Absorption Spectra of the Polyacetylene Films Doped with BF_3

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Optical absorption measurements are carried out on pure and BF_3 doped polyacetylene films over a wide wavelength region (200 cm^{-1}—54000 cm^{-1}). In the lightly doped polymer, the extra peak appears at 870 cm^{-1} and it is assigned to the transition from the valence band to the impurity level. This band becomes more intense at low temperature. For the heavily doped films, the dc conductivity of the $(CH)_x$ fibril is optically estimated to be $\sigma_0=10^4\,\Omega^{-1}\,cm^{-1}$. This value is in good agreement with the calculated value ($\sigma_0=0.8\times10^4\,\Omega^{-1}\,cm^{-1}$) due to the tight binding model.

Polyacetylene is one of the simplest linear conjugated polymers with a single chain structure. Accordingly, many theoretical and experimental studies[1] were reported upon the electronic structure of polyacetylene as a quasi one-dimensional conductor. Shirakawa and coworkers[2-4] succeeded in synthesizing high quality polycrystalline films of $(CH)_x$. The conductivity measured by the four point probe technique was about $10^{-9}\,\Omega^{-1}\,cm^{-1}$ for the *cis*-rich polyacetylene film. Recently, Shirakawa, Heeger, and MacDiarmid and coworkers[5-7] found out that, when flexible, crystalline silvery films of the *cis*-$(CH)_x$ or *trans*-$(CH)_x$ polymer were doped with controlled amounts of electron-attracting species such as chlorine, bromine, iodine, or AsF_5, their electrical conductivity could be systematically varied over a wide range from that of an insulator ($\sigma=10^{-9}\,\Omega^{-1}\,cm^{-1}$) to a metal ($\sigma=10^3\,\Omega^{-1}\,cm^{-1}$). Furthermore, the IR[8] and visible-UV[9-11] absorption spectra were measured upon exposure to vapors of chlorine, bromine, iodine, or AsF_5. Tanaka *et al.*[12] studied the infrared reflection spectra of oriented polyacetylene films, doped with varying concentrations of AsF_5 and iodine, and discussed about the relation between the reflectivity and the conductivity of doped $(CH)_x$ films.

In the present paper, we report the absorption spectra in the 200 cm^{-1}—54000 cm^{-1} region of *cis*-rich polyacetylene films doped with BF_3 and discuss about the electronic structure of the heavily doped $(CH)_x$ films.

Experimental

The *cis*-rich polyacetylene films were prepared from acetylene by treatment of the Ziegler catalyst in hexane at −80 °C as described by Shirakawa and coworkers.[2-4] The films were doped by exposure to the vapor of BF_3 at room temperature. The dopant concentration were determined by weight change of the sample.[17]

The IR transmission measurement of the thick films (*ca.* 5×10^{-3} cm) were taken with Hitachi EPI-L (200 cm^{-1}—700 cm^{-1}) and JASCO IRA-3 (330 cm^{-1}—5000 cm^{-1}) spectrophotometers at room temperature and with a JASCO DS-402G (600 cm^{-1}—4000 cm^{-1}) spectrophotometer at low temperature.

The visible and UV transmission data of the thin films (*ca.* 200 Å) polymerized on the inner surface of the 1 cm quartz cell were measured with JASCO IRA-3 (2500 cm^{-1}—5000 cm^{-1}) and Carl Zeiss M4Q (4000 cm^{-1}—54000 cm^{-1}) spectrophotometers.

Results and Discussion

Linear polyacetylene, $(CH)_x$, is the simplest conjugated organic polymer and the π-electrons on each carbon atom delocalize to form a band. The energy of the π-electrons is calculated by the MO theory,[1,11]

$$\varepsilon(k) = \pm\sqrt{t_1^2+t_2^2+2t_1t_2\cos(ka)} \quad (1)$$

where t_1 and t_2 (>0) are the transfer integrals between successive sites, a the C–C bond length, and k the wave vector. In the absence of bond alternation ($t_1=t_2$), the energy eigenvalues form a band of width $4t$ (Fig. 1-1) which is half-filled with the π-electrons. On the other hand, if one bond is longer than the

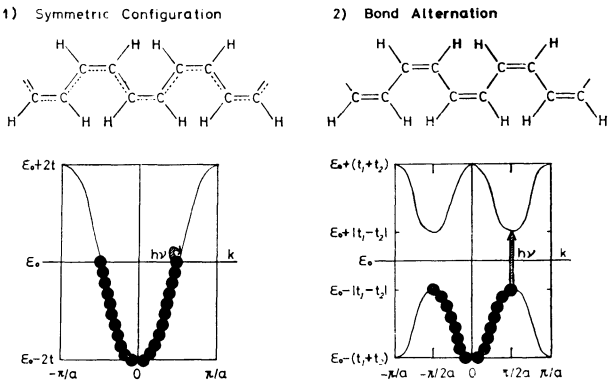

Fig. 1. Energy band diagram for the polyacetylene system.

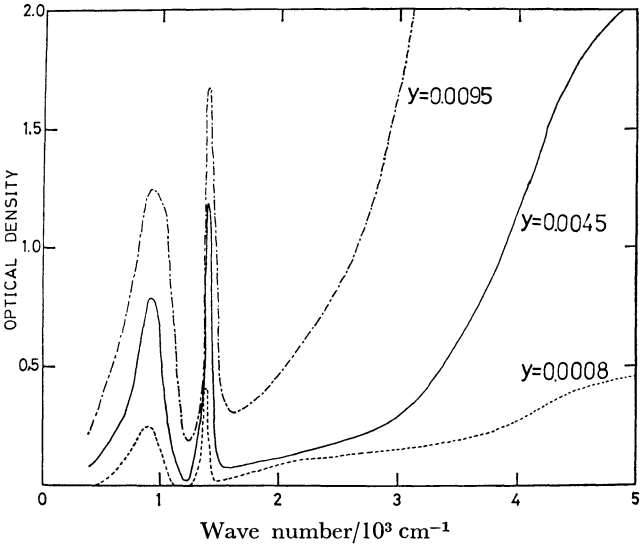

Fig. 2. IR absorption spectra of the thick films (*ca.* 5×10^{-3} cm) of $[CH(BF_3)_y]_x$.

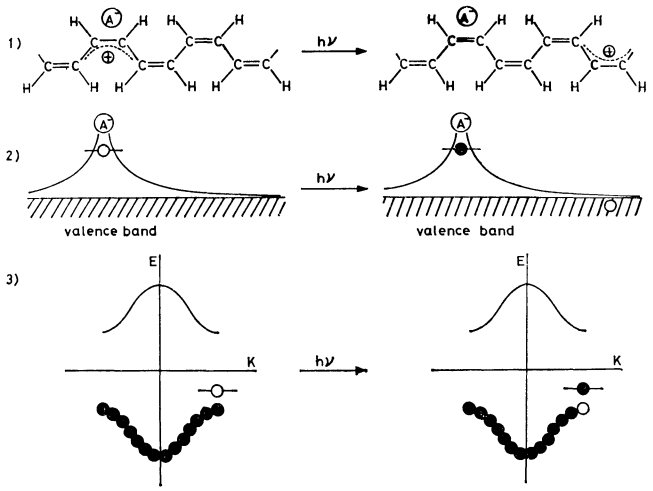

Fig. 3. Character of the 870 cm^{-1} band.
(1) Schematic diagram of acceptor ion (A^-) near a $(CH)_x$ chain. (2) The resulting hole on the polymer chain is bound by the Coulomb potential. (3) The resulting bound state is in the energy gap.

other ($t_1 \neq t_2$), a set of bonding (valence band) and antibonding (conduction band) orbitals is formed and the energy gap in the electronic spectrum is expected as shown in Figs. 1—2.

The absorption spectrum of the undoped polymer has the sharp absorption edge at 12000 cm^{-1} and the peak at 17000 cm^{-1} (Fig. 5, $y=0$). Accordingly, this absorption band can be assigned to the interband transition from the valence band to the conduction band, and shows that the bond alternation is present in the polymer.

In the lightly doped polymer, two infrared peaks of the additional absorption over the undoped sample are observed at 1370 cm^{-1} and 870 cm^{-1} (Fig. 2). The narrow mode at 1370 cm^{-1} was explained by Su, *et al.*[13] as the result of soliton formation in the long chain polyenes.

The broad band at 870 cm^{-1} can be assigned to the transition from the valence band to the hole level by applying the traditional approach in semiconductors. That is, the cation (hole) in the $(CH)_x$ chain is tightly bound to the charge center (A^-) by Coulomb force in a dielectric medium as shown in Fig. 3. Then, the binding energy E of the hole in the screened Coulomb field are given by the following equation,[8,16]

$$-\frac{\hbar^2}{2m^*}\frac{d^2}{dx^2}\psi_n - \frac{e^2}{\varepsilon|x|}\psi_n = E_n\psi_n \tag{2}$$

$$E_n = -\frac{m^*e^4}{2\hbar^2\varepsilon^2}\frac{1}{n^2}. \tag{3}$$

Taking the measured dielectric constant to be $\varepsilon=11$[8] and assuming $m^*/m=1$, the transition from the valence band to the impurity 1s level can be estimated to occur in the vicinity of 900 cm^{-1}. In the thermal equilibrium at room temperature, a few π-electrons can excite from the valence band to the impurity levels. This means that the optical absorption intensity increases at the low temperature. Figure 4 shows the temperature dependence of the 870 cm^{-1} band. The peak is observed at 870 cm^{-1} and located

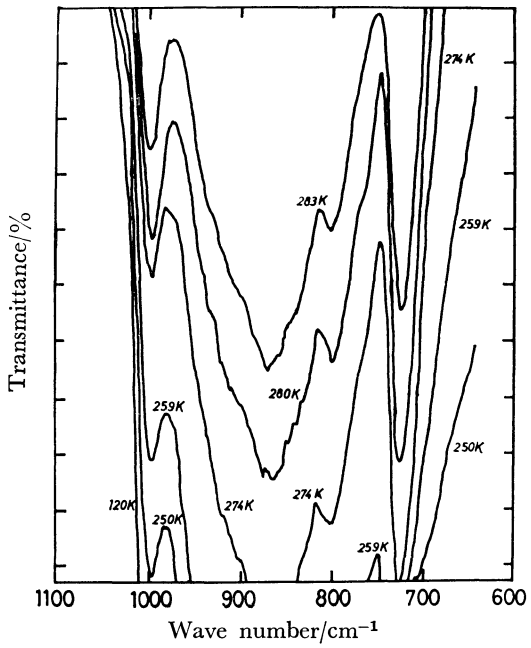

Fig. 4. IR transmission spectra of $[CH(BF_3)_{0.01}]_x$ at various temperature.

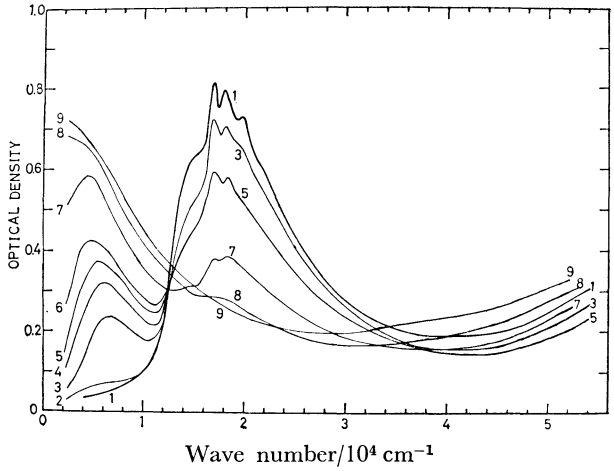

Fig. 5. Absorption spectra of the thin films of $[CH(BF_3)_y]_x$, (1) $y=0$, (2) $y=0.0045$, (3) $y=0.0095$, (4) $y=0.018$, (5) $y=0.025$, (6) $y=0.029$, (7) $y=0.038$, (8) $y=0.051$, (9) $y=0.077$.

between two C–H out of plane bending modes (1015 cm^{-1} in the *trans* isomer and 740 cm^{-1} in the *cis* isomer) and the transmittance of the 870 cm^{-1} band becomes smaller as the temperature decreases.

In addition to the 1370 cm^{-1} and 870 cm^{-1} bands, a broad band appears in the region of 8000 cm^{-1} and the absorption intensity of the interband transition at about 17000 cm^{-1} decreases (Fig. 5). The fact that there is an isosbestic point at 12000 cm^{-1} in the spectra clearly indicates that there is an equilibrium between two absorbing species. Furthermore, the red shift of the broad band suggests that doping removes the bond alternation leading to a uniform bond length as shown in Figs. 1 and 3. That is, the energy gap between the valence and conduction bands becomes small and the metallic state is formed in the heavily doped films. The maximum absorption coefficient of

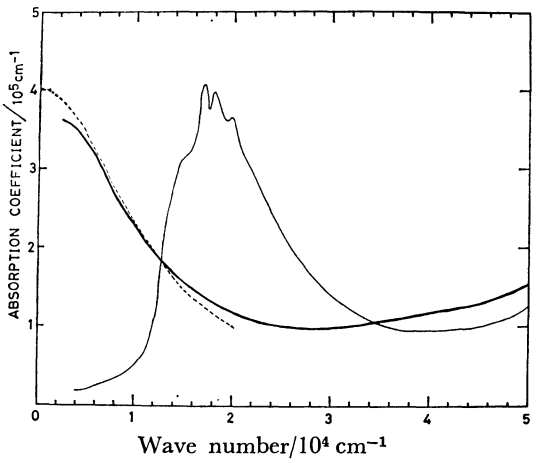

Fig. 6. Comparison between the calculated and observed absorption spectra of the intraband transition band of the metallic doped $(CH)_x$ film.
——: Pure $(CH)_x$, ——: $[CH(BF_3)_{0.077}]_x$, ----: calculated spectra.

the interband transition was determined to be 4×10^5 cm^{-1} near 17000 cm^{-1} by Fincher, *et al.*[11] Accordingly, the absorption coefficient of the intraband transition of the heavily doped films ($y=0.077$) can be estimated as shown in Fig. 6.

The relation between the absorption coefficient $\alpha(\omega)$ and the conductivity $\sigma_1(\omega)$ is given in the following equation,[14]

$$\alpha(\omega)=\frac{4\pi}{n(\omega)c}\sigma_1(\omega)=\frac{4\pi}{n(\omega)c}\frac{\sigma_0^{\text{film}}}{1+\omega^2\tau_0^2} \tag{4}$$

where $n(\omega)$ is the refractive index and c the velocity of light. σ_0^{film} and τ_0 are the dc conductivity of the $(CH)_x$ film and the relaxation time, respectively. These parameter were determined by the optimum fit of Eq. 4 to the experimental data where the refractive index $n(\omega)$ is taken to be unity. The fit was obtained with $\sigma_0^{\text{film}}=1070\ \Omega^{-1}$ cm^{-1} and $\tau_0=0.43\times 10^{-15}$ s. The calculated absorption spectrum based on these values is plotted for comparison with the experimental curves in Fig. 6.

Electron microscopy photographs of $(CH)_x$ films show a fibril structure with typical fibril diameter of about 200 Å. The individual fibrils are randomly oriented and the polymer has the volume filling factor of about $f=1/3$.[11] Then, the dc conductivity σ_0 of the fibrils is given by the next equation,

$$\sigma_0=\sigma_0^{\text{film}}/(f\delta)=10^4\ \Omega^{-1}\text{ cm}^{-1} \tag{5}$$

where δ is the fractional alignment factor ($\delta=1/3$).

In the tight binding approximation, the effective mass m^* of the free carrier is calculated as follows,[15]

$$\frac{m}{m^*}=\frac{4ta^2m}{\pi\hbar^2}=1.1 \tag{6}$$

where t and a are taken to be 3.0 eV and 1.4 Å, respectively. From the measured density of $(CH)_x$ (0.4 g/cm^3) and the filling factor $f=1/3$, the number of π-electrons per unit volume of the fibril can be estimated to be $N=6\times 10^{22}$ cm^{-3}. Then, the plasma frequency ω_p and dc conductivity σ_0 for a metal are written in the conventional form,[15]

$$\omega_p^2=4\pi Ne^2/m^* \tag{7}$$

and

$$\sigma_0=\omega_p^2\tau_0/4\pi. \tag{8}$$

Using the above values for N, m^* and τ_0, ω_p is estimated to be 1.46×10^{16} s^{-1} ($\hbar\omega_p=9.1$ eV) and σ_0 to be $0.8\times 10^4\ \Omega^{-1}$ cm^{-1}. The calculated value of σ_0 is in good agreement with the optically determined value.

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