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"Anomalous" Raman Polarization as Observed in Anthracene Anion

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An example of "anomalous" Raman polarization is presented by measuring the polarization dispersion of a resonant depolarized line of anthracene anion near the first absorption band. The molecular origin of the asymmetric Raman tensor is discussed on the basis of a vibronic effect associated with the resonant electronic level.

Anomalous polarization refers to an unusual aspect of polarization in vibrational Raman scattering, in which the depolarization ratio exceeds the normal maximum value $\rho=3/4$ in isotropic media. This occurs when the scattering tensor becomes appreciably asymmetric under appropriate resonance conditions. Asymmetry of the scattering tensor is by no means unusual in the Raman transition between different electronic states.¹⁾ In vibrational Raman transitions within the non-degenerate ground state, the tensor usually has a virtually symmetric form even when an asymmetry is claimed from the group theory, leading to the well-known rule $\rho\leqq 3/4$.

Deviation from the rule was first demonstrated by Spiro and Strekas for the extreme case of $\rho\simeq\infty$ (inverse polarization) in cytochrome C and hemoglobin.²⁾ This remarkable state of polarization arises from an entirely antisymmetric Raman tensor, which may really exist only in molecules with three-fold or higher symmetry axes. Namely, the orbital degeneracy of electronic excited states contributing to the scattering tensor plays an essential role in bringing about the antisymmetric tensor. Less striking cases of $3/4<\rho<\infty$ were subsequently found in various porphyrins and heme proteins,³⁾ but the tensor asymmetry in those systems could be understood in essentially the same vibronic scheme as in the original high symmetry case. Anomalous polarization of somewhat different origin was also found out in IrX_6^{2-},⁴⁾ where the degeneracy of the electronic ground state is responsible for the tensor asymmetry.

Now, confining our attention to the usual vibrational Raman spectrum in non-degenerate ground state, it may be noted that, from the group theoretical point of view, the scattering tensor is not always symmetric but is rather often asymmetric. Particularly, in lower symmetries without any three-fold or higher axes, which occur in a majority of organic molecules, the tensor of non-totally symmetric vibrations is always asymmetric, so that the depolarization ratio is greater than 3/4. Such an argument is of little significance in ordinary non-resonant Raman observations, where the antisymmetric part of the tensor almost dies out by the nature of wave-functions,⁵⁾ but may become more realistic if an appropriate resonance condition is found. An example substantiating this remark has been given in a previous study on dehydro annulenes of D_{2h} symmetry.⁶⁾ In some point groups, on the other hand, tensor asymmetry is also possible for totally symmetric vibrations: an example of such a type of anomaly was found out very recently in Fe(II)-bis[1-(2′-pyridylmethyleneamino)-2-aminoethane] ion of C_2 symmetry.⁷⁾

In view of the particular significance of anomalous polarization in connection with the vibronic interaction, further experimental evidence should be sought. In this context, we take anthracene anion (An^-) as a promising candidate, because our previous resonance Raman study⁸⁾ of this system recorded a remarkably resonant depolarized line at 1466 cm^{-1}, which is supposed to be 'anomalous' intrinsically. In order to study the behavior of this line more definitely, the polarization dispersion has been carefully measured near the first absorption band.

Experimental

Anthracene anion was prepared by bringing anthracene into contact with metallic sodium in tetrahydrofuran (THF). The Raman spectra were obtained by $\approx 10^{-3}$ mol dm^{-3} THF solutions at room temperature. The intensity and depolarization ratio of 1466 cm^{-1} line were determined by the band area, using 914 cm^{-1} THF line as a standard. Since there exists a weak and broad depolarized band of THF extending over 1400—1550 cm^{-1}, due correction was made by subtracting the contribution from the measured area.

The MCD spectrum was recorded for a $\approx 10^{-6}$ mol dm^{-3} THF solution under the field strength of 10^4 G.

Results and Discussion

The whole span Raman spectrum recorded by 514.5 nm excitation is shown in Fig. 1 by the parallel and perpendicular scattered components. It is observed that the depolarization ratio of 1466 cm^{-1} line is slightly but certainly greater than 3/4 even in this

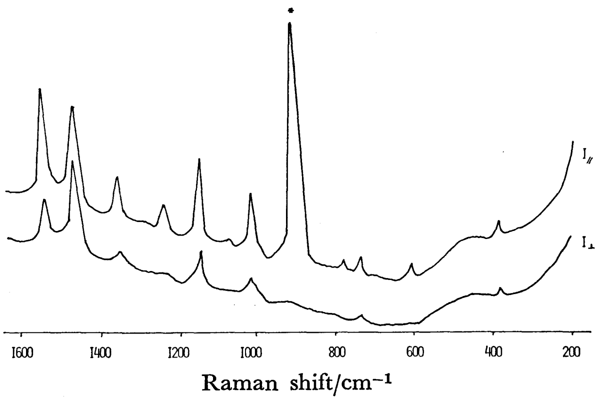


Fig. 1. Resonance Raman spectra of anthracene anion in THF solution by 514.5 nm excitation, obtained by parallel and perpendicular polarization conditions. Solvent line is marked by *.

moderately resonant condition. A partial spectral record of the interesting region is shown in Fig. 2 for some different exciting frequencies; here the dotted line indicates the baseline due to the solvent scattering as estimated in proportion to 914 cm^{-1} THF line. Uniform instrumental sensitivity for the two different analyzer settings has been confirmed by measuring well-defined depolarized lines of a known sample.

Since the deviation of ρ from the normal behavior was rather small in the observed region, the measurement was carefully made by repeated scanning with an alternating polarization sequence. The ρ values averaged for 6—7 records are plotted in Fig. 3 against the exciting laser frequency, together with the intensity plot and absorption curve. Scatter of the data was fairly small, and the composite error including the baseline uncertainty is estimated to be well within 10%. Although accurate measurement was impeded by increasing fluorescence in the more interesting region closer to the absorption maximum, the depolarization ratio has been verified to increase beyond the normal maximum of 3/4 along with the intensity, indicating the resonantly increasing tensor asymmetry.

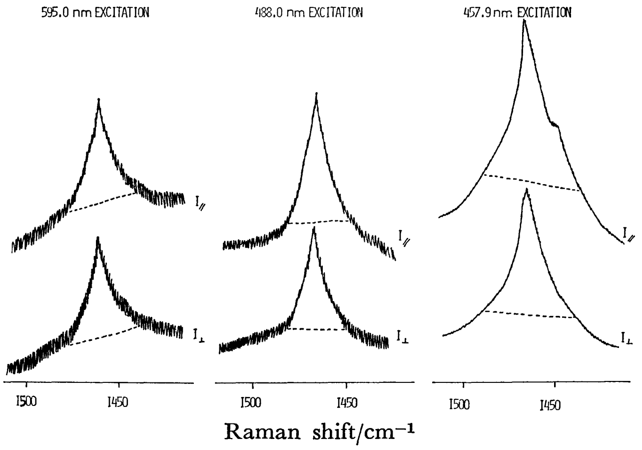


Fig. 2. Changes in polarization features of 1466 cm^{-1} line by different exciting light frequencies, where the dotted line indicates the baseline due to the solvent scattering.

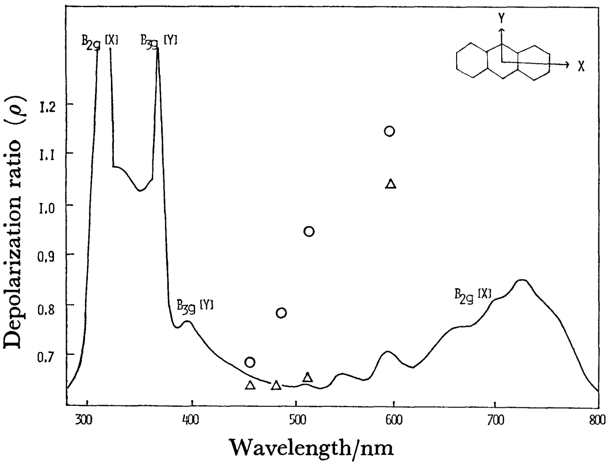


Fig. 3. Polarization dispersion (○) and excitation profile (△) of 1466 cm^{-1} line of anthracene anion in THF solution, with the electronic absorption spectrum.

The ρ value at 457.9 nm excitation is observed to be slightly lower than 3/4 in Fig. 3, in contradiction to the presumably non-totally symmetric nature of 1466 cm^{-1} mode. This is properly ascribed to the effect of a polarized line included in the measured area, because such a signal emerges at about 1450 cm^{-1} in the parallel component of 457.9 nm record as the result of much reduced resonance effect in 1466 cm^{-1} scattering. This polarized line may be reasonably assigned to an a_g mode corresponding to 1480 cm^{-1} of neutral anthracene.

The polarization dispersion as observed above is properly interpreted as due to the vibronic mixing that gives rise to a polarization change of the resonant electronic transition. In order to see the circumstances more precisely, the nature of the relevant electronic states has been investigated by a PPP-SCF-MO calculation and MCD measurement. The polarization of each transition predicted by the calculation is consistent with the sign of the observed ellipticity $[\theta]_M$, assuming B-term contributions in the MCD spectrum. The results are listed in Table 1 and the assignment of transitions is shown in Fig. 3. These results indicate that the first B_{2g} excited state with x-polarized transition moment has a good possibility to vibronically couple with the next B_{3g} states of y-polarization through b_{1g} in-plane vibrations. Then, the b_{1g} Raman tensor having the form $\begin{pmatrix} 0 & \alpha_{xy} & 0 \\ \alpha_{yx} & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}$ can be appreciably asymmetric for exciting laser frequencies sufficiently close to the first absorption band, because in such a resonant condition, the non-zero element is shown to be approximately represented[6]) by the predominant term as

Table 1. Assignment of electronic absorption spectrum for anthracene anion

Observed transition			Calculated transion		
Abs. spectrum	MCD spectrum		PPP-SCF-CI		
Wavelength/nm	Wavelength/nm	$[\theta]_M$	Wavelength/nm	Symmetry type	Direction of polarization
726		+	822	$B_{2g}\leftarrow B_{1u}$	x
400	410	−	485	$B_{3g}\leftarrow B_{1u}$	y
366	365	−	344	$B_{3g}\leftarrow B_{1u}$	y
326	325	+	294	$B_{2g}\leftarrow B_{1u}$	x

$$\alpha_{xy} \propto \frac{\mu_x(\partial\mu_y/\partial Q)_0}{\nu_e+\nu_R-\nu+i\Gamma}, \quad \alpha_{yx} \propto \frac{\mu_x(\partial\mu_y/\partial Q)_0}{\nu_e-\nu+i\Gamma}. \tag{1}$$

Here μ, ν_e, and Γ are the moment, frequency, and damping factor of the resonant B_{1u} (ground)→B_{2g} transition, ν_R and Q are the frequency and normal coordinate of the b_{1g} Raman mode, and ν is the laser frequency. The depolarization ratio is thus given[6)] by

$$\rho = \frac{3}{4}+\frac{5}{4}\left|\frac{\alpha_{xy}-\alpha_{yx}}{\alpha_{xy}+\alpha_{yx}}\right|^2 = \frac{3}{4}+\frac{5}{16}\frac{\nu_R{}^2}{(\nu_e+1/2\nu_R-\nu)^2+\Gamma^2}, \tag{2}$$

which is appreciably greater than 3/4 in the resonant region.

Further insight into the origin of the asymmetric tensor may be obtained by applying Warshel's model,[9)] which approximately represents the transition moment derivative by an assembly of the products of transition monopoles q_i, allocated to individual atoms, and the corresponding components of normal mode vector $L^{i\sigma}$

$$\partial\mu_\sigma/\partial Q = \sum_i q_i L^{i\sigma}(m_i\nu_R)^{-1/2}. \quad m_i\text{: atomic mass} \tag{3}$$

The transition monopoles of the first absorption band as calculated by PPP-SCF-CI method are shown by the circles in Fig. 4.

Since available vibrational data of the anion have been quite insufficient for obtaining $L^{i\sigma}$ accurately, a normal mode calculation has been made for neutral anthracene using the library programs BGLZ and LSMB at the Computer Center, the University of Tokyo. The calculated Raman frequencies are shown in Table 2 together with those observed for neutral and anion species, the force constants being given in Table 3. The vibrational mode of 1466 cm^{-1} anion line may be properly related to ν_{16} and ν_{17} modes of the neutral molecule, which are shown in Fig. 4 by calculated atomic displacements. The MO calculation suggests that the anion mode is more closely allied to the neutral ν_{16} mode, because the change in bond order from neutral to anion predicts a downshift of ν_{16} as large as 87 cm^{-1} in contrast with only 3 cm^{-1} up-shift of ν_{17}. Then, by putting the ν_{16} neu-

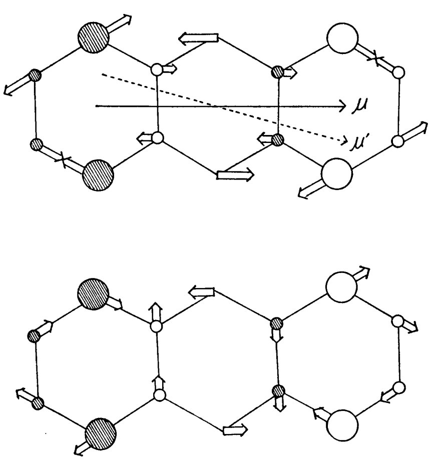


Fig. 4. Transition monopoles of the resonant An$^-$ transition and the atomic displacements of b_{1g} modes of anthracene related with 1466 cm^{-1} An$^-$ mode. Open and hatched circles designate positive and negative transition monopoles respectively. $\mu'-\mu$ gives the change of transition dipole.

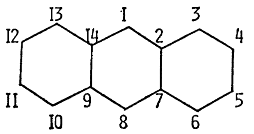
Table 2. Assignment of Raman spectra for anthracene

		Calcd[a)] $\tilde{\nu}$/cm^{-1}	Obsd $\tilde{\nu}$/cm^{-1}		
		Neutral	Neutral		Anion
			CCl$_4$ soln[10)]	Crystal[11)]	THF soln[8)]
a_g	ν_1	3089			
	ν_2	3087			
	ν_3	3085			
	ν_4	1575	1561	1556 s	1545
	ν_5	1472	1479	1480 s	1450
	ν_6	1405	1406	1400 s	1363
	ν_7	1257	1260	1264 vs	1234
	ν_8	1145	1164	1164 vs	1153
	ν_9	1013	1006	1007 vs	1024
	ν_{10}	737		754 vs	738
	ν_{11}	665		625 w	
	ν_{12}	373	394	397 vs	390
b_{1g}	ν_{13}	3092			
	ν_{14}	3086			
	ν_{15}	1669	1634	1632 s	
	ν_{16}	1570		1574 w	1466
	ν_{17}	1346		1346 w	
	ν_{18}	1232		1273 w	
	ν_{19}	1173	1183	1187 vs	
	ν_{20}	1093		1102 w	
	ν_{21}	903		903 w	
	ν_{22}	544	523	521 vs	
	ν_{23}	405			

a) UBFF modified by taking into account the contribution of resonance of 4 Kekulé structures.

Table 3. Force constants for anthracene

Stretching	K(C$_1$-C$_2$)	5.0 mdyn Å^{-1}
	K(C$_2$-C$_3$)	4.3
	K(C$_3$-C$_4$)	6.1
	K(C$_4$-C$_5$)	4.4
	K(C$_2$-C$_7$)	4.4
	K(C-H)	4.8
Deformation	H(C-C-C)	0.30
	H(C-C-H)	0.20
Repulsion	F(C$_1$···C$_3$)	0.70
	F(C$_2$···C$_4$)	0.45
	F(C$_3$···C$_5$)	0.45
	F(C$_1$···C$_7$)	0.45
	F(C$_2$···C$_{14}$)	0.45
	F(C···H)	0.35
Kekulé constant		0.30



tral mode in place of the 1466 cm^{-1} anion mode, we can trace the ultimate source of the off-diagonal tensor elements, Eq. 1, to the wagging motion of $B_{1u} \rightarrow B_{2g}$ transition moment μ_x, which mostly comes from the rotational motion of the four equivalent carbon atoms at 3, 6, 10, and 13 positions which carry the predominant transition monopoles.

"Anomalous" polarization as reported above is by no means a unique occurrence theoretically, but should be observed quite generally as long as it is measured under well-resonant conditions. Nevertheless, it seems still worth investigating in view of its particular significance in studying the vibronic interaction in complex molecules.

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