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Polarized Raman Spectrum of Maleic Anhydride Crystal

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The polarized Raman spectrum of the maleic anhydride single crystal was studied. Prominent polarization behavior of the Raman bands was observed. Assuming the oriented gas model, the relative intensities of the non-totally symmetric intramolecular vibrations in various polarized Raman spectra were studied based on the data of the crystal structure. The assignments of the fundamental vibrational frequencies for maleic anhydride were reinvestigated through the polarization behavior of the Raman bands as well as the normal coordinate calculation.

The infrared and Raman spectra of maleic anhydride were first studied by Mirone and Chiorboli.[1] Most of their assignments were confirmed by the study of the polarized infrared spectrum of the single crystal observed by Di Lauro *et al.*[2] They also carried out the normal coordinate analysis for the in-plane vibrations.[2] Rogstad *et al.*[3] reexamined the vibrational analyses made by earlier workers on the basis of the band contours of the infrared vapor spectrum as well as the isotopic product and sum rules for deuterated molecules.

In this work, the fundamental vibrational assignments are reinvestigated based on the study of the polarized Raman spectrum of the single crystal of maleic anhydride as well as the normal coordinate analyses for in-plane and out-of-plane vibrations.

Experimental

Material. Maleic anhydride obtained from Nakarai Chemicals, Ltd. was purified by zone-refining of about 60 passages followed by sublimation under reduced pressure.

Optical Measurement. The polarized Raman spectrum of maleic anhydride was observed in the single crystal with a JEOL 400T Laser Raman Spectrophotometer. The sample was excited with the 514.5 nm line from an Ar^+ ion laser of Toshiba Model LAI-104-A.

Single crystals were grown in a closed tube by sublimation. Cubic crystals, about $(3\ \mathrm{mm})^3$, were obtained. A well-grown single crystal was selected and the crystal axes were determined by the observation of the birefringence under a polarization microscope. The direction of the crystal growth was selected as the c axis and the two-fold axis of the crystal as the b axis.

The crystal sample was excited with the laser beam polarized along the y axis in the z direction and the Raman scattering was observed in the x direction. The two polarized components of the scattering were analyzed by a polarizer inserted between the sample and the condenser lens. A compensator was placed between the condenser lens and the entrance slit in order to compensate the preferential sensitivity of the spectrophotometer for the light beams polarized along the y and z axes. The crystal was placed in the sample holder equipped with a goniometer in such a way that the crystal axes a, b, and c were parallel to the space-fixed axes x, y, and z. Thus, there are six ways of orientation of the crystal cube and a pair of polarized spectra are observed by the use of the polarizer for each orientation.

Twelve polarized Raman spectra were measured in total. The polarized Raman spectrum was denoted with four symbols following the notation adopted by Porto *et al.*,[4] such as a(ba)c. The letters inside the parentheses refer to the polarization directions of the excitation and scattering light beams in order, and the first and last letters refer to the propagation directions of the excitation and scattering light beams, respectively.

Depolarization measurements of the Raman spectrum were also made in the molten phase.

Calculation of Derived Polarizability Tensors

The crystal structure of maleic anhydride has been determined by Marsh *et al.*[5] Maleic anhydride crystallizes in the orthorhombic system of the space group D_2^4 with four molecules in the unit cell. The projection of the crystal structure on the ab plane is shown in Fig. 1. The correlation among the molecular point group C_{2v}, the factor group D_2, and the site group C_1 of the crystal is given in Table 1. No factor group splitting was observed for the bands due to the molecular vibrations. Thus, the relationship between the two derived polarizability tensors, for the free molecule and the crystal, was derived based on the sim-

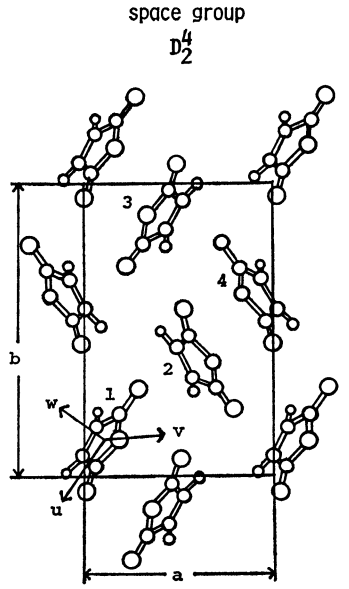

Fig. 1. Projection of the maleic anhydride crystal on the ab plane.

Table 1. Correlation diagram for maleic anhydride crystal

	Molecular group C_{2v}	Site group C_1	Factor group D_2
a_1	α_{uu}, α_{vv}, α_{ww}	a	a
a_2	α_{uv}		b_1
b_1	α_{uw}		b_2
b_2	α_{vw}		b_3

plified oriented gas model.

The evaluation of the matrix elements of the derived polarizability tensors of maleic anhydride was made following the procedures applied for naphthalene and anthracene crystals by Ito *et al.*[6] If the transformation matrix between the molecular-fixed coordinates u, v, w and the crystal fixed a, b, c is expressed by

$$T_1 = \begin{vmatrix} a_u & a_v & a_w \\ b_u & b_v & b_w \\ c_u & c_v & c_w \end{vmatrix}$$

for molecule 1, then the matrices for molecules 2, 3, and 4 are given for the D_2^4 crystal by

$$T_2 = \begin{vmatrix} -a_u & -a_v & -a_w \\ -b_u & -b_v & -b_w \\ c_u & c_v & c_w \end{vmatrix}, \quad T_3 = \begin{vmatrix} -a_u & -a_v & -a_w \\ b_u & b_v & b_w \\ -c_u & -c_v & -c_w \end{vmatrix},$$

and

$$T_4 = \begin{vmatrix} a_u & a_v & a_w \\ -b_u & -b_v & -b_w \\ -c_u & -c_v & -c_w \end{vmatrix},$$

respectively, where a_u is the direction cosine of the a and u axes, and so on. The derived polarizability tensor of a free molecule with respect to a normal vibration Q is given by

$$\alpha'_m(Q) = \begin{vmatrix} \alpha'_{uu} & \alpha'_{uv} & \alpha'_{uw} \\ \alpha'_{vu} & \alpha'_{vv} & \alpha'_{vw} \\ \alpha'_{wu} & \alpha'_{wv} & \alpha'_{ww} \end{vmatrix},$$

where $\alpha'_{uu} = \partial\alpha_{uu}/\partial Q$, and so on. The molecular tensors with respect to the crystal-fixed coordinates are given by

$$\alpha'_{m_1} = T_1 \alpha'_m \tilde{T}_1$$

for molecule 1, and

$$\alpha'_{m_2} = T_2 \alpha'_m \tilde{T}_2$$

for molecule 2, and so on. Under the assumption of the oriented gas model, the polarizability tensor of the unit cell, α_u, is assumed to be

$$\alpha_u = \alpha'_{m_1} Q_1 + \alpha'_{m_2} Q_2 + \alpha'_{m_3} Q_3 + \alpha'_{m_4} Q_4.$$

Using the symmetry coordinates S_{A_1}, S_{B_1}, S_{B_2}, and S_{B_3} appropriate to the four molecule unit cell, the derived polarizability tensors with respect to the unit cell vibrations are given for each symmetry species by

$$\alpha'_u(S_{A_1}) = \begin{vmatrix} A_{aa} & 0 & 0 \\ 0 & A_{bb} & 0 \\ 0 & 0 & A_{cc} \end{vmatrix} \quad \alpha'_u(S_{B_1}) = \begin{vmatrix} 0 & A_{ab} & 0 \\ A_{ba} & 0 & 0 \\ 0 & 0 & 0 \end{vmatrix}$$

$$\alpha'_u(S_{B_2}) = \begin{vmatrix} 0 & 0 & A_{ac} \\ 0 & 0 & 0 \\ A_{ca} & 0 & 0 \end{vmatrix} \quad \alpha'_u(S_{B_3}) = \begin{vmatrix} 0 & 0 & 0 \\ 0 & 0 & A_{bc} \\ 0 & A_{cb} & 0 \end{vmatrix},$$

where the A's are the functions of the direction cosines and of the elements of the derived polarizability tensor of the free molecule.

According to the character table and selection rules for the C_{2v} molecule, we derived simple analytical expressions of A's for the vibrations belonging to the different species of the molecule. These results are given in Table 2.

Table 2. Elements of the derived polarizability tensors of maleic anhydride

	b_1	b_2
A_{aa}	$2a_u a_w \alpha'_{uw}$	$2a_v a_w \alpha'_{vw}$
A_{bb}	$2b_u b_w \alpha'_{uw}$	$2b_v b_w \alpha'_{vw}$
A_{cc}	$2c_u c_w \alpha'_{uw}$	$2c_v c_w \alpha'_{vw}$
A_{ab}	$(a_u b_w + a_w b_u)\alpha'_{uw}$	$(a_v b_w + a_w b_v)\alpha'_{vw}$
A_{ac}	$(a_u c_w + a_w c_u)\alpha'_{uw}$	$(a_v c_w + a_w c_v)\alpha'_{vw}$
A_{bc}	$(b_u c_w + b_w c_u)\alpha'_{uw}$	$(b_v c_w + b_w c_v)\alpha'_{vw}$

	a_2	a_1
A_{aa}	$2a_u a_v \alpha'_{uv}$	$a_u^2 \alpha'_{uu} + a_v^2 \alpha'_{vv} + a_w^2 \alpha'_{ww}$
A_{bb}	$2b_u b_v \alpha'_{uv}$	$b_u^2 \alpha'_{uu} + b_v^2 \alpha'_{vv} + b_w^2 \alpha'_{ww}$
A_{cc}	$2c_u c_v \alpha'_{uv}$	$c_u^2 \alpha'_{uu} + c_v^2 \alpha'_{vv} + c_w^2 \alpha'_{ww}$
A_{ab}	$(a_u b_v + a_v b_u)\alpha'_{uv}$	$a_u b_u \alpha'_{uu} + a_v b_v \alpha'_{vv} + a_w b_w \alpha'_{ww}$
A_{ac}	$(a_u c_v + a_v c_u)\alpha'_{uv}$	$a_u c_u \alpha'_{uu} + a_v c_v \alpha'_{vv} + a_w c_w \alpha'_{ww}$
A_{bc}	$(b_u c_v + b_v c_u)\alpha'_{uv}$	$b_u c_u \alpha'_{uu} + b_v c_v \alpha'_{vv} + b_w c_w \alpha'_{ww}$

Normal Coordinate Calculation

A normal coordinate calculation was performed through the standard ***GF*** matrix method with a Facom M-200 computer at the computer center of Kyushu University. Heiderbrandt *et al.*[7] showed that the maleic anhydride molecule is planar and gave geometric parameters for this molecular structure. We used their geometric parameters for the construction of the ***G*** matrix elements.

The ***F*** matrix elements for the in-plane vibrations were evaluated with the potential field of an improved modification of the Urey-Bradley force field as described in the previous paper.[8] The potential field is given by

$$\begin{aligned} 2V = 2V_{UB} &+ \sum k^o(\Delta r, \Delta r) \\ &+ \sum k^m(\Delta r, \Delta r) + \sum k^m(\Delta R, \Delta R) \\ &+ \sum h^m(\Delta R, \Delta\alpha) + \sum h^m(\Delta R, \Delta\beta) \\ &+ \sum f^o(\Delta\alpha, \Delta\alpha) + \sum f^o(\Delta\beta, \Delta\beta), \end{aligned}$$

where V_{UB} is the basic Urey-Bradley force field, and k, h, and f are due to the valence force field. k^o and k^m are the interaction terms between two stretching coordinates oriented in the ortho and meta positions to each other, respectively, h^m is the interaction term between stretching and bending coordinates oriented in the meta position, and f^o is the interaction term between two bending coordinates oriented in the ortho position. R and α refer to the bond distances and angles constructing the ring, and r and β to the bond distances and angles relating to the C=O and C–H side bonds, respectively.

For the out-of-plane vibrations, the valence force field and ϕ-type torsional coordinates were used. The notations of the force constants Q, q, P, p, and t are the same as those given by Whiffen.[9] The procedure of the calculation was exactly the same as described in the previous paper.[8]

TABLE 3. FORCE CONSTANTS FOR IN-PLANE VIBRATIONS OF MALEIC ANHYDRIDE

$K_{C'=C'}$ [a]	8.34	$F_{C'\cdots H}$	0.53
$K_{C'-C}$	3.67	$F_{C\cdots H}$	0.25
K_{C-O}	2.60	$F_{C'\cdots O}$	0.30
$K_{C'-H}$	4.82	$F_{O\cdots O}$	0.84
$K_{C=O}$	10.46	$k^{o}_{r_H,r_H}$	0.02
$H_{C'-C'-C}$	0.28	$k^{o}_{r_H,r_O}$	0.02
$H_{C'-C-O}$	0.49	$k^{m}_{r_O,r_O}$	0.06
H_{C-O-C}	0.50	$k^{m}_{R,R}$	−0.02
$H_{C'-C'-H}$	0.20	h^{m}_{R,α_O}	0.03
$H_{C-C'-H}$	0.08	h^{m}_{R,α_C}	0.01
$H_{C'-C-O}$	0.28	h^{m}_{R,β_O}	−0.02
H_{O-C-O}	0.66	h^{m}_{R,β_H}	−0.03
$F_{C\cdots C'}$	0.60	$f^{o}_{\alpha,\alpha}$	0.03
$F_{C'\cdots O}$	0.70	$f^{o}_{\beta_H,\beta_O}$	0.03
$F_{C\cdots C}$	0.96	$f^{o}_{\beta_H,\beta_H}$	0.06

Force constants denoted by K, H, F, and k are given in J/dm^2 (=mdyn/Å) units, and those denoted by h and f are in pJ/dm·rad (=mdyn/rad) and aJ/rad^2 (=mdyn·Å/rad^2) units, respectively. a) C′ is a carbon atom bonded to H.

Results and Discussion

The force constants finally obtained after several iterative calculations for the in-plane and out-of-plane vibrations of maleic anhydride are given in Tables 3 and 4, respectively. The calculated frequencies and modes are given in Table 5, together with the experimental results.

The direction cosines were calculated using the X-ray diffraction data given by Marsh *et al.*[5] and the matrix elements of the derived polarizability tensors given in Table 2 were evaluated. The squares of the calculated elements of the derived polarizability tensors, which are proportional to the Raman intensities, are given in Table 6 for the non-totally symmetric vibrations. In this calculation, the values of α'_{uw}, α'_{vw}, and α'_{uv} are taken to be 1.

TABLE 4. FORCE CONSTANTS FOR OUT-OF-PLANE VIBRATIONS OF MALEIC ANHYDRIDE (in aJ/rad^2=mdyn·Å/rad^2)

$Q_{C=C}$	0.35	$p^{o}_{H,H}$	0.045
Q_{C-C}	0.30	$p^{o}_{H,O}$	0.02
Q_{C-O}	0.42	$p^{m}_{O,O}$	0.01
$q^{o}_{C=C,C-C}$	−0.05	$p^{m}_{H,O}$	0.02
$q^{o}_{C-C,C-O}$	−0.02	$t^{o}_{C=C,H}$	−0.14
$q^{o}_{C-O,C-O}$	−0.03	$t^{o}_{C-O,O}$	−0.14
q^{m}	0.02	$t^{o}_{C-C,O}$	−0.14
P_H	0.39	$t^{o}_{C-C,H}$	−0.10
P_O	0.30		

TABLE 5. FUNDAMENTAL VIBRATIONS OF MALEIC ANHYDRIDE

Sym. species	Vibrational mode	Raman				Infrared		Calcd	Obsd
		Liquid			Crystal	Crystal[a]	Vapor[b]		Rogstad et al.
		$\bar{\nu}$/cm^{-1}	Int.	Pol.	Pol.	Pol.	Type	$\bar{\nu}$/cm^{-1}	$\bar{\nu}$/cm^{-1}
a$_1$	ν_1 C-H str.	3124	m	p		//		3124	3117
	ν_2 C=O str.	1843	vs	p		//	B	1851	1852
	ν_3 C=C str.	1592	vs	p		//	B	1591	1592
	ν_4 C-O str.	1240	m	p		//		1236	1235
	ν_5 C-H bend.	1056	s	p		//		1054	1060
	ν_6 C-C str.	870	s	p		//		876	864
	ν_7 ring def.	638	vs	p		//[c]		641	632
	ν_8 C=O bend.	409	m	p		//		408	403
b$_2$	ν_9 C-H str.					⊥	A	3120	3117
	ν_{10} C=O str.	1785	m	dp	bc	⊥	A	1774	1782
	ν_{11} C-C str.	1306	w	dp	bc	⊥		1309	1054
	ν_{12} C-H bend.	1065	m		bc	⊥		1070	1305
	ν_{13} C-O str.	890	vw		bc	⊥	A	897	889
	ν_{14} ring def.	700	w	dp	bc	⊥	A	696	697
	ν_{15} C=O bend.	564	w	dp	bc	⊥	A	574	557
a$_2$	ν_{16} H wag.	766	m	dp	bb, aa			771	959
	ν_{17} ring def.	548	w	dp	bb, aa			544	768
	ν_{18} C=O wag.	269	s	dp	bb, aa			271	275
b$_1$	ν_{19} H wag.	838	vw		cc, aa	⊥	C	840	839
	ν_{20} ring def.	632	m		cc, aa	⊥		631	642
	ν_{21} C=O wag.	188	vw		cc, aa			190	173

a) Observed by Di Lauro *et al.* b) Observed by Rogstad *et al.* c) Observed in this work.

Table 6. Squared values of the elements of the derived polarizability tensors for maleic anhydride

	b_1	b_2	a_2
$(A_{aa})^2$	0.50	0.15	0.45
$(A_{bb})^2$	0.	0.	0.75
$(A_{cc})^2$	0.55	0.20	0.05
$(A_{ab})^2$	0.05	0.15	0.20
$(A_{ac})^2$	0.30	0.10	0.15
$(A_{bc})^2$	0.20	0.60	0.05

It is well known that all Raman bands belonging to one and the same symmetric species, except for the totally symmetric species, show the same polarization behavior in the various different polarized Raman spectra. Thus, the non-totally symmetric Raman bands were clearly classified into the specific symmetry species through the observation of the polarization behavior of the Raman bands. It is expected from Table 6 that the b_1 vibrations appear strongly in the (cc) and (aa) spectra, the b_2 vibrations in the (bc) spectrum, and the a_2 vibrations in the (bb) and (aa) spectra.

The six polarized Raman spectra observed in the different orientations of the single crystal are shown in Fig. 2. The vibrational frequencies observed in the crystal agreed well with the frequencies observed in the liquid.

a_1 Species. The totally symmetric vibrations were straightforwardly identified by depolarization measurements of the Raman bands observed in the molten state. The assignments given for the totally symmetric vibrations were the same as those given by earlier workers,[2,3] except for the C=O stretching (ν_1), C–H bending (ν_5), and ring deformation (ν_7) vibrations. The strong and polarized Raman bands observed at 1848, 1069, and 638 cm^{-1} in the molten state split into doublets, 1856 and 1843, 1065 and 1056, and 638 and 632 cm^{-1}, respectively, in the solid and single crystal. The 1843, 1056, and 638 cm^{-1} bands are stronger in intensity than the other components of the doublets, and do not show the polarization behavior characteristic to the non-totally symmetric species. Therefore, these bands were assigned to ν_2, ν_5, and ν_7 vibrations, respectively, although earlier workers have assigned the weaker components of the doublets, 1856, 1065, and 632 cm^{-1} to ν_2, ν_5, and ν_7 vibrations, respectively. As discussed later, the 1065 and 632 cm^{-1} bands should be assigned to the b_2 and b_1 vibrations, respectively, because of the polarization behavior of the Raman bands. The 1856 cm^{-1} band does not show polarization character of the non-totally symmetric vibrations, and thus, this band was assigned to the combination band of $\nu_{11}+\nu_{15}$ of the a_1 species.

b_1 Species. The non-totally symmetric Raman bands observed in the polarized Raman spectrum were divided into three types according to their relative intensities. The Raman bands of the first type, observed at 838, 632, and 188 cm^{-1}, are characterized by stronger intensity in the (cc) and (aa) spectra

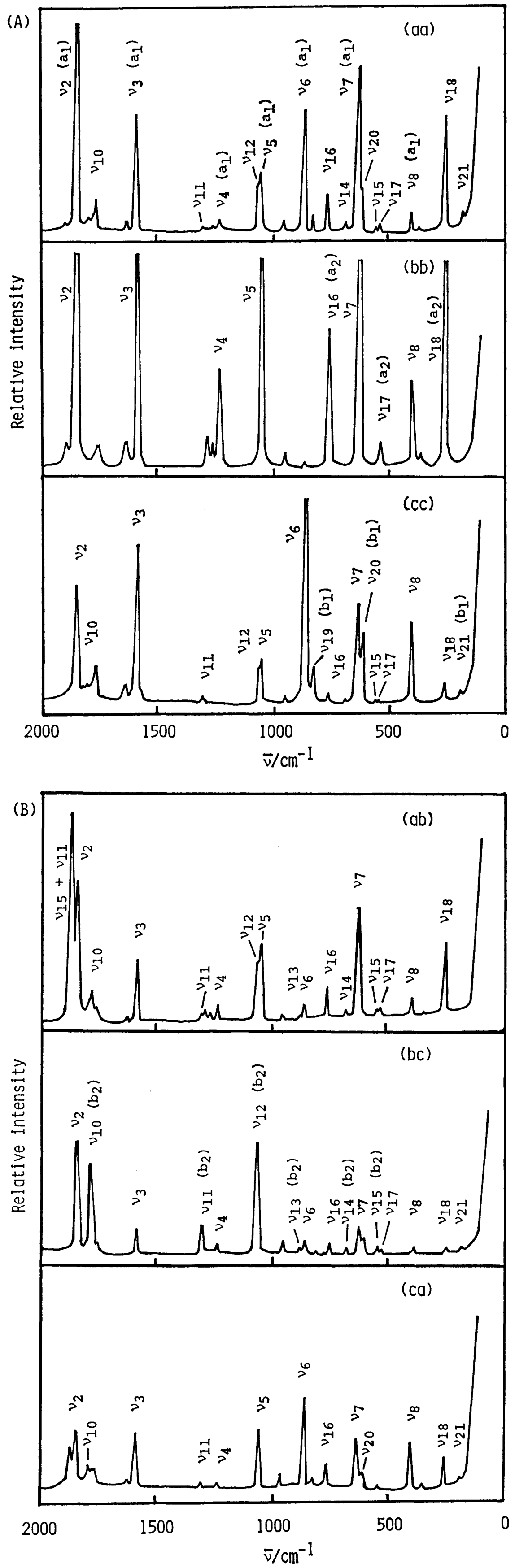

Fig. 2. Polarized Raman spectrum of the maleic anhydride crystal.

(A): (aa), (bb), and (cc) spectra, (B): (ab), (bc), and (ca) spectra.

TABLE 7. VIBRATIONAL ANALYSIS OF THE RAMAN SPECTRUM OF MALEIC ANHYDRIDE

Liquid (60 °C)			Solid		Crystal		Assignment
$\tilde{\nu}$/cm^{-1}	Int.	Pol.	$\tilde{\nu}$/cm^{-1}	Int.	$\tilde{\nu}$/cm^{-1}	Pol.	
			28	vs	28	aa, bb	lattice
			43	sh	43	bc	lattice
			52	vs	52	aa, bb	lattice
			65	vs	65	ab	lattice
			95	sh	95	cc, aa	lattice
			115	sh	115	ac	lattice
			188	vw	188	cc, aa	ν_{21}
270	s	dp	269	s	269	bb, aa	ν_{18}
			371	vw	371	bb, aa	$\nu_7-\nu_{18}$
408	m	p	409	m	409	bb, cc	ν_8
548	w	dp	548	w	548	bb, aa	ν_{17}
564	w	dp	564	w	564	bc	ν_{15}
638	vs	p	632	m	632	cc, aa	ν_{20}
			638	vs	638	bb, aa	ν_7
698	w	dp	700	w	700	bc	ν_{14}
770	m	dp	766	m	766	bb, aa	ν_{16}
			818	vw			$2\times\nu_8$
			838	w	838	cc, aa	ν_{19}
870	s	p	870	s	870	cc, aa, ca	ν_6
			890	vw	890	bc	ν_{13}
956	w	dp	955	w	956	bb, aa	$\nu_8+\nu_{17}$
1069	s	p	1056	s	1056	bb	ν_5
			1065	m	1065	bc	ν_{12}
1237	m	p	1240	m	1240	bb	ν_4
1267	w	p	1267	w	1267	bb	$\nu_8+\nu_6$
1285	w	p	1285	w	1285	bb	$2\times\nu_7$
1310	w	dp	1306	w	1306	bc	ν_{11}
			1567	w	1567	bb, cc	
1591	vs	p	1592	vs	1592	bb	ν_3
1624	m	p	1624	w	1624	bb, cc	$\nu_{15}+\nu_{12}$
1628	w	p	1632	w	1632	bb, cc	$\nu_4+\nu_8$
1737	w		1737	w	1737	bb	$2\times\nu_6$
1748	w		1748	sh	1748	aa, cc	
1754	sh	dp	1753	m	1754	bc	$\nu_5+\nu_{14}$
					1762	bb	$\nu_{14}+\nu_{12}$
1780	m	dp	1785	m	1785	bc	ν_{10}
			1802	vw	1800	bc	$\nu_{15}+\nu_4$
1848	vs	p	1843	vs	1843	bb, aa	ν_2
			1856	m	1856	ab	$\nu_{15}+\nu_{11}$
			1875	vw	1875	bb	$\nu_4+\nu_7$
			1932	vw			
			2110	vw			$2\times\nu_5$
			2118	vw			$\nu_5+\nu_{12}$
			2124	m			$2\times\nu_{12}$
3121	m	p	3124	m	3124	bb, aa	ν_1
			3132	m	3132	cc, bb, bc	$\nu_2+2\times\nu_7$
3180	w	p	3184	w			$2\times\nu_3$

compared with the intensity in the other polarized spectra. The 838, 632, and 188 cm^{-1} bands were observed with weak intensity in the (ca) spectrum and with very weak intensity in the (bc) spectrum, and were hardly detectable in the (bb) and (ab) spectra. The polarization behavior of these bands is consistent with b_1 vibrations according to Table 6. Therefore, these Raman bands were assigned to ring deformation (ν_{19}), H wagging (ν_{20}), and C=O wagging (ν_{21}) vibrations of the b_1 species, respectively.

a_2 Species. The Raman bands of the second type are those appearing strongly in the (bb) and (aa) spectra. A strong Raman band observed at 269 cm^{-1}, a medium intense band at 766 cm^{-1}, and a weak band at 548 cm^{-1} belong to this type. These Raman bands decrease their intensities in the order

of the (bb)>(aa)>(ab)>(ac)>(cc)>(bc) spectra, as can be seen in Fig. 2. Table 6 indicates that these bands should definitely be assigned to the a_2 bands. Therefore, these bands were to be assigned to C=O wagging (ν_{18}), H wagging (ν_{16}), and ring deformation (ν_{17}) vibrations of the a_2 species, respectively. Although Rogstad *et al.* have assigned a Raman band observed at 959 cm^{-1} to the ν_{16} vibration, which shows the a_2 polarization character, we assigned this band to the combination band of $\nu_8+\nu_{17}$, based on the weak intensity of this band as well as the normal coordinate calculation.

b_2 Species. The Raman bands of the third type are characterized by stronger intensity in the (bc) spectrum compared with the intensity in the other spectra. Medium intense bands observed at 1785 and 1065 cm^{-1}, a weak band at 1306 cm^{-1}, and very weak bands at 890, 700, and 564 cm^{-1} belong to this type, as can be seen in Fig. 2. According to Table 6, the Raman bands appearing strongly only in the (bc) spectrum should be assigned to the b_2 bands. Thus, these bands were assigned to the C=O stretching (ν_{10}), C–H bending (ν_{12}), C–C stretching (ν_{11}), C–O stretching (ν_{13}), ring deformation (ν_{14}), and C=O bending (ν_{15}) vibrations of the b_2 species, respectively. Polarization behavior of these bands in the various polarized Raman spectra is consistent with the predicted ones except for ν_{10} and ν_{14} vibrations. Although the vibrations belonging to the b_2 species are expected to appear with about equal intensity in the (aa), (cc), (ab), and (ac) spectra according to Table 6, the intensity of the ν_{10} Raman band is weaker in the (aa) and (cc) spectra compared with that in the (ab) and (ac) spectra. The intensity of ν_{14} Raman band is expected to be strongest in intensity in the (bc) spectrum, but this is not the case in our spectrum. One of the reasons for these discrepancies is considered to be that the oriented gas model is not quite suitable for the prediction of the intensity of the off-diagonal spectra, such as (ab) and (ac), as discussed by Ito *et al.*[6]

The detailed vibrational analysis of the polarized Raman spectrum is given in Table 7.

The assignments given for the fundamental bands based on the polarized Raman spectra are consistent with the polarization behavior and band envelope of the infrared spectrum observed in the crystal and vapor phases, respectively. The agreement between the observed and calculated frequencies is satisfactory.

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