The Resonance Raman Spectrum of the Poly(vinyl alcohol)-Iodine Complex

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(Received May 11, 1972)

The resonance Raman spectra were observed from dilute aqueous solutions of the poly (vinyl alcohol)-iodine complex, using the He–Ne 632.8 nm and Ar$^+$ ion 488.0 nm lines for excitation. Two kinds of poly (vinyl alcohol) were used; one (A) had the degree of polymerization of 500, and the other, (B) 2000. For both samples, the resonance Raman spectra taken with the 632.8 nm line are similar to that of the starch-iodine complex, the intensity of the Raman band at 155 cm^{-1} being strongly enhanced. This band is assigned to the antisymmetric stretching vibration of the I_3^- ion aligned in the helical poly(viny alcohol) molecule. On the other hand, the intensity of the Raman band at 106 cm^{-1} is enhanced for Sample A when the 488.0 nm line is used for excitation. This band is assigned to the symmetric stretching vibration of the I_3^- ion. Its overtones were observed until the sixth. It is clear that the enhancement of the intensities of the 155 and 106 cm^{-1} bands is closely connected with the absorption bands at 670 and 490 nm respectively.

Much work was done on the resonance Raman effect in the pre-laser period.[1] With the recent development of laser-Raman spectroscopy, renewed interest in the resonance Raman effect has been growing both experimentally and theoretically. It seemed that it would be attractive to apply this effect to the study of the molecular structure of trace amounts of colored substances in solution. As the concentration of a colored substance detectable by the resonance Raman effect is very low (*ca.* 10^{-4} mol/*l*) compared with the ordinary Raman effect or the infrared absorption, this method will find various applications not only in physical chemistry, but also in analytical and biological chemistry.

One of the present authors (MT) has studied the resonance Raman spectra observed from dilute aqueous solutions of the starch-iodine complex.[2] The observed Raman bands have been assigned to the vibrations of the I_3^- ions aligned linearly in the cylindrical cavity inside the helical starch molecule. Since poly(vinyl alcohol) (PVA) is known to form a blue complex with iodine, just as starch does, we have taken up this complex in order to check whether or not it is structurally similar to the starch-iodine complex. The results show that the PVA-iodine complex gives a spectrum similar to that of the starch-iodine complex. Under certain conditions, however, a completely different spectrum is observed for the PVA-iodine complex. The details will be reported in the present paper.

Experimental

Sample. Two kinds of PVA samples were used. One (Sample A) had the average degree of polymerization of 500, and the other (Sample B), 2000. Both samples were purchased from the Wako Chemical Co. and were used without further treatment. The tacticities of these polymers are not precisely known. The other reagents were also obtained commercially. The iodine was purified by sublimation.

Each sample solution of the PVA-iodine complex was prepared as follows: 1 cc of a mixed solution of iodine (0.0029 mol/*l*) and potassium iodide (0.12 mol/*l*) was added to 5 cc of a 0.2 wt% aqueous solution of PVA and then the mixture was diluted to 25 cc with boric acid solutions of various concentrations (0.05—0.30 mol/*l*).[3]

In Table 1, the numbering of the sample solutions is given. The concentration of iodine in each sample was 1.1520×10^{-4} mol/*l* as I_2.

TABLE 1. THE NUMBERING OF SOLUTIONS[a)]

PVA	H_3BO_3[b)]					
	0.05	0.10	0.15	0.20	0.25	0.30
DP=500	A–1	A–2	A–3	A–4	A–5	A–6
DP=2000	B–1	B–2	B–3	B–4	B–5	B–6

a) For each solution, the PVA and iodine concentrations are 2.0 wt% and 1.152×10^{-4} mol/*l*, respectively.
b) The concentration of boric acid is expressed in mol/*l*.

Spectral Measurements. The Raman spectra were recorded using a He–Ne laser (632.8 nm) and an Ar$^+$ ion laser (488.0 nm) for excitation. When the He–Ne laser was used, a spectrometer was employed which consisted of a Spex 1401 double monochromator, a photomultiplier, a phase-sensitive detector, and a recorder.[4] Also, a Raman spectrometer constructed by the Kawaguchi Denki Co. and a JEOL JRS-U1 spectrometer were used, both with an Ar$^+$ ion laser. The Raman scattering was observed at right angles to the exciting laser beam, which radiates the sample very close to the quartz-cell wall.

Hitachi EPS-3 and 124 spectrophotometers were used to measure the absorption spectrum in the ultraviolet and visible regions.

Results and Discussion

Figure 1 shows an example of the Raman spectrum

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[1] J. Behringer, "Raman Spectroscopy," ed. by H.A. Szymanski, Plenum Press, New York, N. Y. (1967).

[2] M. Tasumi, *Chem. Lett.*, **1972**, 75.

[3] It might be more reasonable to regard the complex as a ternary one consisting of PVA, iodine, and boric acid. However, we keep the tradionally-used name of PVA-iodine complex. Actually, the complex is formed even without boric acid after the mixed solution of PVA and iodine is left for a long time.

[4] T. Fujiyama and M. Tasumi, *Bunko Kenkyu* (*J. Spectrosc. Soc. Jap.*), **20**, 28 (1971).

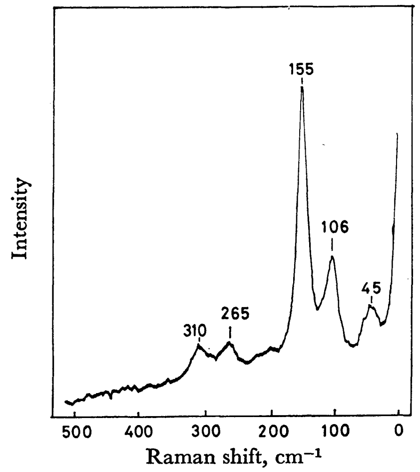

Fig. 1. The Raman spectrum of the solution B–3 taken with the 632.8 nm excitation.

of the PVA-iodine complex obtained with the 632.8 nm line of the He–Ne laser. A close resemblance is found between this and the spectrum reported previously for the starch-iodine complex.[2] It seems reasonable, therefore, to presume that the structure of the PVA-iodine complex is similar to that of the starch iodine complex. In other words, the present result is compatible with the model structure of the PVA-iodine complex proposed by Zwick[5] that a linear polyiodide chain is enclosed by a helical PVA molecule and that the latter, in turn, is surrounded by borates which maintain the PVA helix by forming the –C–O–B–O–C– bridge.

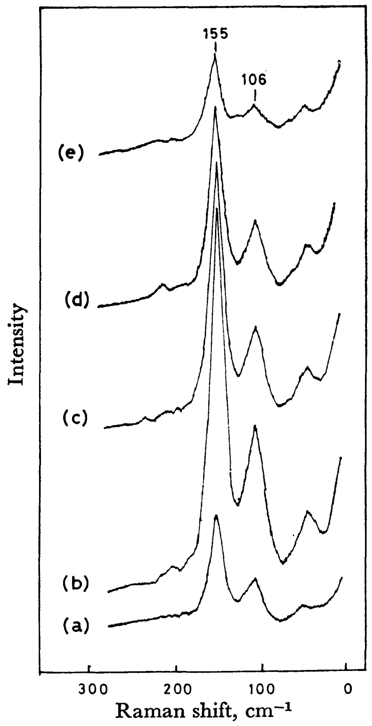

Fig. 2. The Raman spectra of Sample B taken with the 632.8 nm excitation. Iodine concentrations are as I_2:
(a) 2.09×10^{-4} mol/*l*; (b) 1.05×10^{-4} mol/*l*;
(c) 0.52×10^{-4} mol/*l*; (d) 0.26×10^{-4} mol/*l*;
(e) 0.13×10^{-4} mol/*l*.

By analogy with the starch-iodine case, the three bands at 45, 106, and 155 cm^{-1} in Fig. 1 may be assigned, respectively, to the bending, symmetric stretching, and antisymmetric stretching vibrations of the I_3^- ion. The other two, at 265 and 310 cm^{-1}, may be assigned to a combination tone ($265\approx106+155$) and an overtone ($310\approx155\times2$).

In the following part we will discuss various spectral characteristics observed under different conditions.

(1) Effect of the Concentration on the Raman Intensities. Figure 2 shows the dependence of the Raman intensities on the iodine concentration observed for Sample B. The apparent Raman intensity reaches its maximum at the iodine concentration of 1.0488×10^{-4} mol/*l*. A similar tendency was also observed in the solution of Sample A.

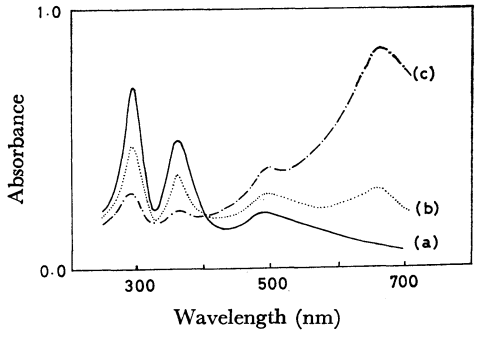

Fig. 3. The absorption spectrum of Sample A in the ultraviolet and visible regions. The solutions used are:
(a), A-1; (b), A-3; (c), A-5.

(2) Correlation between the Absorption and the Raman Spectra. *(a) Ultraviolet and Visible Absorption Spectra*: The absorption spectrum of Sample A in the ultraviolet and visible regions is shown in Fig. 3. The color of the complex varied from red to blue as the concentration of boric acid was increased. The absorption bands at 290 nm and 350 nm are due to the I_3^- ion. The band at 490 nm is close to the absorption wavelength of the I_2 molecule. However, only a small amount of the I_2 molecule would remain in the solutions treated here because of the presence of excess potassium iodide. As the extinction coefficient of the I_2 molecule is small ($\varepsilon=746$ *l*mol^{-1}cm^{-1}), it is unlikely that the 490 nm band in Fig. 3 arises from I_2. Therefore, this band should be assigned to the PVA(Sample

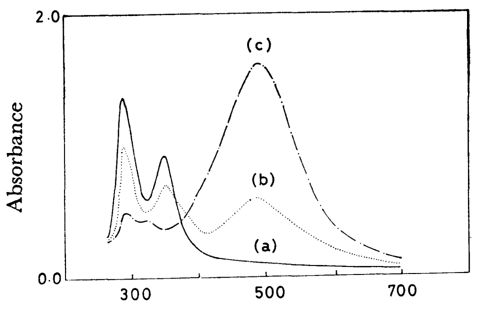

Fig. 4. The absorption spectrum of Sample A in the ultraviolet and visible regions. PVA concentrations are:
(a), 0.04 wt%; (b), 0.2 wt%; (c), 1.0 wt%. No boric acid was added.

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[5] M. M. Zwick, *J. Appl. Polym. Sci.*, **9**, 2393 (1965).

A)-iodine complex. This is supported also by the observation that the intensity of this band increases with an increase in the PVA concentration, while, on the other hand, the intensities of the 290 and 350 nm bands of the I_3^- ion decrease, as is shown in Fig. 4. The band at 670 nm appears very strongly when the boric acid concentration is high.

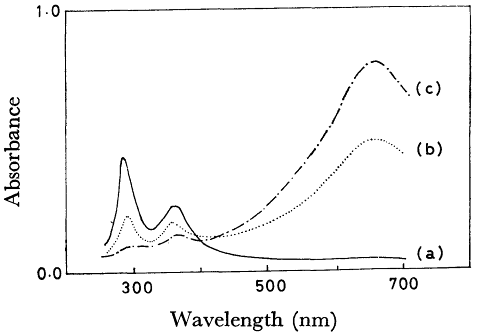

Fig. 5. The absorption spectrum of Sample B in the ultraviolet and visible regions. Boric acid concentrations are: (a), B-1; (b), B-3; (c), B-5.

Figure 5 shows the absorption spectra of the B solution series. The color of the B-1 solution (yellow) was exactly the same as that of the solution of iodine and potassium iodide. This would mean that Sample B does not make a complex with iodine at low boric acid concentrations. At higher boric acid concentrations, Sample B also shows a strong band at 670 nm.

It is noted that the 490 nm band found in the spectra of Sample A is not observed in any of the spectra of Sample B. This difference gives rise to an important effect in the Raman spectra, as will be discussed later.

(b) The Raman Spectra Observed with the 632.8 nm Excitation: The Raman spectra of the A and B solution series are shown in Figs. 6 and 7 respectively; they were obtained with the 632.8 nm line of the He–Ne laser. A marked change may be seen in the spectra of the A solution series. The Raman band at 155 cm^{-1} (the antisymmetric stretching mode) is not observed in the reddish solution A-1. When the color of the complex becomes blue, this band is strongly enhanced. In contrast with this, the intensity of the 106 cm^{-1} band (symmetric stretching mode) remains nearly constant throughout the A solution series, independent of the color of the complex.

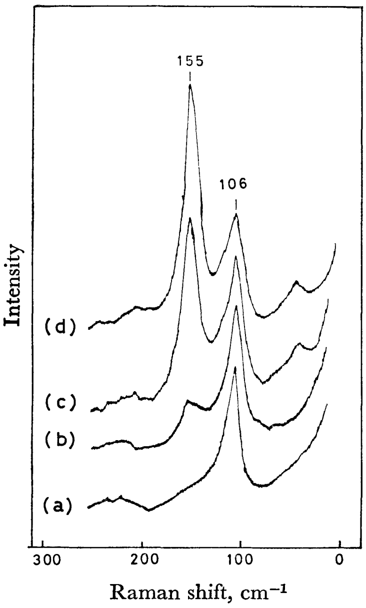

Fig. 6. The Raman spectra of the solution series A taken with the 632.8 nm excitation.
(a), A-1; (b), A-2; (c), A-3; (d), A-5.

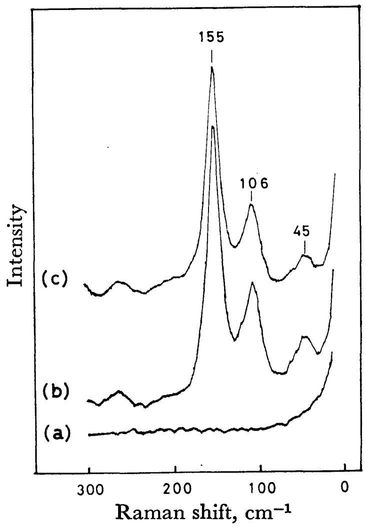

Fig. 7. The Raman spectra of the solution series B taken with the 632.8 nm excitation.
(a), B-1; (b), B-3; (c), B-5.

No Raman bands are observed for the yellow solution B-1. However, as the color becomes increasingly blue upon the addition of the boric acid, strong Raman bands appear for the B-3, B-4, and B-5 solutions.

(c) The Raman Spectra observed with the 488.0 nm Excitation: Figure 8 shows the spectrum of the A-4 solution obtained with the 488.0 nm line of the Ar$^+$ ion laser. It can be noted that the Raman band at 106 cm^{-1} is strongly enhanced and that overtones may be observed until the sixth. The Raman line at 155 cm^{-1} is observed only as a weak shoulder. This is in contrast with Fig. 1, in which the band at 155 cm^{-1}

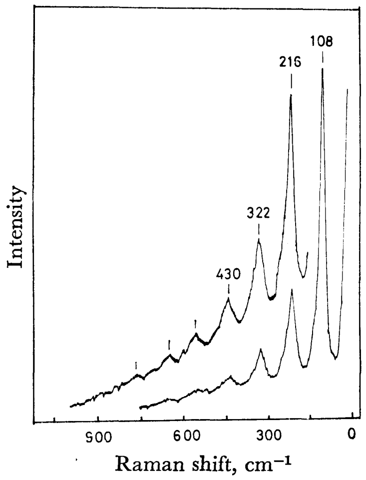

Fig. 8. The Raman spectrum of the solution A-4 with the 488.0 nm line excitation. The solution A-2 gives essentially the same spectrum.

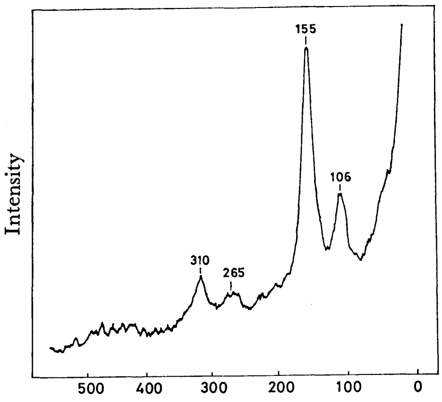

Fig. 9. The Raman spectrum of the solution B-3 taken with the 488.0 nm line excitation.

is much stronger than the band at 106 cm^{-1}.

For Sample B, on the other hand, essentially the same spectra were observed as those obtained with the He-Ne 632.8 nm line (Fig. 9).

The different spectral behavior between Sample A and Sample B with respect to the 488.0 nm excitation seems to be associated with the fact that Sample A has the 490 nm band, which is resonant with the exciting line, whereas Sample B has no such band.

Table 2. Summary of the resonance effect[a)]

Exciting line	Sample					
	PVA-iodine				Starch-iodine[b)]	Free I_3^-
	A		B			
	red	blue	yellow	blue		
632.8 nm	s	s,A	none	s,A	s,A	s
488.0 nm	S	S	none	s,A	s,A	s

a) The capital letters S and A indicate that the intensities of the I_3^- *symmetric* and *antisymmetric* modes are, respectively, enhanced greatly. The small symbol s means that the intensity of the I_3^- *symmetric* stretching is enhanced, but not as greatly as the case indicated by the capital letter.

b) Taken from Ref. 2.

The results obtained above are summarized in Table 2, together with those for the starch-iodine complex and the free I_3^- ion. The Raman spectra of the free I_3^- ion in an aqueous solution are shown in Fig. 10. The measurements were made under much higher I_3^- concentrations than those used in the Raman measurements of the complexes. This indicates that the resonance effect is much weaker for the free I_3^- ion than for I_3^- in the complexes, reflecting the experimental conditions that the exciting wavelengths used are outside the absorption bands of the free I_3^- ion found at 350 and 290 nm (preresonance case).

The following points in Table 2 are most noteworthy:
(i) The intensity of the I_3^- antisymmetric stretching mode is strongly enhanced in the complex state under some conditions, whereas it is only weakly observed in the free state. This is undoubtedly due to the presence of the absorption band of the complex at 670 nm (PVA-iodine) or *ca.* 600 nm (starch-iodine).

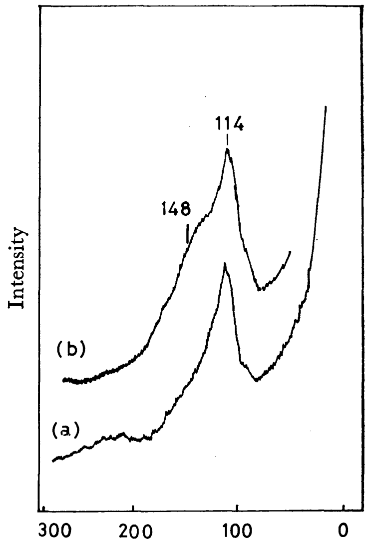

Fig. 10. The Raman spectra of aqueous solutions of potassium iodide.
(a), excited with the 488.0 nm line; (b), excited with the 632.8 nm line.

(ii) The intensity of the I_3^- symmetric stretching mode is enhanced in the free I_3^- spectra. It is strongly enhanced also in the complex-state spectra, instead of the antisymmetric mode, if the exciting wavelength is resonant with the absorption band at 490 nm.

These results clearly show that the alternative enhancement of different Raman bands can be achieved by using the resonance effect. As far as we know, such a clear example of alternative enhancement has not yet been reported. The mechanism which gives rise to the alternative enhancement must be rather complicated. However, we propose a very simple working hypotheses which might be of some value in understanding such a resonance effect: if the direction of a vibrational transition moment of a non-centrosymmetric molecule coincides with that of the electronic transition moment responsible for the resonance effect, the Raman intensity of the relevant vibrations has a chance of being selectively enhanced. As has been discussed in a previous paper,[2)] the transition moment of the 600 nm band of the starch-iodine complex is directed parallel to the linear chain of the I_3^- ion. Therefore, the Raman intensity of the I_3^- antisymmetric stretching mode is enhanced if the 600 nm band is resonant with the exciting wavelength. It seems quite reasonable to expect that the situation is the same for the enhancement of the I_3^- antisymmetric stretching mode of the PVA-iodine complex, though the direction of the transition moment of the 670 nm band of the PVA-iodine complex has not been determined experimentally. On the other hand, the 490 nm band would have its transition moment directed perpendicular to the I_3^- chain, if the working hypothesis described above be true. It is highly probable that the I_3^- ion in the complex deviates slightly from the linear centrosymmetric structure[6)] and, as a result, the transition moment

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[6)] A. G. Maki and R. Forneris, *Spectrochim. Acta.*, **23A**, 867 (1967).

of the I_3^- symmetric stretching mode is directed perpendicularly to the I_3^- chain. In this case, the Raman intensity of this mode may be selectively enhanced by the resonance between the 490 nm band and the 488.0 nm Ar^+ line. However, it should be mentioned that the origin of the 490 nm band is not very clear as yet. It is conceivable that this band is associated with either the tacticity of the polymer or the chain end, since this band is observable only in the spectrum of Sample A. This problem can be clarified only through experiments which utilize well-characterized polymer samples. Also, the validity of that working hypothesis should be tested by choosing suitable molecules, for which not only the molecular structures but also the assignment of the vibrational and electronic spectra are firmly established.