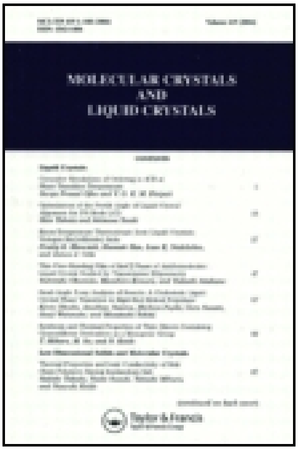

Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics

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Crystal Dynamics and Phase Transition of Glutaric Acid

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CRYSTAL DYNAMICS AND PHASE TRANSITION OF GLUTARIC ACID

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Abstract A crystal-dynamical calculation of the ß phase of glutaric acid was performed with Buckingham potentials under consideration of the low frequency internal modes. The overall agreement with experiments is satisfactory and confirms most of the proposed assignment but two bands have to be modified. The eigenvectors show coupling of internal and external motions and thus demonstrate limitations of the rigid-body model. Model calculations suggest a gradual conformational change to explain the observed anomaly of one mode.The site symmetry changes at the transition to the high temperature phase.

INTRODUCTION

In a previous paper Grip and Samuelsen[1] reported on a study of the phase transition of glutaric acid, $COOH(CH_2)_3COOH$, and of the dynamics of the low temperature ß phase, with Raman spectroscopy. They proposed an assignment of the bands and studied the variation with temperature. It was astonishing to find that one band of the ß phase softened on cooling. In order to describe the dynamics quantitatively, to characterize this band and to get a better insight into the transition mechanism, the low frequency modes were calculated. The single crystal Raman data[1] were supplemented by high-frequency Raman and FIR spectra of both phases from powders.

EXPERIMENTAL

The powder FIR spectra recorded at room temperature were obtained from polyethylene pellets with a Bruker 113v interferometer. The temperature dependent internal Raman spectra were registered from powder with the help of a Jobin-Yvon HG2S spectrometer with the 5145 Å line of an argon-ion laser with an output of about 500 mW and usual accessories for temperature control.

Figure 1 shows the FIR spectrum between 30 and 400 cm^{-1} and reveals the existence of at least five bands at room temperature. The corresponding frequencies are collected in Table III, where the symmetry assignment can only be tentative as no single crystal spectra are available; it is based on the result of the calculation.

The Raman spectra given in Figure 2 shows the changes occuring at the transition. The transition is characterized by a decrease of the number of bands when the temperature is increased from the ß to the α phase (T_c=338 K). Obviously mainly the regions of CH_2 vibrations (stretching, bending) are concerned. Due to the absorptions of the OH groups similar effects could not be observed in the infrared spectrum.

CALCULATIONS

Such a long molecule has internal normal modes which are able to couple with the external modes of vibration of the solid. Thus the crystal calculation has to be done in two steps: a determination of the free molecule modes to be considered, followed by a complete treatment of the crystal.

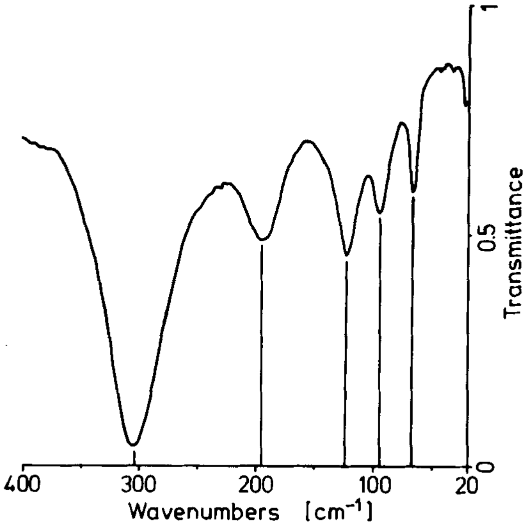

FIGURE 1 Far-infrared spectrum of ß glutaric acid

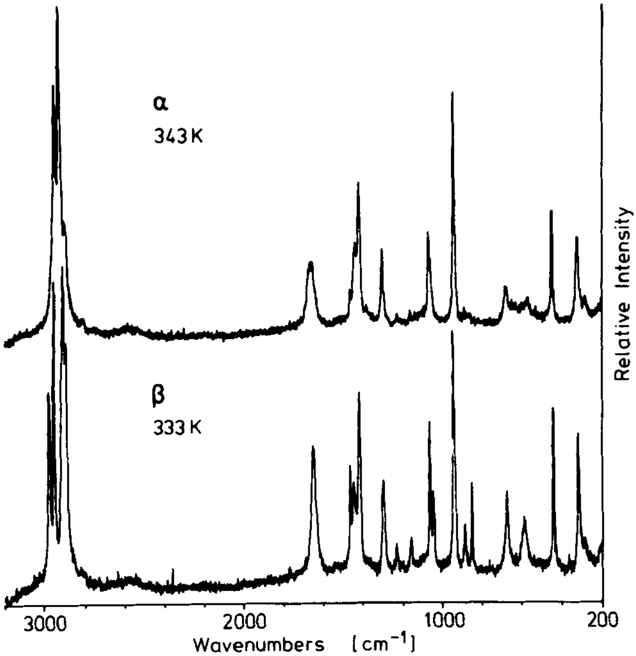

FIGURE 2 Raman spectra of glutaric acid

MOLECULAR AND CRYSTAL STRUCTURE

The crystal structure at 300 K was determined by Morrison and Robertson[2] and analyzed in Ref.1 for spectroscopic applications. It is monoclinic C2/c with Z=4. The molecules form infinite chains through 2.69 Å OH...O hydrogen bonds along the c axis. The molecular long axis is parallel to c. The molecular site has a C_2 symmetry.

FREE MOLECULE CALCULATION

As no structure determination of the free molecule was available, the structure in the crystal was used for the normal coordinate analysis of the free molecule . The force field was transferred from the **alkanes** for the $(CH_2)_3$ group[3] and from oxalic acid for the carboxylic groups[4]. The calculations were performed by using the normal coordinate program package developed by Shimanouchi[5].

We were mostly interested in the lowest frequencies and thus report only the seven internal modes below 300 cm^{-1} in Table I. These values were obtained by modifying the torsional force constants from 0.24 and 1.5 to 0.8 and 1.0×10^{-17} $N.m.rad^{-2}$ for the **alkane** C-C and the $C\text{-}C_{oxalic}$ bonds, respectively, thus taking into account the longer chain in glutaric acid by comparison with oxalic acid and avoiding low frequencies of about 30 cm^{-1} for some torsional motions.

The other internal modes were also calculated and the agreement with the experiment is satisfactory, considering that the calculation treats a free molecule, while the observed frequencies are for hydrogen-bonded molecules. The motions of the CH_2 groups are better reproduced than those of the carboxylic and particularly the OH groups.

TABLE I Low frequency internal modes calculated for the free molecule with C_2 symmetry.

Mode	Symmetry	Frequency (cm^{-1})	Description
I_1	B	271	Deformation CCO_2
I_2	A	257	Deformation CCC
I_3	A	138	Torsion: 36% CCO_2 + 34% CC
I_4	B	129	Torsion CCO_2: 84%
I_5	A	102	Deformation CCC: 58%
I_6	B	52	Torsion CC: 70%
I_7	A	49	Torsion: 49% CC+ 49% CCO_2

CRYSTAL DYNAMICS

The crystal-dynamical calculations were performed with the help of the programs developed by Taddei et al[6]. This approach enables the coupling of the seven modes I_1 to I_7 with the librations and translations, under the influence of intermolecular potentials represented by Buckingham type atom-atom interactions. These potentials were transferred from the ß phase of oxalic acid, which has a similar chain structure[4], for the interactions concerning the oxygen atoms and from Williams[7] for the carbon and hydrogen atoms. Only the parameters of the hydrogen bond were refined. The potentials used are listed in Table II while the calculated frequencies are summarized in Table III. The potential of the hydrogen bond corresponds to an energy of 43.5 kJ/mole and to a force constant of 16 N/m for the experimental minimum. These values are in the right order of magnitude.

TABLE II Atom-atom potentials for glutaric acid. The potential has the form $V=-A/r^6+B\exp(-Cr)$

Interaction	A ($kJ.mole^{-1}.Å^6$)	B ($kJ.mole^{-1}$)	C ($Å^{-1}$)
-C...C-	2378	350075	3.60
-C...H-	523	36694	3.67
-H...H-	114	11110	3.74
=O...O=	1536	208433	3.62
=O...O-	1704	352532	3.69
=O...C-	410	396741	3.71
=O...H-	393	40106	3.75
-O...O-	2960	264568	3.87
-O...C-	565	212368	3.23
-O...H-	343	40106	3.75
Hydrogen bond			
=O...O-	33450	232310	3.215
=O...H-	25	69630	5.235

The agreement between calculation and experiments is satisfactory. It was reached by refining the potentials of the hydrogen bond and by reducing the free molecule frequency for the internal modes I_3,I_4 and I_5 from originally 138, 129 and 102 to the fitted values 103, 100 and 70 cm^{-1}, respectively. This shows that the force field without off-diagonal elements used for the torsional internal coordinates was too simple and could only give a rough description of the free molecule spectrum . This description is sufficient for our purpose as the form of the eigenvectors is only slightly influenced by these terms.

TABLE III Normal modes of glutaric acid at 300 K.

	Experimental		Calculation	
	Freq.[#+]	Assignment[+]	Freq.[#]	Eigenvector[*]
Raman				
A_g	70	R_b	63	$59\%T_z$ $16\%I_7$ $15\%R_z$
	92	T_b	94	$38\%I_7$ $30\%T_z$ $25\%I_5$
	112	Internal	118	$45\%I_3$ $20\%I_5$ $34\%I_7$
	152	Internal	162	$83\%R_z$
	323	Internal	324	$96\%I_2$
B_g	65	R_c	53	$89\%R_x$
	89	T_a	71	$76\%T_y$
	135	R_a	120	$50\%R_y$ $19\%I_4$ $17\%T_x$ $10\%I_6$
	140	T_c	132	$34\%I_6$ $34\%T_x$ $24\%I_4$
	160	Internal	169	$46\%I_4$ $26\%I_6$ $11\%R_y$ $10\%T_y$
	194	Internal	191	$35\%T_x$ $27\%R_y$ $27\%I_6$
	286	Internal	197	$96\%I_1$
FIR				
A_u	95		86	$63\%I_5$ $16\%I_3$ $15\%R_z$
			118	$50\%I_7$ $29\%R_z$ $19\%I_5$
			141	$55\%R_z$ $42\%I_7$
	196		179	$74\%I_3$ $17\%I_5$
			267	$96\%I_2$
B_u	68		84	$95\%R_y$
	125		120	$68\%I_4$ $23\%R_x$
			122	$68\%R_x$ $17\%I_6$ $11\%I_4$
			178	$72\%I_6$ $19\%I_4$
	304		294	$98\%I_1$

[*]) Molecular axes x, y and z correspond to crystal directions c, a^* and b, respectively. [+]) Ref. 1. [#]) In cm^{-1}.

DISCUSSION

The eigenvectors in Table III show couplings between internal and external degrees of freedom which are particularly important and indicate the limitation of the rigid-body approximation used to arrive at the experimental assignment[1] in column 2. The greatest discrepancy appears in the A_g species. For the mode at 92 cm^{-1} the mixing of the internal mode is certainly too high. It is the strongest band of the spectrum and disappears at the phase transition, indicating that it is principally external. The assignments of the bands at 70 and 152 cm^{-1} have to be modified. In fact the rotation around the b direction, which deforms the hydrogen bonds, can be expected at higher frequencies and is calculated at 162 cm^{-1}. On the contrary the antitranslation in b direction, concerning only the van der Waals forces, is calculated at lower frequencies and shared between the 63 and 94 cm^{-1} bands.

The crystal energy is calculated to -93.3 kJ/mole, which is in the order of magnitude expected from the increment method of Bondi[8].

The unusual temperature behaviour of the 89 cm^{-1} B_g mode was tentatively explained in ref. 1 by a gradual conformational change with temperature. This conjecture receives some support by the present calculations which showed that the T_y motion is particularly sensitive to the conformation: in one run the C_{2v} symmetry was artificially imposed on the molecular site. While the frequencies of the internal modes were modified only within a few wavenumbers and most lattice modes by 10-15 cm^{-1}, the T_y mode became unstable (imaginary) in this symmetry.

Since the high-temperature structure (α phase) is not known, the crystal dynamics calculations could not be extended to this phase. Experimentally the Raman spectra of Figure 2 show intensity variations around T_c in the regions 2900-3000 (CH_2 stretching), 1430-1470 (CH_2 bending), 1050-1250 and 550-700 cm^{-1}. Heating by only 10 K across the phase transition, some bands almost completely lose their intensities (2980, 1475, 1230, 1155, 890 and 850 cm^{-1}), while frequency shifts are small. This fact suggests either a change in the site symmetry, implying a modification of the selection rules, or a reduction of the size of the unit cell, reducing the number of components due to the crystal field splitting. The latter argument corroborates with the previous observation[1] of a decreased number of lattice bands in the α phase.

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