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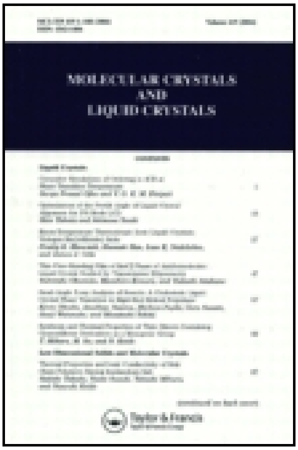

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Infra-Red Intensities of the Lattice Modes of Molecular Crystals

M. Sanquer [a] & O. Contrras [a]
[a] Département de Physique, Cristalline et Chimie Structurale, E.R.A. au C.N.R.S. No. 015, Universite de Rennes, avenue du Général Leclerc, 35031, Rennes-Cedex, (France)

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Infra-Red Intensities of the Lattice Modes of Molecular Crystals

M. SANQUER and O. CONTRERAS

Département de Physique Cristalline et Chimie Structurale, E.R.A. au C.N.R.S. No. 015, Universite de Rennes, avenue du Général Leclerc, 35031 Rennes-Cedex (France)

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Starting from calculated eigenvectors and the known electrical properties of molecules a quantitative evaluation of the intensities of lattice modes in molecular crystals is carried out. Results of the calculations are compared with experimental data for benzene, durene, naphtalene.

INTRODUCTION

A few years ago the long wavelength infra-red spectra of molecular crystals became available.[1–3] Absorption bands with wave numbers less than 100 cm^{-1} were attributed to translational motion of molecules as a whole in the lattice and so were named lattice modes.

The intensity of a band is defined as $\int k(\nu)\,\mathrm{d}\nu$ Mulliken[4] where ν is the frequency in cm^{-1} and $k(\nu)$ is the absorption coefficient. The integration is to be carried out over all the absorption range and this causes serious difficulties, especially in the case of overlapping bands. Experiments should be carried out if possible on monocrystalline samples where the separation of the various species is possible when working with polarised light. No experimental quantitative value for crystals of large molecules was available in the literature until Sataty[5] measured the intensity of I. R. lattice modes of polycrystalline benzene.

Thereafter we shall consider the molecule as rigid as this has very little effect on the lattice modes.[6]

Group theory predicts the number and the polarisation of lattice modes but gives no information on the intensities and it is known from experiment that

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these intensities are quite different one from another and they are sometimes not observed due to special conditions.

Schnepp[7] has given a theory of intensities of lattice modes in molecular crystals. His work is however limited to the study of simple molecular crystals (N_2, CO_2). Hadni[1] and Luty[8] discuss only the polarisation of the Bu mode in a monoclinic crystal. Moreover the above cited authors use models which seem to us not realistic for crystals made of large molecules. As a typical molecule, benzene has a diameter of about 5 Å and in the crystal some atoms on different molecules may be at a distance of less than 2.5 Å. It is easy to predict that the induced field will be quite different at the center of the molecule and at external points. In view of the notable success of atom–atom interaction description of molecular crystals we think that a more detailed model should be useful in the study of the infra-red intensities.

THE MODEL AND METHOD OF CALCULATION

The intensity arises from the interaction of the molecules so that an oriented gas model has no value as it predicts zero intensities. Moreover, eigenvectors associated with the frequencies are needed but these are now easily obtained even for complex molecular crystals based on the atom–atom interaction approximation.[9] The calculated eigenvectors are obtained from calculations with a precision better than the calculated frequencies as the former are quite independent of the particular values choosen for interaction coefficients.[9]

The simplest model describing the electrical properties of a molecule is that of an assembly of bonds. To each bond is associated a dipole and three values characterising the polarisability of the bond; numerical values are available in the literature.[10,11] These values have been determinated from physical properties which have no relation to the present problem; moreover they are characteristic of the bond rather than of the molecule and so our method will be useful for most molecular crystals. There remains however an uncertainty about the exact location of the polarisable units; we choose to locate them at the mid point of the bonds for definiteness.

In the electrical harmonic approximation one has to evaluate $(\partial\mu/\partial Q)^2$ Schnepp.[7] μ is the induced dipole moment in the whole crystal; Q denotes the normal coordinate corresponding to a given frequency.

Thus we calculate the dipole M induced on a polarisable bond by the motion of all dipoles on surrounding molecules; there are three contributions.

I) Dipole arising from the rotation of the polarisable unit in a constant field

II) Induced field due to the rotation of dipoles

III) Induced field due to the variation of distances between the dipoles and the polarisable unit.

TABLE I

Electrical properties of bonds in molecules

Bond	P Debye[a]	αL[b]	αT	αV (10^{-23} cm^3)
C_{ar}—C_{ar}	0.0	0.224	0.021	0.059
C—C	0.0	0.099	0.027	0.027
C—H	0.42	0.064	0.064	0.064

αL = polarisability along the bond
αT = perpendicular to the bond in the plane of the molecule
αV = perpendicular to the bond and the molecular plane.
[a] From Gribov.[11]
[b] From Lefevre.[10]

Only the last term has to be evaluated in centrosymmetric crystals.

The field induced by dipole P at distance R is

$$E = P \cdot \nabla^2(I/R) \tag{1}$$

where ∇ is the usual gradient operator. Thus,

$$\frac{\partial E}{\partial Q} = P \cdot \nabla^3(1/R) \cdot \frac{\partial R}{\partial Q} \tag{2}$$

and

$$\left(\frac{\partial M}{\partial Q}\right) = \alpha \cdot \left(\frac{\partial E}{\partial Q}\right) \tag{3}$$

where α is the polarisability tensor of the bond referred to crystal-fixed axis.

The dipoles induced on each bond are summed to give the dipole induced in the molecule. The dipole induced in the crystal is then the sum of the dipoles induced in all molecules of the crystal. Group theory imposes that these dipoles are to be the same for translationally equivalent molecules and differ only by a phase factor for molecules related by a symmetry operation which is not a simple translation. The induced dipole is then projected on the observation axis, Luty.[8] As an exact knowledge of the eigenvectors is necessary, the present calculations were added to a general Fortran IV programm claculating the frequencies and eigenvectors (available on request from the first author). Let us consider now some specific examples.

Benzene

Benzene is orthorhombic Pbca, D_{2h}^{15} with four molecules in the unit cell so that there are six I. R. active frequencies, two polarised along each cristallographic axis. The intensities of these bands were measured recently by Sataty[5] using a polycrystalline sample.

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TABLE II

Calculated intensity for benzene I.R. active lattice bands. All values have been given relative to the highest B_{1u} mode to facilitate comparison with experimental data.

	ν_{cal} (Ref. 9)	ν_{exp} (Ref. 5)	I_{cal}	I_{exp} (Ref. 5)
B_{1u}	71	77	0.90	0.15
$E \parallel a$	87	93	1.(29 D.)	1.(20 D.)
B_{2u}	56	60	0.03	0.23
$E \parallel b$	103	108	0.37	0.90
B_{3u}	54	72,5	0.08	0.08
$E \parallel c$	100	105	1.62	1.60

The results of the intensity calculations are given in Table II together with Sataty's experimental frequencies

The absolute value calculated for the B_{1u} highest mode is 29 Darks, very nearly the experimental value (20 Darks).

The calculated intensities do not fit very well with the experimental values given by Sataty. Our calculated values apparently are in better agreement with the spectra published by Wyncke[12] which were recorded using monocrystalline samples. The lack of good quantitative data prevent us to try any fitting of the model. The calculated values given in Table II have been obtained using 20°K extrapolated crystallographic parameters.[9] Use of 270°K parameters led to a strong decrease of the intensities—the lowest frequency bands being much more affected—no experimental data are available to confirm the validity at this quasi harmonic model.

Durene

Durene is monoclinic $P2_1/a$, C_{2h}^5 with two molecules in the unit cell. The lack of quantitative data led us to record again the far I. R. spectrum of a monocrystalline sample of durene.

This crystal was chosen because

a) The intensities of the three expected bands are quite low and of comparable value.[1]

b) The dynamical properties of zero wave vector phonons have been extensively studied in the literature.[6]

The spectra were recorded on a Beckman I. R. spectrometer RIIC F100, *ab* platelets were studied with the electric vector successively along *a* and along *b* as these directions are also the axes of the indicatrix. Relatively large thicknesses were used (0.92, 1.42, 2.50 mm) and the result obtained (in Table III) are precise to only 20%. We think however that the relative values are much

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TABLE III

Calculated intensities for durene crystal using two electrical molecular models a and b (see the text).

	ν_{cal} cm^{-1} (Ref. 6)	ν_{exp} cm^{-1} (Ref. 1)	I^{a}_{cal}	I^{b}_{cal}	I^{Darks}_{exp}
A_u	34	37	0.57	0.58	0.40
$E /\!/ b$	58	68	1.34	2.0	0.80
B_u	67	65	1.36	3.7	1.30
$E \perp b$					

more precise, in particular the order of relative intensity is well established. Two models were used for evaluating I. R. intensities

a) A simple model using the value of Table I for dipoles and polarisabilities of the benzene ring. The C—H bonds of the methyl groups were allowed to have a dipole moment of 0.3 D, Gribov[11] and polarisabilities of the benzenic hydrogen.[10]

b) A more complex model allowing for anisotropy of the polarisability of C—H bonds (0.085, 0.045, 0.045 × 10^{-23} cm^3 Amos[13]) and a small dipole on C—C_{ar} bond (0.15 D).

Results quoted in Table III show that the model *b* gives a more valuable description of the relative intensities.

The number of unknowns is too great to permit any definitive conclusion about the electrical properties of the bonds. The study provides clues such as that the values given by Amos for the anisotropies of C—H bonds are apparently too large. C—C_{ar} is slightly polar with positive charges on the methyl carbon. It is shown that the I. R. intensities of lattice bands can be accounted for by what we know about the electrical properties of bonds.

Naphtalene

Naphtalene is also monoclinic $P2_1/a$ with two molecules in the unit cell. The I. R. intensities were calculated using dipole and polarisabilities of Table I. Results of the calculations are given in Table IV. No quantitative measure-

TABLE IV

Calculated I.R. lattice mode intensities for naphtalene crystal

	ν_{cal} cm^{-1} (Ref. 14)	ν_{exp} cm^{-1} (Ref. 3)	I_{cal}(Darks)
A_u	60	55	2
$E \parallel b$	95	98	23
B_u	74	75	36
$E \perp b$			

ment is available in the literature. Calculation shows however that the A_u band at 55 cm^{-1} is relatively very weak and this explains why it has been observed by some authors[2,3] and not by others[1]

CONCLUSION

We have shown that I. R. intensities of lattice modes can be related to intrinsic properties of molecules. The results obtained can be used to make band attributions in spectra of polycrystalline samples with the same cautions as frequency calculations.

Conclusions about the electrical properties of bonds should perhaps be deduced from careful experiments on monocrystalline samples, but a first result of this work is that the electrical distortion of the molecules need not necessarily be invoked in the course of the translational motion. It has already been shown that the mechanical distortion is also negligible even in such deformable molecules as durene.[6] The general method described here shall be applied to the calculation of relative Raman lattice mode intensities in cases where the oriented gas model approximation fails (halogenobenzenes).

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