(b) Centrosymmetric crystal

Making use of ($B2$) and ($B3$) in (28) and then using the substitution that $y_P^{c^2}=2x$ we obtain for the two-atom case

$$\langle y_N y_P^c\rangle=\frac{2\sigma_2}{\pi^{3/2}}\int_0^1(1-x)^{-1/2}\ {}_1F_1\left(-\tfrac{1}{2};\tfrac{1}{2};\frac{-\sigma_1^2}{\sigma_2^2}x\right)\mathrm{d}x$$
$$=\frac{4\sigma_2}{\pi^{3/2}}\ {}_2F_2\left(-\tfrac{1}{2},1;\tfrac{1}{2},\tfrac{3}{2};\frac{-\sigma_1^2}{\sigma_2^2}\right) \qquad (B12)$$

where we have made use of equation (16) on page 47 of Sneddon (1961). Putting $n=\frac{1}{2}$ in equation ($A13$) of Parthasarathy & Srinivasan (1967) we obtain for the many-atom case that

$$\langle y_N y_P^c\rangle=\frac{2}{\pi}\ {}_2F_1\left(-\tfrac{1}{2},-\tfrac{1}{2};\tfrac{1}{2};\sigma_1^2\right). \qquad (B13)$$

Making use of equation (7.4) on page 24, equations 4(ii) on page 44 and 1(vii) on page 42 of Sneddon (1961) we can simplify ($B13$) as

$$\langle y_N y_P^c\rangle=\frac{2}{\pi}\left[\sigma_2+\sigma_1\sin^{-1}(\sigma_1)\right]. \qquad (B14)$$

In obtaining ($B14$) we have also made use of the result that

$$\tan^{-1}(x)=\sin^{-1}\left(\frac{x}{\sqrt{(1-x^2)}}\right).$$

References

Booth, A. D. (1945). *Phil. Mag.* **36**, 609.
Buerger, M. J. (1967). *Crystal Structure Analysis*, p. 589. New York: John Wiley.
Foster, F. & Hargreaves, A. (1963*a*). *Acta Cryst.* **16**, 1124.
Foster, F. & Hargreaves, A. (1963*b*). *Acta Cryst.* **16**, 1133.
Luzzati, V. (1952). *Acta Cryst.* **5**, 802.
Parthasarathy, S. (1966). *Z. Kristallogr.* **123**, 27.
Parthasarathy, S. & Srinivasan, R. (1967). *India J. Pure Appl. Phys.* **5**, 502.
Slater, L. J. (1960). *Confluent Hypergeometric Functions.* Cambridge Univ. Press.
Sneddon, I. N. (1961). *Special Functions of Mathematical Physics and Chemistry*. London: Oliver & Boyd.
Srikrishnan, T. & Srinivasan, R. (1968). *Z. Kristallogr.* **127**, 427.
Wilson, A. J. C. (1949). *Acta Cryst.* **2**, 318.
Wilson, A. J. C. (1969). *Acta Cryst.* **B25**, 1288.

Acta Cryst. (1972). A**28**, 432

The Molecular Packing of Solid II Cyclobutane by Means of Spectroscopic Data and Potential Energy Calculations

By E. Castellucci, M. G. Migliorini and P. Manzelli

Istituto di Chimica Fisica, Università di Firenze, Via G. Capponi 9, 50121-*Firenze, Italy*

(*Received* 6 *March* 1972)

The molecular packing of solid II cyclobutane has been calculated starting from the knowledge of the site symmetry (point group D_2) and of two possible symmetries of the primitive unit cell (D_2 and D_{2h} factor group symmetry), derived from analysis of the infrared and Raman spectra. Crystal potential energy has been calculated for 13 orthorhombic space groups using the packing program written by Williams. The calculation was based on a pairwise potential of Buckingam type, widely tested on a large number of hydrocarbon crystal structures and properties. The energy was calculated as a function of the unit cell parameters (length of the cell edges), considering the molecules as rigid bodies and leaving the crystal symmetry unchanged. The results show the packing corresponding to space group *Ccca* to have the lowest calculated potential energy. The spectroscopic results allowed some changes to be made in the previous assignment of the fundamental frequencies of cyclobutane and cyclobutane-d_8.

Introduction

Several low temperature infrared and Raman studies on molecular crystals have been carried out in recent years with the aim of determining the crystal structure when X-ray data were not available. In order to restrict the choice of the possible structures compatible with the spectral data, simple closest-packing arguments and, when available, the comparison between calculated and observed density, have often been used.

A different approach to this problem concerns the calculation of the structure using the structural information obtained from the analysis of the crystal spectra. At any given temperature and pressure the most stable structure is governed by the arrangement of molecules that has the lowest free energy. Assuming the zero point lattice energy to be comparable for a number of possible close-packed structures, one can reasonably assume that the most probable structure is the one with the lowest calculated lattice energy.

Cyclobutane offers an attractive possibility for this kind of investigation since: (i) the molecular geometry has been widely investigated; (ii) the molecule possesses only C and H atoms; (iii) infrared spectra in polarized light of oriented crystals have been obtained, which are of help in deriving structural information. Point (ii) is very important for calculating the minimum energy crystal structure since different sets of semi-empirical atom–atom potential parameters exist in the literature which have been widely tested on a number of experimental crystal properties and structures of aromatic and aliphatic hydrocarbons (Williams, 1967). It is widely accepted that cyclobutane has a puckered equilibrium configuration with D_{2d} symmetry and a dihedral angle of about 32°. The evidence for this has been given by electron diffraction experiments (Almenningen, Bastiansen & Skancke, 1961), by an unpublished vibrational analysis of Lord and Rea quoted by Lord & Nakagawa (L & N) (1963), by relative intensity measurements of CH_2 rocking vibrations (Dows & Rich, 1967) and by high resolution n.m.r. spectra in a nematic solvent (Meiboom & Snyder, 1970). Recently Ueda & Shimanouchi (U & S) (1968) reproduced by calculation the frequency values and intensity of the sidebands on the low wavenumber side of the 2878 cm^{-1} fundamental in the cyclobutane gas infrared spectrum. They assigned these bands in terms of a puckering structure and calculated the inversion barrier, the energy levels of the puckering potential and the dihedral angle. Some extended observations of puckering structures were very recently reported by Stone & Mills (S & M) (1970), and by Miller & Capwell (M & C) (1971), who were also able to measure some pure puckering transitions in the low frequency gas phase Raman spectrum. These authors extended this study to fully deuterated cyclobutane. Barrier height and dihedral angle calculated by these authors agree very well with those deduced by U & S.

Solid cyclobutane is known (Rathjens & Gwinn, 1953) to exist in two crystal forms, one stable between 182 and 145°K (solid I) and the other one stable below 145°K (solid II). An X-ray investigation (Carter & Templeton, 1953), the heat of fusion, the large heat of transition, and the poor thermal conductivity of solid I are consistent with dynamical rotational disorder in the high temperature form, whereas powder patterns of solid II show this to have an ordered structure.

The present paper reports on the infrared spectrum in polarized light of the lower temperature crystal form of cyclobutane. The fully deuterated sample has also been studied in a polycrystalline form. By use of the mixed-crystal technique the nature of the crystal splittings has been established. Far infrared as well as Raman spectra of solid II of both isotopic species have also been recorded and analysed.

Some changes have been made in the assignment of L & N for C_4H_8 and C_4D_8 fundamentals. A new assignment has been proposed based on criteria which will be given below.

Site and factor group analysis has been applied to the study of the spectra of the crystal and the results used in the calculation of the crystal energy of a number of structures.

Experimental

Normal cyclobutane was prepared in good yield *via* a Wurtz ring closure reaction (Connor & Wilson, 1967). Some lighter impurities were detected by gas chromatography. These gave rise to some infrared absorptions which completely disappear after purification by gas chromatography. Cyclobutane-d_8 from Mallinckrodt Co. (U.S.A.) containing more than 95% deuterium was used without further purification. Mixed samples of 1:40 C_4H_8:C_4D_8 and C_4D_8:C_4H_8 used in the isotopic dilution experiments were prepared by mixing the vapors in a 1:40 molar ratio.

Infrared spectra between 4000 and 250 cm^{-1} were measured on a Perkin–Elmer Model 225 grating spectrometer. The Perkin–Elmer grid polarizer unit was used for polarization measurements. A conventional low-temperature cell, equipped with external caesium iodide windows was used. Samples to be studied were sprayed directly onto a CsI support cooled at liquid nitrogen temperature. The polycrystalline films were repeatedly annealed at temperatures not higher than −140°C, (to avoid sublimation). No changes in the spectra were observed after annealing.

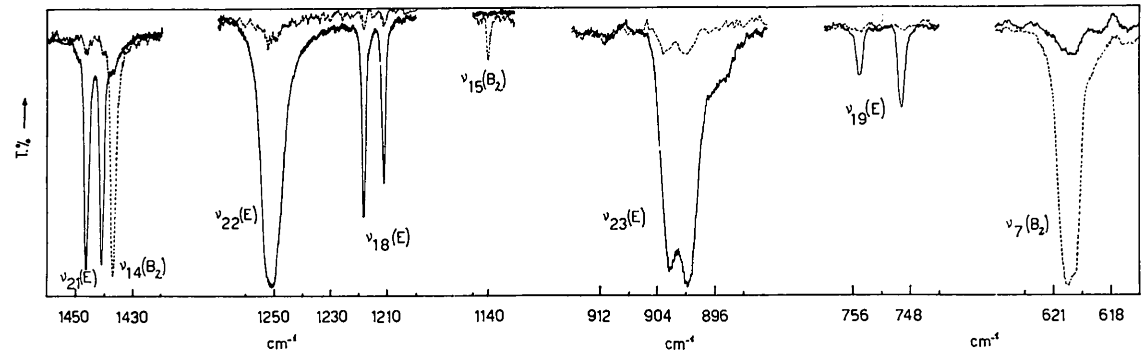


Fig. 1. Infrared spectrum in polarized light of an oriented film of solid II C_4H_8. Full line and dotted line spectra refer to a relative sample–polarizer orientation corresponding to the minimum (β polarization) and maximum (α polarization) intensity of the 1437 cm^{-1} band respectively. The modes are labelled according to the symmetry of the free molecule (D_{2d} symmetry).

Oriented polycrystalline films of C_4H_8 were obtained by slow cooling of the liquid film between two KBr windows with 50μ lead spacers under a suitable temperature gradient. Owing to the high volatility of cyclobutane (b. p. 12°C under atmospheric pressure) the liquid film was prepared maintaining sample and windows at about -40°C in a dry box.

The infrared spectra from 40 to 250 cm^{-1} were obtained on a Perkin–Elmer Model 301 and on a Hitachi FIS-30 far-infrared spectrometer. The cryostat employed in this spectral region was equipped with polyethylene or silicon windows. A large amount of cyclobutane was sprayed onto the internal window to obtain appreciable intensity of the bands.

Raman spectra were recorded with a Cary 81 instrument equipped with an argon ion laser source, using the 4880 Å line for excitation. A low temperature sample cell of very high scattered energy yields for 90°

Table 1. *Vibrational spectrum of* C_4H_8

Frequencies in cm^{-1}; α, β polarization of the infrared bands (see text); *vs*, very strong; *s*, strong; *m*, medium; *w*, weak; *vw*, very weak; *sh*, shoulder; *br*, broad.

Mode*		Assignment	L & N†	Raman (liq.)	Pol.	Raman (cryst.)	I.R. (cryst.)	Pol.	Solid sol. (1:40 in C_4D_8)
		Lattice vibrations				84*w* 96*w* 103*wbr*	81·4*w* 94·6*w*		
ν_1	A_1 A_{1g}	CH sym. str.	2895	2924*vs*	P	2922*s*			
ν_2	A_1 A_{1g}	CH_2 deformation	1443	1470*wbr*		1469*m*			
ν_3	A_1 A_{1g}	Ring breathing	1001	1005*vs*	P	1006*vs*			
		–^{13}C				996*w*			
ν_4	B_1 A_{1u}	CH_2 twisting	[1220]			1233*vw*			
ν_5	A_2 A_{2g}	CH_2 wagging	[1260]			1258*vw*			
ν_6	B_2 A_{2u}	CH antisym. str.	2987	2975*sh*		2975*w*	2973*s*	α	2975*s*
ν_7	B_2 A_{2u}	CH_2 rocking	627			626*vw*	624*vs*	α	626*s*
		–^{13}C					623*sh*		623·5*w*
ν_8	B_1 B_{1g}	CH_2 wagging	1219	1220*wbr*		1220*s*			
ν_9	B_1 B_{1g}	Ring deformation	926	927*m*	dp	929*vs*			
		–^{13}C				918*vw*			
ν_{10}	A_1 B_{1u}	CH antisym. str.	{2975}	2937*w*	P	2932*m*			
ν_{11}	A_1 B_{1u}	CH_2 rocking	741						
ν_{12}	A_1 B_{1u}	Ring puckering	200	200*wbr*		249*w* 220*vw*			
ν_{13}	B_2 B_{2g}	CH sym. str.	{2890}	2890*w*		2890*w*	2898*w*	α	2899*w*
ν_{14}	B_2 B_{2g}	CH_2 deformation	1443	1439*wbr*		1442*sh*	1437*s*	α	1440·5*s*
ν_{15}	B_2 B_{2g}	Ring deformation	1001			1140*m*	1139·5*w*	α	
ν_{16}	A_2 B_{2u}	CH_2 twisting	[1225]			1228*vw*			
ν_{17}	E E_g	CH antisym. str.	2952	2954*s*	dp	2960*s* 2950*s*	2962*w* 2958*w*	β β	2963*w* 2958*w*
ν_{18}	E E_g	CH_2 twisting	1223			1221? 1218*sh*	1218·5*m* 1211·5*m*	β β	1219*m* 1217·5*m*
ν_{19}	E E_g	CH_2 rocking	749			752*w* 746*w*	755*w* 749*w*	β β	754*vw* 751*w*
ν_{20}	E E_u	CH sym. str.	2890	2865*m*	dp	2861*s*	2865*vs* 2862*vs*	β β	2864*vs*
ν_{21}	E E_u	CH_2 deformation	1447	1443*w*		1445*m* 1443*w*	1446·2*s* 1441·0*s*	β β	1445·8*s* 1441·2*s*
ν_{22}	E E_u	CH_2 wagging	1257	1250*vw*		1252*vw*	1252·5*vs* 1251·2*vs*	β β	1254*vs* 1253*vs*
ν_{23}	E E_u	Ring deformation	898	900*sh*		907*w* 895*w*	902·2*vs* 899·8*vs*	β β	901·5*vs* 900·2*vs*

* The upper species refer to D_{2d} molecular point symmetry and the lower ones to D_{4h} symmetry.

† Lord & Nakagawa (1963).

observation was employed. The spectra were always recorded after annealing the sample.

Polarization measurements on liquid cyclobutane have been performed with the back-scattering arrangement of the Cary 81 laser instrument.

Results

The results of the infrared measurements as well as the Raman data are summarized in Tables 1 and 2 for C_4H_8 and C_4D_8 respectively. The polarized light infrared spectrum of C_4H_8 solid II is shown in Fig. 1 and refers to a relative sample–polarizer orientation corresponding to the minimum (β polarization) and maximum (α polarization) intensity of the 1437 cm^{-1} band. The Raman spectrum of liquid C_4H_8 in polarized light agrees with that reported by Rathjens, Freeman, Gwinn & Pitzer (1953). No previous spectra in polarized light of C_4D_8 exist for comparison.

Vibrational assignment

The vibrational assignment of cyclobutane was first proposed by Wilson (1943) on the basis of a planar

Table 2. *Vibrational spectrum of* C_4D_8

Several weak bands due to partially deuterated species have been ignored; frequencies in cm^{-1}; *vs*, *s*, *m*, *w*, *vw*, *sh*, and *br*: see Table 1.

Mode*		Assignment	L & N†	Raman (liq.)	Pol.	Raman (cryst.)	I.R. (cryst.)	Solid sol. (1:40 in C_4H_8)
		Lattice vibrations				55*wbr* 73*w* 84*w*	71·8*w* 82*w*	
ν_1	A_1 A_{1g}	CD sym. str.	{2120}	2170*s*	P	2168*s*		
ν_2	A_1 A_{1g}	CD_2 deformation	1160	1166*s*	P	1165*s*		
ν_3	A_1 A_{1g}	Ring breathing	882	884*vs*	P	884·5*vs*		
ν_4	B_1 A_{1u}	CD_2 twisting	[870]	905*vw*	dp	908*w*		
ν_5	A_2 A_{2g}	CD_2 wagging	[950]			1017*vw*		
ν_6	B_2 A_{2u}	CD antisym. str.	2242	2247*sh*		2247*sh*	2242·5*s*	2241*m*
ν_7	B_2 A_{2u}	CD_2 rocking	483				483·7*vs*	481·2*s*
ν_8	B_1 B_{1g}	CD_2 wagging	1078	1042*w*	dp	1040*w*		
ν_9	B_1 B_{1g}	Ring deformation	746	747*m*	dp	750·5*vs*		
ν_{10}	A_1 A_{1u}	CD antisym. str.	[2240]	2234*s*	P	2231*s*		
ν_{11}	A_1 A_{1u}	CD_2 rocking	[600]					
ν_{12}	A_1 B_{1u}	Ring puckering	?			199*w* 144*vw*		
ν_{13}	B_2 B_{2g}	CD sym. str.	{2120}	2143*m*	dp?	2140*m*		
ν_{14}	B_2 B_{2g}	CD_2 deformation	1040	1080*m*	dp	1075*m*	1071*s*	1076·5*s*
ν_{15}	B_2 B_{2g}	Ring deformation	{938}			925*w*		
ν_{16}	A_2 A_{2u}	CD_2 twisting	[920]			891*w*		
ν_{17}	E E_g	CD antisym. str.	2230	2223*sh*		2224*m*	2234*m*	2235*w* 2229*w*
ν_{18}	E E_g	CD_2 twisting	938	946*m*	dp	944*m* 941·8*m*		
ν_{19}	E E_g	CD_2 rocking	556	560*m*		559*w* 554*w*	561·5*w* 556*w*	558*vw* 556·3*vw*
ν_{20}	E E_g	CD sym. str.	{2120}	2120*wbr*		2118*w*	2120*m* 2117*m*	2120*m* 2117*m*
ν_{21}	E E_u	CD_2 deformation	1048	1050*sh*	dp	1052*w* 1048*w*	1049·5*s* 1048·8*s*	1048·2*m* 1047·5*m*
ν_{22}	E E_u	CD_2 wagging	1078	1030*sh*	dp	1035*sh*	1034*m*	1034·5*m* 1033·8*m*
ν_{23}	E E_u	Ring deformation	734	728*sh*	dp	724*m*	731·5*vs* 729·1*vs*	729·7*vs* 728·3*vs*

* † See footnotes of Table 1.

ring of D_{4h} symmetry. As a result of the discrepancy between the entropy measurements and the values calculated from spectroscopic data with the assumption of a planar carbon skeleton, it became necessary to consider the possibility of a non-planar ring, and to interpret the spectra in terms of D_{2d} symmetry (Rathjens and coworkers).

Successive reinterpretations of the spectra by L & N were based on a normal coordinate analysis using as a basis for the calculation the assignment made by Lord and Rea of bent cyclobutane. The authors recognized that the molecule is definitely non-planar, yet it approximates the D_{4h} structure.

We checked L & N's frequencies for correct species assignment using our polarization and solid solution infrared data. As a result some changes in the previous assignment have been introduced. Moreover, applying the isotopic shift rule, Raman polarization data of the liquid, and band intensity considerations, a nearly complete assignment of the vibrations of cyclobutane has been proposed.

We based our interpretation mainly on the spectra of solid cyclobutane. This procedure was justified by the following experimental features:

(1) the intensity pattern of the bands does not change much in going from the liquid to the solid;

(2) the shifts of the frequencies from the liquid to the crystal are only a few wavenumbers;

(3) the transitions that would be inactive for the free gaseous molecule are expected to appear weakly in the spectrum of the solid where the molecule has a lower symmetry.

Assuming a bent structure for the free molecule the vibrational modes are distributed among the irreducible representations of D_{2d} as follows:

$$6A_1+2A_2+3B_1+5B_2+7E\,.$$

Only the B_2 and E modes are allowed in the infrared. The E and B_2 modes are allowed also in the Raman, while the A_1 and B_1 modes are only Raman-active. A_2 modes are inactive both in the infrared and Raman.

The bands observed in the polarized light infrared spectrum of C_4H_8 can be grouped into two clearly distinct groups with opposite polarization character (see Fig. 1 and Table 1). The discussion of their assignment follows.

E modes

Bands with β polarization are split into two components, and belong therefore to the E species. The degeneracy is lifted by the crystal symmetry. The bands split also in the solid solution spectrum into two components. The agreement with L & N's assignment is complete apart from a small shift with respect to the liquid and gas.

No polarized light infrared spectrum of C_4D_8 has been obtained. Nevertheless, the solid solution spectrum permitted the re-assignment of the bands at 1034 and 1071 cm^{-1} to the proper symmetry species. The band at 1034 cm^{-1}, assigned by L & N to a CD_2 deformation of B_2 species, is single in the pure crystal spectrum but splits into two components in solution. On the other hand the 1071 cm^{-1} band, assigned by L & N to the E species is single in both spectra. We then reversed the assignment of ν_{14} and ν_{22}, taking for ν_{14} the band at 1071 cm^{-1} and for ν_{22} the band at 1034 cm^{-1}.

B_2 modes

The bands of C_4H_8 exhibiting α polarization belong to the B_2 species. These bands are single in the solid solution spectrum. We agree with L & N's assignment except for ν_{15}, which is a ring deformation, for which they choose the value of 1001 cm^{-1}. We have seen no band in our spectra around this frequency. A band of medium intensity whose polarization is of α type occurs at 1139·5 cm^{-1}. No combinations or overtones of this polarization are possible in this frequency range and thus we assign this band to ν_{15}. The ring strain can account for the relatively high frequency of this mode. In the cyclopropane molecule (Bates, Sands & Smith, 1969) the highest ring mode occurs at about 1190 cm^{-1} and in cyclopentane (Schettino, Marzocchi & Califano, 1969) at 1030 cm^{-1}.

The assignment of ν_{14} of C_4D_8 has been discussed previously. Small changes in the assignment of ν_8 and ν_{15} were introduced in order to account for the isotopic shift product rule.

A_2 modes

Vibrations belonging to these species are active in the crystal but their intensity is expected to be very low. Some weak features have been chosen in our spectra of both isotopic species at about the frequencies reported by L & N.

A_1 modes

There is no evidence in our infrared spectra of bands of these species so that the assignment of the A_1 modes is based only on the analysis of the Raman spectra.

The assignment of ν_{12}, the ring puckering mode, has to be discussed in rather more detail. L & N gave the values 200 and 151 cm^{-1} for C_4H_8 and C_4D_8 respectively. Recently, M & C report for the ring puckering vibration of solid II cyclobutane $-h_8$ and $-d_8$ the Raman values of 220 and 144 cm^{-1} respectively. M & C also found evidence for a band at 245 cm^{-1} which they assigned to a lattice mode of solid II C_4H_8. We observed all these features and also a band at 199 cm^{-1} in the Raman spectrum of solid II C_4D_8. However, the assignment of the band at 245 cm^{-1} to a lattice mode of the C_4H_8 crystal seems to us highly questionable owing to its relatively high frequency. In fact, external modes of molecular crystals usually do not exceed 200 cm^{-1}. Looking at similar molecules, *e.g.* cyclopropane and cyclopentane, the highest lattice frequencies observed are 108 and 116 cm^{-1} respectively.

We prefer to assign the bands at 245 and 220 cm^{-1} of C_4H_8 and 199 and 144 cm^{-1} of C_4D_8 to transitions between different levels of the puckering motion. This requires some excited levels to be still populated at the temperature of the experiment (~80°K). The effect of the crystal field on the molecular mode accounts for the shift to higher frequency of the ring puckering vibration.

B_1 *modes*

We have modified the assignment of ν_8 of C_4D_8 following the new evidence of ν_{22} in the infrared spectrum of the solid solution. In fact, in the region around 1040 cm^{-1} of the Raman spectrum three bands appear, two weak and one of medium intensity. The two weak bands have easily been assigned to E modes owing to their multiplicity and their infrared counterpart. The band of medium intensity at 1040 cm^{-1} can then be assigned to ν_8.

We shall not discuss the assignment of CH and CD stretching modes owing to the great complexity arising in the corresponding spectral region from the occurrence of overtones and combinations of lower lying modes. Tentative changes of L & N's assignment are reported in Tables 1 and 2 for normal and fully deuterated cyclobutane.

Site and factor group symmetry

The most important information we derive from the infrared and Raman spectra is the absence, in the former, of bands belonging to the A_1 and B_1 irreducible representations of the molecular point group D_{2d}. When the crystal structure is unknown, the site symmetry (subgroup of the molecular point group) can be tested systematically from the agreement between the observed spectrum and the selection rules for each symmetry. This procedure leads usually to the identification of a restricted number of possible site symmetry groups. In the case of solid II cyclobutane the only site group whose mapping into the molecular group D_{2d} allows only Raman activity for the A_1 and B_1 modes is the D_2 group.

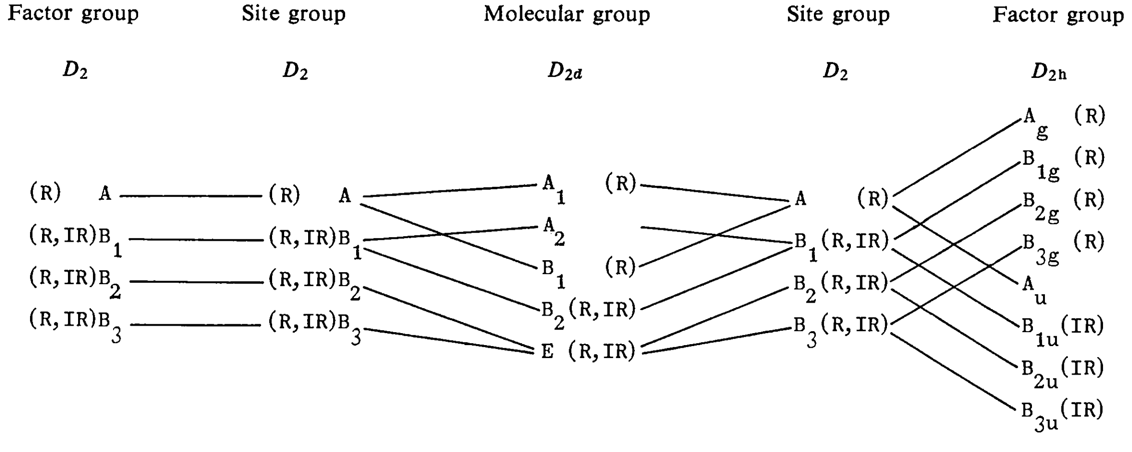
The correlation between the molecular point group D_{2d} and the site group D_2 predicts also the activation of E and B_2 modes in the Raman and of A_2 modes in the Raman and infrared spectra. The relevant piece of information, that the A_1 and B_1 modes do not have infrared counterparts, allows then the immediate identification of a unique site symmetry for the molecules in the crystal. The choice of the D_2 site symmetry leads to the exclusion of triclinic and monoclinic crystal systems. On the other hand solid II cyclobutane is not cubic (Carter & Templeton, 1953) and a hexagonal or trigonal crystal symmetry is highly improbable for an ordered structure owing to the fourfold symmetry of the cyclobutane molecule.

Mention has already been made of the polarization behaviour of the various components of molecular fundamentals in the solid II C_4H_8 spectrum. This is consistent both with a tetragonal structure with the unique axis lying parallel to the plates and with an orthorhombic structure whose crystal planes parallel to the plates are (*hk*0) or (*h*0*l*) or (0*kl*).

The mapping of the site group species into the factor group (which describes the symmetry of the complete primitive cell) can be tested against band multiplicity and polarization, infrared–Raman coincidence, and the number of observed lattice vibrations. D_2 site symmetry allows only two possible orthorhombic factor groups, while three factor groups are possible if the crystal structure is tetragonal. The orthorhombic factor groups are the D_2 and D_{2h} and the tetragonal factor groups are the D_{2d}, D_{4h} and D_4 groups. For all factor groups, A_1 and B_1 modes remain Raman active only and no choice is possible on this basis.

Table 3. *Correlation diagram for the mapping of the D_{2d} molecular point group into D_2 and D_{2h} factor groups through D_2 site group*

R = Raman active; IR = infrared active.



If the numbers of band components in the Raman and in the infrared are considered, a definite choice between an orthorhombic and a tetragonal structure can be made. The mapping of the molecular group D_{2d}, through the site group D_2, into the orthorhombic factor groups D_2 and D_{2h} (see Table 3) reveals that the A_1 and B_1 bands have to be single, whereas for D_{2d}, D_4 and D_{4h} tetragonal factor groups these bands have to be double. The modes of A_2 and B_2 species have to be single and those of E species double in every case.

E species bands show in all the spectra a double structure and B_2 bands are single except in one case, *i.e.* ν_7 in the infrared spectrum of normal cyclobutane. The band corresponding to this mode exhibits two components (see Fig. 1). The lower one maintains its frequency but decreases strongly in intensity in the solid solution spectrum. Relative intensity and wavenumber separation between the main peak and the weaker one suggest then that this must be due to cyclobutane-^{13}C present in about 4% concentration. In the pure crystal spectrum there is probably a borrowing of the intensity of the weaker band from the main peak. Satellites due to ^{13}C also appear on the lower frequency side of $\nu_3(A_1)$ and $\nu_9(B_1)$ in the Raman spectrum of solid II C_4H_8. Bands belonging to A_1 and B_1 species are always single. Then the experimental evidence (only one component for A_1 and B_1 species bands) favours the orthorhombic structure.

The only spectroscopic means left for distinguishing between the two possible orthorhombic factor groups, D_2 and D_{2h}, is the inspection of the infrared and Raman spectra for coincidence. Observation of frequency coincidence would support a non-centrosymmetric unit cell (D_2 factor group), while non-coincidence would support a centrosymmetric unit cell (D_{2h} factor group). For a D_{2h} factor group symmetry and D_2 site symmetry, A_2 and B_2 molecular modes originate two unit cell modes, one infrared and one Raman active, whereas A_1 and B_1 modes originate only one Raman active mode and E modes originate two Raman and two infrared crystal modes (see Table 3).

A D_2 factor group symmetry yields instead only one crystal mode for each molecular vibration (two for the degenerate ones) active in the infrared and Raman except for A_1 and B_1 modes which are Raman active only (see Table 3). It can be seen from Tables 1 and 2 that in every case in which a molecular mode gives rise to detectable Raman lines, they never coincide with the infrared counterparts. In most cases the difference between the infrared and Raman frequencies is small, and lies within the limits of the experimental errors. In three cases, however, the differences seem large enough (ν_{18}:ir 1218·5, 1211·5 − R(1221), 1218; ν_{23}:ir 902·2, 899·8 − R907, 895 of C_4H_8 and ν_{23}:ir 731·5, 729·1 − R724 of C_4D_8) to be taken as real. Also in the low frequency region no coincidence occurs between the observed Raman and infrared lattice bands, although, since the differences in frequency are of the order of the experimental errors, this cannot be used as a decisive proof.

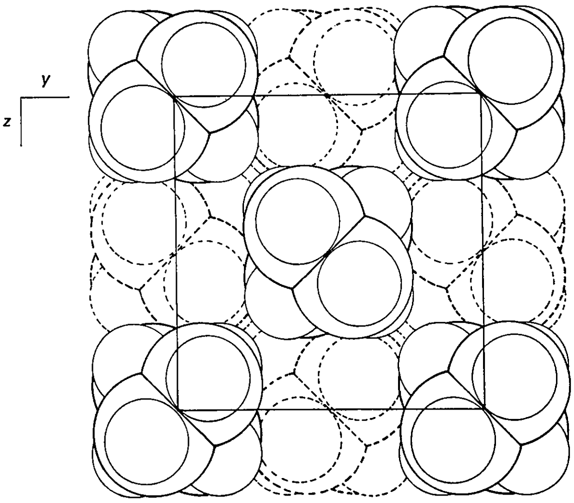


Fig. 2. Calculated packing of the cyclobutane crystal according to space group *Ccca*, viewed along the x direction. Molecules with $x=\frac{1}{2}a$ are drawn with dotted lines. Thicker lines indicate C atoms; thinner indicate H atoms. Van der Waals radii used in the drawing are 1·3 and 1·8 Å for H and C atoms respectively. The *bc* unit cell face has been also indicated.

We conclude therefore that from the spectroscopic data alone the crystal structure of solid II cyclobutane can be known to the point of the symmetry of the occupied sites and of a choice between D_2 and D_{2h} orthorhombic factor groups. Reference to *International Tables for X-ray Crystallography* (1969) reveals that non-centrosymmetric space groups Nos. 2, 3, 4, 5 and 9 do not contain D_2 sites, and can thus be discarded. Similarly, of the 28 space groups isomorphous with the factor group D_{2h}, Nos. 1, 5–19, 25, 27 and 28 do not contain D_2 as sites and can likewise be discarded. We can carry the analysis no further on spectroscopic grounds alone, and are left with the rather large assortment of 13 possible space groups.

We can make a reasonable choice among these possibilities if we assume that the molecules of cyclobutane are packed in the crystal as closely as their geometry allows, *i.e.* with the least possible unoccupied space consistent with the van der Waals radii of the hydrogen and carbon atoms.

Molecular packing calculation

Using the structural information derived from the spectroscopic data, a calculation of the minimum energy packing of solid II C_4H_8 was carried out with the program *PACK*3 written by Williams (1964, 1965). This was made possible because of the existence of sets of potential parameters relating to C···C, C···H and H···H contacts which have been widely tested on a large number of hydrocarbon structures and properties. Moreover, the requirements of the site symmetry immediately constrain the molecules to fixed orientations and positions reducing the adjustable parameters to only three, *i.e.* to the length of the cell edges.

The method involves selection of all the space groups compatible with the symmetry of the molecule in the crystal and, for each of them, minimization of the lattice energy by variation of the cell dimension. Here the exp-6 type atom–atom potential (set IV of Table II, Williams, 1967) was imposed as a condition and the crystal structure was allowed to change to minimum energy starting from reasonable cell parameters obtained from interlocking of molecules arranged according to the selected unit cell symmetry. Molecular geometry and dimension are those of a rigid gaseous molecule with D_{2d} symmetry and were taken from Almenningen *et al.* (1961) and from U & S (1968). The summation of the pairwise interactions between the atoms of the reference molecule and those of the surrounding ones was terminated at a distance of 7·0, 6·5 and 6·0Å for C···C, C···H, and H···H interactions respectively. Above these values the calculation gives practically constant values of the energy.

Different minima in the crystal potential energy curve corresponding to the same unit cell symmetry, have been sought starting from various initial packings having different cell parameters, obtained by contacting in different ways the countours of the molecules. The molecular shape used in this calculation reduced noticeably the number of starting models. In fact, on account of the fourfold symmetry of the molecule only two fixed orientations at the site, of the three required by D_2 site symmetry, needed to be considered. Moreover, a number of packings thus obtained actually have tetragonal symmetry and we discarded them by selection rule requirements. The results of the calculation are shown in Table 4 where the energetically more favoured orthorhombic space groups are reported.

The order of decreasing energy for the space groups in the Table corresponds to that of decreasing specific volume (cm^3.g^{-1}), with non-significant exceptions when similar energies are calculated for different space groups. This is in agreement with the closest packing principle (Kitaigorodskii, 1961).

The packing corresponding to the space group *Ccca*, which has the lowest calculated crystal energy, is shown schematically in Fig. 2. There are four molecules per unit cell related two by two by centres of symmetry, *i.e.* there are two molecules per primitive unit cell. The structure may be thought of as made up of layers related by screw axes.

We conclude that the use of the minimum potential energy as a criterion for a choice of the most probable among a series of unknown structures is very useful provided good transferable potential functions exist. Another very important requirement concerns the structural information regarding the primitive unit cell symmetry (site symmetry, factor group symmetry). In fact we were able to perform a reliable calculation mainly because the high symmetry of the site strongly reduces the number of structural parameters to be adjusted, *e.g.* the dimensions of the energy space.

The authors would like to thank Professor S. Califano for helpful criticisms and suggestions and Dr F. D. Verderame for his encouragement in the early stages of this work. The work was supported by the Italian Consiglio Nazionale delle Ricerche and in part by the US Department of the Army (Washington D. C.), under Contract No. DAHC15-69-C-0183.

References

Almenningen, A., Bastiansen, O. & Skancke, P. N. (1961). *Acta Chem. Scand.* **15**, 711.
Bates, J. B., Sands, D. E. & Smith, W. H. (1969). *J. Chem. Phys.* **51**, 105.
Carter, G. F. & Templeton, D. H. (1953). *Acta Cryst.* **6**, 805.
Connor, D. S. & Wilson, E. R. (1967). *Tetrahedron Letters*, p.4925.
Dows, D. A. & Rich, N. (1967). *J. Chem. Phys.* **47**, 333.

Table 4. *Cell edge lengths, crystal packing energy and unit cell specific volume (UCSV) of the orthorhombic space groups compatible with the data obtained from the spectra of solid* II *cyclobutane*

a, *b*, and *c* parameters (Å), are along the *x*, *y*, and *z* crystal reference axes respectively (see also Fig. 2).

Space group	*a*	*b*	*c*	2*E*(kcal.mole^{-1})	UCSV (cm^3.g^{-1})
Fmmm	10·43	10·43	9·88	−8·42	1·44
*F*222	5·15	10·34	9·66	−8·86	1·38
Cmma	10·38	10·38	4·28	−11·25	1·24
Pccm	4·28	5·13	10·39	−11·46	1·22
*P*222	4·28	5·13	5·14	−11·64	1·21
*C*222	4·32	9·63	5·12	−12·50	1·14
Cccm	4·31	9·66	10·36	−12·65	1·16
Ibam	4·28	9·68	10·35	−12·69	1·15
*I*222	4·28	9·67	5·11	−12·75	1·14
Pnnn	5·10	9·56	4·31	−12·85	1·12
Pban	4·29	9·66	5·12	−12·89	1·14
Fddd	4·31	9·62	19·81	−13·63	1·10
Ccca	4·33	9·60	9·63	−14·23	1·07

International Tables for X-ray Crystallography (1969). Vol. I. Birmingham: Kynoch Press.
KITAIGORODSKII, A. I. (1961). *Organic Chemical Crystallography*. New York: Consultants Bureau.
LORD, R. C. & NAKAGAWA, I. (1963). *J. Chem. Phys.* **39**, 2951.
MEIBOOM, S. & SNYDER, L. C. (1970). *J. Chem. Phys.* **52**, 3857.
MILLER, F. A. & CAPWELL, R. J. (1971). *Spectrochim. Acta*, **27**A, 947.
RATHJENS, G. W. JR, FREEMAN, N. K., GWINN, W. D. & PITZER, K. S. (1953). *J. Amer. Chem. Soc.* **75**, 5634.
RATHJENS, G. W. JR & GWINN, W. D. (1953). *J. Amer. Chem. Soc.* **75**, 5629.
SCHETTINO, V., MARZOCCHI, M. P. & CALIFANO, S. (1969). *J. Chem. Phys.* **51**, 5264.
STONE, J. M. R. & MILLS, I. M. (1970). *Molec. Phys.* **18**, 631.
UEDA, T. & SHIMANOUCHI, T. (1968). *J. Chem. Phys.* **49**, 470.
WILLIAMS, D. E. (1964). USAEC Report *IS*-1042.
WILLIAMS, D. E. (1965). *Science*, **147**, 605.
WILLIAMS, D. E. (1967). *J. Chem. Phys.* **47**, 4680.
WILSON, T. P. (1943). *J. Chem. Phys.* **11**, 369.

Acta Cryst. (1972). A**28**, 440

An Improvement in the Algorithm for Absorption Correction by the Analytical Method

BY N. W. ALCOCK*
Department of Molecular Sciences, University of Warwick, Coventry, CV4 7AL, England
G. S. PAWLEY
Department of Physics, University of Edinburgh, Edinburgh, EH9 3JZ, Scotland
AND C. P. ROURKE
Department of Mathematics, University of Warwick, Coventry, CV4 7AL, England
WITH AN APPENDIX BY M. R. LEVINE
Department of Physics, University of York, York, YO1 5DD, England

(*Received* 10 *February* 1972)

The most time-consuming step in the analytical method for absorption correction is the examination for each Howells polyhedron of the large number of tetrahedra formed from all possible sets of one auxiliary point with the faces of previously found tetrahedra. In the present method, a formula is presented for the absorption of a polyhedron (a slice) with two parallel faces, which are planes of constant absorption. With this formula, the absorption of a Howells polyhedron can be calculated, with much less effort, by systematically dividing it into slices.

Introduction

Absorption correction by the analytical method has the immense advantage over numerical integration of being exact, but it suffers from being slower in most circumstances. This paper presents an alternative method of calculation that increases the speed; it may also be of value in other problems concerned with absorption and extinction.

The nomenclature used is that of De Meulenaer & Tompa (1965) and Alcock (1970), and a sample calculation is presented based on the example of the latter.

The analytical calculation has several sections for each reflexion. These are, with the relative times taken (by the Fortran program *ABSCOR* running within the X-Ray 63 system):

(i)	calculation of the diffraction angles and general overheads,	9%
(ii)	finding the auxiliary points,	29
(iii)	selecting those points which are the vertices of each Howells polyhedron,	11
(iv)	calculating the transmission for each Howells polyhedron,	51

Stages (iii) and (iv) are considered here. Stage (iii) can be reduced by storing for each point a list of the Howells polyhedra it can contribute to, once the point is found. This leaves stage (iv) as the most important.

A Howells polyhedron is defined as the portion of a crystal which is reached by rays entering the crystal through one particular face and leaving through one particular face (possibly the same one). This means (De Meulenaer & Tompa, 1965) that within the polyhedron, the loci of points of constant absorption are a series of parallel planes on which the rays have constant path length in the crystal. These planes may be arbitrarily oriented in relation to the polyhedron vertices and faces. In the original method, the explicit formula for the transmission of a general tetrahedron is used. The polyhedron is split up into its component tetrahedra by considering all combinations of a face and a vertex, and discarding those not producing genuine tetrahedra.