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Author's Review

## Lattice Dynamics and Intermolecular Forces in Organic Molecular Crystals

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Recent developments in the theory and the application of determination of intermolecular forces are discussed for the computer simulation of the lattice dynamics of organic molecular crystals. Different atom-atom potentials for carbon, hydrogen, halogens, oxygen and nitrogen are presented. The influences of hydrogen bonds and multipolar forces are illustrated with some examples. Such potentials are applied to glutaric and squaric acid, hexachloroethane, malononitrile and parachlorobenzamide.

### INTRODUCTION

With the development of the Fourier transform far infrared spectrometers and the laser-Raman spectroscopy the frequency domain from 300 to some  $\text{cm}^{-1}$  has become available to study the vibrations of the molecules as a whole in an organized crystal lattice, the so-called lattice modes. Parallel theoretical developments for the calculation of these modes with the help of a normal coordinate analysis or lattice-dynamical calculation have led to a very rapid evolution of the tools for interpretation of the spectra and of their use in the study of different problems since the first publications 20 years ago.<sup>1-5</sup> Three main directions can roughly be distinguished in the present research: 1) further development of the methods in order to extend the field of application (intensity calculations, consideration of anharmonicity) or the precision of the analysis (multipolar interactions, anisotropic potentials), 2) use of experimental results in certain series of substances in order to study intermolecular potentials (transferability of parameters, relative importance of the Coulomb forces or hydrogen bonds), 3) application of known potentials to study the dynamics of crystals with complicated structure or such effects as phase transitions.

Several books and reviews have appeared during the last years dealing with lattice vibrations,<sup>6-9</sup> the study of phase transitions<sup>10</sup> or the use of the atom-atom potential model.<sup>11</sup> Thus, there is no need for another overall review. In this paper we shall concentrate on some recent results concerning the field of organic molecular crystals. After a short chapter summarizing the background of the theory three parts will discuss the three topics mentioned above.

## THEORETICAL BACKGROUND

In the study of molecular crystals the forces between the atoms can mostly be divided into two groups separated by more than one order of magnitude: intramolecular forces corresponding to energies in the order of 400 kJ/mole and intermolecular forces with energies lower than 20 kJ/mole. Consequently, the total potential  $V$  can be written as

$$V = V_{\text{inter}} + V_{\text{intra}}$$

The intramolecular potential can mostly be transferred from the study of the isolated molecule as the molecular structure hardly changes from the gaseous or liquid to the solid state. The intermolecular potential between two molecules, on the other side, can further be divided into three components according to

$$V_{\text{inter}} = V_{\text{vW}} + V_{\text{C}} + V_{\text{HB}}$$

$V_{\text{vW}}$  represents the van-der-Waals forces consisting of two terms: an attractive one corresponding to dispersion (London) interactions and a repulsive one caused by the Pauli exclusion rule when the overlap of the electronic clouds becomes too high as atoms come closer. According to a proposal of Kitaigorodsky<sup>12</sup> these forces are usually represented as a sum of atom-atom participations.

$$V_{\text{vW}} = \sum_i \sum_j V_{ij}$$

where  $i$  and  $j$  run over all atoms  $i$  of the first molecule and over  $j$  of the second one. The most common functions used are of the Lennard-Jones

$$V_{ij} = -\alpha/r_{ij}^6 + \beta/r_{ij}^m \quad \text{with } 6 < m < 14$$

or of the Buckingham type

$$V_{ij} = -A/r_{ij}^6 + B \exp(-Cr_{ij})$$

where  $\alpha$ ,  $\beta$ ,  $m$ ,  $A$ ,  $B$  and  $C$  are parameters depending only on the nature of atoms  $i$  and  $j$ . These potentials are functions of the interatomic distance only and thus isotropic. A critical compilation and review of the already existing potentials, applied to different physical properties, has been presented very recently by Pertsin.<sup>11</sup>

$V_{\text{C}}$  represents the Coulombic part of the potential produced by the electric field caused by the charge distribution in the crystal. It can be fundamentally treated with two formalisms. The first one consists of assigning a partial charge to each atom and thus adding a third term to the atom-atom function according to the Coulomb law. In the second approach, the multipole expansion is used and a series of multipoles is assigned to each molecule. The first approach has the advantage of adding just one term to the atom-atom sum. The main disadvantage is that the whole summation has to be performed over very long distances because the  $1/r$  Coulombic function converges very slowly. The second formalism only requires a long summation of molecule-molecule interactions and permits the use of experimentally determined dipole and, if known, quadrupole moments. The multipole expansion is theoretically valid only if the intermolecular distances are long in comparison with the molecular size. Correspondingly higher moments should

also be considered for large molecules. In fact, as far as only the frequencies are concerned, the approximation seems to work rather nicely.<sup>6,7</sup>

$V_{\text{HB}}$  represents the possibility of finding hydrogen bonds in the crystal structure. The corresponding potential can be defined as a Lippincott-Schroeder function<sup>13</sup>, two heads to tail oriented Morse curves<sup>14</sup> or any other suitable function. A commonly used technique consists of rewriting the Buckingham function as

$$V = \frac{\varepsilon \cdot \lambda}{\lambda - 6} \left[ - (r/r_0)^6 + \frac{6}{\lambda} \exp \{ \lambda (1 - r/r_0) \} \right]$$

where  $\varepsilon$ ,  $r_0$  and  $\lambda$  mean the energy, equilibrium distance and steepness of the repulsive part, respectively.<sup>15</sup> It is possible to define the corresponding energy and force constant (second derivatives) for the hydrogen bond distance  $r_0$  and thus determine the three parameters of the potential curve. The potentials defined above are used for the calculation of lattice frequencies. The theory has been extensively discussed by Califano and Schettino.<sup>6,7</sup> The basic idea is that lattice vibrations can be determined as the eigenvalues (frequencies) and corresponding eigenvectors (normal coordinate or form of the vibration) of the matrix  $\mathbf{D}$ , the elements of which can be written as

$$D_{\mu l}^{\nu m}(\mathbf{k}) = \sum_{\beta} \exp(-2\pi i \mathbf{k} \cdot \mathbf{r}_{\beta}) (\partial^2 V / \partial Q_{1\mu l} \partial Q_{\beta\nu m})_0$$

where  $\mathbf{k}$  is the wave vector indicating the phase shift of neighbouring unit cells,  $\mathbf{r}_{\beta}$  is a vector between unit cell  $\beta$  and reference cell 1,  $V$  is the already discussed potential:  $\mu$ ,  $\nu$  number the molecules in the unit cell, while  $l$  and  $m$  define the degrees of freedom (translation, rotation or internal) considered in the calculation.<sup>16</sup> For IR and Raman active modes the wave vector is practically zero so that the exponential term is equal to unity: all unit cells vibrate in phase at the centre of the Brillouin zone.

This method was developed in different groups, particularly in Florence in the group around Califano.<sup>7</sup> It represents a great improvement of the former approach of Shimanouchi<sup>17,18</sup> with a greater flexibility to study the different components of the crystalline potential quantitatively.

#### RECENT THEORETICAL DEVELOPMENTS

The extensive use of the method led to two main conclusions. On one hand, the ability to reproduce the observed spectra makes the method useful for the study of intermolecular forces and for a quantitative assignment of the spectra. On the other hand, as the study became more precise with the help of high quality experimental data, the discrepancies could be analyzed. Subsequently, theoretical development became necessary in order to improve agreement between the observed and calculated spectra. Finally, the success achieved led to further works treating other spectral properties.

The most important improvements made in the last years are: the consideration of many-body interactions<sup>19</sup>, of polarization interactions<sup>20</sup> as complements to the usual atom-atom and electrostatic potentials and the consideration of the anisotropy of the atom-atom potential.<sup>21</sup> A calculation of the lattice energy and of the vibrational frequencies of ammonia by Giua and Schettino<sup>20</sup> showed that the contribution of the polarization interactions is small but not negligible, at least for this small molecule. Some frequencies

shift by 9% while the participation to the crystal energy reaches 3.0 out of 33.5 kJ/mol. Burgos and Bonadeo<sup>19</sup> performed a similar study of acetylene with the inclusion of three-body interactions. Unfortunately, only the results for the energy are available, but already at this level a participation of the order of 7% of the total energy arises from three-body interactions, and this effect balances polarization interactions. It turns out that for crystals of larger molecules, where numerous atom-atom interactions exist, such effects neutralize each other and can be disregarded in the first approximation.

Reversely, the effects due to the anisotropy of crystal fields cannot be neglected. For crystals containing nitrogen, oxygen or heavier atoms the spherical symmetry assumed for the atoms does not hold. In a study of squaric acid<sup>22</sup>, a substance with a marked two-dimensional character due to strong hydrogen bond building layers of molecules, the inter-layer compressional mode could not be reproduced accurately with isotropic potentials. Bonadeo proposed to take into account the anisotropy of the atom-atom potential by using a distribution of multipolar pseudo-moments over the whole molecule.<sup>23</sup> Calculations of chlorine<sup>21,23</sup> show an improvement of the results but lead to an increase of the number of parameters introduced. To sum up, the effects of the three-body and polarization interactions and of the anisotropy can be handled, but the improvement causes a rapid increase of computing time and of the number of parameters. Such calculations are very useful for a precise understanding of the dynamical processes and of the components of the intermolecular potential in crystals of small molecules. But due to the complexity of the treatment they can hardly be used for larger molecules. Similarly to the competition in quantum chemistry between *ab initio* and semi-empirical methods, we can use the complete method for small molecules in the lattice-dynamical treatment and a more empirical approach for large molecules by using transferable atom-atom potentials and the lower terms (dipole and quadrupole) of the multipole expansion.

Apart from these potential studies, a lot of work has also been done in order to extend the application field of the method. The aim of these trials is to test the eigenvalues of the secular problem (frequencies) on one hand and the quality of the corresponding eigenvectors, *i.e.* the form of the vibrations on the other hand. One method is the calculation of vibrational intensities. The IR and Raman intensities are proportional to the square of the derivative with respect to the normal coordinate of the dipole moment and the polarizability tensor, respectively. In this way, the quality of the normal coordinate can be tested.

The theory has been developed by Luty *et al.*<sup>21</sup> and Schettino and Califano<sup>25</sup> and overcomes a lot of shortcomings of the oriented gas model. Gamba and Bonadeo<sup>26</sup> used this formalism in the study of the orthorhombic and cubic phases of acetylene. Their results are summarized in Table I. Due to the particular structure of both phases the form of the vibrations is fixed by symmetry conditions so that errors in the results can only originate from limitations in the intensity calculations and not from errors in the eigenvectors. Such comparisons are made difficult by the poor reliability of the available experimental data, as mentioned by Cardini and Schettino



TABLE I  
*Vibrational Intensities of the Lattice Modes of Acetylene*<sup>26</sup>

	Freq. (cm <sup>-1</sup> )	Relative intensities			
		Obs.	a	b	c
IR					
<i>Orthorhombic</i>	132	100	0	100	100
	96	60—70	0	55	75
<i>Cubic</i>	90	100	0	100	100
	62	30	0	51	36
Raman					
<i>Orthorhombic</i>	133		2	0.3	14
	88.6	vs	100	100	100
	86.4		43	38	54
	85	s	64	48	80
<i>Cubic</i>	61	w	5	4	11
	38	m	4	4	6
	20	vs	100	100	100

a: oriented gas model

b: molecule centered multipoles

c: molecules distributed multipoles

w, m, s and vs mean weak, medium, strong and very strong intensity, respectively.

for naphthalene.<sup>27</sup> The results in Table I reveal that by comparison with the oriented gas model the introduction of dipolar and quadrupolar polarizabilities leads to a remarkable improvement of the relative intensities. A nice agreement is observed in column c where the electric properties are distributed over all the atoms, instead of being assigned to each molecule. This corresponds to the consideration of higher order multipole moments and polarizabilities. In that case it can be shown that also the absolute intensities become rather accurate. This observation indicates that like in the case of the frequency calculation a precise description requires consideration of higher terms of multipole expansion. A drawback of these results is the necessity to have numerous parameters for an accurate calculation, which are mostly unknown for larger molecules, so that the complete treatment will probably remain limited to small molecules. An alternative attempt was undertaken by Bleckmann and Thibud<sup>28</sup> for oxamide. Using the fact that the crystal is triclinic with  $Z = 1$ , they tried to calculate the Raman intensity of the lattice modes with the CNDO method using a finite field perturbation formalism. Although the relative intensities seem to be rather satisfactory, they give no absolute values and thus no answer to the question whether the CNDO method could reproduce the spectra of such a crystal with hydrogen bonds or not. Since the intermolecular interactions were only considered for distances shorter than 3.4 Å, the method can not be evaluated by this single trial. Anyway, because of the need of computer time for this type of calculations<sup>29</sup>, it will be applicable only to crystals with small unit cells containing small molecules.

As a counterpart to this discussion of alternative methods for intensity calculations, it can be mentioned that, if the conditions of the oriented gas model are roughly fulfilled, this quick method works rather nicely, as shown for hexachloroethane, although the translational and librational degrees of freedom couple in the normal modes.<sup>30</sup>

In addition to the intensity calculations, consideration of anharmonic processes is also a means to test the potential, because the third and fourth derivatives of the potential are implied and supplementary experimental values as the band halfwidth and profile can be taken into account. A good example of such a study was given by della Valle *et al.*<sup>31</sup> with a calculation of naphthalene at 4 K leading to a good agreement with experimental values. The results obtained confirm the validity of the potential developed for the intensity calculation and the potential studies reported in the next section, thus showing the complementarity of all these studies.

As a conclusion of this section on recent theoretical works, a formalism has been developed in order to describe all the properties of the spectra: frequencies, intensities, band widths and profiles. This method is able to describe the spectra and give informations about the intermolecular potential and a precise description of crystal dynamics. The applications are limited by the fact that a complete study is very computer-time consuming. On the other hand, numerous parameters are needed which are usually unknown for larger molecules so that they have to be guessed or used as fitting parameters in the calculation. For large molecules the effects just discussed seem to compensate for each other to a large extent so that the simpler methods exposed in the introduction can be used as the first approximation.

#### POTENTIAL STUDIES

Twenty years ago aromatic hydrocarbons, naphthalene and anthracene, were the subjects of the first studies performed.<sup>1,2,4</sup> Many of the most recent results are again concerned with this class of compounds: naphthalene<sup>31-33</sup>, anthracene<sup>34,35</sup>, phenanthrene.<sup>36</sup> The atom-atom potentials for carbon and hydrogen atoms are well defined<sup>12,37</sup> and have been shown to be transferable to various hydrocarbons. As the structural and dynamical data (including dispersion curves) of naphthalene and anthracene are well-known at a temperature<sup>32,34</sup> as low as about 10 K or under pressure<sup>33</sup>, it was possible to analyze the details of the potential. By using only an atom-atom potential for naphthalene<sup>32</sup> the splitting of about 16 cm<sup>-1</sup> for the two highest frequencies could not be reproduced, some other vibrations showing deviations of about 20%. All these features are improved when the quadrupole moment is included into the calculation.<sup>31</sup> The results given in Table II for vibrations at the centre of the Brillouin zone show the quality of the agreement obtained. The overall agreement is also satisfactory in the Brillouin zone, whereby some discrepancies can be analyzed and interpreted in terms of anisotropy of the atom-atom potential in agreement with the intensity calculation.<sup>27</sup> A similar conclusion can be drawn from the comparison with the Grüneisen parameters.<sup>33</sup>

In the case of anthracene the calculation was performed at the atom-atom level, but under consideration of the internal »butterfly« modes which are able to couple with the external degrees of freedom because of their energy gap of only 20 cm<sup>-1</sup>.<sup>34,35</sup> This coupling could also be followed over

TABLE II  
*Lattice Frequencies (in  $\text{cm}^{-1}$ ) of Crystalline Naphthalene at 6 K<sup>31</sup>*

Symmetry	Calculation	Experimental
$A_g$	113	112
	84	83
	55	64
$B_g$	129	130
	84	79
	51	54
$A_u$	112	107
	57	57
$B_u$	75	80

the entire Brillouin zone in different directions and is in qualitative agreement with the experience.

The overall transferability of the C and H potentials is used in the studies of acetylene<sup>38,39</sup> and hexadiyne.<sup>40</sup> Here again the necessity of including multipoles became evident and it was found that also the atom-atom potentials had to be fitted. It seems that the general validity of the method is not applicable to small linear molecules. Obviously, the inclusion of multipoles higher than quadrupole is not sufficient to improve the results. In Ref. 39 the potential developed for the orthorhombic phase is not transferable to the cubic phase. For 2,4-hexadiyne the trial of using a simple atom-atom potential also led to a qualitative agreement only.

Further, several works were concerned with the intermolecular potentials for heteroatoms: halogens, oxygen and nitrogen. In a series concerning the lattice modes of hexasubstituted ethanes we studied hexachloro- and hexabromoethane<sup>30,41</sup> and used the experimental single crystal spectra in order to check the applicability of nine chlorine and four bromine potentials. Under consideration of lattice energy, equilibrium conditions and vibrational frequencies, only two out of the nine chlorine potentials gave reliable results: those developed by Bates and Busing<sup>42</sup> and Hsu and Williams.<sup>43</sup> Under closer inspection both potentials are very similar and it is interesting to note that both have been developed under separate consideration of the electrostatic interaction and represent only the van-der-Waals forces. As hexachloroethane has neither a dipole nor a quadrupole moment, such potentials are particularly well suited for this kind of calculation.

A similar treatment of bromine was not so satisfactory because there are rather large discrepancies even for the best potential proposed by Hill.<sup>44</sup> It is probable that for this large atom the polarization interaction becomes fairly important and can no longer be neglected if a good agreement is required. A recent crystallographic work has shown that such atoms are no longer isotropic<sup>45</sup> so that the Lennard-Jones or Buckingham potential forms are no longer valid. Kirin proposes an alternative treatment of these data consisting of the shortening of the bond length<sup>46</sup>, which can be correlated to the fact that Williams was obliged to use shorter CH bonds than the experimental ones.<sup>37</sup> Potentials for oxygen atoms are somewhat more difficult to treat as the chemical nature of the atom could be of importance. In an earlier paper on succinic anhydride, we proposed a potential including

parameters for —O— and =O atoms.<sup>47</sup> In recent years, this potential was tested for the  $\alpha$  and  $\beta$  phases of oxalic acid<sup>48</sup>, for squaric acid<sup>49</sup>, glutaric acid<sup>50</sup>, parachlorobenzamide<sup>51</sup> and is now being tested for malonic acid. The results concerning the transferability are summarized in Table III. First of all, the oxygen atoms of squaric acid cannot be distinguished significantly in the calculation so that this potential was refined as if only one atomic species was present. The corresponding parameters can thus hardly be compared with the other ones. The differences between both atom types for other crystals are significant and particularly important for the B parameter while the scattering of each value is smaller. Finally, the usual combining rules for the cross terms (C...O, H...O and =O...O) are clearly not valid in this case.<sup>52</sup> These parameters are different from those reported by Pertsin<sup>11</sup> and from those gathered by Filippini *et al.*<sup>53</sup>. But by transferring the potential of the  $\beta$  phase of oxalic acid to glutaric acid without any change a very satisfactory agreement was obtained.<sup>50</sup> Similarly, the use of the potential for double bonded oxygen in a calculation of parachlorobenzamide was satisfactory.<sup>51</sup> We feel that the potential determined is suitable for calculations of crystals with oxygen atoms of the same type. For other oxygen atoms, like in furan or other, these parameters can only be used as start values of a fitting process.

Further information about the details of the crystal field could be obtained for each individual analysis. As already mentioned for hydrocarbons,

TABLE III  
Atom-atom Potential\* for Oxygen Atoms  $V = -A/r^6 + B \cdot \exp(-C \cdot r)$

Interaction	A (kJ·mole <sup>-1</sup> ·Å <sup>6</sup> )	B (kJ/mole)	C (Å <sup>-1</sup> )
—O...H	377	40106	3.804
	343 <sup>a, b</sup>		3.748 <sup>a, b</sup>
	636 <sup>c</sup>		3.569 <sup>c</sup>
=O...H	393	40106	3.748
	636 <sup>c</sup>		3.569 <sup>c</sup>
—O...C	1738	212368 396741 <sup>c</sup>	3.733
	565 <sup>b</sup>		3.168 <sup>a</sup>
	3475 <sup>c</sup>		3.228 <sup>b</sup> 3.738 <sup>c</sup>
=O...C	410	396741	3.713
	3475 <sup>c</sup>		3.738 <sup>c</sup>
—O...O—	2960	264568	3.870
=O...O=	1855	208433	3.756
	1536 <sup>b</sup>		3.395 <sup>a</sup>
			3.623 <sup>b</sup>
=O...O—	6695	352532	3.816
	1704 <sup>b</sup>		3.384 <sup>a</sup>
			3.690 <sup>b</sup>
			3.813 <sup>c</sup>

\* Reference is the potential in succinic anhydride<sup>47</sup>. Variations are indicated as <sup>a</sup> for  $\alpha$  oxalic acid, <sup>b</sup> for  $\beta$  oxalic acid<sup>48</sup> and <sup>c</sup> for squaric acid<sup>49</sup>.

the multipolar forces must be considered and yield 11 and 14% of the crystal energy for  $\alpha$  and  $\beta$  oxalic acid, respectively, but only 3% for squaric acid when moments up to quadrupole are introduced. The influence on the frequencies cannot easily be characterized; some frequencies increase while others decrease by values reaching 10–15  $\text{cm}^{-1}$ . Concerning the atom-atom potential in both forms of oxalic acid, the C...O= interactions shorter than 3.2 Å, *i. e.* shorter than the sum of the van-der-Waals radii, had to be treated with parameters different from those reported in Table III. Such very short interactions turned out to be purely repulsive. Their nature is not well understood yet but is probably in correlation with the high density of both crystalline forms. In squaric acid, as already mentioned, the interlayer compression mode can by no means be obtained at the frequency required from the experience although the remaining overall agreement is very satisfactory. Due to the strong two-dimensional character of the structure this fact is probably caused by the anisotropy of the crystal field and particularly of the shortest C...O interactions ranging from 3.17 to 3.31 Å. The analysis of these results indicates that a possible way to account for the transferability problem could be to determine parameter sets for classes of chemically similar substances instead of trying to obtain more universal potentials which lead to a poor agreement, at least for the spectral properties.<sup>53</sup>

Recent work concerning nitrogen mainly treats the molecules of imidazole<sup>54,55</sup>, 2,2'-bipyridine<sup>56</sup> and tetracyanoethylene.<sup>57,58</sup> In his book Pertsin analyzes the development of different potentials particularly showing the convergence of the work of Gamba and Bonadeo<sup>59</sup> for the calculation of azabenzenes and the modification by Luty of the potential proposed by Govers.<sup>60,61</sup> The works cited above treat other types of molecules for which these potentials are not applicable. In the two papers handling tetracyanoethylene the authors come back to the original Govers potential because it reproduces the dispersion curves better than the revisited version by Luty. But the agreement is far from being satisfactory, with discrepancies reaching 20–30% between experience and calculation.<sup>58</sup> The authors suggest the necessity of including electrostatic interactions which could correspond to the similar effect observed in hydrocarbons with triple bonds.

The other papers confirm the validity of an old parameter set developed for heterocycles.<sup>62</sup> This potential turns out to be very well transferable to imidazole<sup>54</sup>, as well as 2,2'-bipyridine<sup>56</sup>, leading to reasonable energies and accurate vibrational frequencies. The second paper on imidazole proposes another potential but neither gives a comparison with other potentials nor compares any result with those published two years earlier by Majoube<sup>54</sup>, where the agreement, particularly for the lattice modes, seems to be better. Anyway, in both papers the force constant of the hydrogen bond, calculated as the sum of the corresponding N...N and N...H interactions, is 0.24 N/cm, *i. e.* clearly smaller than in previous works. The potential of Ref. 62 was also successfully used in the calculation of the spectra of parachlorobenzamide.<sup>51</sup>

As an intermediate conclusion of this chapter on the intermolecular potentials the following summary can be given:

— the atom-atom approach is useful for describing the van-der-Waals forces, but must mostly be supplemented with electrostatic interactions expressed as atomic charges, molecule centered multipoles or distributed multipoles.

— the anisotropy of the atom-atom potential can be taken into account with pseudo-multipoles. It is particularly necessary to consider this effect for small or linear molecules.

— this approach enables the analysis of different components of the intermolecular field for the energy, as well as for lattice vibrations.

— due to mathematical correlation the B and C parameters of the Buckingham potential are not independent so that complementary information is necessary to determine, for example, the value of C.

The results summarized here show that transferable potentials exist and lead to reliable results.

#### APPLICATION OF KNOWN POTENTIAL FOR DYNAMICAL STUDIES

In this section some recent results of our group will illustrate typical applications of dynamical studies with the help of the method discussed before.

#### *Rigid-body Approximation and its Limitations — Glutaric Acid*<sup>50</sup>

Glutaric acid,  $\text{COOH}-(\text{CH}_2)_3-\text{COOH}$ , crystallizes in two phases. The  $\alpha$  phase at room temperature is monoclinic ( $C2/c$ ) with  $Z = 4$ . The molecules build infinite chains with  $2.69 \text{ \AA}$   $\text{OH} \dots \text{O}$  hydrogen bonds. The structure of the  $\beta$  phase (stable for  $T > 338 \text{ K}$ ) is not known. Before studying the phase transition it was necessary to determine the possible existence of couplings between internal degrees of freedom (expected as low as  $50-100 \text{ cm}^{-1}$ ) and external motions, *i. e.* to test the validity of the rigid-body approximation. The vibrational spectrum of the free molecule was calculated with the help of the Shimanouchi program<sup>17</sup> under application of the force field of oxalic acid for carboxylic groups<sup>48</sup> and of alkanes<sup>63</sup> for the central part of the molecule. This leads to the spectrum the seven modes of which situated under  $300 \text{ cm}^{-1}$  are reported in Table IV. Then, using the program package of Taddei *et al.*<sup>16</sup>, the molecule was introduced into the crystalline surrounding and allowed to interact with the external degrees of freedom. The intermolecular potential was transferred from the  $\beta$  form of oxalic acid where a similar chain structure exists. The results are presented in Table V. In order to obtain the agreement reported it was necessary to assume that the frequency of internal modes  $I_3$ ,  $I_4$  and  $I_5$  had to be reduced from 138, 129 and 102 to 103, 100 and  $70 \text{ cm}^{-1}$ , respectively. This correction corresponds to the facts that the intramolecular potentials are probably not just transferable and that the molecular field is slightly perturbed in the crystal. Under consideration of rough approximation the agreement is satisfactory. It turns out that only eight out of 22 normal modes can be considered as pure. All other show couplings between internal and external motions ( $B_g$   $135 \text{ cm}^{-1}$ ) or of internal motions together ( $A_g$   $112 \text{ cm}^{-1}$ ). Thus, the experimental assignment obtained from the rigid body approximation can only be indicative.<sup>88</sup> Particularly, the  $A_g$  mode at  $152 \text{ cm}^{-1}$  is assigned by the calculation to a lattice mode.



TABLE IV

Low Frequency Internal Modes Calculated for the Free Molecule of Glutaric Acid With  $C_2$  Symmetry

Mode	Symmetry	Frequency (cm <sup>-1</sup> )	Description
I <sub>1</sub>	B	271	Deformation CCO <sub>2</sub>
I <sub>2</sub>	A	257	Deformation CCC
I <sub>3</sub>	A	138	Torsion: 36% CCO <sub>2</sub> + 34% CC
I <sub>4</sub>	B	129	Torsion CCO <sub>2</sub> : 84%
I <sub>5</sub>	A	102	Deformation CCC: 58%
I <sub>6</sub>	B	52	Torsion CC: 70%
I <sub>7</sub>	A	49	Torsion: 49% CC+ 49% CCO <sub>2</sub>

In a further trial to see the dependence on the conformation of the alkane chain we found out that, when going from a  $C_2$  to a  $C_{2v}$  molecular symmetry, the most sensible mode was not a coupled, but a rather pure one ( $B_g$  89 cm<sup>-1</sup>) which could be involved in the mechanism of phase transition, because it experimentally shows a strong abnormal temperature variation (softening on cooling).

TABLE V

Normal Modes of Glutaric Acid at 300 K

	Experimental		Calculation	
	Freq. # <sup>+</sup>	Assignment <sup>+</sup>	Freq. #	Eigenvector*
Raman				
A <sub>g</sub>	70	R <sub>b</sub>	63	59% <sub>0</sub> T <sub>z</sub> 16% <sub>0</sub> I <sub>7</sub> 15% <sub>0</sub> R <sub>z</sub>
	92	T <sub>b</sub>	94	38% <sub>0</sub> I <sub>7</sub> 30% <sub>0</sub> T <sub>z</sub> 25% <sub>0</sub> I <sub>5</sub>
	112	Internal	118	45% <sub>0</sub> I <sub>3</sub> 20% <sub>0</sub> I <sub>5</sub> 34% <sub>0</sub> I <sub>7</sub>
	152	Internal	162	83% <sub>0</sub> R <sub>z</sub>
	323	Internal	324	96% <sub>0</sub> I <sub>2</sub>
B <sub>g</sub>	65	R <sub>c</sub>	53	89% <sub>0</sub> R <sub>x</sub>
	89	T <sub>a</sub>	71	76% <sub>0</sub> T <sub>y</sub>
	135	R <sub>a</sub>	120	50% <sub>0</sub> R <sub>y</sub> 19% <sub>0</sub> I <sub>4</sub> 17% <sub>0</sub> T <sub>x</sub> 10% <sub>0</sub> I <sub>6</sub>
	140	T <sub>c</sub>	132	34% <sub>0</sub> I <sub>6</sub> 34% <sub>0</sub> T <sub>x</sub> 24% <sub>0</sub> I <sub>4</sub>
	160	Internal	169	46% <sub>0</sub> I <sub>4</sub> 26% <sub>0</sub> I <sub>6</sub> 11% <sub>0</sub> R <sub>y</sub> 10% <sub>0</sub> T <sub>y</sub>
	194	Internal	191	35% <sub>0</sub> T <sub>x</sub> 27% <sub>0</sub> R <sub>y</sub> 27% <sub>0</sub> I <sub>6</sub>
	286	Internal	197	96% <sub>0</sub> I <sub>1</sub>
FIR				
A <sub>u</sub>	95		86	63% <sub>0</sub> I <sub>5</sub> 16% <sub>0</sub> I <sub>3</sub> 15% <sub>0</sub> R <sub>z</sub>
			118	50% <sub>0</sub> I <sub>7</sub> 29% <sub>0</sub> R <sub>z</sub> 19% <sub>0</sub> I <sub>5</sub>
			141	55% <sub>0</sub> R <sub>z</sub> 42% <sub>0</sub> I <sub>7</sub>
	196		179	74% <sub>0</sub> I <sub>3</sub> 17% <sub>0</sub> I <sub>5</sub>
			267	96% <sub>0</sub> I <sub>2</sub>
B <sub>u</sub>	68		84	95% <sub>0</sub> R <sub>y</sub>
	125		120	68% <sub>0</sub> I <sub>4</sub> 23% <sub>0</sub> R <sub>x</sub>
			122	68% <sub>0</sub> R <sub>x</sub> 17% <sub>0</sub> I <sub>6</sub> 11% <sub>0</sub> I <sub>4</sub>
			178	72% <sub>0</sub> I <sub>6</sub> 19% <sub>0</sub> I <sub>4</sub>
	304		294	98% <sub>0</sub> I <sub>1</sub>

\* Molecular axes x, y and z correspond to crystal directions c, a\* and b, respectively.

<sup>+</sup> Ref. 88.

# In cm<sup>-1</sup>.

Several studies of this kind have been performed. Natkaniec *et al.*<sup>64</sup> studied the coupling of the phenyl ring torsion with the rotations and translations for biphenyl over the Brillouin zone, showing that this motion is distributed mainly between three normal modes which exchange their character over the whole zone. Surprisingly, a similar potential trial applied to 2,2'-bipyridine<sup>56</sup> led to the opposite conclusion that the rigid-body approximation works. For squaric acid<sup>49</sup>, oxalic acid<sup>48</sup> and malononitrile<sup>73</sup>, where the frequency gap is of the order of 70, 30 and 20  $\text{cm}^{-1}$ , respectively, the couplings were always smaller than 10%. Thus, a general conclusion cannot be drawn, but all these results show that the rigid-body approximation has to be used and interpreted very carefully.

### Dispersion Curves and Sound Velocities — Squaric Acid<sup>65</sup>

Squaric acid ( $\text{H}_2\text{C}_4\text{O}_4$ , 1,2-dihydrocyclobutenedione) has attracted much interest due to the phase transition at about 100 °C, connected with a disorder of the proton in the hydrogen bond. The ordered phase at room temperature belongs to the monoclinic system,  $P2_1/m$  with  $Z = 2$ , where the molecules build layers through strong hydrogen bond ( $\text{O}\cdots\text{O} = 2.55 \text{ \AA}$ ) (Figure 1). In order to interpret the experimental dispersion curves obtained by inelastic neutron scattering it is very useful to dispose of the calculated eigenvectors in the corresponding directions of the Brillouin zone. For squaric acid the Brillouin

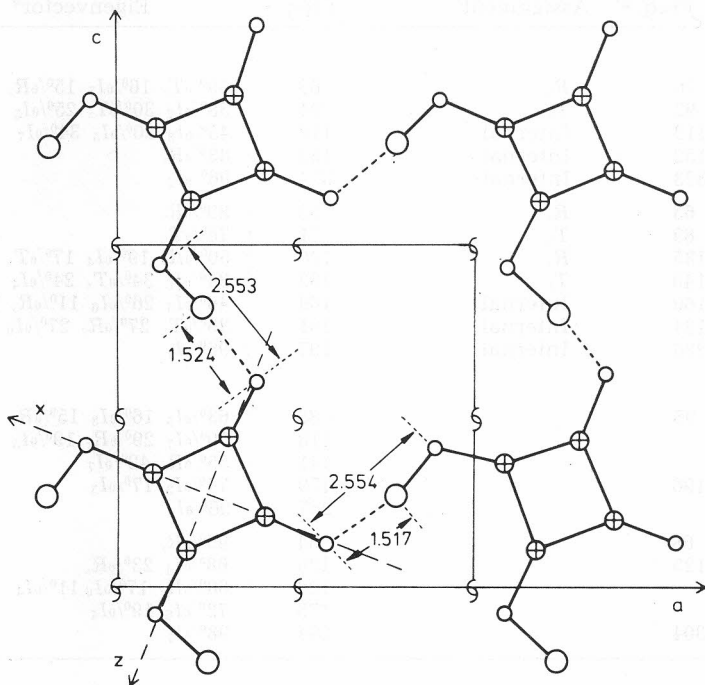


Figure 1. Crystal and molecular structure of squaric acid in a layer. Small, large and crossed circles represent O, H and C atoms, respectively.

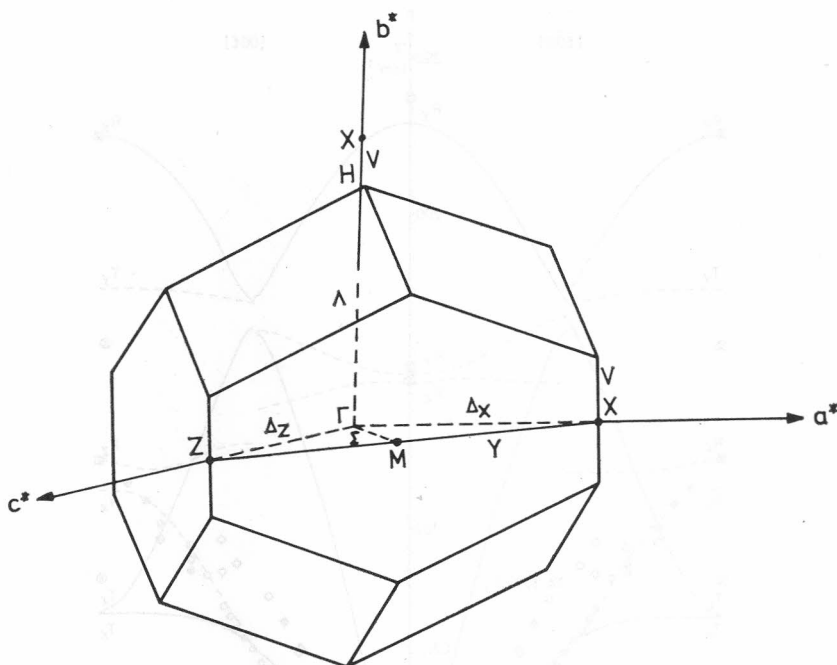


Figure 2. Brillouin zone and particular points of the pseudo-tetragonal unit cell according to Koster.<sup>87</sup>

zone is shown in Figure 2; the calculations were performed from  $\Gamma$  to X and Z over  $\Delta_x$  and  $\Delta_z$ , from  $\Gamma$  to H and X over  $\Lambda$  and V.

The relations in directions  $\Delta_x$  and  $\Delta_z$  are reported in Figure 3. The overall agreement is good as the main features of the four acoustic branches are reproduced. Strong similarity of both directions in the crystal is evident from the picture of the experimental as well as of the calculated data. Figure 4 shows the results in direction  $\Lambda$  where both transversal acoustic modes (TA) are so close that they cannot be distinguished experimentally. The discrepancy in the potential leading to a calculated frequency of  $177.5 \text{ cm}^{-1}$  for the inter-layer compression mode, which is far too high, explains the divergence between the calculated and the observed longitudinal acoustic (LA) mode. From the steepness of the acoustic modes around  $\Gamma$  it is possible to calculate the sound velocities in the corresponding direction. Some examples given in Table VI are compared with the experimental values of neutron and ultrasonics measurements. They reveal the quality of the potential obtained at the centre of the zone.

Such calculations are useful for an understanding of crystal dynamics. In recent years, they were performed for biphenyl<sup>64</sup>, naphthalene<sup>32</sup>, anthracene<sup>34</sup>, 2,3-dimethylnaphthalene<sup>66</sup>, imidazole<sup>55</sup>, tetracyanoethylene<sup>57</sup> and *p*-chloroaniline<sup>67</sup>. Particularly for crystals of large molecules the distinction of the different branches is very difficult to perform on an experimental basis only and a calculation is often necessary in order to orientate the experimental work.

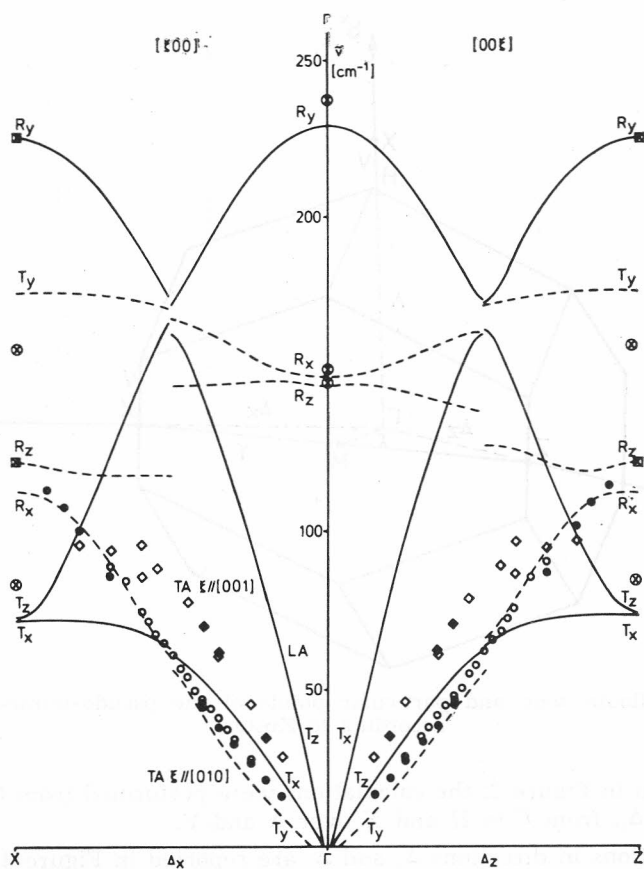


Figure 3. Dispersion relations in directions  $\Delta_x$  and  $\Delta_z$ . Full and dashed lines represent planar and non-planar modes, respectively. Circle and rhombus represent transverse modes polarized parallel to b and c, respectively. Full symbols indicate deuterated samples. IR and Raman bands are given at  $\Gamma$  and X (Z) points. At X (Z) point only the bands present in the ordered low-temperature phase are indicated.

### Amplitude of Vibrations — Hexachloroethane<sup>30</sup>

Hexasubstituted ethanes build a class of molecules with a nearly spherical external appearance so that most of them exist in at least one orientationally disordered phase (plastic crystal) below the melting point. A study of hexachloroethane was performed in order to try to understand the mechanism of the onset of disorder.

Cruickshank developed a model of thermal motions for rigid molecules supposing no coupling of translations and rotations.<sup>68</sup> Following this model the mean square amplitude of libration is given by

$$\langle \varphi^2 \rangle = (h/8 \pi^2 I \nu) \coth (h\nu/2 kT)$$

where  $I$  is the moment of inertia and  $\nu$  the frequency. If the unit cell contains more than one molecule, more than one libration exists for each inertial

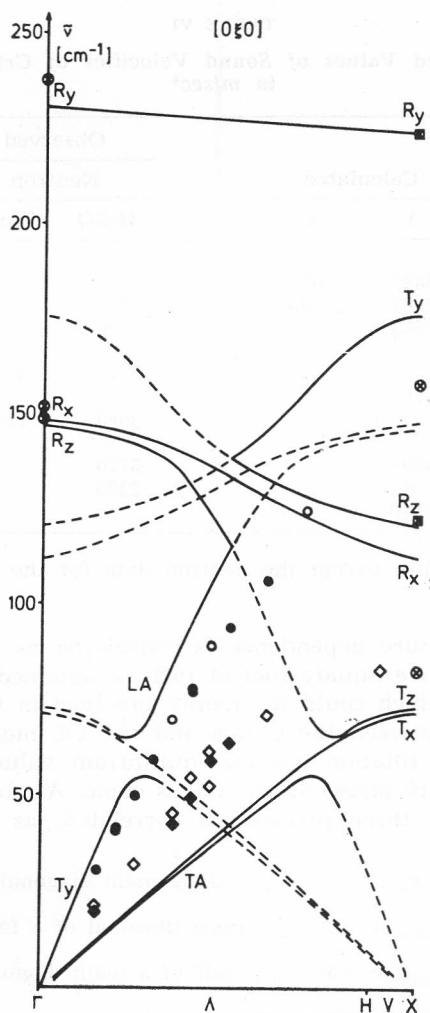


Figure 4. Dispersion relations in direction  $\Lambda$ . Circle and rhombus represent LA and TA modes, respectively. The zone-folded curves are indicated by dashed lines.

axis according to the symmetry and the mean value of the corresponding frequencies is used. At room temperature, crystalline hexachloroethane is orthorhombic,  $Pnma$  ( $D_{2h}^{16}$ ), with four molecules in the unit cell on sites  $m$  ( $C_s$ )<sup>69</sup> (Figure 5). The lattice-dynamical study already cited, using the potential of Bates and Busing<sup>30,42</sup>, leads to the results given in Table VII for the Raman spectrum. The amplitudes of libration were estimated by using the method of Cruickshank and assuming that the rotations are uncoupled, which is approximately true for  $B_{1g}$  and  $B_{3g}$ , but could be more problematic for  $A_g$  and  $B_{2g}$ . The experimental frequencies at 294 and 140 K were used to calculate the values given in Table VIII. Under consideration of the rather drastic simplifications introduced the agreement is good. The high amplitude of the  $R_y$  motion is interesting; particularly if the lowest  $R_y$  mode ( $A_g$  21  $\text{cm}^{-1}$ ) showing

TABLE VI

Calculated and Observed Values of Sound Velocities of Crystalline Squaric Acid in m/sec\*

Direction, mode	Calculated		Observed		Ultrasonics <sup>86</sup> H <sub>2</sub> SQ
			Neutron		
	$\Delta_z$	$\Delta_x$	H <sub>2</sub> SQ	D <sub>2</sub> SQ	
$\Lambda$ (100)					
LA	6835	6710			5755
TA out-of-plane	2008	2005	2125	2010	2010
TA in-plane	2583	2650	3190	3250	3375
$\Lambda$ (010)					
LA	3822		3245	3220	3060
TA	1411( $T_x$ )				
TA	1337( $T_z$ )		2080	1955	
$\Sigma$ (101)					
LA	6899		5770		5040
TA out-of-plane	2084		2370		2010
TA in-plane	3640				4400

\* All at room temperature except the neutron data for the  $\Sigma$  direction which are taken at 91 °C.

the strongest temperature dependence is considered as a single vibration, a value of 263 degrees<sup>2</sup>, *i. e.* square root of 16.2°, is obtained for  $\langle \varphi^2 \rangle$ . This value hints at the motion which could be mainly involved in the inset of disorder. Angle  $\theta$  (Figure 5) between the *c* axis and the CC molecular bond (*z* axis) modulated by the  $R_y$  rotation has an equilibrium value of 12.5° at 300 K. In the high temperature phase the crystal is cubic. A monoclinic intermediate phase also exists; all three phases are correlated, as shown by Gerlach<sup>70</sup> (Figure 6):

$$a_{\text{ortho}} = c_{\text{mono}} = \sqrt{3} a_{\text{cubic}} \text{ along main diagonal (111)}$$

$$b_{\text{ortho}} = b_{\text{mono}} = \sqrt{2} a_{\text{cubic}} \text{ along diagonal of a face (110)}$$

$$b_{\text{ortho}} = a_{\text{mono}} = \sqrt{3/2} a_{\text{cubic}} \text{ half of a main diagonal (111)}$$

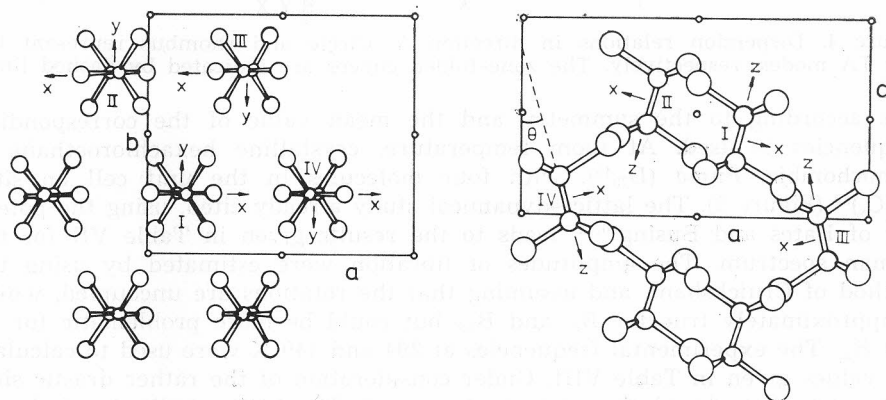


Figure 5. Unit cell of hexachloroethane at 294 K.<sup>69</sup>  $\theta = 12.5^\circ$ .



TABLE VII

*Frequencies and Eigenvectors of Crystalline Hexachloroethane With the Bates-Busing Potential<sup>42</sup> at 300 K<sup>a</sup>*

	Frequency		Eigenvector					
	Observed	Calculated	$T_x$	$T_y$	$T_z$	$R_x$	$R_y$	$R_z$
$A_g$	21.0	19.9	0.15	0.0	-0.69	0.0	0.71	0.0
	28.5	31.9	-0.84	0.0	-0.47	0.0	-0.28	0.0
	34.0	38.5	-0.53	0.0	0.55	0.0	0.65	0.0
$B_{1g}$	29.5	25.7	0.0	0.05	0.0	-0.99	0.0	0.03
	—	56.7	0.0	0.15	0.0	0.04	0.0	0.99
	—	58.9	0.0	0.94	0.0	0.05	0.0	0.15
$B_{2g}$	—	27.8	0.20	0.0	-0.96	0.0	0.22	0.0
	37.0	39.4	0.51	0.0	0.29	0.0	0.81	0.0
	55.0	50.5	-0.84	0.0	-0.05	0.0	0.54	0.0
$B_{3g}$	30.0	27.9	0.0	0.63	0.0	-0.25	0.0	0.73
	46.0	43.5	0.0	0.34	0.0	0.94	0.0	0.03
	—	49.8	0.0	-0.70	0.0	0.23	0.0	0.68

<sup>a</sup> Axes are defined in Figure 5.

As the molecule reaches the value of  $12.5^\circ$  according to  $R_y$ , it becomes obviously parallel to the main diagonal of the cubic cell. Thus, for direction  $y$  the disorder can already exist in the monoclinic intermediate phase. The second transition from the monoclinic to the cubic structure corresponds to the appearance of disorder for the two remaining rotational degrees of freedom. Cheam and Krimm<sup>71</sup> also successfully used the same formalism in the study of diketopiperazine, a crystal in which the rotations and translations are separated by symmetry and where the internal modes do not couple with the external ones. On the contrary, in the already discussed case of biphenyl where such couplings occur, Bonadeo and Burgos<sup>72</sup> had to extend the calculation method in order to include the lowest internal mode. It turns out that the high amplitude of libration around the long molecular axis can be reproduced without assuming a double-well potential.

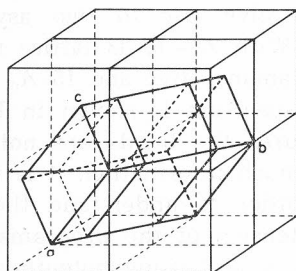


Figure 6. Comparison of the cubic disordered and orthorhombic ordered cells of hexachloroethane.

### Phase Transitions With Soft Mode — Malononitrile<sup>73</sup>

Malononitrile,  $\text{CH}_2(\text{CN})_2$ , shows the rare existence of reentrant phase transitions in the solid state.<sup>74</sup> The room temperature monoclinic  $\gamma$  phase unit cell transforms to a triclinic one between 295 and 141 K. It becomes monoclinic again, with parameters similar to those of the  $\gamma$  phase for lower temperature. Both phase transitions are accompanied by a soft mode.<sup>75</sup> One of the aims of this calculation was to obtain a quantitative description of these modes. As it can be expected of such a small molecule, the effects discussed in the preceding sections have to be considered. The dipole, as well as the quadrupole, moment act very strongly on some normal modes and the atom-atom potential of the nitrogen atoms had to be modified by comparison with the literature; neither the potentials cited by Pertsin<sup>11</sup> nor our potential discussed in the preceding chapter<sup>62</sup> were able to reproduce the spectra. Particularly, the  $\text{N}\cdots\text{H}$  interaction led to instable modes with imaginary frequencies. After fitting the parameters, the soft mode observed between 0 and  $15\text{ cm}^{-1}$  was calculated at the lowest frequency, but much too high between 35 and  $43\text{ cm}^{-1}$  depending on the calculation model and on the phase considered. This fact can be due to the high anharmonicity which is expected from this type of motion. The eigenvector was calculated as a combination of a translation ( $38^\circ/\theta$ ) parallel to  $z$  and a libration ( $36^\circ/\theta$ ) around  $y$  ( $z$  and  $y$  correspond roughly to the  $a$  and  $b$  crystal axes, respectively) with some further smaller participations. These values correlate nicely with the crystallographic results which show a rotation of  $3.5^\circ$  around  $b$  and a translation of 0.6 pm along  $a$  at the transition.<sup>76</sup> This example shows that although the frequencies are not reproduced very accurately, the general form of the mode is comparable with the results of crystallography. A similar result could be obtained for the mode softening at the phase transition of parachlorobenzamide.

### Interpretation of the Spectra of Crystals with Complicated Structure — Parachlorobenzamide<sup>51</sup>

Apart from its interesting phase transitions,  $p$ -chlorobenzamide is also a good example of a crystal for which a calculation is necessary in order to ascertain the spectral assignment. At room temperature, the triclinic unit cell contains six molecules consisting of three crystallographically non equivalent pairs. The A molecules build one centrosymmetric dimer (Figure 7) while B and C molecules give rise to two asymmetric dimers through  $\text{NH}\cdots\text{O}$  hydrogen bonds.<sup>77</sup> With  $Z = 6$ , 33 lattice modes are expected. They can be classified as 18  $A_g$  Raman active and 15  $A_u$  infrared active vibrations. The corresponding Raman spectrum is shown in Figure 8. Obviously, even at relatively low temperatures the bands are not well resolved and since deuteration does not give much information, it is necessary to try a lattice-dynamical calculation in order to understand the spectra. The simulation was performed with an extension of the programs of Ref. 16 for non-equivalent molecules by Burgos *et al.*<sup>78</sup> using potentials without any fitting process.<sup>37,42,48,62</sup> The results are indicated as bar spectrum at the bottom of Figure 8. The main features of the spectrum are reproduced and the eigen-

vector of one mode showing a strong softening by temperature increase is calculated as expected from crystallographic data.

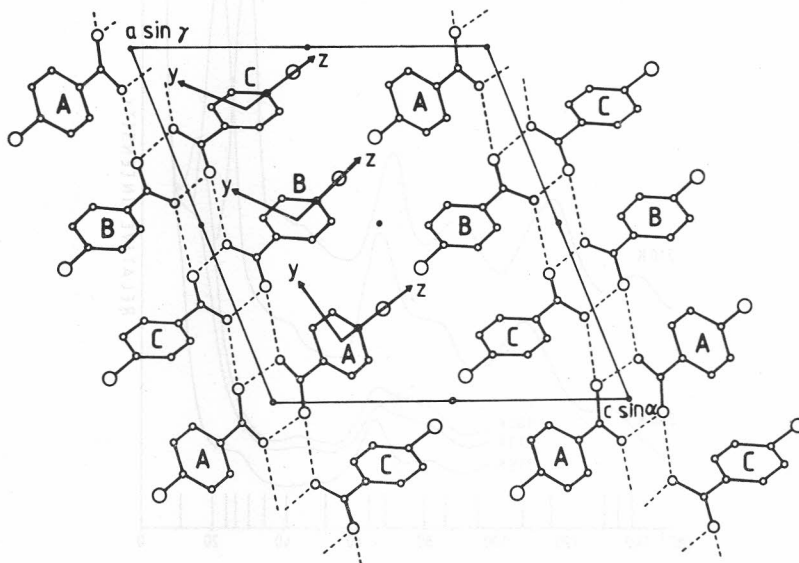


Figure 7. Unit cell of *parachlorobenzamide*.<sup>77</sup>  $x$ ,  $y$  and  $z$  are the molecular axes of inertia.

Similar studies were performed for 1,3,5-trioxane<sup>79</sup>, cyclopropane<sup>80</sup>,  $\alpha$ -glycine<sup>81</sup>, chloranil<sup>82</sup>, l-cocaine hydrochloride<sup>83</sup>, stearic acid<sup>84</sup>, and furane<sup>85</sup>. Except for cyclopropane and trioxane, the crystals treated were complicated or symmetry data as help for the assignment were not available;<sup>85</sup> the calculation could be used as a means to determine the assignment of the bands observed.

TABLE VIII

*Square Root of the Mean Square Amplitude  $\langle q^2 \rangle$  of Crystalline Hexachloroethane in Degrees*

		Raman	Crystallography <sup>69</sup>
294 K	$R_x$	5.1	5.0
	$R_y$	7.1	4.7
	$R_z$	3.7 <sup>a</sup>	5.5
140 K	$R_x$	3.0	2.8
	$R_y$	3.9	2.6
	$R_z$	2.1 <sup>a</sup>	3.3

<sup>a</sup> For non observed librations the calculated frequencies were used.

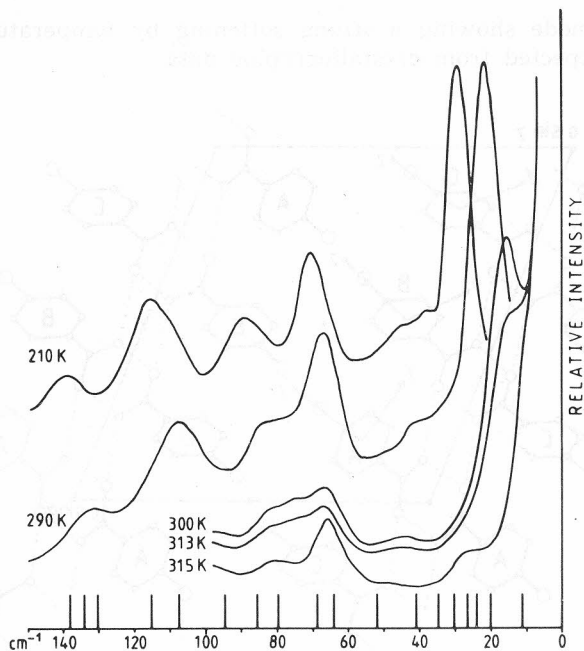


Figure 8. Observed and calculated (bars at the bottom) Raman spectra of *p*-chlorobenzamide. Note the softening from 30 to 10  $\text{cm}^{-1}$  of the lowest mode.

#### CONCLUSION

The examples presented here show that after twenty years of development the use of the lattice modes and of computer simulation that study the dynamics on the one side and the intermolecular forces on the other side yield very valuable informations. For small molecules or symmetric crystals very elaborate methods enable a fine analysis of the forces and a quantitative description of the dynamics. Larger crystals cannot be treated so precisely but the results can be used in order to improve the spectral analysis (assignment) or to follow the mechanism of phase transitions. As the determined potentials seem to be transferable to molecules with similar chemical properties, they could be useful for other domains where there is a similar need for potentials, *i. e.* molecular dynamics and mechanics.

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**SAŽETAK****Dinamika rešetke i intermolekulske sile u organskim molekulskim kristalima***D. Bougeard*

Razmatra se najnoviji razvoj teorije i primjene određivanja intermolekulskih sila u organskim kristalima numeričkom simulacijom. Prikazani su različiti potencijali atom-atom za ugljik, vodik, halogene, kisik i dušik. Utjecaji vodikovih veza i multipolnih sila ilustrirani su primjerima. Takvi potencijali primjenjeni su na glutarnu i kvadratnu kiselinu, heksakloretnan, malononitril i para-klorbenzamid.