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Phonon Dynamics in the Low Temperature Phase of Crystalline Chloranil

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Frequencies and eigenvectors of phonons in the low-temperature phase of chloranil are calculated using the usual harmonic, nonbonded atom–atom interaction and rigid-body approximations. Results show that these approximations are sufficiently good to draw interesting conclusions for the conditions of the phase transition and on the nature of the potential double well in which the molecules are at low temperature.

INTRODUCTION

Tetrachloroparabenzoquinone (chloranil) is a very interesting molecular crystal. A soft mode was observed for the first time for a molecular crystal by Raman experiments (Hanson[1]). This soft mode is associated with the second order phase change which occurs at 94 K. The existence of this second order transition was already known from quadrupolar resonance spectroscopy.[2,3]

Rey-Lafon[4] has published a complete Raman spectrum of chloranil in the low temperature phase at 30 K. On the other hand, only 5 bands of the 9 expected in the F.I.R. spectrum were observed in the same study. Results of inelastic neutron scattering by chloranil have been published by Ellenson and Kjems[5] but the phonon frequencies were measured only at some special points of the Brillouin zone (soft phonon).

Precise structures of both phases of chloranil are available. The high temperature phase has been resolved from X-ray diffraction experi-

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ments by Chu *et al.*[6] at room temperature and by Van Weperen *et al.*[7] at 110 K. These studies show that the molecule conserves the same shape as the temperature is lowered. The low temperature phase has been elucidated by Terauchi *et al.* at 77 K.[8] At T_c ($\simeq$94 K) there is a doubling of the unit cell along the *c* axis and the molecular displacements correspond principally to a staggered rotation about axes perpendicular to the molecular planes. The high temperature phase belongs to space group $P\,2_1/a$ while the low temperature phase belongs to space group $P\,2_1/n$ (equivalent to $P\,2_1/a$ but with a different distribution of symmetry elements). The number of molecules in the unit cell goes from $Z = 2$ to $Z = 4$. Recently Baudour *et al.*[9] have determined by neutron diffraction the variation of molecular rotations over a large temperature range, from 10 K to 89 K. This study shows that in the low temperature phase the molecules rotate not only around their normal axis but also, with an amplitude approximately half, around an in plane axis passing through the two oxygen atoms.

THE QUASI-HARMONIC APPROXIMATION

Before doing any calculation we need to know the structure of the crystal: its space group and the position of the molecules in the unit cell. Thus, we cannot make any prediction about the phase transition. We can only test the consistency of the model and try to explain the origin of the phase transition.

There is some a priori reason to believe that a quasi harmonic model should throw light on the nature of the chloranil phase transition. There exists a very short C—O nonbonded distance in this compound and:

a) in the high temperature phase the short C—O nonbonded distance becomes shorter at low temperature, 2.85 Å at 293 K[6] 2.77 at 110 K.[7]

b) the low temperature phase space group corresponds to a lengthening of this short bond. Thus the phase transition in chloranil is simply a question of different packing when going from the larger (high temperature) cell to the smaller (low temperature) cell. (If the doubling of *c* is not taken into account).

The basic deficiency of a quasi harmonic model is to use fixed well-defined atomic positions although we know that the atoms move continuously due to the existence of phonons. Methods taking into ac-

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count the motion of atoms require summations on the Brillouin zone and consequently are very tedious and expensive in terms of calculational time.

Chloranil is still too complex a crystal to be studied by methods of self-consistent phonons.[10] Bonadeo[11] estimates to 10% the approximative error due to the quasi harmonic approximation when calculating energies in some chlorobenzenes; but it is evident that such an error will depend strongly on the crystal studied and more on the particular calculated physical property.

THE RIGID BODY APPROXIMATION

Chloranil is not so rigid a molecule as other aromatic compounds. Indeed internal modes as low as 80 cm^{-1} were attributed by Yamada *et al.*[12] to the distortion of the benzene ring; this value is just the value expected for the highest external mode. However, since from molecular packing the strong external tension playing an essential role in the transition mechanism will be applied to the O atoms and the lowest frequency involving these O atoms is at 470 cm^{-1},[12] and since Van Weperen[7] at 110 K and Chu[6] at 293 K found the same molecular configuration, the molecule may be considered as rigid.

THE ATOM-ATOM INTERACTION

Kitaigorodski[13] has reviewed the possible descriptions of molecular crystals. He has shown that a reasonable way to describe a molecular crystal composed of rigid molecules is to consider them as a sum of interacting nonbonded atoms. A particularly useful potential is the Buckingham type potential $V(r) = A \exp(-Br) - C/r^6$ where r is the distance between the nonbonded atom-pair, and A, B, C are empirical parameters. There are some difficulties about the choice of these empirical parameters as very different values are attributed to the same atom pair by different authors.

In chloranil the packing will be strongly influenced by the presence of chlorine atoms and we choose the set of parameters describing the Cl—Cl pair given by Mirsky[14] who gives a discussion of the merits of various sets of interaction parameters proposed by different authors for pairs involving the Cl atom.

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The choice of parameters used to describe the C—O nonbonded interaction will be quite difficult as there exist very short C—O nonbonded distances in chloranil (2.85 Å at ambient temperature,[6] 2.77 Å at 110 K[7]). It is generally admitted that this short C—O nonbonded distance arises from the existence of charges on C and O atoms. This is confirmed by the fact that the atoms involved in such short distances bear opposite charges.[15] One knows that in aromatic systems a C=O bond acts as a dipole which can approach 3 Debyes: for example 2.90 D in benzophenone.[16]

Effectively it appeared quite clearly in our study that a model neglecting the charges between C and O atoms and using the potential parameters of Kitaigorodski[17] for C—O pair, together with Mirsky[14] parameters for Cl—Cl pair, did not give physically reasonable results. The C—O nonbonded interaction was too repulsive and the structure calculated with this model did not agree with the experimental one for any value of observed lattice parameters.

Thus, we tried to use a more complete model including charges between C and O atoms. But the charges necessary to obtain a physically meaningful result were too large ($\mu \simeq 5$ D for the C=O bond) if we accepted the Kitaigorodski[17] parameters for the C—O nonbonded pair. So we were led to suppose that the O atom has a very low repulsion potential as compared with Cl or C atoms so that O and C atoms in chloranil can have a short nonbonded distance. We thus chose to ascribe to the O atoms the softest potential we found in the literature, namely the potential proposed by P. de Santis[18] for describing O—O nonbonded pair, and we deduce the C—O potential parameters by the following combining rules:[13]

$$V_{\mathrm{CO}} = A \exp(-Br) - C/r^6$$

with

$$C = (C_{\mathrm{CC}} C_{\mathrm{OO}})^{1/2} \quad B = 1/2(B_{\mathrm{OO}} + B_{\mathrm{CC}})$$

B_{CC}, B_{OO}, C_{CC}, C_{OO} are the corresponding terms for C—C and O—O nonbonded pairs. We chose to fit the repulsion term by the condition that there is a minimum potential for some distance R (Van der Waals radius) such that:

$$A = 6(C/B)R^{-7} \exp BR$$

The usual Van der Waals distance of 3.20 Å between C and O atoms gives the potential parameters of Table I (together with the values proposed by Mirsky and P. de Santis for other atom pairs). For C and O

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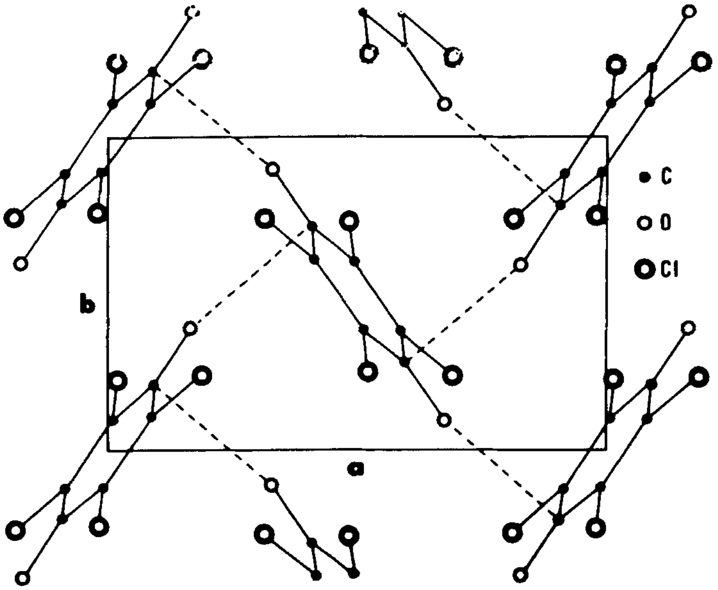

FIGURE 1 The short C—O interatomic distances in chloranil (from Ref. 6).

atoms involved in short intermolecular distances an electrostatic potential $V = Q_O Q_C / r$ is added with $Q_C = -Q_O = 2\ 10^{-10}$ e.s.u. This electrostatic term considered alone has a minimum for a position corresponding to the high temperature phase. With the values of the parameters given above, the total potential, sum of Van der Waals and electrostatic interactions, reproduces well the structural position of chloranil at 10 K.

Thus we construct a simplified model for studying the potential variation in the crystal of chloranil. In this model the interaction potential

TABLE I

Semi-empirical parameters used to describe non-bonded atom–atom interactions in chloranil. $V = A \exp(-Br) - C/r^6$. For C and O atoms involved in short intermolecular distances $V = Q_O Q_C / r$ is added with $Q_C = -Q_O = 2\ 10^{-10}$ e.s.u.

Atom pair	A (kcal mole^{-1})	B (Å^{-1})	C (kcal mole^{-1} Å^6)
C—C	71600	3.68	421
C—Cl	17685	2.97	1120
C—O	33427	4.006	207.3
Cl—Cl	4580	2.26	2980
Cl—O	16001	3.29	551
O—O	30000	4.33	102

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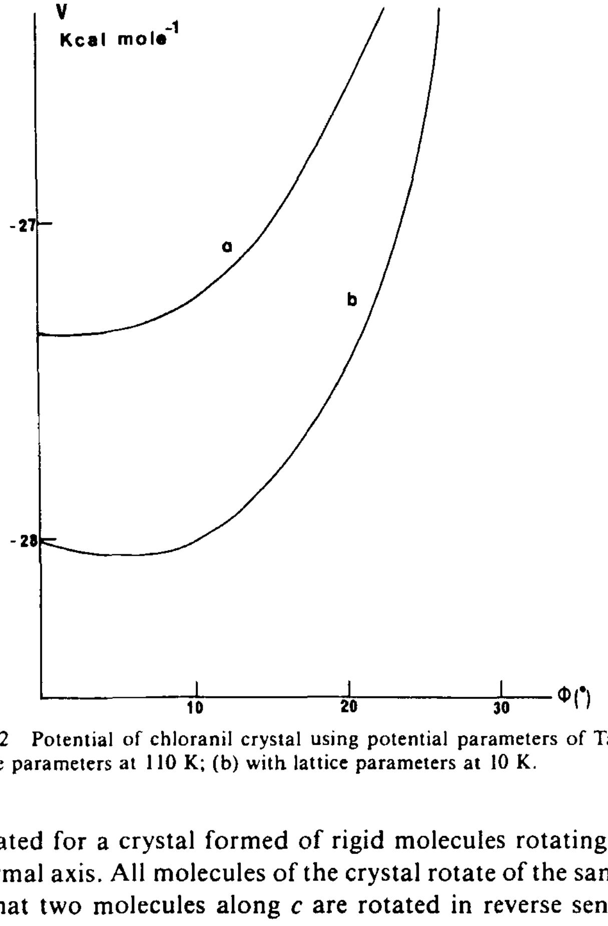

FIGURE 2 Potential of chloranil crystal using potential parameters of Table I; (a) with lattice parameters at 110 K; (b) with lattice parameters at 10 K.

is calculated for a crystal formed of rigid molecules rotating around their normal axis. All molecules of the crystal rotate of the same angle except that two molecules along *c* are rotated in reverse sense. This gives a potential curve with one parameter: the angle ϕ of rotation of one molecule. The minimum potential should be the equilibrium position (Figure 2). Thus the variation with temperature is represented by the variation of the lattice parameters which are held fixed during the rotation of the molecules.

LATTICE DYNAMIC CALCULATION

Frequencies and eigenvectors are obtained by solving the secular equation

$$|F^{\mu\nu}(k) - \lambda\delta^{\mu\nu}| = 0$$

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for any value of the k-vector (wave vector). $F^{\mu\nu}$ is the second derivative of the crystal energy versus dynamic variables generated from molecular libration and translation. In the special case of chloranil there are two molecules in the asymmetric unit in the low temperature phase and the motions of these two molecules will be independent.

Each molecule being on a center of inversion there is no mixing between translations and librations for $k = 0$. Results of calculation with the structural data at 10 K are given in Table II for the g modes (Raman active in the center of the Brillouin zone). These are compared with Rey-Lafon[4] observed frequencies at 30 K. Unhappily there is no good infrared data to compare with the calculated u modes.

We have also calculated the phonon frequencies and eigenvectors for the high temperature phase of chloranil. To compare with the values calculated in the low temperature phase, one must calculate the frequencies and eigenvectors for two points in the Brillouin zone namely the (0, 0, 0) and (0, 0, 0.5) points (Tables III, IV).

Thus there is not an important variation in the calculated eigenvectors in the two phases. In the low temperature phase we are led to describe the motion of the two independent molecules by six parameters (three librations for each independent molecule) and the main change when going to the high temperature phase is that the motion can be described by three parameters only in the special chosen Brillouin zone points.

TABLE II

The Raman active modes in the low temperature phase of chloranil (10 K)

		Eigenvector						
	ν_{cal}	L_1	M_1	N_1	L_2	M_2	N_2	ν exp(30°K) (4)
Ag	18.4	0.02	0.29	0.39	0.04	0.21	0.45	11
	48.2	−0.01	−0.27	0.34	0.05	0.442	0.331	41
	51.2	0.022	0.36	0.33	0.082	0.32	−0.37	50
	58.2	−0.12	−0.42	0.32	−0.135	0.39	0.16	53
	64.5	0.48	−0.14	0.08	0.47	0.04	0.10	86
	79.3	−0.49	−0.019	−0.01	0.50	0.019	0.51	88
Bg	23.0	−0.37	0.41	0.24	−0.24	0.49	0.16	22
	37.1	0.046	0.23	0.34	−0.08	0.20	0.52	44
	52.8	−0.07	−0.27	−0.48	−0.02	−0.14	0.40	50
	59.7	0.12	−0.40	0.23	0.22	0.42	0.19	52
	64.7	−0.48	−0.14	0.17	−0.44	0.11	0.03	88
	84.8	0.49	−0.07	−0.00	−0.50	0.04	0.13	93

L, M, N are respectively the long, middle and normal axes for the two molecules in the asymmetric unit.

TABLE III

Calculated frequencies for the high temperature phase (110 K) of chloranil (for $k = 0$)

Sym	ν	L	M	N	a	b	c	ν exp(293°K) (4)
Ag	42.9	0.00	−0.19	−0.68				31
	44.9	−0.05	0.67	0.19				43
	69.7	0.70	0.04	0.02				79
Bg	32	0.07	0.33	0.62				16
	52.6	−0.21	0.60	0.29				47
	58.0	−0.67	−0.15	0.16				78
Au	37.28				0.15	0.0	0.69	37
	70.5				0.69	0.0	0.15	62
Bu	55.35					0.70		61

DISCUSSION

The potential interaction model predicts at low temperature a double well type of potential which progressively moves into a single-well potential at high temperature. This is in striking contrast with the view of Richardson[2] who made the hypothesis that at high temperature the potential double well still subsists but that the molecule ignores it by doing very large amplitude librations. This is also in contrast with biphenyl where within the same approximation exactly the reverse situation is found. In biphenyl at high temperature the calculated double well potential is deeper and larger than at low temperature.[19] This arises mainly from the fact that in biphenyl the phase transition, which is also

TABLE IV

Calculated frequencies and eigenvectors for (0, 0, 0.5) point of Brillouin zone for the high temperature phase ($P\ 2_1/a$) of chloranil (110 K).

ν cm^{-1}	L	M	N	a	b	c
12.0	0.04	−0.37	−0.59	0.0	0.0	0.0
19.0	0.00	0.64	0.30	0.0	0.0	0.0
25.4	0.00	0.0	0.0	0.11	0.70	0.11
34.0	0.00	0.0	0.0	0.70	0.10	0.06
35.4	0.00	0.0	0.0	0.10	0.11	0.69
46.6	0.00	0.0	0.0	0.06	0.09	0.70
47.5	0.04	0.30	0.30	0.0	0.0	0.0
53.6	0.52	0.30	0.00	0.0	0.0	0.0
54.5	0.0	0.0	0.0	−0.70	−0.090	0.0
57.2	−0.60	0.28	−0.22	0.0	0.0	0.0
69.1	0.0	0.0	0.0	0.70	0.0	−0.1
75.1	0.70	−0.02	0.03	0.0	0.0	0.0

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governed by a soft-mode phonon,[20] arises from an intramolecular degree of freedom.

The often admitted view that symmetry breaking in the low temperature phase comes from the condensation of a mode of the high symmetry phase is confirmed by our eigenvector calculation. In particular it is found that the low-temperature phase may include a rotation along the middle axis together with rotation along the normal to the molecule. These results are in agreement with recent structural studies (Baudour *et al.*[9] see Tables II and IV).

The soft mode effect is totally ignored by the quasi-harmonic approach as the calculated phonon frequencies always decrease with the increase in lattice parameters. This was expected since the soft mode is a typical effect of anharmonicity.

It is possible to relax the rigid body approximation as an internal field has been proposed by A. Girlando[21] but no important change is to be expected from this refinement except perhaps on the highest external calculated frequencies.

We proposed a set of atom–atom potential parameters for describing the C—O non-bonded interaction in chloranil. This set is certainly not unique. But more data on the properties of this compound are needed to widen our knowledge of the physical reason for such a short non-bonded interatomic distance.

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