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Raman Polarizability for Some Totally Symmetric Normal Vibrations of Naphthalene and Maleic Anhydride

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The values of the Raman polarizability of some totally symmetric normal vibrations of naphthalene and maleic anhydride were estimated from the analysis of the polarized Raman spectra observed in single crystal. For the totally symmetric ring vibrations of naphthalene the principal elements of the Raman polarizability in the molecular plane are about isotropic and the principal element perpendicular to the molecular plane has the value almost one-half of the values of the in-plane elements. For the totally symmetric C=O and C=C stretching vibrations of maleic anhydride the Raman polarizability shows quite anisotropic character.

The polarizability is one of the important molecular constants and provides the information about the dynamic behavior of the electronic charge in a molecule. The Raman polarizability, which is related to the intensity of the Raman band, corresponds to the variation of the polarizability due to molecular vibrations.

Experimental determination of the values of the principal elements of the Raman polarizability has been made by various workers[1—4] through the observation of the degree of depolarization of the rotational Raman bands for small linear and symmetric (or nearly symmetric) top molecules in gas phase. The principal elements of the Raman polarizability of these molecules can be definitely determined from the degree of depolarization because of the symmetry of the molecular vibrations. However, the measurement of the degree of depolarization for large polyatomic molecules in gas phase was very difficult. This difficulty was overcome by Ebata et al.[5] recently using high sensitive observation of the stimulated Raman pumping and mass-selected resonance enhanced multiphoton ionization double resonance spectroscopy. They measured the degree of depolarization of the ν_1 Raman band of jet-cooled benzene and determined the relative values of the principal elements of the Raman polarizability.

Three approaches to the calculation of the polarizability have been made by Hudis and Ditchfield,[6] Sadlej,[7] and Helgaker and Almlöf.[8] Very recently Darling and Schlegel[9] used a new method combining these three approaches and obtained strikingly good results for the calculation of the polarizability of small molecules such as H_2 and C_2H_4.

The polarized Raman spectrum in single crystal has been used for the assignment of the non-totally symmetric normal vibrations of molecules.[10—12] In this work the polarized Raman spectrum is used for the determination of the relative values of the principal elements of the Raman polarizability of some totally symmetric vibrations of naphthalene and maleic anhydride, and the relation between the Raman polarizability and the mode of molecular vibration is studied. Well-grown single crystals can be easily obtained and the modes of normal vibrations were explicitly determined for naphthalene and maleic anhydride. In naphthalene the normal vibrations are delocalized whole over the molecule[10] and thus the molecular vibrations cause swing of the electronic charge over the molecule, while the normal vibrations in maleic anhydride are fairly localized on particular bonds[11] and thus the electronic charge could not swing over the molecule by vibrations. It is interesting to study how such electronic behavior caused by the vibrations affects the Raman polarizability for these molecules.

It will be shown in this work that the polarized Raman spectrum in single crystal is very useful to the experimental determination of the relative values of the principal elements of the Raman polarizability and to the study of the relation between the Raman polarizability and the mode of molecular vibration.

Experimental

Material. Naphthalene and maleic anhydride obtained from Wako Pure Chemical Industries and Nacalai Tesque, respectively, were purified by zone refining of about 100 passages.

Optical Measurement. The polarized Raman spectra of naphthalene and maleic anhydride were observed in single crystal with a JEOL 400T Laser Raman Spectrophotometer. The samples were excited with the 514.5 nm line from an Ar^+ ion laser of Spectra Physics 168B.

Single crystals of naphthalene and maleic anhydride well grown by the Bridgman method were quite transparent and no cracking was found under polarization microscope inspection. A well grown single crystal was cut along the cleavage plane (*ab* and *bc* planes in the naphthalene and maleic anhydride crystals, respectively) and then cut out in a cube of about (5 mm)^3. The crystal axes were determined under polarization microscope. The naphthalene crystal belongs to the monoclinic system of the space group C_{2h}^5 with two molecules in the unit cell.[13] The two edges of the cube of the crystal sample were cut to be parallel to the crystal *a* and *b* axes and the third edge was cut to be perpendicular to both the *a* and *b* axes and made the angle of 32 ° to the crystal *c* axis. This direction is called c' axis hereafter. The maleic anhydride crystallizes in the orthorhombic system of the space group D_2^4 with four molecules in the unit cell.[14] The three edges of the sample cube were cut to be parallel to the crystal *a*, *b*, and *c* axes, respectively.

The polarized Raman spectrum was observed with the back scattering method in the following way. The sample cube was placed on the sample holder equipped with a goniometer in such a way that one of the planes of the cube, say *ab* plane, was set to be perpendicular to the optical axis of the spectrophotometer, an edge of this plane being parallel to the slit. The propagation direction of the laser beam was set to be parallel to the optical axis of the spectrophotometer. The polarization direction of the laser beam was first set to be parallel to the crystal *a* axis of the *ab* plane and the *aa* and *ab* polarized Raman spectra were observed. Then the polarization direction of the laser beam was turned to be parallel to the *b* axis of the plane using the half- wave plate and the *bb* and *ab* polarized spectra were observed. In this way the *aa*, *bb*, and *ab* polarized Raman spectra were observed successively in the one crystal orientation. This crystal orientation will be called as the *ab* plane orientation hereafter. In the *ac* and *bc* plane orientations, where the sample cube was placed in such a way that the *ac* and *bc* planes of the cube were set to be perpendicular to the optical axis of the spectrophotometer, respectively, the *aa*, *cc*, *ca* and the *bb*, *cc*, *bc* polarized Raman spectra can be observed, respectively. This experimental procedure could greatly shorten the observation time of the polarized Raman spectra and could sufficiently reduce sublimation of the crystal sample compared with the 90° scattering method. This advantage remarkably improved the accuracy of the measurement of the relative intensity of the polarized Raman bands.

The degree of depolarization of the Raman bands in molten phase was measured in a rectangular cell with the backscattering method. The optical alignment was set in such a way that the degree of depolarization of the totally symmetric ν_1 Raman band of liquid carbon tetrachloride becomes as small as possible. The value of the degree of depolarization measured for the ν_1 band of carbon tetrachloride with this method is 0.007, while the most reliable value at present is 0.0039.[15]

Calculation of the Raman Polarizability

In the oriented gas model approximation, the relative intensities of the Raman bands due to the totally symmetric molecular vibrations observed in the *aa*, *bb*, *cc*, *ab*, *bc*, and *ca* polarized Raman spectra are expressed by the following proportional equations if the principal axes of the Raman tensor coincide with the molecular axes,[10,11]

$$\sqrt{I_{aa}} \propto a_x^2\alpha'_{xx} + a_y^2\alpha'_{yy} + a_z^2\alpha'_{zz}, \tag{1}$$

$$\sqrt{I_{bb}} \propto b_x^2\alpha'_{xx} + b_y^2\alpha'_{yy} + b_z^2\alpha'_{zz}, \tag{2}$$

$$\sqrt{I_{cc}} \propto c_x^2\alpha'_{xx} + c_y^2\alpha'_{yy} + c_z^2\alpha'_{zz}, \tag{3}$$

$$\sqrt{I_{ab}} \propto a_x b_x\alpha'_{xx} + a_y b_y\alpha'_{yy} + a_z b_z\alpha'_{zz}, \tag{4}$$

$$\sqrt{I_{bc}} \propto b_x c_x\alpha'_{xx} + b_y c_y\alpha'_{yy} + b_z c_z\alpha'_{zz}, \tag{5}$$

$$\sqrt{I_{ca}} \propto c_x a_x\alpha'_{xx} + c_y a_y\alpha'_{yy} + c_z a_z\alpha'_{zz}, \tag{6}$$

where I_{aa} is the band intensity in the *aa* polarized spectrum, a_x is the direction cosine between the crystal *a* and molecular *x* axes, α'_{xx} is the *xx* element of the Raman polarizability, and so on. The *x* axis is taken perpendicular to the molecular plane and the *y* and *z* axes are in the plane with the *z* axis passing through the central C–C bond for naphthalene and being prependicular to the C=C bond for maleic anhydride.

Let's $\gamma_1 = \alpha'_{xx}/\alpha'_{zz}$ and $\gamma_2 = \alpha'_{yy}/\alpha'_{zz}$. Since the proportionality factors in Eqs. 1, 2, 3, 4, 5, and 6 are equal under the same experimental condition, Eqs. 1 and 2 give the following linear relationship between γ_1 and γ_2

$$\gamma_2 = \frac{\sqrt{I_{bb}}a_x^2 - \sqrt{I_{aa}}b_x^2}{\sqrt{I_{aa}}b_y^2 - \sqrt{I_{bb}}a_y^2}\gamma_1 + \frac{\sqrt{I_{bb}}a_z^2 - \sqrt{I_{aa}}b_z^2}{\sqrt{I_{aa}}b_y^2 - \sqrt{I_{bb}}a_y^2}. \tag{7}$$

Eqs. 1 and 4, and Eqs. 2 and 4 give the similar linear equations

$$\gamma_2 = \frac{\sqrt{I_{ab}}a_x^2 - \sqrt{I_{aa}}a_x b_x}{\sqrt{I_{aa}}a_y b_y - \sqrt{I_{ab}}a_y^2}\gamma_1 + \frac{\sqrt{I_{ab}}a_z^2 - \sqrt{I_{aa}}a_z b_z}{\sqrt{I_{aa}}a_y b_y - \sqrt{I_{ab}}a_y^2} \tag{8}$$

$$\gamma_2 = \frac{\sqrt{I_{ab}}b_x^2 - \sqrt{I_{bb}}a_x b_x}{\sqrt{I_{bb}}a_y b_y - \sqrt{I_{ab}}b_y^2}\gamma_1 + \frac{\sqrt{I_{ab}}b_z^2 - \sqrt{I_{bb}}a_z b_z}{\sqrt{I_{bb}}a_y b_y - \sqrt{I_{ab}}b_y^2}, \tag{9}$$

respectively. From the measurement of the intensity of the bands in the *aa*, *bb*, and *ab* polarized spectra observed for the ab plane orientation the three linear equations, two of which are linearly independent, are obtained for the values of γ_1 and γ_2. The crossing point of the three straight lines for these linear equations gives the γ_1 and γ_2 values, from which the relative values of principal elements of the Raman polarizability for the totally symmetric molecular vibrations can be obtained.

The degree of depolarization ρ is expressed by

$$\rho = \frac{1.5\{(\gamma_1-\gamma_2)^2+(\gamma_2-1)^2+(1-\gamma_1)^2\}}{5(\gamma_1+\gamma_2+1)^2+2\{(\gamma_1-\gamma_2)^2+(\gamma_2-1)^2+(1-\gamma_1)^2\}}. \tag{10}$$

Thus the degree of depolarization can be drawn by the contour map with respect to the γ_1 and γ_2 values.[16]

If the experiment is carried out in ideal condition, the three crossing points regarding to the γ_1 and γ_2 values obtained from the *ab*, *ac*, and *bc* plane orientation spectra should coincide to each other and also should lay on the contour map of the degree of depolarization.

Results and Discussion

The polarized Raman spectra of the naphthalene and maleic anhydride crystals are essentially the same as those given by Suzuki et al.[10] and Ishibashi et al.[11] Since the relative intensity of the polarized Raman bands must be measured accurately in order to obtain the values of the Raman polarizability from Eqs. 7, 8, and 9, the fairly strong Raman bands free from overlapping with other bands should only be selected. The Raman bands due to the ν_5 and ν_8 ring vibrations of naphthalene observed in the ab plane orientation and the ν_2 (C=O stretching) and ν_3 (C=C stretching) vibrations of maleic anhydride observed in the *ab* and *bc* plane orientations satisfy these conditions. These vibrational modes are illustrated in Fig. 1.

Substituting the values of direction cosine between the crystal and molecular axes of the naphthalene crystal and the intensity of the ν_5 bands in the *aa*, *bb*, and *ab* polarized spectra observed for the *ab* plane orientation into Eqs. 7, 8, and 9 one obtains the equations

$$\gamma_2 = -3.62\gamma_1 + 2.40,$$

$$\gamma_2 = 39.3\gamma_1 - 14.2,$$

$$\gamma_2 = 5.24\gamma_1 - 1.03.$$

The three straight lines for these equations are drawn in Fig. 2, together with the contour map of the degree of depolarization. The crossing point of these straight lines is located at the position of $\gamma_1 = 0.4$ and $\gamma_2 = 1.0$, and these values give the relative values of the principal elements of the Raman polarizability α'_{xx}, α'_{yy}, α'_{zz} to be 0.4, 1.0, and 1.0 for the ν_5 vibration. In the same way, the three lines for the γ_2 and γ_1 equations for the ν_8 vibration of naphthalene were obtained and these lines are drawn in Fig. 2, together with the contour map of the degree of depolarization. The crossing point of these lines is located at $\gamma_1 = 0.5$ and $\gamma_2 = 1.4$ and the relative values of the Raman polarizability α'_{xx}, α'_{yy}, α'_{zz} are obtained to be 0.5, 1.4, and 1.0 for the ν_8 vibration of naphthalene. These values are given in Table 1. In naphthalene the polarized Raman spectra observed for the *ac'* and *bc'* plane orientation could not give enough intensity to measure the values of the Raman polarizability accurately.

The straight lines for the γ_2 and γ_1 linear equations obtained from the intensities of the ν_2 and ν_3 bands in the polarized Raman spectra of maleic anhydride observed for the *ab* and *bc* plane orientations were drawn in Fig. 3. The crossing points of the lines for the ν_2 and ν_3 bands obtained for the *ab* plane orientation are very closely located at the crossing points for the ν_2 and ν_3 bands obtained for the *bc* plane orientation, respectively. The crossing point obtained for the *ab* crystal orientation is more reliable than that of the *bc* plane orientation because the intensity of the bands observed for the former orientation is much stronger than that observed for the latter orientation. The crossing point obtained for the *ab* plane orientation is located at $\gamma_1 = 0.7$ and $\gamma_2 = 3.8$ and the relative values of the Raman polarizability α'_{xx}, α'_{yy}, α'_{zz} obtained from these values are 0.7, 3.8, and 1.0 for the ν_2 vibration. The crossing point for the ν_3 vibration is located at $\nu_1 = 0.06$ and $\gamma_2 = 0.8$ and the relative values of the Raman polarizability α'_{xx}, α'_{yy}, α'_{zz} are obtained to be 0.06, 0.8, and 1.0 for the ν_3 vibration. The intensity of the bands in the *ac* plane orientation spectra of maleic anhydride was too weak to evaluate the Raman polarizability accurately.

The results obtained for naphthalene will be discussed first. The values of α'_{yy} and α'_{zz} are nearly equal to each other and the value of α'_{xx} is about one half of the values of the in-plane elements α'_{yy} and α'_{zz} for both the ν_8 and the ν_5 vibrations. This may be due to the fact that the modes of the ν_8 and ν_5 vibrations delocalize over the molecule, that is, all atoms in the molecule vibrate simultaneously in the molecular plane, and the electronic charge swings along the *y* and *z* axes almost equally. The in-plane molecular vibrations also

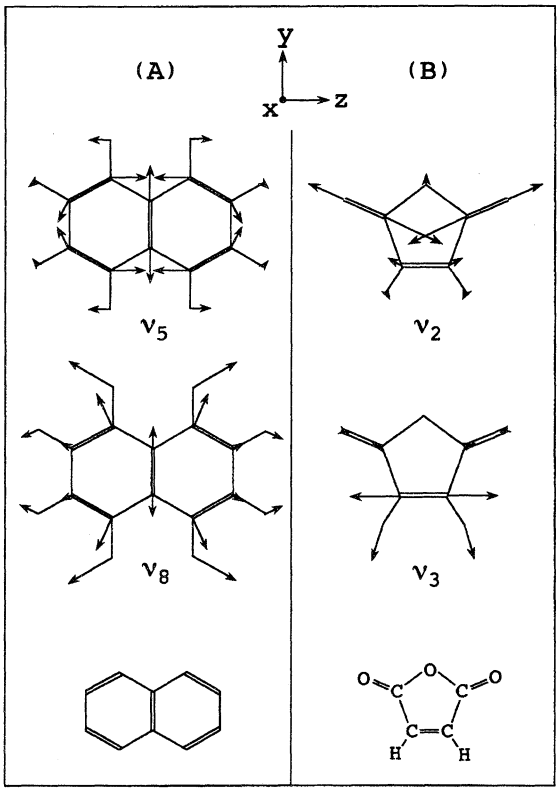

Fig. 1. Modes of the ν_5 and ν_8 vibrations of naphthalene (A) and the ν_2 and ν_3 vibrations of maleic anhydride (B).

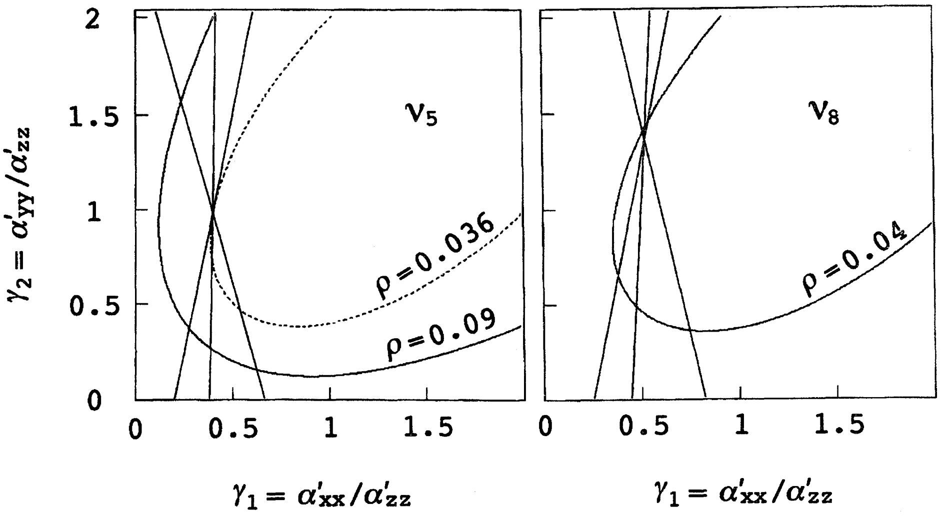

Fig. 2. The straight lines for the γ_1 and γ_2 linear equations obtained from the ν_5 and ν_8 bands of the polarized Raman spectra observed for the *ab* plane orientation of the naphthalene crystal and the contour map of the degree of depolarization observed for molten naphthalene.

Table 1. Relative Values of the Principal Elements of the Raman Polarizability and Degree of Depolarization for the Totally Symmetric ν_5 and ν_8 Vibrations of Naphthalene and ν_2 and ν_3 Vibrations of Maleic Anhydride

Molecule	Vibrational mode	Relative Raman polarizability			Degree of depolarization	
		Obsd			Obsd	Calcd[a]
		$\alpha'_{xx}/\alpha'_{zz}$	$\alpha'_{yy}/\alpha'_{zz}$	$\alpha'_{zz}/\alpha'_{zz}$		
Benzene	$\nu_1^{b)}$	0.68	1.0	1.0	0.008	
Naphthalene	ν_5	0.4	1.0	1.0	0.09	0.036
	ν_8	0.5	1.4	1.0	0.04	0.038
Maleic anhydride	ν_2	0.7	3.8	1.0	0.18	0.141
	ν_3	0.06	0.8	1.0	0.12	0.109

a) Value calculated from the Raman polarizability by Eq. 10. b) Taken from Ref. 5.

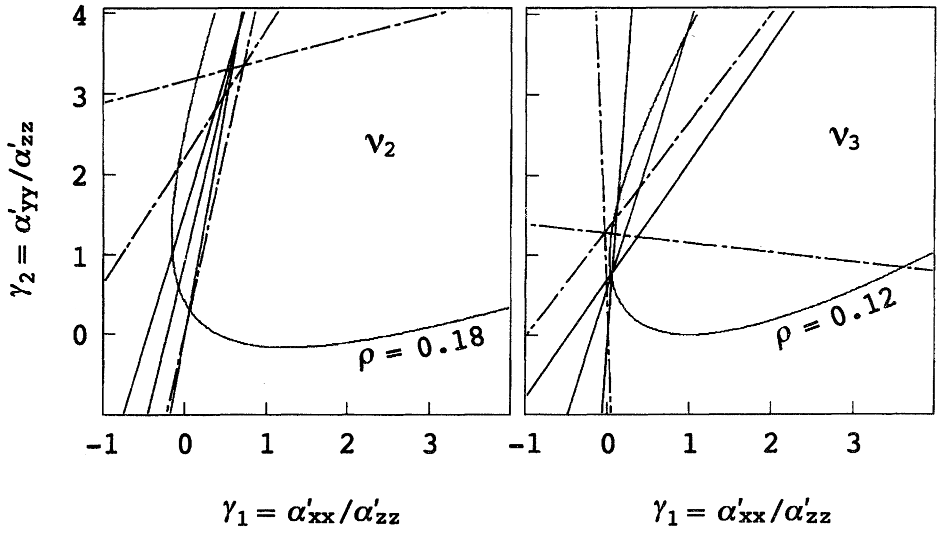

Fig. 3. The straight lines for the γ_1 and γ_2 linear equations obtained from the ν_2 and ν_3 bands of the polarized Raman spectra observed for the *ab* (—) and *bc* (–··–) plane orientations of the maleic anhydride crystal and the contour map of the degree of depolarization observed for molten maleic anhydride.

cause fairly large swing of the electronic charge along the x axis. This situation is quite similar to that in benzene. In benzene the value of $\alpha'_{xx}/\alpha'_{zz}$ is reported to be 0.68 for the ν_1 vibration by Ebata et al.[5] This value was calculated from the degree of depolarization 0.008 observed by the simulated Raman-UV optical double-resonance spectroscopy. These results indicate that the Raman polarizability for the totally symmetric ν_1 vibration of benzene is approximately spherical, that is, the principal out-of-plane element of the Raman polarizability has fairly large value comparable to values of the principal in-plane elements due to fairly large swing of the electronic charge along the normal of the benzene ring.

For the Raman polarizability of maleic anhydride the swing of electronic charge along the y axis caused by the ν_2 vibration is expected to be larger than that along the z axis as can be seen in Fig. 1 and therefore the principal elements of the Raman polarizability in the molecular plane are expected to be anisotropic. In accordance with the expectation the relative value of α'_{yy} is larger than the value of α'_{zz}. The in-phase combination of the two C=O stretching vibrations may induce the swing of the electronic charge over the molecule. As the result the swing of the electronic charge along the x axis may be induced and this leads to the value of α'_{xx} being fairly large as in the case of the totally symmetric ring vibrations of benzene and naphthalene. On the other hand the relative value of α'_{xx} for the ν_3 vibration is very small compared with values of α'_{yy} and α'_{zz} different from the other vibrations described above. This may be due to the fact that the ν_3 vibration is almost localized on the C=C bond and this vibrational mode may not induce the large amplitude of the swing of the electronic charge over the molecule.

The values of the degree of depolarization estimated from the Raman polarizability by Eq. 10 are 0.036 and 0.038 for the ν_5 and ν_8 vibrations of naphthalene and 0.141 and 0.109 for the ν_2 and ν_3 vibrations of maleic anhydride, respectively, while the observed values of the degree of depolarization for these four vibrations are 0.09, 0.04, 0.18, and 0.12, respectively. These values are given in Table 1. The agreement between the calculated and observed degree of depolarization is fairly satisfactory and this fact suggests that the relative value of the Raman polarizability obtained in this work is fairly reliable.

In conclusion the relative value of the principal elements of the Raman polarizability of the totally symmetric vibrations can be estimated fairly well by analyzing the polarized Raman spectrum in single crystal and the interesting relation between the Raman polarizability and vibrational mode is able to be discussed.

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