_2, B_2, C_2 are the coefficients relative to atom pairs 1–1 and 2–2 respectively, the potential function of the atom pair 1–2 may be deduced by some "combination rules." The most widely used are of the type (A, B, C are relative to the atom pair 1, 2)

$$B = (B_1B_2)^{1/2} \qquad C = (C_1 + C_2)/2$$

for the repulsive term. If we suppose a "Van der Waals radius" for each atom, potential function must be minimum for $2R_1$, $2R_2$, and $R_0 = R_1 + R_2$, so that

$$A/B = \tfrac{1}{6}R_0^7 \exp(-CR_0)$$

In our computer programme we admit explicitly such relations, although they may be relaxed at any moment of the calculation.

J_{lm} is calculated differently according to the physical properties involved. Some particular assumptions were made concerning lattice frequencies. It is supposed that eigenvectors do not depend on the coefficients of the potential function. We have seen elsewhere that this is a very good approximation.[1] The elements J_{lm} are calculated as lattice sums of analytical derivatives and the calculation must be made at each cycle of the least squares process.

The weight matrix W is defined to give appropriate importance to each calculated quantity. In particular, frequencies are weighted proportionally to $(\omega_i^2)^{-1}$ where ω_i is the value in cm^{-1} of the experimental frequency.

RESULTS AND DISCUSSION

Molecular Structure

Using the interaction parameters of Liquori,[17] the position of the CH_3 groups was that given in Figure 1, i.e., with a hydrogen atom in the ring plane. This was confirmed by neutron diffraction.[4] However, Kitaïgorodsky's parameters[18] predict a rotation of 12 degrees of the methyl groups,[19] in conflict with experimental data. This shows that the carbon-hydrogen pair has a much more repulsive term at short distance than the hydrogen–hydrogen pair. The calculated barrier rotation height of the CH_3 group depends on the set used: 0.3 kcal/mole with William's parameter;[20] 3 kcal/mole with Kitaïgorodsky's parameters[18] and 1.2 kcal/mole with Liquori's parameters.[17]

All sets of parameters predict in the molecule a very low methyl libration frequency for the gear-like motions 1 and 2 of Figure 2 and a very high frequency for the other motions 3 and 4. There is no experimental evidence in durene for this latter result. However, in hexamethyl benzene a non gear-like motion of CH_3 was found around 1050 cm^{-1}.[21]

Values of the calculated frequencies are of course very different according to the constants set used. If we use set of ref. 17 two gearlike frequencies were found about 60 cm^{-1} and two non gear-like frequencies about 680 cm^{-1} (in the free molecule). Our model does not exclude the existence of a low-lying non gear like mode but this would suppose that the repulsive term for H–H pair is much weaker than generally admitted.

Rigid Body Motion

In a first calculation we made use of a molecular model with an average methyl–methyl interaction but the results were not satisfactory, as already remarked on in a preceding paper.[22] Indeed, an imaginary low frequency was obtained in the antisymetric mode B_g and a nonnegligible departure between rotation and inertial axes.[23] As Prince *et al.*,[4] have recently located the hydrogen atoms of the methyl groups it was then possible to use a refined model with confidence.

If we take the potential functions of Williams[20] we obtain frequencies and eigenvectors as given in Table I. We note that the peculiarities of the durene low frequency spectra are very well predicted. There is notably an inversion of axes. The frequency along *M* axis is considerably higher than around *L* axis though the moment of inertia around *M* is twice that around *L*.

TABLE I

Calculated frequencies using Williams parameters[20]

		Eigenvectors						
Sym	ν_{cal}	*L*	*M*	*N*	*a*	*b*	*c**	ν Exp (6)(7)
Ag	41	−0.15	−0.01	0.948				(32)
	87	0.98	0.05	0.15				72
	141	−0.05	0.99	0.01				103
Bg	24	0.16	0.00	0.98				32
	82	0.98	0.02	−0.14				72
	135	−0.02	0.99	0.02				103
Au	40				−0.22	0.0	0.97	37
	69				0.97		0.22	68
Bu	76							65

L, *M*, *N*: inertial axes (Figure 1)
a, *b*, *c**: crystallographic axes.

The motion occurs predominantly around the inertial axis. This conclusion is well verified by experiment[6] and indicates that the atom–atom interaction model predicts the correct eigenvectors, the structure being known with some accuracy. These conclusions could be reached using any of the potentials currently used in the literature. This confirms the results on benzene[1]: eigenvectors are largely independent of the exact potential function used.

Potential parameter refinement

As found by Taddei *et al.*,[24] the least squares equation led to an almost singular characteristic determinant. This shows that the coefficients of the Buckingham potential are in fact not independent, or else, that an almost as good a fit may be obtained using different sets of potential parameters. A way of avoiding this difficulty is to vary only one type of parameter. But parameters so calculated depend on the values which were chosen as starting point; different results are obtained according to the variables we begin to refine: there is a competition between the coefficients B and C. Furthermore there is a compensation between the different terms: a weak repulsive hydrogen term being balanced by a strong repulsive carbon term and vice-versa. Thus we think that it is necessary to search for solution in another way.

We then propose to retain the potential parameters which give reasonable values for internal reorientation barrier heights, methyl libration frequencies and a good molecular configuration. It would be tempting to introduce there molecular calculated properties in the least squares equations, but this is not desirable because of the great uncertainty of the experimental data. The internal barrier height is known to lie between 1.4 and 2 kcal/mole. Of the 8 methyl librations frequencies only two are reported in the literature.[10,25] However the internal properties can be used to provide clues for predicting the features of the potential parameters. In particular the H–H repulsion term must be much less important than is generally assumed and as a result the C–H repulsion term must be much more important. There is no difficulty with the attractive term as all authors agree to give them always the same order of magnitude (see Table 1, Ref 1) this attractive term can also be compared with values obtained from other methods. Following these principles we obtain the parameter coefficients of Table II.

Non rigid Body Motion

Results of the calculated frequencies are given in Table III. We see that the coupling between internal and external modes is very weak. This fact is not accidental and is mainly due to the kinetic energy associated with methyl

TABLE II

Set† of refined parameters (kcal/mole, Å)

Atom pair	A	$B.10^{-3}$	C
C–C	329.2	1816	4.3840
C–H	137.8	25.6	4.6488
H–H	26.9	0.3618	2.7601

† For this set the only combination rule retained is $B_{CH} = (B_{C} \cdot B_{H})^{1/2}$

TABLE III

Calculated frequencies

	Ag			Bg			Au		Bu
a	45	83	114	25	81	103	36	59	67
b	44	78	106	23	78	101	34	58	67
c	(32)	72	102	32	72	102	37	68	65

Motion of the molecule

	Ag		Bg		Au		Bu	
a			147	175				
b	205	216	189	226	197	210	198	209
c		187	163	197*		(189–194)		

Methyl librations

a = rigid-body calculation using set of Table II
b = non rigid body calculation with the same set
c = experimental values (6), (7), (8), (9)
* at 25 K.

libration modes which is very small compared with the rigid body motion energy. There is a strong kinetic decoupling between the internal and the external modes. Such phenomenon is also observed using another molecular model.[11] Thus it is proved that the separation between internal and external modes may remain valid even though frequencies have the same order of magnitude. This assumption was used by experimenters since long ago.

We can also clarify what may be understood by semi-internal modes.[26] Methyl libration is typically such a mode because the hydrogen atoms have a large displacement. The influence of the external field is very important (half of the calculated energy comes from the external field).

It is thus expected that such frequencies, although internal, will show characters of external modes (temperature dependence, dispersion). This is in striking contrast with other modes in which the carbon atoms have important displacements. These latter modes are little influenced by the crystal field and although their frequencies may be very low they remain quasi pure internal modes.[11]

CONCLUSION

We have pointed out the difficulty of obtaining a good set of parameters for potential functions, in order to reproduce experimental data with a good fit. Nevertheless it seems that repulsive terms commonly used in the literature to describe H–H interactions are too large, more especially if we agree with some authors[10] that all methyl librations occur in the region 100–200 cm^{-1} instead of in higher regions. We think this is also the reason why Kitaïgorodsky's parameters are not so good: the repulsive terms are the most important we have found in the literature for H–H interactions: at the opposite of Bartell's parameters with which we have obtained better results.[1]

A good interpretation of low internal frequencies of durene is needed to get insight into the internal field and this should help us to find good parameters to describe physical properties of the molecule and the crystal. We have shown that good interpretation of the low frequency I.R. and Raman spectra may be obtained, starting from many atom–atom potential functions. However, as we know that many proposed parameters can give almost as good results we propose to retain functions giving good values for internal properties of molecules since inter- and intramolecular distances are of the same order.

In the study of the crystal properties no allowance was made for anharmonicity. This may be a serious cause of errors.[1] Data on low temperature crystallographic structure are still lacking for durene. Another cause of errors may come from the neglect of other terms than those in r^{-6} in the potential functions. We have already shown that electrostatic term is negligible[27] but term in r^{-8} or higher may be important. A trial to reproduce molecular properties with Lennard–Jones potential would also be valuable.

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