

The 1320-nm Excited FT-Raman Spectra of Lightly Iodine-Doped *trans*-Polyacetylene

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Abstract : The FT-Raman spectra of *trans*-polyacetylene films doped lightly with iodine were obtained with the 1320-nm laser line. The observed Raman bands are attributed to positively charged domains created by acceptor doping. The observed Raman wavenumbers of the ν_2 (CC stretch), ν_3 and ν_4 bands (mixed of CC stretch and CH in-plan bending) of iodine-doped form are slightly higher than those of the corresponding bands of pristine *trans*-polyacetylene, whereas the contrary is the case for ν_1 band (C=C stretch) of iodine-doped form. In particular, these upshifts of the ν_2 and ν_3 bands are distinguished from the downshifts of these bands in donor doping. The origin of doping induced Raman bands is discussed in terms of solitons and polarons.

Keywords : *trans*-polyacetylene, raman spectroscopy, iodine doping.

Introduction

trans-Polyacetylene (PA) [(CH=CH)_n] is a prototype of conducting polymers.^{1,2} This polymer shows high electrical conductivity of more than 10⁵ S/cm when chemically doped with electron acceptors (such as iodine, AsF₅, FeCl₃, and HClO₄) or electron donors (such as alkali metals). The electrical conductivity of PA increases dramatically when the dopant content is less than 1 mol% per CH unit.^{3,4} On the other hand, the Pauli spin susceptibility which indicates the metallic density appears suddenly at a dopant concentration of about 6 mol%/CH unit (critical value)^{4,5} for donor doping or about 7 mol%/CH unit for acceptor doping,⁶ and doped PA can be thus regarded as a metal. When the dopant concentration is below the critical value, charged solitons that have charges but no spin have been proposed as spinless charge carriers.¹ However, a complete understanding of the mechanism of electrical conduction has not been achieved yet, though several arguments have been proposed. In particular, the SSH (Su, Schrieffer and Heeger) continuum models have stimulated many theoretical researchers about

PA.^{7,8} Some spectroscopic methods to identify soliton have been developed. The existence of neutral solitons on *trans*-PA has been certified by ESR (Electro Spin Resonance) spectroscopy. By recent dynamic studies using nano or pico-second spectroscopy, the information about the production of charged soliton pairs after photoexcitation and their relaxation by recombination into polaron etc., has been provided.⁹⁻¹¹ According to the A. J. Heeger *et al.*,¹²⁻¹⁶ the charged solitons appear in PA that have been doped or photo-excited. For such samples electronic transition to the soliton level and transitions due to vibrations around a soliton are also observed in the infrared spectrum.¹⁴⁻²⁰

Recently, we have demonstrated the usefulness of resonance Raman spectroscopy in the characterization of self-localized excitations existing in the doped PA.^{21,22} The resonance Raman spectra of the doped PA film and its pristine *trans*-PA excited with laser lines between 363.4- and 1064-nm have shown the large changes with the exciting laser wavelengths.²³⁻²⁶ In particular, the observed frequency dispersion of pristine *trans*-PA has been explained in terms of the existence of segments having various conjugation lengths,²² and the effective conjugation coordinate model²³ originating from the amplitude-mode theory. Zerbi and co-workers²³ have attributed the observed Raman spectra to

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undoped chains remaining in doped PA, because the intensities of the Raman bands arising from doped domains are expected to be very weak on the basis of their theoretical considerations. In previous papers,^{25,26} however, we have attributed the observed Raman bands of Na-doped *trans*-PA to doped domains for the following reasons: (1) The Raman bands of doped domains can be observed because of the resonance enhancement effect, which is not taken into account in the effective conjugation coordinate model. (2) The Raman spectra of heavily Na-doped *trans*-PA are quite similar to those of the charged species of polyenes.²⁶ Lefrant and co-workers^{27,28} have also ascribed the observed Raman bands to doped domains. Tanaka *et al.*²⁹ reported the 632.8-nm excited Raman spectra of *trans*-PA doped with Na at various concentrations. However, Raman spectra show no significant changes in the case of pristine *trans*-PA at dopant concentrations less than about 8 mol%. Accordingly, Raman spectra taken with a laser line of wavelength longer than 1064 nm are expected to be more informative, because the electronic absorption of Na-doped PA appears from visible to infrared spectrum.^{4,29} We were first to report on the Raman spectra of lightly sodium doped PAs with the 1320-nm laser line.³⁰ We have shown that the Raman spectra of lightly doped PA with sodium are considerably different from those observed with its pristine *trans*-PA.

In this paper, we newly report the Raman spectra of lightly doped PAs with iodine, as the electron acceptor, with the 1320-nm laser line.

Experimental

The *cis*-rich PA films prepared according to Shirakawa's method³¹ at -78°C were thermally isomerized to *trans*-PA films at 180°C for 60 min. The *trans*-PA films were doped with iodine on gas phase in a completely sealed ampoule. The dopant concentrations were controlled by the contacting time between *trans*-PA films and iodine gas as a dopant. Five iodine-doped PA films were prepared under the various doping concentration from 1.5 to 7.8 wt%. The iodine concentrations of the doped PA samples (sample No. 1-5) were 1.5, 2.1, 3.9, 7.4, and 7.8 wt%. The dopant contents of iodine doped PA were calculated from the weight increase after doping.

Raman spectra taken with the 1064- and 1320-nm laser line were measured on a JEOL JIR 5500 Fourier transform (FT) spectrophotometer modified for Raman measurements. A laser line was provided from a continuous-wave Nd:YAG laser (CVI YAG-MAX C-92). Then laser beam was passed through an interference filter to remove spontaneous emission lines. The InGaAs and Ge detectors were used for Raman measurements with 1064- and 1320-nm excitations, respectively. Especially, for the 1320-nm laser line, the Raman scattered light was collected with a 90° off-axis parabolic mirror in a backscattering configuration, and was passed

through three long-wavelength-pass dielectric filters (Omega) to eliminate the Rayleigh scattered light. Raman measurements on this FT spectrophotometer were made at a spectral resolution of 4 cm^{-1} .

Results and Discussion

In Figures 1 and 2, Raman spectra of lightly iodine doped PA observed with the 1064- and 1320-nm excitation are newly presented. The Raman spectra of the lightly sodium doped PA are consistent with the results previously reported with 1320-nm laser line.³⁰

The Raman spectra of pristine *trans*-PA taken with the 1064- and 1320-nm lines are shown in Figures 1 (a) and 2 (a), respectively. Five bands are observed at 1459-1462, 1290, 1172, 1068, and 1008 cm^{-1} , which are denoted as the ν_1 , ν_2 , ν_3 , ν_4 , and ν_5 bands, respectively. The ν_1 , ν_2 , and ν_4 bands are undoubtedly assigned to Raman-active fundamentals²¹⁻²³ for an infinite planner polyene chain (C_{2h} symmetry). The ν_3 band has been attributed to the $\delta = \pi$ mode (where δ is the phase difference between the adjacent $-\text{CH}=\text{CH}-$

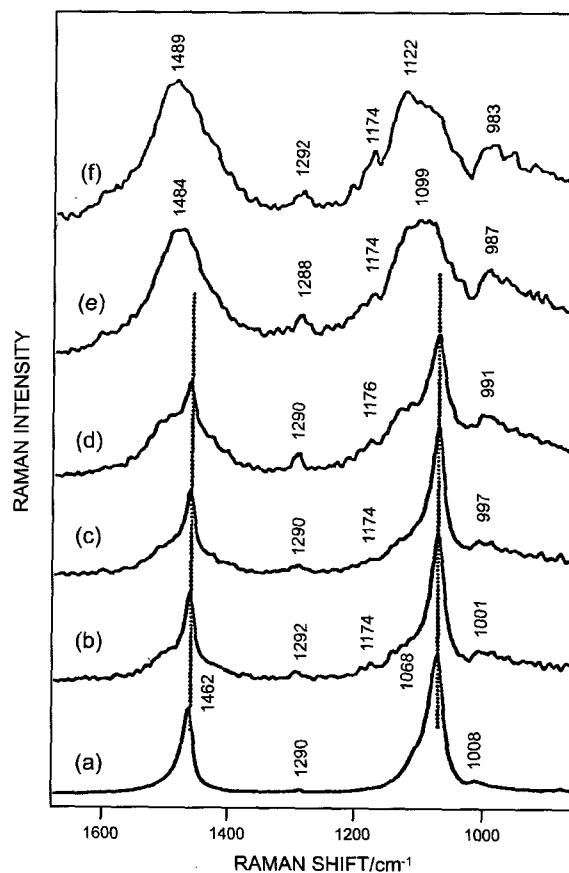


Figure 1. The 1064-nm excited Raman spectra of (a) pristine *trans*-polyacetylene and (b)-(f) iodine-doped *trans*-polyacetylene: (b) 1.5 wt% ; (c) 2.1 wt% ; (d) 3.9 wt% ; (e) 7.4 wt% ; (f) 7.8 wt%.

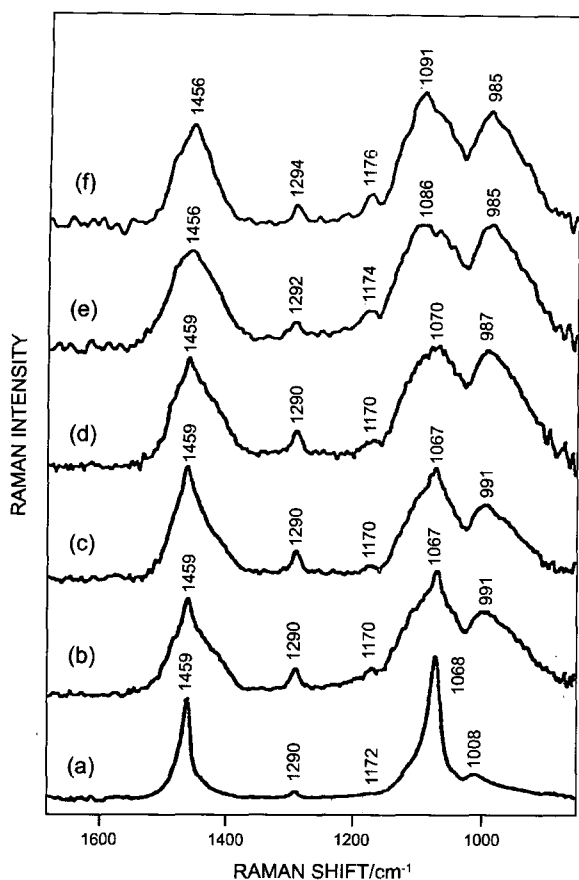


Figure 2. The 1320-nm excited Raman spectra of (a) pristine *trans*-polyacetylene and (b)–(f) iodine-doped *trans*-polyacetylene: (b) 1.5 wt%; (c) 2.1 wt%; (d) 3.9 wt%; (e) 7.4 wt%; (f) 7.8 wt%.

units) of the ν_4 branch,³² in which neighboring $-\text{CH}=\text{CH}-$ units move in opposite directions. The Raman bands corresponding to ν_1 , ν_2 , ν_3 , and ν_4 are also observed for α,ω -di-*tert*-butylpolyenes,³³ although the Raman band corresponding to ν_3 is not observed for unsubstituted polyenes. The ν_5 band has been attributed to the in-phase ($\delta=0$) CH out-of-plane bending on the basis of the frequency shifts of ^{13}C and ^2H substitutions.³⁴ The ν_3 and ν_5 bands, which are Raman-inactive for an infinite planer chain, probably appear in the Raman spectrum because of symmetry lowering due to the distortion of the polyene chain. Tasumi *et al.*³⁴ have pointed out that the in-phase CH out-of-plane bending mode appears in the Raman spectra of some carotenoids due to the distortion of the polyene chain.

The Raman spectra of iodine-doped PA taken with the 1064- and 1320-nm laser lines are shown in Figure 1(b)–(f) and Figure 2(b)–(f), respectively. The iodine concentrations of the doped PA samples are 1.5, 2.1, 3.9, 7.4, and 7.8 wt%, respectively. The 1064-nm excited Raman spectra of 1.5, 2.1, and 3.9 wt% iodine doped PA (Figure 1(b), (c), and (d)) do not show large spectral changes from its neutral species

(Figure 1(a)). However, as we can see from Figure 1(e) and (f), the 7.4, and 7.8 wt%, doped samples clearly show doping-induced new bands in the 1484–1489 (ν_1), 1174–1176 (ν_3), and 1099–1122 (ν_4) cm^{-1} ranges.

Figure 2(b)–(f) illustrates the 1320-nm excited Raman spectra of lightly doped PA with iodine. The spectra show small but significant spectral changes with increasing iodine concentration, although the dopant concentrations are less than 3.9 wt%. The spectral characteristics are as follows: For the ν_1 band, a new peak with shoulder is observed at 1456 cm^{-1} . This wavenumber is slightly lower than that observed at 1459 cm^{-1} for pristine *trans*-PA (Figure 2(a)). This downshift of ν_1 band has also been reported in the lightly doped PA with sodium with 1320-nm line,³⁰ which was explained in terms of negative solitons generated by sodium doping. This ν_1 band group shifts upward with decreasing Raman excitation wavelength. In particular, the large wavenumber range dispersion for the ν_1 band can be explained by the existence of the charged domains with various localization lengths. These domains have different electronic absorptions, and the Raman bands arising from a domain are resonantly enhanced when the wavelength of excitation laser line is located within the electronic absorption of the same domain. For this reason, the wavenumber position of ν_1 band with 1064-nm line is observed at 1489 cm^{-1} (Figure 2(f)).

The ν_2 band is observed between 1290 and 1294 cm^{-1} . This wavenumber position is slightly higher than that observed at 1290 cm^{-1} for pristine *trans*-PA (Figure 2(a)). However, in the case of donor-doping, the wavenumber of the ν_2 band has been reported at lower position than that of pristine *trans*-PA. Similar upshifts of the ν_2 wavenumbers (1292–1296 cm^{-1}) are close to that of a positively charged model compounds; i.e. 1302 cm^{-1} of the radical cation of 1,6-diphenyl-1,3,5-hexatriene.³⁶ These upshifts upon acceptor doping are in contrast to the downshifts to the ν_2 band upon donor doping.

The ν_3 band is weak in intensity between 1170 and 1176 cm^{-1} and shows small upshifts with increasing iodine concentration. However, in the case of donor-doping,³⁰ the wavenumber of the ν_3 bands has been reported at lower position (between 1167 and 1169 cm^{-1}) than that of pristine *trans*-PA (1172 cm^{-1}).

For the ν_4 band, a broad peak is observed at about 1070–1091 cm^{-1} range. This wavenumber position is also higher than that observed at 1068 cm^{-1} for pristine *trans*-PA (Figure 2(a)). The ν_4 band is also upshifted with decreasing excitation wavelength such as ν_1 band. This shift of the ν_4 band is probably due to the existence of various localization lengths of the doped domains. The widths of ν_1 and ν_4 bands of iodine-doped *trans*-PA are much broader than those of Na-doped *trans*-PA.

The ν_5 band undergoes downshifts and its intensity

Table I. Observed Raman Frequencies of Lightly Doped PA with Iodine and Its Assignments¹⁹

Raman Frequencies (cm ⁻¹) of Lightly Iodine-doped PA Excited with 1320-nm Laser Line	Infrared Frequencies (cm ⁻¹) of Lightly Iodine-doped PA ¹⁹	Assignments ^{19,30}
1456 cm ⁻¹ (strong), ν_1	888 cm ⁻¹ (strong and broad)	C=C (stretch)
1292-1294 cm ⁻¹ (weak), ν_2	1288 cm ⁻¹ (strong)	C-C (stretch)
1170-1176 cm ⁻¹ (weak), ν_3	1397 cm ⁻¹ (strong)	CH (in-plan banding) or mixed CH
1070-1091 cm ⁻¹ (strong), ν_4	-	band and CC stretch

increases markedly as the iodine concentration increases. The strong intensity of the ν_5 band may arise from the mixing of the CH out-of-plane bending mode with the CC stretching due to distortion of charged domains in the polyene chain. In the infrared spectra of lightly doped PA with iodine, three characteristic absorption bands were also observed at the 1397 (CH bending), 1288 (CC stretch) and 888 cm⁻¹(C=C stretch).¹⁹ Su *et al.*³⁷ reported that the charged solitons that have charges but no spin act as the spinless charged carriers when the dopant contents are below the critical value, i.e., 6-8 mol%. The tentative assignments of the Raman and infrared absorption¹⁹ bands of lightly doped PA are summarized in Table I.

As described above, the doping-induced Raman bands of lightly doped PA with iodine as the acceptor dopant is clearly different from that of pristine *trans*-PA. A similar observation was made by our previous studies on lightly doped PA with sodium as the donor dopant.³⁰ According to the Kivelson and Heeger,³⁸ when *trans*-PA is doped with dopant, solitons or polarons are expected to be form. A soliton has C_{2v} local symmetry, whereas a polaron has C_{2h} local symmetry. Concerning the Raman studies of lightly iodine doped PA, there are not many reports on doping-induced Raman bands associated with charged domains. However, the present observation suggests that the observed doping-induced Raman bands are due to the positive solitons because the doping levels are below the critical value.

Summary

Raman spectra obtained from lightly doped *trans*-PA with iodine are quite different from those of pristine *trans*-PA. The observed Raman bands of doped *trans*-PAs are attributed to the charged domains generated by doping. The wavenumber of the ν_1 band (C=C stretching) varies with the wavelength of excitation laser line. The wavenumber of the ν_1 band in the 1320-nm line is located at lower position than that of pristine *trans*-PA. Small but significant upshifts of ν_2 and ν_3 bands are observed upon acceptor doping in contrast to the downshifts of these bands for donor doping.

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