CHEMISTRY LETTERS, pp.75-78, 1972. Published by the Chemical Society of Japan

RESONANCE RAMAN SPECTRUM OF THE STARCH-IODINE COMPLEX

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Resonance Raman spectrum of the starch-iodine complex was observed in dilute aqueous solution. Three Raman bands observed at 163, 115, and 56 cm^{-1} are assigned, respectively, to the antisymmetric stretching, symmetric stretching, and bending vibrations of the I_3^- ion aligned linearly in the helical starch molecule.

Recently interest in the resonance Raman scattering is increasing. In this paper we discuss the resonance Raman spectrum obtained from dilute aqueous solution of the starch-iodine complex which is well known for its blue color.

(1) Samples. The following two samples of the starch-iodine complex were prepared. Original solution of Sample I contained soluble starch (0.2 mg/cc), iodine (0.000863 mol/ℓ), and potassium iodide (0.00236 mol/ℓ). Original solution of Sample II contained the soluble part of amylose (ca. 0.01 mg/cc), iodine (0.000863 mol/ℓ), and potassium iodide (0.00236 mol/ℓ). These were diluted to various concentrations as required. The solutions of both samples showed very broad absorption bands in the visible region. The absorption maximum was found at 588 nm for Sample I and at 637 nm for Sample II. This means that both soluble starch and amylose used here have wide molecular-weight distributions, the maxima of distribution being at the chains consisting of 60 and 300 glucose units, respectively.1)

(2) Measurements of Raman spectra. The Raman spectra were recorded using a He-Ne laser (632.8 nm) and an Ar^+ ion laser (514.5 nm) for excitation. When the He-Ne laser is used, a spectrometer was employed which consists of a Spex 1401 double monochromator, a photomultiplier, a phase-sensitive detector, and a recorder.2) Also, a Raman spectrometer constructed by Kawaguchi Denki Co. was used 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. In Fig. 1 is shown the Raman spectrum of Sample I which was obtained with the He-Ne laser. The concentration was 1/10 of the original solution. No ordinary Raman effect would be observed at such a low concentration. So, it seemed most likely that the bands at 163, 115, and 56 cm^{-1} were made observable by the resonance effect. In order to confirm this view, following observations were made.

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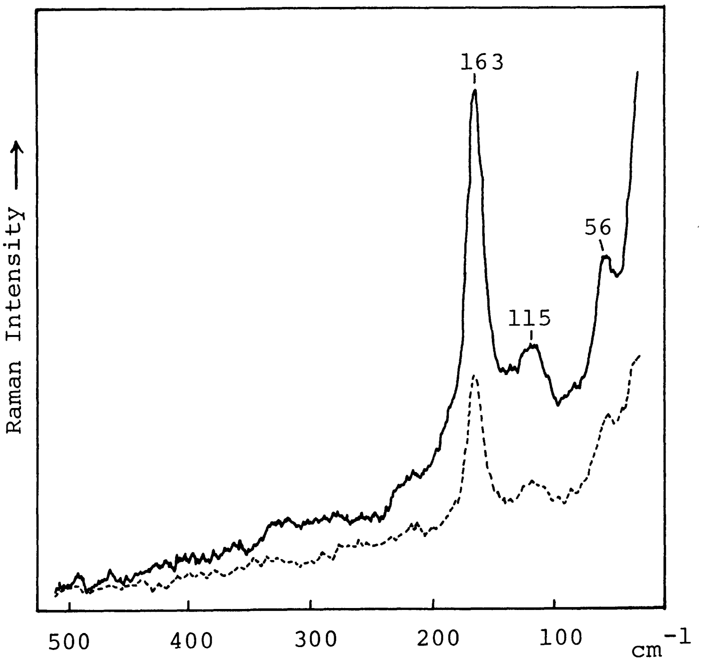

Fig. 1. Raman spectrum of Sample I taken with 632.8 nm excitation. Solid and broken curves indicate, respectively, the polarized and depolarized spectra.

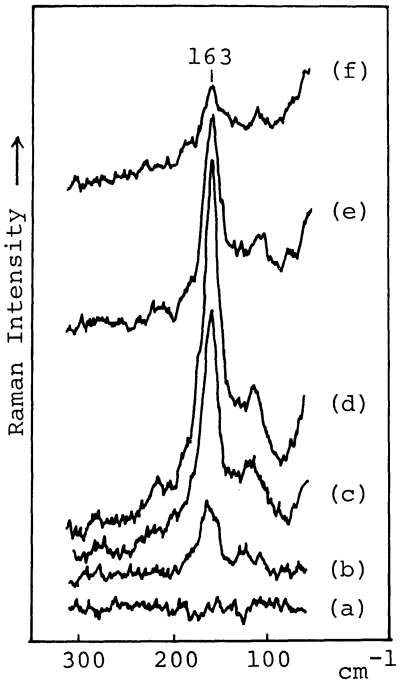

Fig. 2. Raman spectra of Sample I at various concentrations. (a) Original solution; (b), (c), (d), (e), and (f) are for the solutions diluted to 1/2, 1/4, 1/10, 1/20, and 1/40 of the original concentration.

Effect of concentration. Fig. 2 shows the changes in the intensities of the Raman bands with the concentration of Sample I. Sample II showed essentially the same spectrum and concentration dependence. Apparent Raman intensity reaches its maximum at the concentration of 1/10 of the original solution. In Fig. 3 the apparent intensity of the 163 cm^{-1} band is plotted against concentration. This parallels qualitatively the results obtained for the I_2^+ ion in fluorosulfonic acid[3] and the I_2 molecule in chloroform.[4]

Effect of temperature. The blue color of the starch-iodine complex is known to disappear with increasing temperature. The Raman bands also disappear completely at about 60°C, as shown in Fig. 4. At 60°C the solution is colorless. This indicates that the coloration and the Raman bands may be attributable to the same origin.

Spectral changes with excitation wavelength. So far, the results of measurements with the He-Ne laser were shown. It is interesting to see the changes of the Raman spectrum with shorter wavelength excitation. In Fig. 5 is shown the spectrum of Sample I obtained with the 514.5 nm line of the Ar^+ ion laser. Sample II gave almost the same spectrum. It is noted that two new bands are found at 324 and 474 cm^{-1}. These may be assigned to the first and second overtones of the 162 cm^{-1} band. This result strongly suggests that the present case falls into the category of the "rigorous" resonance Raman effect.[5] Holzer, et al., have studied the resonance Raman spectra of the halogen gases.[6] They have concluded that intense overtone bands appear when the laser wavelength used for excitation is shorter than the con-

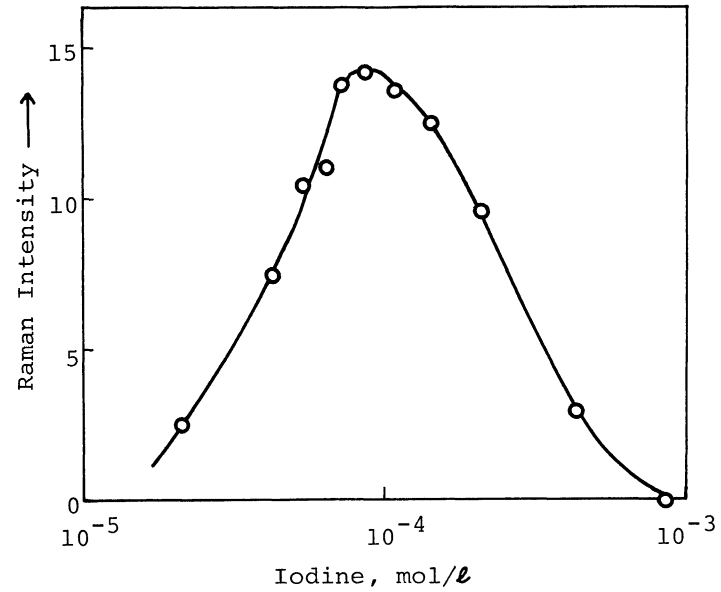

Fig. 3. Concentration dependence of the intensity of the $163\ cm^{-1}$ band. For convenience, iodine concentration is taken as the abscissa. The ordinate is proportional to recorder deflection.

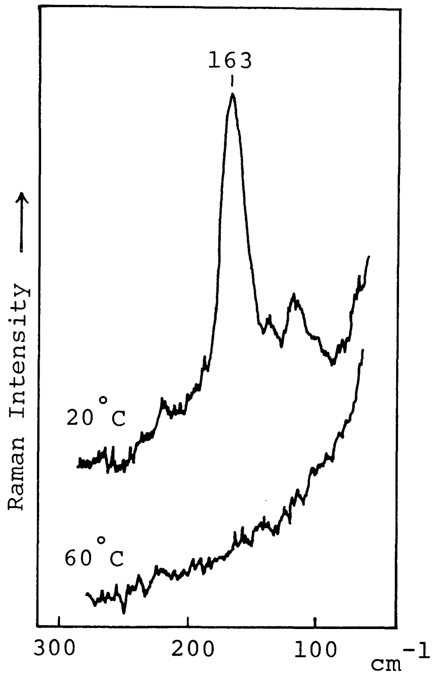

Fig. 4. Temperature dependence of the Raman spectrum of Sample I.

vergence limit of the sample molecule. On the other hand, Mortensen has reported the resonance Raman spectrum of the I_2 molecule in chloroform solution.[4)] He showed that, whether the exciting frequency is above or below the convergence limit, the spectrum of the I_2 molecule in solution resembles closely the gas-phase spectrum excited above the convergence limit. It is found in the present study that both Samples I and II give the same spectral behavior for either 632.8 or 514.5 nm excitation. This result, as well as Mortensen's, indicates that the condition for the appearance of overtone bands from solution might be more complex than that for the gas phase. The peak positions in Fig. 5 are slightly different from those in Fig. 1. Since these spectra were recorded using different spectrometers, such small discrepancy would be due to instrumental error.

(3) Band assignments. A number of studies have been conducted in order to elucidate the structure of the starch-iodine complex. We wish to show that the present results may be most reasonably interpreted by assuming the I_3^- ions aligned linearly and interacting strongly with one another in the cylindrical cavity formed by the helical starch molecule. Such a structure was proposed previously[7)] and supported by the X-ray diffraction analysis of the HI_3-benzamide complex (a model of the starch-iodine complex).[8)] The vibrational analysis of the I_3^- ion has been carried out by Maki and Forneris.[9)] According to them, the antisymmetric stretching, symmetric stretching, and bending vibrations are found at $148\ cm^{-1}$ (KI_3), $114\ cm^{-1}$ (KI_3), and $69\ cm^{-1}$ (CsI_3). We have also observed the Raman spectrum of the aqueous solution of KI_3 (Fig. 6). Comparing this with the spectrum of the starch-iodine complex, we assign the 163, 115, and $56\ cm^{-1}$ bands of the complex to the antisymmetric stretching, symmetric stretching, and bending vibrations, respectively, of the I_3^- ion included in the starch helix. In Fig. 6 the antisymmetric stretching vibration band at $148\ cm^{-1}$

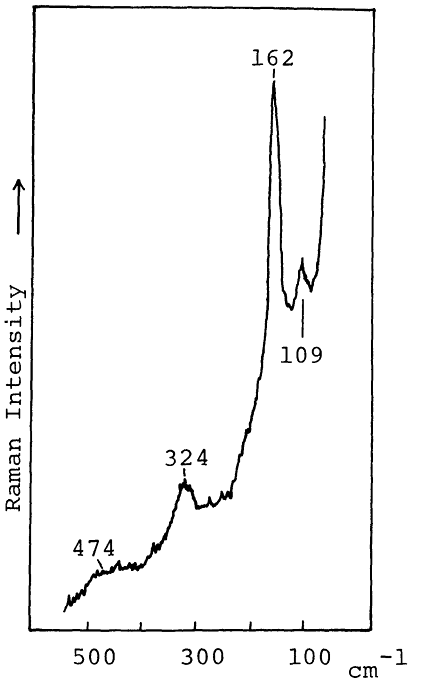

Fig. 5. Raman spectrum of Sample I taken with 514.5 nm excitation.

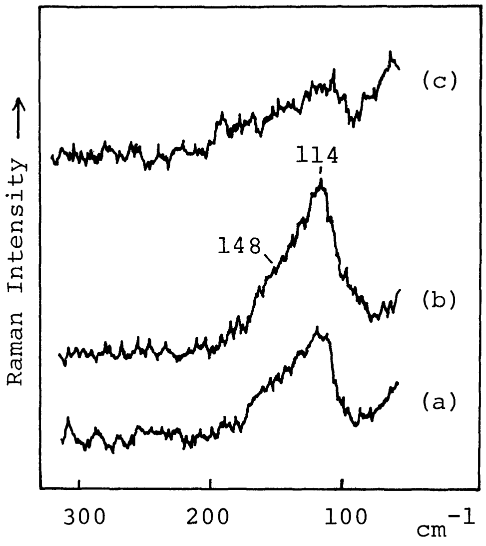

Fig. 6. Raman spectra of aqueous solutions of potassium iodide. (a) 0.5 mol/ℓ, (b) 0.1 mol/ℓ, (c) 0.0086 mol/ℓ.

is weaker than the symmetric stretching vibration band at 114 cm^{-1}. This is quite reasonable since the I_3^- ion is only slightly deviated from the $D_{\infty h}$ symmetry.9) For the $D_{\infty h}$ symmetry the antisymmetric stretching mode is inhibited in the Raman effect. In Fig. 1, on the other hand, the antisymmetric stretching vibration band is shifted to 163 cm^{-1} and has higher intensity than the symmetric stretching vibration band at 115 cm^{-1}. This indicates that the intensity of the antisymmetric stretching mode is far more enhanced by the resonance effect. The transition moment of the visible absorption around 600 nm was shown to be parallel to the starch helix axis,10) i.e., it is parallel to the postulated chain of the I_3^- ion. The transition moment of the antisymmetric stretching mode also must be parallel to that direction. Therefore, the coincidence of the electronic and vibrational trasition moments might be the cause which gives rise to the specific enhancement of the intensity of the antisymmetric stretching mode.

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(Received November 15, 1971)