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RAMAN STUDIES ON DONOR-DOPED *TRANS*-POLYACETYLENES

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The Raman spectra of donor-doped *trans*-polyacetylenes have been studied. They are different from the Raman spectra of either intact or acceptor-doped *trans*-polyacetylene. A model structure of donor-doped *trans*-polyacetylene is proposed.

Polyacetylene has been found to show high electrical conductivity when doped with controlled amounts of electron-acceptors (such as iodine, AsF_5, and SO_3) or electron-donors (such as sodium and potassium).[1-3] In a previous paper[4] we reported the Raman and absorption (ultraviolet through infrared) spectra of acceptor-doped *trans*-polyacetylene and proposed a structure model. In this communication the Raman spectra of donor-doped *trans*-polyacetylene will be reported.

Preparation of polyacetylene samples and measurements of the Raman spectra were carried out in the same way as described earlier,[4] except that the alkali doping was performed by treating the *trans*-polyacetylene films with tetrahydrofuran solution of alkali naphthalide (*ca*. 0.5M) for 30 minutes. The amount of alkali in the doped sample could not be determined but the electrical conductivity of the doped sample was comparable to that of the sample heavily doped with iodine. Alkali-doped polyacetylene was found very unstable and, therefore, care was taken not to expose the doped film to air. The absorption spectrum in the ultraviolet and visible regions was published elsewhere.[5] We are now trying to observe the infrared spectra of alkali-doped polyacetylenes without exposing the sample to air, and the results will be reported separately.

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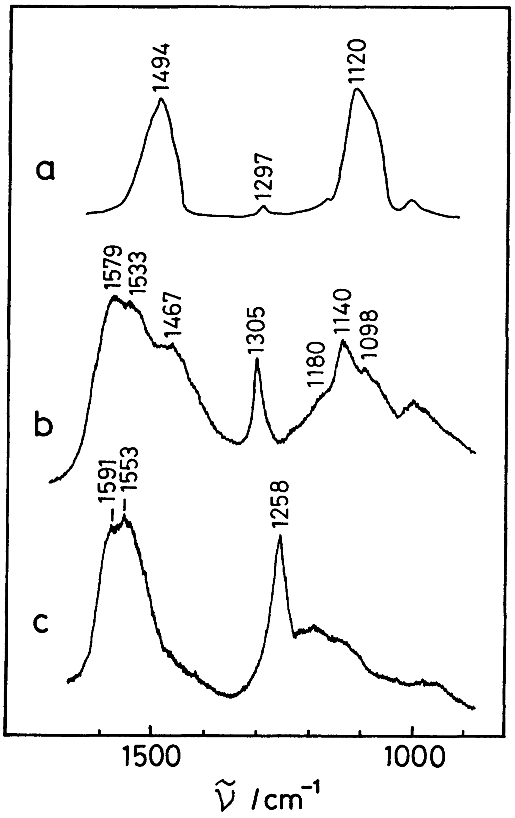
In Fig. 1 the Raman spectrum of Na-doped *trans*-$(CH)_x$ is compared with those of intact and AsF_5-doped *trans*-$(CH)_x$. As is obvious in this figure, the Raman spectra of donor-doped and acceptor-doped *trans*-$(CH)_x$ are different from each other. Although a more detailed experimental study of the Raman spectra of donor-doped *trans*-$(CH)_x$ is still to be carried out, the results so far obtained (including those not shown in Fig. 1) can be summarized as follows. (1) Na-doped and K-doped *trans*-$(CH)_x$ show essentially the same spectra. (2) The ν_2 band which is found at about 1300 cm^{-1} in the spectra of both intact and acceptor-doped *trans*-$(CH)_x$ is missing. Instead, a relatively sharp band is observed at about 1260 cm^{-1} independently of the excitation wavelength. (3) The ν_1 bands (due to the C=C stretching) are found at 1591 and 1553 cm^{-1}, whereas the corresponding band of intact



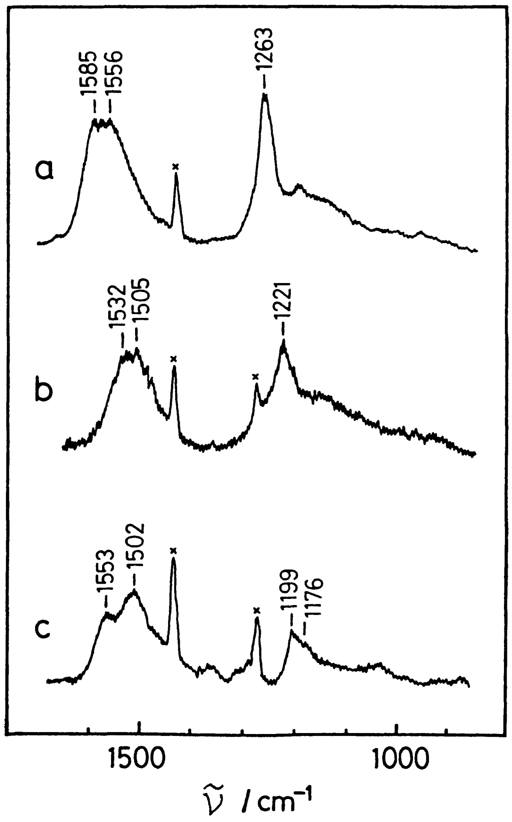


Fig. 1.(left) Raman spectra of *trans*-$(CH)_x$ and doped *trans*-$(CH)_x$ observed with 488.0-nm excitation. a, *trans*-$(CH)_x$; b, AsF_5-doped *trans*-$(CH)_x$; c, Na-doped *trans*-$(CH)_x$.

Fig. 2.(right) Raman spectra of doped *trans*-$(CH)_x$ taken with 441.6-nm excitation. a, Na-doped *trans*-$(CH)_x$; b, Na-doped *trans*-$(^{13}CH)_x$; c, K-doped *trans*-$(CD)_x$. The bands with x are due to spontaneous emissions from the He-Cd laser.

trans-$(CH)_x$ is located at 1494 cm^{-1}. There is little indication of the ν_1 bands below 1460 cm^{-1} which were observed for acceptor-doped *trans*-$(CH)_x$ and were assigned to the skeletal vibration of the doped part. (4) The peak wavenumbers and band shape of ν_1 depend on the excitation wavelength. With 632.8-nm excitation a broad band was observed at about 1540 cm^{-1}.

The Raman spectra of donor-doped *trans*-$(CH)_x$, *trans*-$(^{13}CH)_x$, and *trans*-$(CD)_x$ are shown in Fig. 2. The spectra in Figs. 2a and 2b show that on ^{13}C substitution the two major bands (ν_1 and the 1260-cm^{-1} band) of the normal species are shifted to lower frequencies by about 50∿40 cm^{-1}. This indicates that the 1260-cm^{-1} band of the normal species arises from the C-C stretching vibration possibly of the doped part (designated as D_D in Fig. 3, see below). In the spectrum of K-doped *trans*-$(CD)_x$ (Fig. 2c) the band around 1200-1150 cm^{-1} would be due to the corresponding vibration. However, it is possible that the ν_2 band of intact polymer in the sample has some contribution to the same band.

On the basis of the above results a structure model of donor-doped *trans*-$(CH)_x$ may be proposed, though more studies are undoubtedly necessary to assign the observed individual bands to specific vibrational modes. When *trans*-$(CH)_x$ is doped with a donor, an electron is transferred from the donor to the polymer and the negatively charged parts are produced along the polymer chain. Conjugation of *trans* double bonds is disrupted by the introduction of these negatively charged parts and as a result shortened segments of conjugated *trans* double bonds are produced (P_{D1} and P_{D2} in Fig. 3). The Raman bands at 1595-1550 cm^{-1} (Fig. 1c) may be assigned to the 'gerade' C=C stretching vibrations of P_{D1} and P_{D2}. The ν_1∿ν_4 pattern characteristic of the resonance Raman spectra of intact and acceptor-doped *trans*-$(CH)_x$ is not clear in the case of donor-doping.

The dependence of the Raman intensities on excitation wavelength is now under study in relation to the very broad absorptions extending from the visible to near-infrared region.[5] A normal coordinate analysis for the model structure depicted in Fig. 3 is also in progress to clarify the assignments

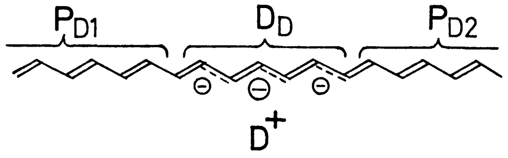


Fig. 3. A structure model for donor-doped *trans*-$(CH)_x$.
D_D, negatively charged part; P_{D1}, P_{D2}, conjugated *trans* double bonds perturbed by doping; D^+, donor.

of individual bands. The results of these experimental and theoretical studies will be reported elsewhere.

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