J. Phys. Chem. 1981, 85, 1789-1794

Electronic Spectra and Structures of Polyiodide Chain Complexes

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Electronic spectra and electronic structures of triiodide, pentaiodide, and polyiodide chain complexes are investigated by electronic and Raman spectral measurements on nine single crystals of complexes with theoretical considerations. The assignments of optical bands are presented by the exciton and electronic exchange interactions of the triiodide and the pentaiodide chain or their mixed system. The resonance Raman spectra of these complexes are measured and discussed with an attempt to estimate the contents of I_3^- and I_5^- species in the chain.

Recently an active interest has revived in the quasi-linear polyiodide chain compounds, because of varieties of structures and physical properties. In particular accurate X-ray analysis of the complex crystals by Herbstein and his co-workers[1-3] and Saenger and his group[4,5] revealed many ordered and disordered structures of the iodide chain in various crystals. Marks and his co-workers[6-8] showed the potentiality of resonance Raman scattering and the Mössbauer effect in the study of the structure of polyiodide chain compounds.

In this paper we present reflection spectra of crystals of linear iodide chain compounds in order to find the relation between the electronic spectra and the structures of these quasi-linear systems. These results will provide basic information on the origin of the color of iodide chain complexes. The nature of the intermolecular interaction in the quasi-linear system will be discussed.

Experimental Section

CsI_3. Crystals of CsI_3 were obtained from a mixed solution of 20 mL of water and 5 mL of methyl alcohol containing 1 g of iodine and 5 g of CsI. They grew as large black prismatic crystals with a metallic luster of a steel blue color and elongated along the *c* axis with (110) and (001) faces.

$(Xanthotoxin)_2 \cdot KI_3$. Reddish-brown rhombuses of $(\text{xanthotoxin})_2 \cdot KI_3$ crystals were obtained from ethyl alcohol solution of equivalent amounts of xanthotoxin, potassium iodide, and iodine.

Tetra-n-butylammonium Triiodide. Crystals were obtained as black laths of irregular shape from a methyl alcohol solution of $(n\text{-Bu})_4NI$ and iodine. The most reflective direction was identified as the *c* axis by taking X-ray photographs.

$(Benzamide)_2 \cdot HI_3$. Crystals of $(\text{benzamide})_2 \cdot HI_3$ were prepared by adding 5 g of benzamide to 10 mL of HI aqueous solution (57%), including 5 mL of water and 1 g of iodine according to the procedure of Moor and Thomas,[9] and highly reflective black plates were obtained.

$Caffeine \cdot H_2O \cdot HI_3$. The complexes were prepared by mixing an acetic acid solution of caffeine with an aqueous solution of potassium iodide and iodine and subsequently adding hydrochloric acid into the mixture. Dark greenish needle-shaped crystals with metallic luster and elongated along the *c* axis were obtained from the above solution.

$(Trimesic\ Acid \cdot H_2O)_{10} \cdot HI_5$. Faintly brownish crystals with copper luster were obtained from a hot aqueous solution of trimesic acid, hydroiodic acid, and iodine.

$(Benzophenone)_9 \cdot (KI)_2 I_7 \cdot CHCl_3$. Benzophenone complex was prepared from a chloroform solution of equivalent amounts of benzophenone, iodine, and potassium iodide. Black hexagonal plates with a vertical section of golden luster were obtained from the above solution by gradual evaporation of the solvent.

$(\alpha\text{-}Cyclodextrin)_2 \cdot LiI_3 I_2 \cdot 8H_2O$. Black hexagonal columnar crystals were obtained from a hot aqueous solution of stoichiometric equivalents of a α-cyclodextrin, iodine, and lithium iodide. The linear polyiodide chain was found parallel to the elongation direction of the column.

$(\alpha\text{-}Cyclodextrin)_2 \cdot Cd_{0.5} I2I_2 \cdot 26H_2O$. Very thin needle-shaped crystals with golden luster were obtained from a hot aqueous solution of stoichiometric equivalents of α-cyclodextrin (α-CD), cadmium iodide, and iodine. The long axis of the crystal was identified as the *c* axis by taking X-ray photographs.

Reflection spectra of these polyiodide crystals, except the last compound, were measured over a range of 12 000~40 000 cm^{-1} by using a microscopic reflection spectrophotometer equipped with Glan-Thompson and Rochon prism polarizers. Absorption spectra were obtained through the Kramers-Kronig (K-K) transformation from these reflection spectra. Absorption spectra of the $(\alpha\text{-cyclodextrin})_2 \cdot Cd_{0.5}I2I_2 \cdot 26H_2O$ crystal were measured by a microscopic transmittance spectrophotometer.

Resonance Raman spectral measurements for the KI disks were carried out on a JRS-400D Raman spectrophotometer with the 5145-Å excitation.

Results and Discussion

Before discussion of the spectra of the polyiodide chain compounds, a brief survey will be made of the electronic structure and the spectra of iodide and triiodide ions.

Spectrum of Iodide Ion. The electronic spectrum of the iodide ion in aqueous solution was studied by Franck and Scheibe[10] in 1928 and reviewed by Rabinowitch.[11] Two

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(1) F. H. Herbstein and M. Kapon, *Philos. Trans. R. Soc. London, Ser. A*, **291**, 199 (1979).

(2) F. H. Herbstein and M. Kapon, *Z. Kristallogr.*, in press.

(3) F. H. Herbstein, M. Kaftory, M. Kapon, and W. Saenger, *Z. Kristallogr.*, in press.

(4) M. Noltemeyer and W. Saenger, *Nature (London)*, **259**, 629 (1976).

(5) F. Cramer, U. Bergmann, P. C. Manor, M. Noltemeyer, and W. Saenger, *Ann. Chem.*, **1976**, 1169 (1976).

(6) R. C. Teitelbaum, S. L. Ruby, and T. J. Marks, *J. Am. Chem. Soc.*, **100**, 3215 (1978).

(7) T. J. Marks, *Ann. N. Y. Acad. Sci.*, **313**, 594 (1978).

(8) R. C. Teitelbaum, S. L. Ruby, and T. J. Marks, *J. Am. Chem. Soc.*, **102**, 3322 (1980).

(9) F. J. Moore and R. M. Thomas, *J. Am. Chem. Soc.*, **36**, 1928 (1914).

(10) J. Franck and G. Sheibe, *Z. Phys. Chem., Abt. A*, **139**, 22 (1928).

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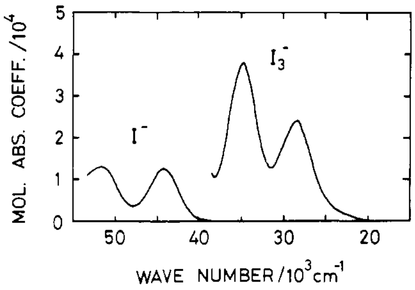

Figure 1. Absorption spectra of I^- and I_3^- in aqueous solutions of KI and KI + I_2, respectively.

peaks were found in the 50 000-cm^{-1} region with a doublet structure of $\Delta\nu = 7500$ cm^{-1}. A typical solution spectrum of iodide ion is illustrated in Figure 1. The doublet was interpreted as the splitting of $^2P_{3/2}$ and $^2P_{1/2}$ states of the iodine atom by the spin-orbit coupling. The electronic spectrum was explained as due to the electron transfer from I^- to the surrounding hydrate water molecules. The molar absorption coefficients are 13 700 at 44 300 cm^{-1} and 17 000 at 51 800 cm^{-1}.

Spectrum of Triiodide Ion. Two strong peaks were observed in the spectrum of triiodide ions in aqueous solution at 28 400 and 34 700 cm^{-1} with a separation of $\Delta\nu = 6300$ cm^{-1}, as shown in Figure 1. The splitting may be due to the spin-orbit coupling; the atomic energy level scheme is conserved in the isolated triiodide ion.

Gabes and his co-workers[12,13] calculated semiempirical molecular orbitals of symmetrical triiodide ion and discussed the electronic spectra of several trihalides. According to the calculation, the strong absorption bands in the 30 000-cm^{-1} region were assigned to the $\sigma_g \rightarrow \sigma_u^*$ and $\pi_g \rightarrow \sigma_u^*$ transitions. Although we agree to the assignment of the $\sigma_g \rightarrow \sigma_u^*$ transition, the $\pi_g \rightarrow \sigma_u$ transition is not acceptable for the following reasons. First, the intensity of the 28 400-cm^{-1} band (C band in Gabe's paper) is too strong as the forbidden $\pi_g \rightarrow \sigma_u^*$ transition. Secondly, the polarization character of the transitions is the same for the 28 400- and 34 700-cm^{-1} bands, as is discussed later in the text, and this is not in agreement with Gabes's assignment. A more plausible explanation for the 28 400-cm^{-1} band is that it arises from the splitting of the iodine $^2P_{3/2}$ and $^2P_{1/2}$ states by the spin-orbit coupling.

The electron population of the σ_g orbital is on both end atoms, while that of the σ_u^* orbital is larger on the central atom. The character of the electronic transition is an electron transfer from the end atoms to the central one; therefore, an atomic iodine state might appear on the end atoms and the splitting of the atomic state will be observed. A reasonable explanation for the absence of C bands in IBr_2^- and ICl_2^- of Gabes's spectra is given as follows. The electron affinities of bromine and chlorine are greater than those of iodine; therefore, an excess charge may be localized more on the end bromine and chlorine atoms than on the end iodine atom. Therefore, the bromine or chlorine atomic states which do not show distinct splittings may be involved in the electron-transfer spectra. For this reason the strong bands at 28 400 and 34 700 cm^{-1} of I_3^- are ascribed to the $\sigma_g \rightarrow \sigma_u^*$ transitions split by the spin-orbit coupling.

Crystalline Spectra of Isolated Triiodide Ions. The crystals of CsI_3 are elongated prisms with (110) and (001) faces where the reflectivities were measured along the *c*, *a*, and *b* axes. The crystalline structure was determined by Tasman et al.[14] and Runsink et al.[15] The triiodide ions lie on the (100) plane, as shown in Figure 2A, and the electronic transition moment has no component along the *a* axis. Actually the reflectivity along the *a* axis is the smallest (Figure 2B), in harmony with the above-mentioned assignment of the $\sigma_g \rightarrow \sigma_u^*$ transition. If the $\pi_g \rightarrow \sigma_u^*$ transition is involved with the 27 000-cm^{-1} band, it should have a component along the *a* axis, because it could be active when the σ_u^* orbital includes s character.

The Kramers-Kronig transformation of the reflectivities along the *b* and *c* axes is shown in Figure 2C. It is desirable to measure the reflectivity beyond 40 000 cm^{-1} and to include it in the K-K transformation. The spectral range, however, is beyond our spectrophotometer, and it was difficult to measure in this range. In the present study the main absorption band of polyiodide crystal exists in the lower energy region, and the reflectivity in the 40 000-cm^{-1} region drops less than 20%. Therefore, an error might not be serious even if we did not consider the high-energy data in the K-K transformation. The peaks are found at 27 000 and 33 000 cm^{-1}, and they correspond to the 28 400- and 34 700-cm^{-1} bands of I_3^- in aqueous solution. The intensities along the *c* and *b* axes are expected to be proportional to the square of the projections of transition moment along the *c* and *b* axes estimated 1:0.70 from the crystal structure, and the observed dichroic ratio between them is 1:0.72, which is in good agreement with this expectation.

The same polarization character of the two bands supports the above-mentioned assignment in that they belong to the same electronic origin split by the spin-orbit coupling.

The crystal of CsI_3 has a space group of *Pmcm* and has a possibility of Davydov splitting along each crystalline axis. In fact, the Davydov splittings amounting to 660 and 400 cm^{-1} are found for the first and second bands between the *b* and *c* axes, respectively, as shown in Figure 2C.

It should be stressed that the interaction between the adjacent iodide ions in this crystal is not strong because the iodide ions are separated from each other by a fairly large distance (~4 Å) and the σ orbital of the end atom does not directly overlap with those of the nearest neighbors.

The crystalline structure of (xanthotoxin)$_2$·KI_3 was determined by Herbstein and Kapon,[2] and the projection of molecules is shown in Figure 2D. The triiodide ions are arranged nearly parallel to the *b* axis. The reflectivities were measured with the developed plane along and perpendicular to the *b* axis. The reflectivity shows three peaks at 25 400, 32 500, and 38 800 cm^{-1}. Accidentally the organic chromophore is situated with the transition moment along the same direction with the triiodide ion, and it has three transitions at 33 000 ($\epsilon = 3200$), 40 000 ($\epsilon = 6400$), and 46 250 cm^{-1} ($\epsilon = 6400$) in methyl alcohol solution.

The Kramers-Kronig transformation of the reflectivity also shows three peaks, and it appears that the triiodide spectrum overlaps with that of the organic chromophore (Figure 2F). No strong band is found perpendicular to the *b* axis, which is in harmony with the $\sigma_g \rightarrow \sigma_u^*$ assignment for the triiodide spectrum. The absorption peaks at 27 500 and 32 000 cm^{-1} are due to the triiodide ion, and parts of the 32 000- and 37 000-cm^{-1} bands are ascribed to the xanthotoxin molecule. In harmony with no direct iod-

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(11) E. Rabinowitch, *Rev. Mod. Phys.*, **14**, 112 (1942).

(12) W. Gabes and M. A. M. Nijiman-Meester, *Inorg. Chem.*, **12**, 589 (1973).

(13) W. Gabes and D. J. Stufkens, *Spectrochim. Acta, Part A*, **30**, 1835 (1974).

(14) H. A. Tasman and K. H. Boswijik, *Acta Crystallogr.*, **8**, 59 (1955).

(15) J. Runsink, S. Swen-Walstra, and T. Migchelsen, *Acta Crystallogr., Sect. B*, **28**, 1331 (1972).

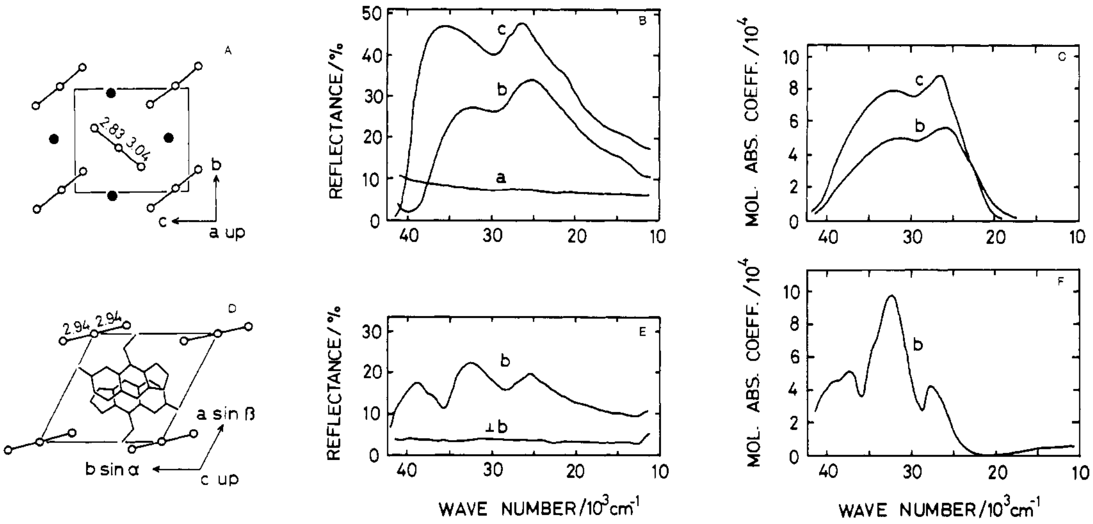

Figure 2. (A) Crystal structure of CsI_3. (B) Polarized reflection spectra of CsI_3 crystal along the *a*, *b*, and *c* axes. (C) Polarized absorption spectra of the CsI_3 crystal obtained by the K–K transformation of the reflection spectra. (D) Crystal structure of (xanthotoxin)$_2$·KI_3. (E) Polarized reflection spectra of the (xanthotoxin)$_2$·KI_3 crystal along and perpendicular to the *b* axis. (F) Polarized absorption spectrum of the (xanthotoxin)$_2$·KI_3 crystal obtained by the K–K transformation of the reflection spectrum.

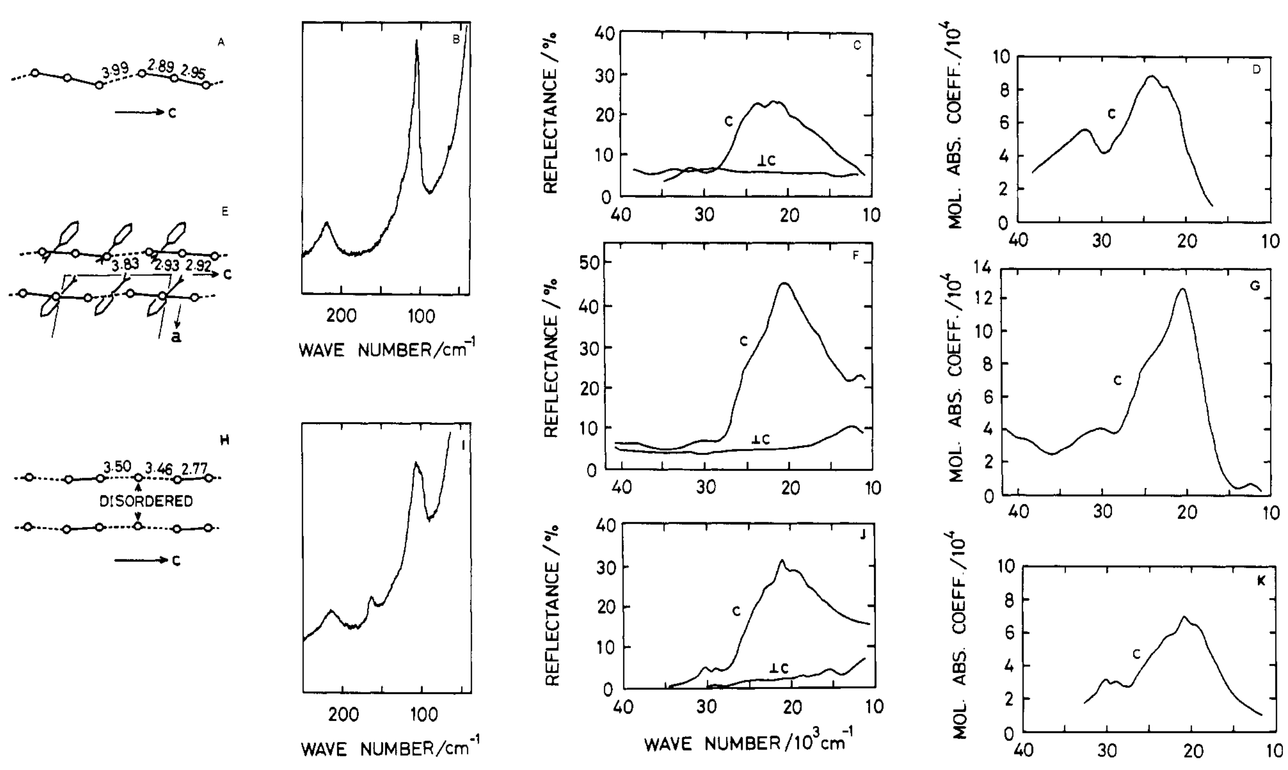

Figure 3. (A) Structure of linear triiodide chain in the tetra-*n*-butylammonium triiodide crystal. (B) Resonance Raman scattering of the tetra-*n*-butylammonium triiodide crystal with 5145-Å excitation. (C) Polarized reflection spectra of the tetra-*n*-butylammonium triiodide crystal. (D) Polarized absorption spectrum of the tetra-*n*-butylammonium triiodide crystal obtained by the K–K transformation of the reflection spectrum. (E) Double-strand structure of triiodide chains in the (benzamide)$_2$·HI_3 crystal. (F) Polarized reflection spectra of the (benzamide)$_2$·HI_3 crystal along and perpendicular to the *c* axis. (G) Polarized absorption spectrum of the (benzamide)$_2$·HI_3 crystal obtained by the K–K transformation of the reflection spectrum. (H) Double-strand structure of linear triiodide chains in the caffeine·H_2O·HI_3 crystal. (I) Resonance Raman scattering of the caffeine·H_2O·HI_3 crystal with 5145-Å excitation. (J) Polarized reflection spectra of the caffeine·H_2O·HI_3 crystal along and perpendicular to the *c* axis. (K) Polarized absorption spectrum of the caffeine·H_2O·HI_3 crystal obtained by the K–K transformation of the reflection spectrum.

ine–iodine interaction in the crystal, the electronic spectrum shows a pattern of isolated triiodide ion.

Crystalline Spectra of Linear Triiodide Chain. Herbstein et al.[2,3] recently studied three crystals containing triiodide ions which are arranged in a quasi-linear way in the channels surrounded by a matrix of counterions or organic molecules. In tetra-*n*-butylammonium triiodide crystal each channel contains a single triiodide chain, while in (benzamide)$_2$·HI_3 and caffeine·H_2O·HI_3 crystals, parallel chains are formed within a channel (Figure 3A,E,H).

The Raman spectra of tetra-*n*-butylammonium triiodide and caffeine·H_2O·HI_3 were recorded as shown in Figure 3, B and I, where the characteristic Raman lines of the triiodide ion at 108 cm^{-1} were observed in both crystals. In addition, an extra line at 166 cm^{-1}, which might be ascribed to the I_5^- ion, appeared weakly in the caffeine·H_2O·HI_3

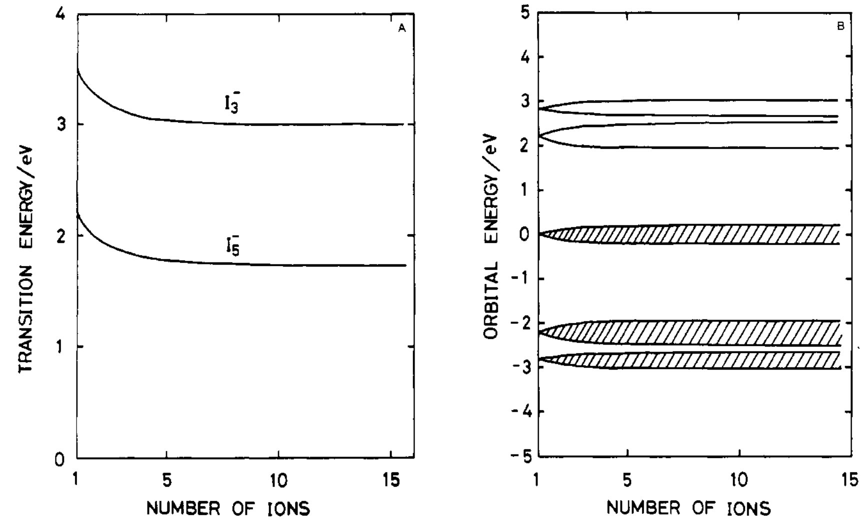

Figure 4. (A) Transition energies of linear chain systems of I_3^- and I_5^- calculated by the Hückel MO method. (B) Broadening of the energy levels of the Hückel MO of linear pentaiodide system. The hatched levels are the occupied ones by the valence electrons.

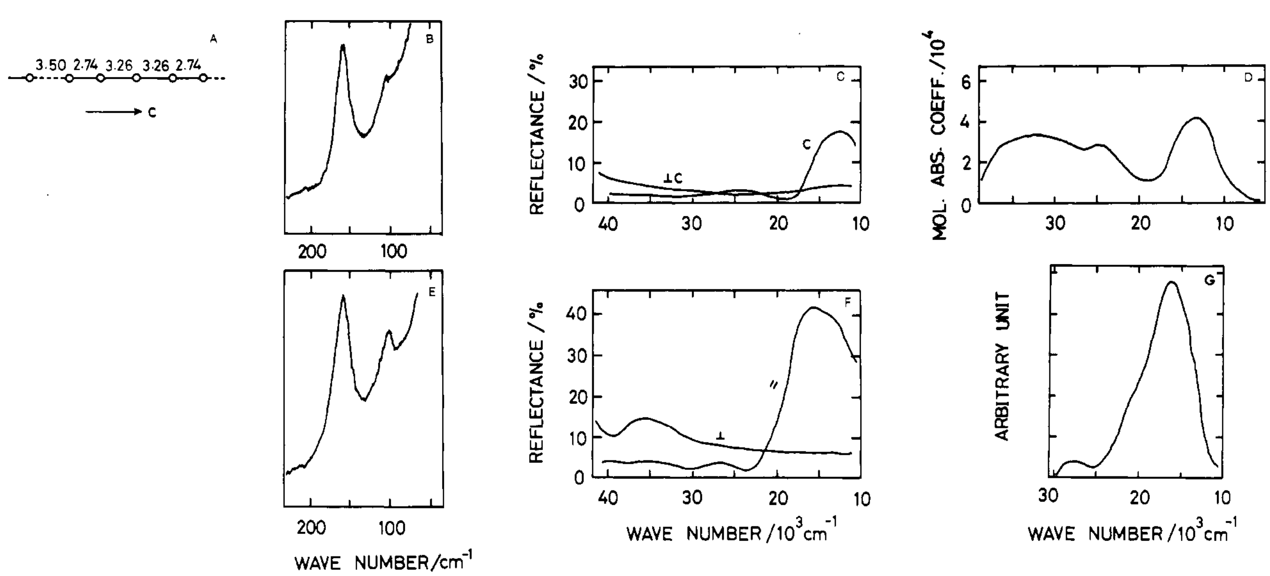

Figure 5. (A) Structure of linear pentaiodide chain in the (trimesic acid·$H_2O)_{10}$·HI_5 crystal. (B) Resonance Raman scattering of the (trimesic acid·$H_2O)_{10}$·HI_5 with 5145-Å excitation. (C) Polarized reflection spectra of the (trimesic acid·$H_2O)_{10}$·HI_5 crystal along and perpendicular to the c axis. (D) Polarized absorption spectrum of the (trimesic acid·$H_2O)_{10}$·HI_5 crystal obtained by the K–K transformation of the reflection spectrum. (E) Resonance Raman scattering of the (benzophenone)$_9$·$(KI)_2I_7$·$CHCl_3$ crystal with 5145-Å excitation. (F) Polarized reflection spectra of the (benzophenone)$_9$·$(KI)_2I_7$·$CHCl_3$ crystal parallel and perpendicular to the polyiodide chain (assumed). (G) Polarized absorption spectrum of the (benzophenone)$_9$·$(KI)_2I_7$·$CHCl_3$ crystal obtained by the K–K transformation of the reflection spectrum.

crystal. According to the disordered structure of the triiodide ion in the caffeine·H_2O·HI_3 crystal reported by Herbstein,[3] the possibility of the existence of I_5^- ion is considered as a minor component. In other words, the Raman line at 166 cm^{-1} is in accord with the disordered structure of the triiodide chain.

The reflectivity of tetra-*n*-butylammonium triiodide crystal was measured parallel and perpendicular to the *c* axis, and the reflectivity is strongest parallel to the iodide chain, as shown in Figure 3C. The Kramers–Kronig transformation of the reflectivity gives a spectrum shown in Figure 3D, where the peak is found at 24 000 cm^{-1}.

The reflectivity of (benzamide)$_2$·HI_3 was measured with the (100) plane (Figure 3F), parallel and perpendicular to the triiodide chain. The reflectivity is strongest along the chain direction at 20 500 cm^{-1}, and other weak humps are found in the 12 000-cm^{-1} region along parallel and perpendicular directions of the chain axis. The absorption spectrum along the chain direction was calculated by the Kramers–Kronig transformation, as shown in Figure 3G.

The reflectivity of caffeine·H_2O·HI_3 was measured parallel and perpendicular to the *c* axis, and the maximum along the chain direction was found at 21 000 cm^{-1}. The tail of reflectivity extends to the lower energy region, which is in contrast with the single-chain system. The spectral pattern resembles that of the double-chain one, (benzamide)$_2$·HI_3. The Kramers–Kronig transformation of the reflectivity gives the absorption spectra as shown in Figure 3K.

The comparison of the spectra of the triiodide chain with the isolated triiodide (Figure 2, B and C) shows that the doublet of spin–orbit coupling is found in the 21 000- and 30 000-cm^{-1} region with $\Delta\nu \simeq 9000$ cm^{-1} for the double chain and 24 000 and 31 000 cm^{-1} for the single-chain crystals. However the band shape is greatly changed; i.e., the first band (~21 000 cm^{-1}) is much stronger than the second band (~30 000 cm^{-1}). This assignment of the split band should be confirmed by other means. The red shift for the first peak is ca. 3000 cm^{-1} for the single chain and 6000 cm^{-1} for the double chain as compared with the

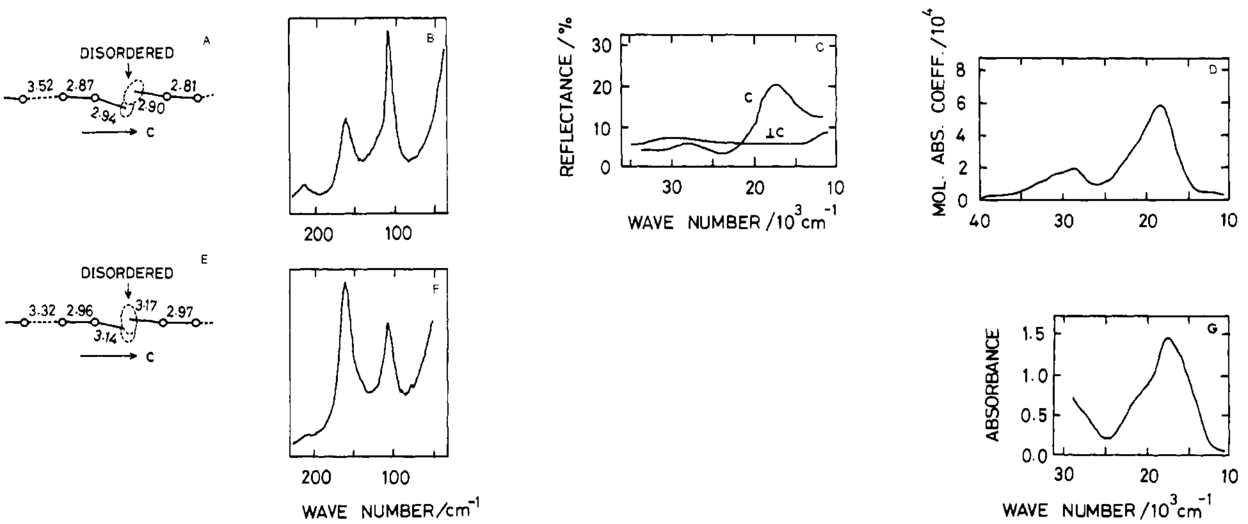

Figure 6. (A) Structure of linear pentaiodide chain in the $(\alpha\text{-cyclodextrin})_2\cdot LiI_3I_2\cdot 8H_2O$ crystal. (B) Resonance Raman scattering of the $(\alpha\text{-cyclodextrin})_2\cdot LiI_3I_2\cdot 8H_2O$ crystal. (C) Polarized reflection spectra of the $(\alpha\text{-cyclodextrin})_2\cdot LiI_3I_2\cdot 8H_2O$ crystal along and perpendicular to the *c* axis. (D) Polarized absorption spectrum of the $(\alpha\text{-cyclodextrin})_2\cdot LiI_3I_2\cdot 8H_2O$ crystal obtained by the K-K transformation of the reflection spectrum. (E) Structure of linear pentaiodide chain in the $(\alpha\text{-cyclodextrin})_2\cdot Cd_{0.5}I2I_2\cdot 26H_2O$ crystal along and perpendicular to the *c* axis. (F) Resonance Raman scattering of the $(\alpha\text{-cyclodextrin})_2\cdot Cd_{0.5}I2I_2\cdot 26H_2O$ crystal. (G) Polarized absorption spectrum of the $(\alpha\text{-cyclodextrin})_2\cdot Cd_{0.5}I2I_2\cdot 26H_2O$ crystal.

crystalline spectra of the isolated triiodide.

All absorption curves so far presented show a subbands which are ascribed to the spin–orbit splitting. In addition each absorption peak is associated with a very broad envelope, which is considered as arising from vibrational progressions and other mechanisms. The vibrational energy of the iodine-containing bond may be relatively small, but the electronic perturbation to each energy level caused by the polarizable iodine atoms will be significant to broaden the band shape.

The calculation of the exciton band shift for the linear chain triiodide system was performed with a model structure of ions arranged linearly separated by 9.66 Å. The magnitude of the shift is largely dependent on the size of the transition moment. If the whole intensity is afforded to the first peak, the shift is calculated to be -2000 cm^{-1}. Actually the intensity is distributed between the two peaks, and a reasonable shift may be -1000 cm^{-1}, one-third of the observed shift. The rest of the shift may be due to the electron-exchange effect between the triiodide ions in the one-dimensional chain.

For the double triiodide chain crystals, the exciton interaction was calculated by the slab sum method. The results showed that the allowed transition should be blue shifted by 330 cm^{-1} for $(\text{benzamide})_2\cdot HI_3$ crystal and 1470 cm^{-1} for caffeine$\cdot H_2O\cdot HI_3$ crystal. In fact both spectra showed large red shifts as shown in Figure 3, G and K. If the electron-exchange effect is the major source of the red shift, then it should be ca. -2000 cm^{-1} for the single linear triiodide chain and $-6000\sim-7000$ cm^{-1} for the double chain. The shifts are apparently large as compared with single-chain crystals; hence, a cooperative effect between the chains may be occuring.

Another reason for the red shift, which is conceivable for caffeine$\cdot H_2O\cdot HI_3$, is a mixing of I_5^- ion in the chain; the lower energy absorption tail might be ascribed to the minor I_5^- ion.

The calculation of Hückel-type MO for the model structure of a large number of triiodide chains, separated by 3.8 Å, is shown in Figure 4A. With a β value to give a reasonable fit to the monomer triiodide spectrum, and with the inter-iodide resonance integral taken to be proportional to the $5p\sigma$–$5p\sigma$ overlap integral, we obtain the energy-level shift of ca. -4000 cm^{-1}. Therefore, the combined effect of the dipole–dipole interaction in the exciton state and the electron-exchange interaction might be the origin of the large red shift found in the linear triiodide systems.

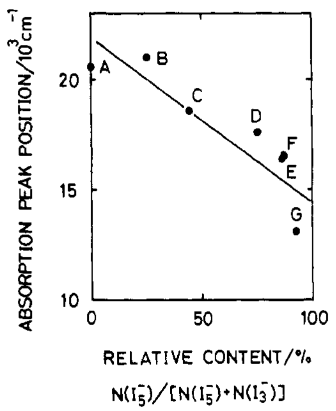

Figure 7. Linear relationship between the position of absorption peak and the content of I_5^- species in several polyiodides, $N(I_5^-)/[N(I_5^-) + N(I_3^-)]$, estimated from the relative Raman intensities with the 5145-Å excitation: (A) $(\text{benzamide})_2\cdot HI_3$; (B) caffeine$\cdot H_2O\cdot HI_3$; (C) $(\alpha\text{-cyclodextrin})_2\cdot LiI_3I_2\cdot 8H_2O$; (D) $(\alpha\text{-cyclodextrin})_2 Cd_{0.5}I2I_2\cdot 26H_2O$; (E) $(\text{benzophenone})_9\cdot(KI)_2I_7\cdot CHCl_3$; (F) amylose–polyiodine complex; (G) $(\text{trimesic acid}\cdot H_2O)_{10}\cdot HI_5$.

Crystalline Spectra of Linear Pentaiodide Chain. A few examples of linear pentaiodide chain systems are known: Herbstein and Kapon[16] reported on the crystal structure of $(\text{trimesic acid}\cdot H_2O)_{10}\cdot HI_5$, where the linear I_5^- chain exists as shown in Figure 5A, but the arrangements of the chains in the crystal are not correlated to each other to give a regular lattice. The complex $(\text{benzophenone})_9\cdot(KI)_2I_7\cdot CHCl_3$ is another probable system including a $(I_5^-)_x$ chain. The structure has not yet been solved, but the chemical composition suggests that it may consist of three I_5^- species and one I_3^-, and the electronic spectrum shows that it is probably a linear chain system. The existence of the pentaiodide ion in several complexes has been suggested by Marks et al.[6-8] by using a resonance Raman spectra.

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(16) F. H. Herbstein and M. Kapon, *Acta Crystallogr., Sect. A*, 28, S74 (1972).

The Raman spectrum of (trimesic acid$\cdot$$H_2O$)$_{10}$$\cdot$$HI_5$ was measured as shown in Figure 5B, which is nearly in agreement with the reported one.[6-8] It exhibits a strong 163-cm^{-1} line and a weak 107-cm^{-1} line and their combination and overtones. The intensity ratio of 163- and 107-cm^{-1} lines is almost independent of the excitation wavelength. The line at 163 cm^{-1} is characteristic of a $(I_5^-)_x$ chain. The peak frequency of the weak band, 107 cm^{-1}, coincides with that of $(I_3^-)_x$ or I_3^-.

Two alternative interpretations are possible concerning the assignment of these bands. One of them is that 107 cm^{-1} is inherent in $(I_5^-)_x$ as well as $(I_3^-)_x$ or I_3^- since the combination band of the 163- and 107-cm^{-1} bands is observed at 264 cm^{-1}.[8] The other is that the 107-cm^{-1} band is solely due to $(I_3^-)_x$ or I_3^- embedded in the $(I_5^-)_x$ chain. The appearance of the combination band is explained by a resonance effect of excitonic excited state covering both the I_5^- and I_3^- species, and the ground states of both species may be simultaneously excited by a Raman process to give a combination band.

The Raman spectrum of benzophenone polyiodide is quite similar to that of the trimesic acid polyiodide, as shown in Figure 5E, and is relatively independent of the excitation wavelength. If we take the latter interpretation about the 108-cm^{-1} band, the complex is considered to consist largely of $(I_5^-)_x$ and to a lesser extent of $(I_3^-)_x$ chains, which is consistent with chemical composition. In this case a combination band at 267 cm^{-1} is observed for the reason mentioned above.

The reflection spectra of (trimesic acid$\cdot$$H_2O$)$_{10}$$\cdot$$HI_5$ were measured along the *c* axis and perpendicular to it, as shown in Figure 5C. The Kramers–Kronig transformation of the reflectance spectrum gave a peak at 13 000 cm^{-1}, which is a characteristic of the linear $(I_5^-)_x$ chain, while higher ones are ascribed to the organic chromophore. Although the crystalline structure of benzophenone polyiodide is not known, the reflectivity was measured as shown in Figure 5F. Along the strongest reflective direction broad peaks are found at 13 000 and 16 000 cm^{-1}, and the Kramers–Kronig transformation of the reflectivity gives a single peak at 16 400 cm^{-1}.

The color of amylose–iodine complex has been attributed to the linear iodine chain, but its character has not been clarified. Marks found I_5^- species in the amylose–iodine complex, and the origin of the characteristic color might be assigned to the I_5^- or its linear array, $(I_5^-)_x$. In an accompanying paper[17] we found that a single I_5^- species in the shortest amylose complex in aqueous solution absorbs at 17 900 cm^{-1}, while the iodide complex in the longer amylose chain absorbs at 16 700 cm^{-1}.

With the structure of (trimesic acid$\cdot$$H_2O$)$_{10}$$\cdot$$HI_5$ shown in Figure 5A, the magnitude of the dipole interaction and the electron-exchange effects can be calculated. The oscillator strength of the transition of the single I_5^- species was estimated as $f = 1.45$, and the size of the transition moment is 2.73 Å. When these values were used, the dipole–dipole interaction energy was calculated as −1120 cm^{-1}. Experimentally the shift of the linear pentaiodide system is −4900 cm^{-1} as compared with the above-mentioned value; therefore, the rest, −3800 cm^{-1}, may be due to the electron-exchange effect. The interatomic distance between I_5^- ions is 3.5 Å, and a large electron-exchange effect is expected for this system.

The Hückel MO calculation with the inclusion of the interaction between I_5^- ions was performed, and the result is shown in Figure A and B. It is found that the band broadening occurs for both filled and empty bands (Figure 4B). Thus the bandwidth of the valence band was estimated as 0.5 eV for the linear pentaiodide chain. The large red shift of the pentaiodide chain in trimesic acid monohydrate channel is thus explained by both the dipole interaction and the electron-exchange effect. The absorption peak of the polyiodide chain in the benzophenone crystal may be interpreted as being due to the mixed chain of the pentaiodide and triiodide.

Crystalline Spectra of Cyclodextrin Pentaiodide Complexes. The crystalline structures of α-cyclodextrin–iodine complexes were studied by Saenger and his co-workers,[4,5] and several crystalline types were described. In the channel of α-cyclodextrin rings, the polyiodide chain is elongated and disordered I_5^- and $I_3^-\cdots I_2$ species are located.

Two typical types of crystalline spectra are shown in Figure 6C for $(\alpha\text{-CD})_2Li^+I_5^-\cdot 8H_2O$ and in Figure 6G for $(\alpha\text{-CD})_2Cd_{0.5}{}^+I_5^-\cdot 26H_2O$. The X-ray results for these two crystals show that the Li salt contains the disordered $I_3^-\cdots I_2$ chain while Cd salt includes the disordered I_5^- chain.

The Raman spectra of these complexes are shown in Figure 6, B and F, and characteristic lines of both $(I_5^-)_x$ and $(I_3^-)_x$, 161- and 107-cm^{-1} bands, respectively, are found with varying proportion. This result does not mean a discrepancy of Raman and X-ray results, because the varied composition of I_5^- and $I_3^-\cdots I_2$ chains will give the disordered X-ray results with an emphasis on the major component. Therefore, it is likely that the Li complex contains more $I_3^-\cdots I_2$ than I_5^- and vice versa for Cd complex. The relative intensity of 161- and 107-cm^{-1} bands is dependent strongly on the excitation wavelength; the 107-cm^{-1} band is intensified with the excitation of shorter wavelength light, and the 161-cm^{-1} band is enhanced with the excitation of a longer one.

The crystalline reflection spectra were measured with the Li complex parallel and perpendicular to the *c* axis (Figure 6C). The Kramers–Kronig transformation of the reflectivity gives a spectrum peaked at 18 600 cm^{-1}, as shown in Figure 6D. Another small peak is found at 28 800 cm^{-1}, which may be another doublet component of spin–orbit coupling.

The crystals of Cd complex are too small to be measured by the reflection technique. We measured the transmittance spectrum by a microscopic method and obtained the absorption spectrum as shown in Figure 6G. The absorption peak is found at 17 600 cm^{-1} for the Cd complex along the *c* axis.

We attempted to estimate the relative contents of I_5^- and I_3^- species in the complexes from the relative Raman intensities of 163- and 107-cm^{-1} bands supposing the 107-cm^{-1} band to be inherent in I_3^- species and using the fact that the intensity ratio of I_5^- and I_3^- peaks is ca. 1:2 in the Raman spectrum of a mixture of equivalent amounts of (benzamide)$_2$$\cdot$$HI_3$ and (trimesic acid$\cdot$$H_2O$)$_{10}$$\cdot$$HI_5$ crystals. If we plot the electronic absorption peaks against the estimated relative contents of several polyiodide complexes, a smooth line is obtained, as shown in Figure 7, suggesting an approximate correlation between them.

Therefore the extent of the disorder of the polyiodide chain in the complex may be estimated from those plots. However, the intensities of both lines are dependent on the excitation wavelength; hence, caution must be taken in measuring Raman intensities and considering the composition of the complexes.

Acknowledgment. We are grateful to Professor F. H. Herbstein for sending us preprints of unpublished results.

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[17] J. Tanaka and M. Takeuchi, to be submitted for publication.