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The Low Temperature n-π^* Absorption Spectra of the Cyclohexane-1,4-dione Crystal

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Cyclohexane-1,4-dione is an aliphatic ketone with two carbonyl groups. The absorption due to the n-π^* transition of the carbonyl group extends from the 30000 cm^{-1} to the 42000 cm^{-1} region. The transition is symmetrically forbidden and is assigned to the A_1-A_2 transition in the C_{2v} system. The spectra in the crystal and in a solution of EPA at 77°K show only prominent carbonyl stretching vibrations. The polarized single crystal absorption spectra at 4.2°K are composed of many sharp lines; the vibrational structures are analyzed in detail. The 0-0 transition is observed at 31408 cm^{-1}; the distinct basic frequencies of the excited state are 1096, 790, 557, 375, 247, and 122 cm^{-1}, while the lattice vibrations are 61, 32, and 22 cm^{-1}. The transition is explained by the vibronic coupling mechanism, assuming the C_{2v} symmetry for the carbonyl group. Two different types of progressions are noticed; one is induced by the out-of-plane b_2-type vibration, while the other is allowed by the a_2-type vibration. The dichroic properties of the crystal spectra allowed the assignment of the vibrational modes. These vibrations are compared with the infrared and Raman spectral data.

There have been many experimental and theoretical studies of the n-π^* transitions of aliphatic and aromatic carbonyl compounds.[1] The first vibrational analysis of the spectra of formaldehyde was made by Herzberg,[2] who thus established the vibrational intervals for the carbonyl stretching frequency. Complete rotational analysis was made by Dieke and Kistiakowsky[3] on formaldehyde; they concluded that the n-π^* transition is polarized in plane and perpendicular to the carbonyl axis. Brand[4] and Robinson[5], by absorption and emission spectral measurements, determined that the configuration of formaldehyde in the singlet excited states is non-planar. Pople and Sidman[6] studied the mechanism of the vibronic coupling in formaldehyde and concluded that most of the intensities of the perpendicularly polarized bands arose from the mixing of the A_2 ($n\pi^*$) state with the $B_1(n\sigma^*)$ state by the perturbation of the b_2-type vibration. These result may be applicable to the interpretation of n-π^* transitions in more complex aliphatic aldehydes and ketones.

The asymmetric carbonyl compounds are known to show the optical rotatory dispersion in the n-π^* transition regions, and the octant rule has been found to hold for the complex carbonyl compounds.[7] Mason[8] discussed the optical activity of the carbonyl

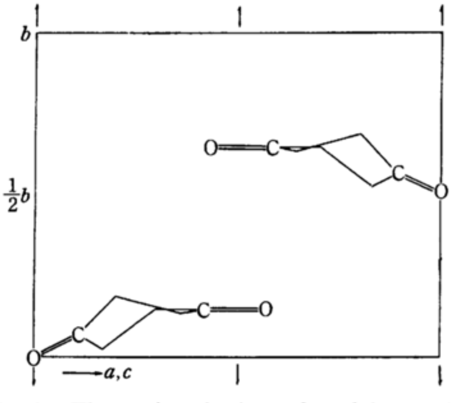

Fig. 1. The projected view of cyclohexane-1,4-dione on to the (10$\bar{1}$) plane according to the X-ray results. The absorption spectra were photographed through this plane. One carbonyl axis is nearly parallel to the [10$\bar{1}$] axis, while another is inclined to the b and [10$\bar{1}$] directions. The molecular C_2 axis is nearly perpendicular to both carbonyl groups.

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compounds and suggested that the parallel component to the carbonyl axis is important in any interpretation of the optical activity. The transition moment along the carbonyl axis may be produced by *a* vibronic coupling through the a_2-type vibration or by the other kinds of perturbations[9)]

In this paper the vibrational analysis of the spectra of aliphatic ketone at low temperatures will be presented with a view to elucidating the mechanism of the intensity gain. Cyclohexane-1,4-dione is a cyclic diketone, as is shown in Fig. 1. The polarized absorption spectra of this diketone at 4.2°K shows several vibrational progressions; the detailed analysis of these progressions gives unambiguous assignments for the vibrational modes and for the mechanism of the vibronic coupling. The vibrational frequencies for the excited states are compared with the infrared and Raman spectral data.

Experimental

The cyclohexane-1,4-dione was the product of Nakarai Chem., Ltd., Kyoto, Japan; it was recrystallized from an ethanol solution and was used immediately after preparation because the crystal is not stable at room temperature.

The spectrum of the solution in EPA at the temperature of liquid nitrogen was recorded on a Cary spectrophotometer model 15. Crystal absorption experiments at the temperatures of liquid nitrogen and liquid helium were carried out on a Shimadzu GE-100 spectrograph equipped with a Bausch & Lomb grating, as has been reported before.[10)] A standard Zeiss hydrogen lamp was employed as the radiation source. The smaple was mounted between two black paper masks, placed between quartz disks. The crystal axes were checked by a polarizing microscope and by the X-ray photographic method. The light incident upon the sample was a plane polarized by a rotable Glan-Thompson calcite polarizer; it was focussed with the appropriate lens system on the spectrograph slit. The exposure times ranged from 4 to 12 min with a slit width of 0.1 mm using Kodak 103a-0 photographic plates. Reference ion-arc spectra were photographed adjacent to each absorption spectrum. This molecule has the symmetry of C_2 in the crystal, but the two-fold axis is nearly perpendicular to the carbonyl axes. The carbon atoms attached to the carbonyl carbon are coplanar with the oxygen atom; the projection of molecules analyzed by Mossel and Romers[11)] and Groth and Hassel[12)] is shown in Fig. 1. Two carbonyl groups are separated by the saturated bonds; therefore, the chromophores are considered to be nearly independent of each other, although they are related by the symmetry operation. From a rigorous point of view, there should be an exciton interaction between the chromophores, however, no detectable effect can be found on the absorption spectra. Therefore, a treatment based on the independent system will be used in the following dissussion. The spectrum of the solution at 77°K is shown in Fig. 2. It shows several maxima, but the vibrational intervals are not so clear as those in the crystal spectrum. The crystal spectrum at 77°K shows several progressions of 1100 cm^{-1}; these may be assigned to the carbonyl stretching. However, no other vibrational modes can be detected clearly.

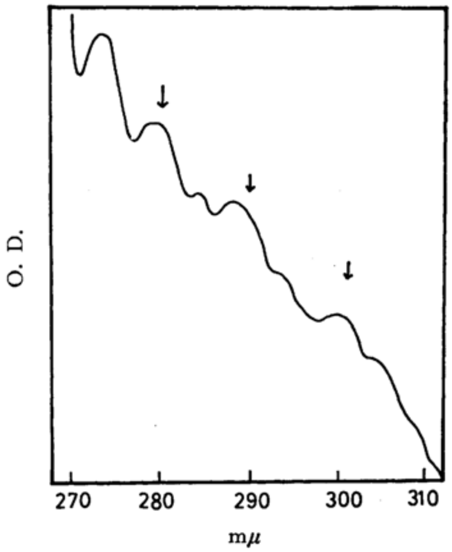

Fig. 2. The spectra of cyclohexane-1,4-dione in the E.P.A. solution at 77°K.
Ordinate: The optical density in arbitrary unit.
Abscissa: Wavelength in mμ.
The arrows indicate the position of the frequencies of the carbonyl stretching.

Vibrational Analysis of the 4.2°K Crystal Spectra

The single crystal spectra at the temperature of liquid helium are shown in Fig. 3 for the light polarized parallel and perpendicular to the *b* axis. At 4.2°K each vibrational envelope is composed of many sharp lines. No detectable splitting between the *b* and the [10$\bar{1}$] axis has been found; this supports the independent-system approach. Several characteristic fundamental vibrational frequencies have been observed along the *b* and the [10$\bar{1}$] axes; some of them are peculiar to the [10$\bar{1}$] axis. The spectrum starts with a sharp line at 31408 cm^{-1}; this line we assigned to the 0–0 transition for several reasons. No trace of any absorption to the red of this origin could be found in crystals up to 0.2 mm in thickness. The appearance of the weak 0–0 band and the subsequent strong vibrational bands are consistent with the vibrational progression built on a forbidden transition. Definite proof is given by the observation of the highest

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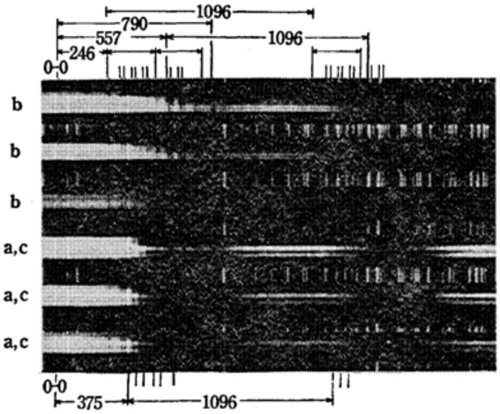

Fig. 3. The polarized absorption spectra at liquid-helium temperature showing the details of first and second band systems. Three different exposure times (12, 8 and 4 min) were used. The basic vibrations, which are common to both *b* and [10$\bar{1}$] axes spectra, are indicated on the top of the spectra. The vibration which is peculiar to the [10$\bar{1}$] axis spectrum is indicated in the bottom.

energy fluorescence band of the same origin, but no fluorescence has been observed with this compound. The frequencies, intensities, and assignments of the absorption bands are shown in Table 1. The carbonyl stretching progressions are observed up to the fourth level. Only the first member of each of the progressions is accompanied by many sharp lines, and the dichroic properties are clearly observed. The second member can be analyzed to some extent, but analysis is difficult for the higher members.

The important vibrational frequencies found along the [10$\bar{1}$] direction are 375 cm^{-1} and 1096^{-1}. The progression of 1096 cm^{-1}, which is common to the *b*-axis spectrum, can safely be regarded as the stretching mode of the carbonyl group because it is already established with other carbonyl compounds.$^{2)}$ The frequency is greatly reduced as compared with that of the ground state. If we suppose the local symmetry of the carbonyl group to be valid for the discusssion of the excited state of the present molecule, then the carbonyl stretching mode has a symmetry of a_1. It is reasonable

TABLE 1. ABSORPTION BANDS OF CYCLOHEXANE-1,4-DIONE CRYSTAL AT 4.2°K

Frequency cm^{-1}	$\Delta\nu$ cm^{-1}	Intensity	Assignment	Frequency cm^{-1}	$\Delta\nu$ cm^{-1}	Intensity	Assignment
31408		w	0-0	32494	1086	m	
31654	246	m	+247	32518	1110	vw	
31718	310	s	+247+61	32548	1134	vw	
31741	333	s	+247+61+24	32578	1170	vw	
31782	374	vs, w	+375	32596	1188	vw	
31795	387	w		32639	1231	vw	
31815	407	vs*, w	+375+32	32664	1256	w	
31842	434	w*, vw	+375+32×2	32681	1273	vw	
31866	458	vw		32705	1293	w	
31904	496	vs*, s	+375+122	32743	1335	m	
31937	529	s*, vw	+375+122+32	32774	1366	w	+1096+247+23
31965	557	vs	+557	32815	1407	vw	+1096+247+61
31986	578	s	+557+21	32840	1432	s	+1096+247+61+24
31997	589	w		32880	1472	m	+1096+375
32025	617	vs	+557+61	32901	1493	m	+1096+375+32
32045	637	vs	+557+61×2+20	32922	1514	m	
32069	661	m		32946	1538	s	+1096+375+32×2
32103	694	vs	+(694)	32965	1557	m	
32123	715	s	+(694)+21	32996	1588	w	
32141	733	s		33019	1611	w	
32149	741	s	+(741)	33043	1635	w	
32168	760	vw	+(741)+19	33080	1672	vs	+1096+557+21
32198	790	vs	+790	33134	1726	vs	+1096+557+61+21
32222	814	vw	+790+24	33163	1755	m	
32254	846	s	+790+61	33193	1785	vs	+1096+(694)
32288	880	m		33246	1838	w	+1096+(741)
32332	924	w		33266	1856	m	
32347	939	vw		33282	1874	m	
32407	999	m		33300	1892	m	+1096+790
32432	1024	m					

Intensity designations are: s, strong; m, medium; w, weak; vw, very weak.
When two intensity designations are written *a*, *c* axis absorptions are marked by *.

that this frequency is often coupled with other type of vibrations.

From the arrangement of the molecule in a unit cell shown in Fig. 1, the symmetry properties of the vibronic state can be discussed. The component parallel to the carbonyl axis (A_1 type) can be strongly observed, particularly along the $[10\bar{1}]$ direction. In order for us to find the symmetry-forbidden n-π^* state (A_2 state) along the carbonyl axis, the vibronic coupling with the a_2-type vibration should be operative. The observed band at 0–0+375 cm^{-1} is thus shown to correspond to the vibronically-a_2-coupled state. This band is only weakly observed in the b-axis direction. For the molecule having an exact C_{2v} symmetry, the a_2-type vibration is not effective for the vibronic intensity borrowing. For molecules of a lower symmetry such as this diketone, the strict geometry of the C_{2v} system does not hold; the a_2-type torsion will induce the electronic transitions vibronically. The band progression starting at 31782 cm^{-1} should, therefore, be assigned to the component parallel to the carbonyl axis, which is itself produced by the coupling with the a_2-type torsional mode. The lattice vibration of 30 cm^{-1} is found only along the $[10\bar{1}]$ direction.

It is noteworthy that no important progressions have been found which are observed only along the b axis. In a previous paper the out-of-plane component of the n-π^* transition was rejected on the grounds of the measurement of several crystals.[9)]

It has been confirmed again in the present research that no particular b_1-type vibration is associated with the induction of the B_2 excited state, which is active in the out-of-plane of the carbonyl group. The transitions polarized parallel to the other directions, in the plane and perpendicular to the carbonyl axis, will be found along both the b and the $[10\bar{1}]$ directions. The vibrations of 247, 557, and 790 cm^{-1} are regarded as b_2-type vibrations, which will mix the B_1 excited level with the forbidden A_2 n-π^* state. The small spacings of 60 cm^{-1} and the doublet structure of 20 cm^{-1} may be assigned to the lattice vibration. It is remarkable that the 60 cm^{-1} and 20 cm^{-1} intervals are associated with the 247, 557, and 790 cm^{-1} vibronic states.

The infrared and Raman spectra of this molecule in the crystalline state show the corresponding frequencies of 60, 122, 247, 375, 557, and 790 cm^{-1}. These frequencies are compared with the present values for the excited state in Table 2. It is noticeable that the frequencies assigned to the excited state nearly coincide with the values given for the ground state except for the carbonyl stretching mode.

TABLE 2. COMPARISON OF VIBRATIONAL FREQUENCIES

Frequencies of the ground state		Frequencies of the excited state by electronic spectra (cm^{-1})
Infrared (cm^{-1})	Raman (cm^{-1})	
		20(m)
54(s)		60(m)
114(s)		122(w)
160(s)	179(m)	
238(s)	236(s)	247(m)
365(m)	360(m)	375(s)
413(m)		
435(s)	431(m)	
507(m)		
522(m)		
560(s)	543(s)	557(s)
589(m)	573(m)	
	600(w)	
805(vs)	746(vs)	790(s)
	824(w)	
873(m)	903(w)	
	920(w)	
943(s)		
965(vs)	975(w)	
	1023(w)	
1064(s)	1074(m)	
1090(s)		
1144(vs)		
1163(m)	1172(w)	
1271(s)	1247(w)	
1312(s)	1324(m)	
1326(m)	1324(m)	
1342(m)		
1404(s)	1430(s)	
	1528(w)	
	1562(w)	
1598(m)	1591(w)	
1705(vs)	1720(vs)	1097(vs)
	1757(w)	

Intensity designations are: s, strong; m, medium; w, weak; vw, very weak.

The quantitative estimate of the intensity of the component of the a_2-type induced A_1-excited state is rather difficult because of the complexity of the spectra, but an approximate value would be about 20% of the total n-π^* transition intensities. The result is very closely connected with the theory of the optical activity. A theoretical discussion of the mechanism of the intensity gain will be presented in a separate paper.

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