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Low-frequency Lattice Vibrations and Intermolecular Forces of the 9,10-Anthraquinone Crystal

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The low-frequency Raman active lattice vibrations of the 9,10-anthraquinone single crystal were measured at various temperatures from 26°C to −190°C, and the symmetry species of the observed Raman bands were determined by polarization measurements. From a comparison between the observed and calculated frequencies, it seems that Dashevsky's potential expresses well the intermolecular potential of the 9,10-anthraquinone crystal. It was also found that the temperature dependence of lattice vibrations can be explained reasonably with this potential.

The lattice vibrations of molecular crystals have attracted great attention because of their importance in the elucidation of the intermolecular potentials in crystals. One of the most important characteristics of the low-frequency lattice vibrations of molecular crystals is the great dependence of the frequencies upon the temperature. The frequency shifts due to changes in the temperature are generally different for different lattice vibrations; they often amount to 20—30% of the frequencies in the region from room temperature to the temperature of liquid nitrogen. These characteristics may be utilized in the study of the intermolecular potentials. Unfortunately, however, in molecular crystals it is very seldom that crystal structures at various temperatures over a wide range are well known in detail. For this reason, the highly useful experimental data of the effects of the temperature have been neglected.

One of the crystals whose structures have been determined at various temperatures over a wide range is the 9,10-anthraquinone crystal; Lonsdale *et al.* have reported the crystal structures at 20.5, −12.5, −72, −112, and −170°C.[1] It is, therefore, a good example

1) K. Lonsdale, H. J. Milledge, and K. El Sayed, *Acta, Crystallogr.*, **20**, 1 (1966).

Table 1. Observed lattice vibrations of 9,10-Anthraquinone (cm^{-1})

−190°C	−165°C	−145°C	−122°C	−88°C	−54°C	−27°C	0°C	26°C	Assign.
73	73	73	73	72	71	69	68	66	A_g
63	63	62	62	60	58	57	56	51	A_g
36	36	35	35	32	32	30	29	27	A_g
92	91	91	90	89	87	86	84	82	B_g
63	63	62	61	60	60	60	58	57	B_g

for use in testing the intermolecular potentials at various temperatures.

In the present experiment, the polarized Raman spectra of the low-frequency lattice vibrations of the single crystal of 9,10-anthraquinone were measured at various temperatures, and assignments of the observed Raman bands were given. The results obtained were then used to examine the intermolecular potentials proposed by various authors.

Experimental

9,10-Anthraquinone was purified by repeated zone refinements, and the single crystal was grown by Bridgman's method. The single crystal used in the Raman measurements was about $4\times5\times8$ mm, one of the edges of the crystal being parallel to the crystallographic b axis, which was determined by taking oscillation X-ray photographs.

The optical arrangement for the measurement of the polarized Raman spectra is almost the same as that reported previously.[2] A He-Ne gas laser of 6328 Å (Japan Electron Optics Laboratory Co., 50 mW) and a Nalumi model 750 Z-1200 double monochromator combined with a cooled head-on-type photomultiplier tube, followed by a photon-counting detector, were used for taking the Raman spectra.

The temperature of the single crystal was controlled in the region between room temperature and −190°C by regulating the flow speed of cooled nitrogen gas introduced into a cryostat. Even at the lowest temperature, no cracking of the crystal occurred, so the polarization experiments were carried out successively.

Results and Assignments

The crystal structure of 9,10-anthraquinone belongs to a monoclinic system, space group $C_{2h}^5-P2_1/a$, and it contains two molecules in a unit cell.[1] The optically-active lattice vibrations can therefore be divided into two parts; six librational modes ($3A_g+3B_g$) and three translational modes ($2A_u+B_u$). The vibrations of the g species are active only in the Raman spectrum, while those of the u species are active only in the infrared spectrum. The three A_g and three B_g Raman active lattice vibrations should be differentiated by means of a polarization experiment; that is, when the single crystal is excited by incident light polarized parallel to the b axis of the crystal, the Raman lines of the A_g and B_g vibrations should appear in the spectra of the $b_{//}$ and $b_{\perp}$ components of the scattered light respectively. Figure 1 shows typical spectra obtained in this way at 26 and −122°C. It may be seen that all the Raman lines except one of the B_g species are clearly identified.

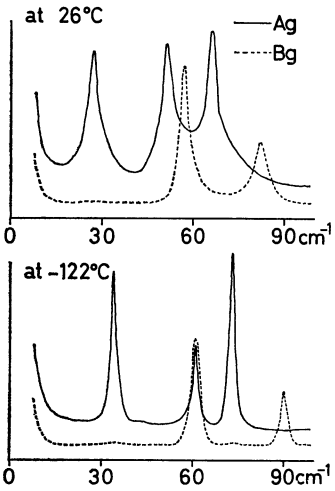


Fig. 1. Polarized Raman spectra of 9,10-anthraquinone single crystal.

The frequencies observed at various temperatures are summarized in Table 1, together with their assignments.

A Raman line of 115 cm^{-1} has been reported in the Raman measurement at room temperature by Singh *et al.*,[3] who assigned it to the lattice vibration. In our measurements, however, we were unable to find any Raman lines in the neighbourhood of 115 cm^{-1}. Instead, we found a weak Raman line at 148 cm^{-1}, which appears preferentially in the B_g spectrum. It is probably due to the combination band of 66 cm^{-1} (A_g) and 82 cm^{-1} (B_g).

Calculation of Lattice Vibrations

The calculation of lattice vibrations was performed in a rigid-body approximation according to the **GF** matrix method developed by Shimanouchi *et al.*[4,5] The intermolecular potential used was approximated by the sum of the atom-atom pair-by-pair potentials of the form:

$$V(r) = -Ar^{-6} + B\exp(-Cr),$$

where r is the interatomic distance and where A, B, and C are constants characteristic of the kind of atom pair. The potential of this type has often been used with great success in the calculation of many properties of molecular crystals, such as lattice vibrations, specific heat, and elastic constants.

We employed several sets of values of A, B, and C as proposed by different authors for the H···H and

2) M. Suzuki, T. Yokoyama, and M. Ito, *Spectrochim. Acta*, **24A**, 1091 (1968).

3) S. N. Singh and R. S. Singh, *ibid.*, **24A**, 1591 (1968).

4) T. Shimanouchi, M. Tsuboi, and T. Miyazawa, *J. Chem. Phys.*, **35**, 1597 (1961).

5) T. Shimanouchi and I. Harada, *ibid.*, **41**, 2651 (1964).

Table 2. Parameters in atom-atom potentials

		Ste I	Set II	Set III	Set IV
H···H	A	2.501	0.3960	0.3420	0.1487
	B	27.79	291.8	45.80	63.15
	C	3.740	4.860	4.082	4.640
C···C	A	3.717	2.487	2.390	3.293
	B	517.3	291.8	272.0	261.9
	C	3.600	3.580	3.546	3.520
O···O	A	2.459	2.459	2.459	2.459
	B	670.4	670.4	670.4	670.4
	C	4.330	4.330	4.330	4.330

A: units of mdyn. Å^7 B: mdyn. Å C: Å^{-1}

C···C atom pairs; they are the values proposed by Williams[6] (Set I), Kitaigorodsky[7] (Set II), Bartell-Crowell[8] (Set III), and Dashevsky *et al.*[9] (Set IV). For O···O, the values given by Dashevsky *et al.*[9] were always used. The values of A, B, and C used in the calculations are summarized in Table 2. The values for the heteroatom pairs were taken as follows;

$$A_{ab} = \sqrt{A_{aa} \times A_{bb}},$$
$$B_{ab} = \sqrt{B_{aa} \times B_{bb}},$$
$$C_{ab} = (C_{aa} + C_{bb})/2$$

for a···b.

The crystal structures of 9,10-anthraquinone at 20.5, −12.5, −72, −112, and −170°C have been reported by Lonsdale *et al.*[1] Therefore, the calculations were made for the structures at these temperatures by taking account of all the interactions of interatomic distances shorter than 3.2, 3.5, 3.5, 3.6, 4.0, and 4.1 Å for H···H, H···O, H···C, O···C, O···O, and C···C respectively. These limits were selected for the following reasons: (1) For the distances over these limits, the force constants are generally very small, (2) the numbers of the atom pairs to be included are almost the same over the range from 20.5°C to −170°C, and (3) when the limits of interactions are extended to 4.5 Å, the number of the atom pairs to be included increases about twice, but the calculated frequencies and eigen vectors change only a little.

Table 3. Observed and calculated frequencies at 20.5°C (cm^{-1})

	Set I	Set II	Set III	Set IV	Obsd[a]
A_g	124	117	102	73	66
	88	72	71	52	52
	53	38	40	30	28
B_g	133	123	109	77	73
	104	94	86	62	58
	83	71	68	50	—

a) Interpolated values to 20.5°C from Table 1.

The frequencies of lattice vibrations calculated under the above restrictions are given in Table 3. It may be seen that the calculated frequencies with the potentials of Set IV agree reasonably with the observed Raman frequencies, while the potentials of the other sets give higher frequencies. In Table 4, the frequencies obtained with the potentials of Set IV and the atomic coordinates at various temperatures are listed, together with the approximate vibration modes for 20.5°C.

Discussion

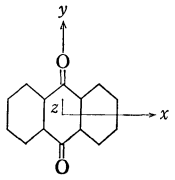
In the preceding section, we noted a great difference in the calculated frequencies between the potentials of Set I—III and Set IV. An inspection of the crystal structures shows that there exist interatomic pairs involving hydrogen atoms of short distances. Especially, we have a very short H···H distance of 2.2 Å, and found that the great difference in the calculated frequencies is mainly to be ascribed to the difference in the potentials of the H···H pair (and thereby of the H···C and H···O pairs) in the region of the short distances.

Beside the calculated lattice vibrational frequencies, their dependences upon the temperature provide a good check to see which potentials are more realistic. The observed and calculated frequency shifts of the indi-

Table 4. Calculated values with Set IV at various temperatures (cm^{-1})

	−170°C	−112°C	−72°C	−12.5°C	20.5°C	Approx. modes[a, b]		
A_g	85	81	81	78	73	61% R_x,	36% R_y,	3% R_z
	62	59	57	53	52	2% R_x,	21% R_y,	77% R_z
	36	34	33	31	30	37% R_x,	43% R_y,	20% R_z
B_g	90	86	85	82	77	39% R_x,	60% R_y,	1% R_z
	67	67	65	63	62	30% R_x,	11% R_y,	59% R_z
	54	54	52	50	50	31% R_x,	29% R_y,	40% R_z

a) R_x means rotational oscillation around x axis of molecule, and so on.
b) x, y, and z axes are chosen as follows;



6) D. E. Williams, *J. Chem. Phys.*, **45**, 3770 (1966).
7) A. Kitaigorodsky, *J. Chim. Phys.*, **63**, 9 (1966).
8) Cited by D. A. Oliver and S. H. Walmsley, *Mol. Phys.*, **17**, 617 (1969).
9) V. G. Dashevsky, V. T. Struchykov, and Z. A. Akoppayan, *Zhr. Struk. Khim.*, **7**, 594 (1966).

TABLE 5. FREQUENCY SHIFTS BETWEEN 20.5°C AND −170°C (cm^{-1})

	Set I	Set II	Set III	Set IV	Obsd
A_g	17	19	15	12	8
	16	16	14	10	9
	7	6	6	6	8
B_g	19	20	16	13	8
	8	9	7	5	5
	7	7	6	4	—

vidual lattice vibrations between 20.5 and −170°C are given in Table 5. It may be seen that the calculated shifts with Set IV are of the same order of magnitude as the observed ones, while the calculated shifts with the other sets give larger shifts. This difference was found again to be ascribable mainly to the difference in H···H potentials in the region of short distances.

The fact that both the lattice vibrational frequencies and their shifts induced by the temperature change are well reproduced with the potentials of Set IV seems to indicate the preferability of the H···H potential of Set IV over those of the other sets, especially in the region of short interatomic distances.