Ultraviolet Photoelectron Spectroscopy of Alkaline-Metal Doped Polyacetylene

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Sodium- and potassium-doped highly conducting polyacetylenes were studied by ultraviolet photoelectron spectroscopy (UPS) using synchrotron radiation. Upon doping, the UPS spectra immediately show a large shift toward the higher binding energy side relative to E_F. At intermediate doping level, a new state is created in the empty energy gap region. The gap state in the UPS spectra is assigned to the charged soliton band. This is the first direct observation of emission from the charged soliton state in doped polyacetylene. At heavily doped level, the quasi-metallic density of states is found just below the Fermi level and the broadening of the UPS spectra occurs at the regions of C 2_p and C 2_s levels. However, no finite density of states was observed at the Fermi level in the case of unoriented polyacetylene. This result is in contrast to the case of oriented polyacetylene doped with perchlorate, where the existence of a finite density of states at E_F is reported. The spectral shape of UPS near the Fermi level is in accordance with Tomonaga–Luttinger liquid model of strong electron correlated system. Ab initio molecular orbital calculations taking account of nearest-neighbor chain effect gives a good description of the UPS for all the C 2s, C 2pσ, and C 2pπ bands.

During the last decade, photoelectron spectroscopy (PES) of conducting polymers has provided useful information for the electronic structure and electronic interaction. Numerous works have been performed utilizing X-ray photoelectron spectroscopy (XPS) and ultraviolet photoelectron spectroscopy (UPS) to examine the valence and core level electronic structures of neutral and doped conducting polymers.[1—8] In particular, valence electronic levels, which are directly affected by the change in electronic population, can be probed more easily with UPS. However, the highest occupied π states are usually difficult to observe, because of the low photoionization cross section of C 2p orbitals forming these states and the structural disorder of the polymer chains. In p-type doped conducting polymer, the position of Fermi level, E_F, is found to shift to the higher binding energy side when going from the neutral to the highly doped form.[1] Several groups have reported on p-type doped conducting polymers such as AsF_5-doped polyacetylene,[1] ClO_4^--doped polypyrrole,[2] and PF_6-doped poly(3-hexylthiophene).[4] However, only a few works have been reported on the electronic structure of n-doped polymers.[8]

Polyacetylene, $(CH)_x$, is an insulator without doping, but changes into the metallic state by either n- or p-type doping. In our previous study of UPS spectra of perchlorate-doped (p-type doped) polyacetylene,[9] we found a finite density of states at E_F in the heavily doped regime. As for n-type doping, the conductivity is reported to reach a value of 1.3×10^4 S cm^{-1} by potassium doping.[10] In this paper, we will report on the UPS of alkaline-metal doped polyacetylene. The spectral changes in the highest occupied valence states were followed during stepwise doping, and the observed UPS spectra directly showed the changes in the electronic structure. Such spectral features are discussed with the aid of theoretical calculations on doped polyacetylene and its model compounds.

Experimental

Thin polyacetylene films were synthesized using the high-temperature aged catalyst prepared with Tsukamoto's method[11] in a glove box. The catalyst was cast with uniform thickness of 1 µm on a flat glass plate. Acetylene monomer gas of six-nine grade was passed over the catalyst cooled at −78 °C for a few minutes. After polymerization, the film was stripped from the glass plate, washed repeat-

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edly with toluene, put carefully on a molybdenum substrate, and then dried in vacuo. Typical thickness of the film was around 0.5 μm.

Photoelectron spectra were measured at the beamline 8B2 in the UVSOR Facility, Institute for Molecular Science. The Fermi level of the sample was referred to that of a gold film evaporated in situ. The photon of 40 eV energy was used with the incident angle of 50° from surface normal, and the photoelectrons were collected in normal emission from the sample surface. The total energy resolution of the spectrometer was about 200 meV, as judged from the Fermi edge of gold.[12] Thin films of about 0.5 μm were used for measurements of pristine polymer for avoiding sample charging at UPS measurements due to ionization. The charging effect could be avoided by limiting the photocurrent below 30 pA by inserting an appropriate mesh in the optical path.

Immediately after synthesis, polyacetylene contains 93—95 percent of *cis* form. For measuring both *cis*- and *trans*-forms, synthesized fresh film was kept in an argon-filled vessel which was cooled at −78 °C before UPS measurement to avoid isomerization to *trans*-form at room temperature. The *cis*-film was completely isomerized to *trans*-form in the preparation chamber attached to the UPS spectrometer at 200 °C for 1 h. After the UPS measurements, the content of the *cis*-form was evaluated from infrared absorption measurements. The *cis–trans* isomerization were completed at this condition. The results for these undoped films and their discussions are reported elsewhere.[9] After the isomerization were completed, sodium or potassium doping of *trans*-polyacetylene was carried out in situ at 170±10 °C in the preparation chamber (base pressure 5×10^{-8} Torr, 1 Torr=133.32 Pa) using a SAES alkaline metal getter source. Subsequently the doped films were transferred to the measurement chamber (base pressure 1×10^{-10} Torr). The SAES getter was heated with a current of 5.8—6.5 A d.c. to evaporate alkaline metal. The amount of metal deposited onto the polymer film was monitored by a quartz thickness monitor. The potassium doping levels were determined from the ICP analysis after UPS measurements. After doping, the films were heated in the spectrometer up to 473 K for 1 h in the preparation chamber for the acceleration of the alkaline-metal migration and removing the excess alkaline-metals condensed on the surface; we confirmed that the spectrum was not changed by heating.

Ab initio SCF-MO calculations for simplified model systems of doped states were carried out by Gaussian 92 program[13] at the Computer Center of Institute for Molecular Science. The basis set for the calculation was 3-21G. Also explicit energy band structures of doped polyacetylene for the π levels were calculated by Pariser–Parr–Pople's (P–P–P) method[14] by using the structural data obtained by the ab initio method.

Results and Discussion

UPS Spectra of Na-Doped Polyacetylene. Figure 1 shows the UPS spectra of Na-doped polyacetylene at increasing doping levels. The abscissa is the binding energy E_b from the vacuum level (E_{vac}). The curve (a) is the spectrum of undoped film, where the top of the valence band is at 0.9 eV below E_F. A shoulder at 8 eV is absent in the film manipulated exclusively under inert gas or vacuum. This shoulder is thus ascribed to a defect induced by exposure to air for a few minutes before the film is introduced into the spectrometer.[9] Curve (b) of Fig. 1 illustrates UPS of lightly Na-doped film, where E_F shifts to the lower binding energy side by 0.8 eV from E_{vac}. The expanded spectra in this region with energy standard relative to E_F are illustrated in

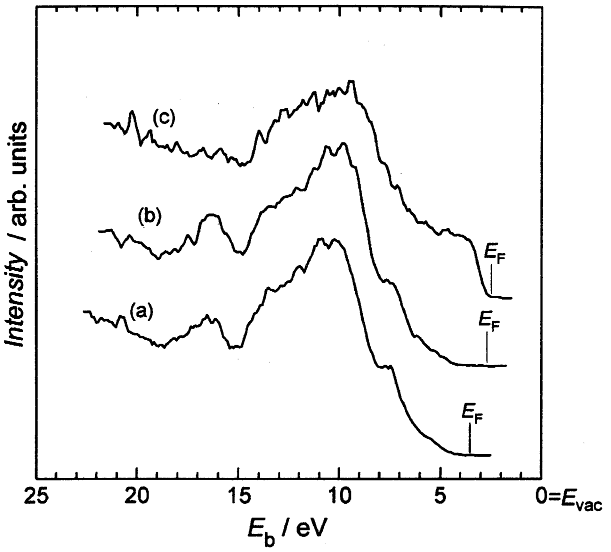

Fig. 1. Changes of the UPS spectra of Na-doped polyacetylene: (a) *trans*-polyacetylene, (b) lightly Na-doped, and (c) heavily Na-doped polyacetylene.

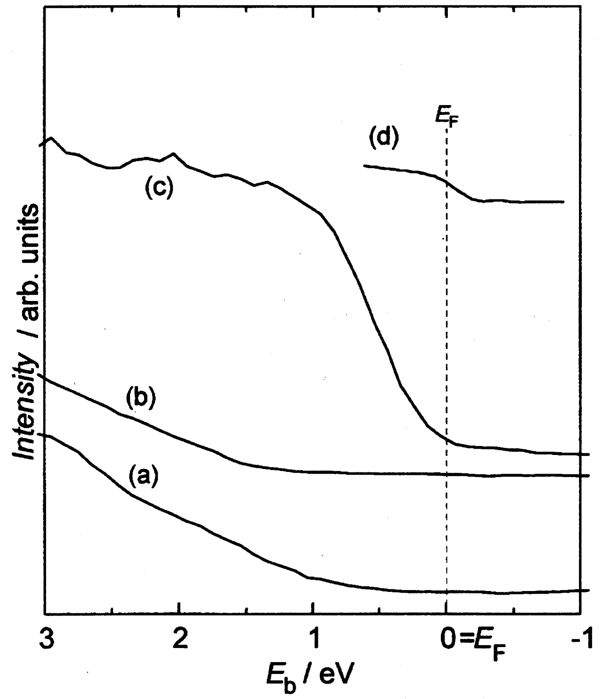

Fig. 2. The expanded UPS spectra near E_F for (a) *trans*-polyacetylene, (b) lightly Na-doped, (c) heavily Na-doped polyacetylene, and (d) metallic Na evaporated film on Au film. The location of E_F is determined from the Fermi edge of Au evaporated film.

Fig. 2, where curve (b) shows a downward shift of the valence band relative to E_F.

By further doping to the saturated level, the UPS spectrum changed drastically and the occupied state extended close to E_F (Fig. 1(c) and Fig. 2(c)), but a sharp Fermi-edge was not observed at the top of the occupied state. The position of E_F was still shifted toward E_{vac} by about 0.25 eV compared to the lightly doped regime (Fig. 2(b)).

Because we were afraid of possible presence of metallic sodium on polyacetylene, we also measured the UPS spectrum of Na evaporated on a gold substrate; this is shown in Fig. 2(d). The spectrum is much different from that for the heavily Na-doped polyacetylene in Fig. 2(c). Also we heated the heavily doped film at 200 °C for 1 h in the preparation chamber for removing the excess sodium, and confirmed that the spectrum was not changed by heating. Moreover, even when sodium film remained on the surface of polyacetylene, the sodium valence band emission near E_F is very weak due to the small cross section of Na 3s levels.[15] In addition, Na 2p emission of the heavily doped polyacetylene film was found at 31.1 eV relative to E_F, which was a 0.6 eV higher binding energy than that of sodium metals (30.5 eV). The shift might be caused by the formation of the sodium ion. These results indicate that the density of states near E_F can be assigned to the emission from the quasi-metallic band of the heavily doped polyacetylene chain.

UPS Spectra of K-Doped Polyacetylene. The UPS spectra of K-doped polyacetylene for increasing doping levels are shown in Fig. 3, and those of by expanded scale near E_F are shown in Fig. 4. The K concentrations for intermediate stages were estimated from the exposure time to K vapor, resulting in 0.02±0.01 (c), 0.03±0.01 (d), 0.06±0.01(e), and 0.10±0.01(f) mole per repeat unit of $(CH)_x$ chain, respectively. The K content of the films (y) was estimated on the assumption that the evaporated K atoms on the film are uniformly distributed in the film. At initial stage of doping (Fig. 4b and 4c), the UPS spectra peaks shift to the higher binding energy side relative to E_F as in the case of the lightly Na-doped polyacetylene. The shift may be caused by the generation of a new state in the energy gap, although such a peak could not be seen in the initial stage of doping because of its small content of dopant. At intermediate doping levels (Fig. 4d and 4e), a new state appears in the originally empty electron energy gap (the band gap). The position of the new level shifts toward E_F with increasing doping, as shown in Fig. 4. At intermediate doping level of (d), the new state appears at 1.0 eV below E_F. This broad peak moves uniformly toward E_F with increasing doping level.

In the case of Na-doped polyacetylene, this state could not be observed as mentioned in the preceding section. This might be caused by the difference of migration ratio caused by the difference of ion radius between sodium and potassium. Another possibility is the different vapor pressure between sodium and potassium. Excess potassium may be easily removed by heating. Effective doping might occur in the case of potassium doping than in the case of sodium. However, the details of just why these two systems are different is not clear at this time.

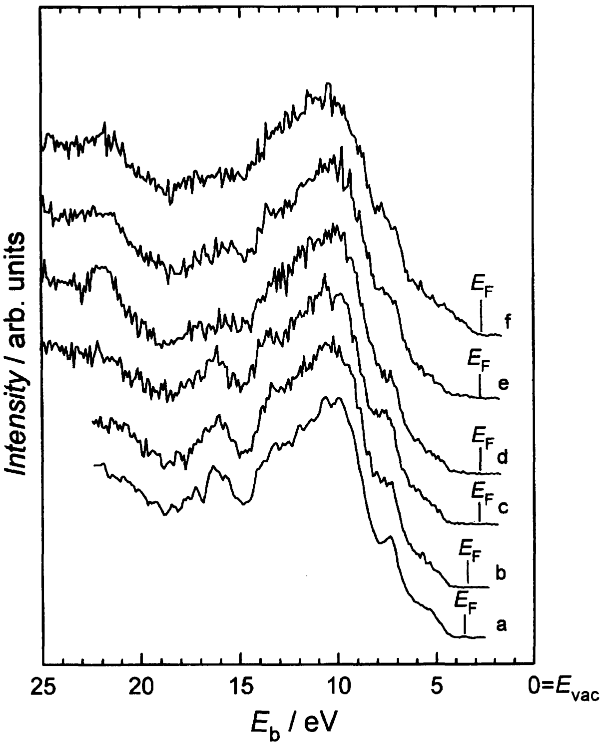

Fig. 3. Changes of the UPS spectra of K-doped polyacetylene for increasing dopant concentration.

By further doping to the stage (f) with $(CHK_y)_x$, $y=0.10\pm0.01$, a finite density of states was found just below E_F as for the case of Na-doped polyacetylene. In stage (f), the position of E_F was still shifted about 0.11 eV (Fig. 3) from the intermediately doped film (e), where $y=0.06\pm0.01$. In the Raman spectral study of Na-doped polyacetylene,[16] new Raman lines appear at $y>0.085$, and the spectra changed completely into a new pattern at the stage of $y=0.13$. Moreover, Chung et al.[17] found an insulator–metal transition at a critical dopant concentration from the magnetic susceptibility measurement. They found Pauli spin susceptibility to be independent of dopant concentration from $y=0.08$ to 0.15. In the heavily doped region, the appearance of a large density of states near E_F thus corresponds to the transition found in the Raman spectra and magnetic susceptibility studies.

Comparison of the UPS Spectra of Doped Polyacetylene to the Charged Soliton and Polson Model Calculations. We will discuss the observed spectra described above by comparing with theoretical calculations. We have proposed that the charged soli-

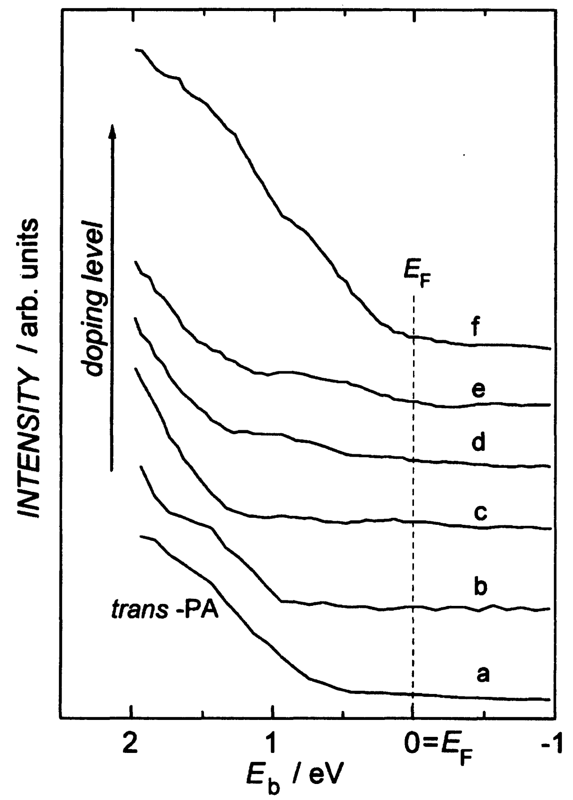

Fig. 4. Expanded UPS spectra of K-doped polyacetylene in the low binding energy region.

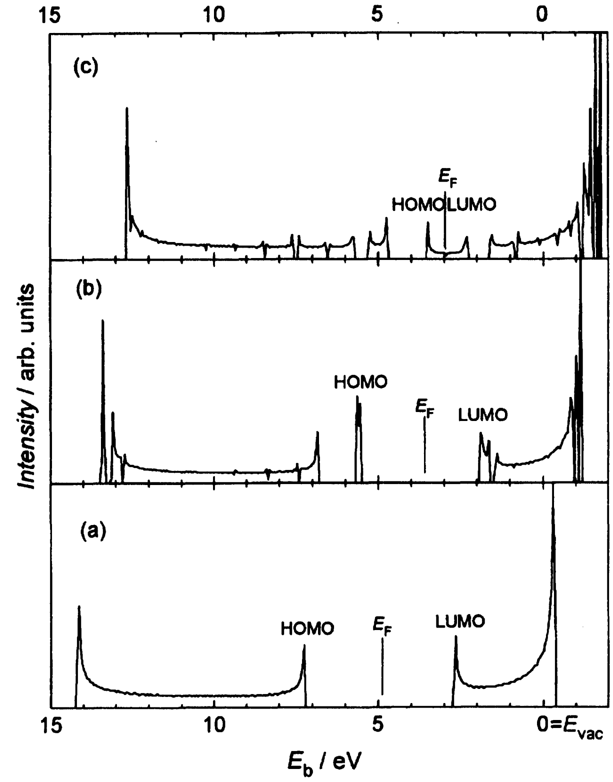

Fig. 5. The calculated density of states of (a) *trans*-polyacetylene, (b) lightly Na-doped charged soliton chain, and (c) heavily Na-doped polson chain.

tons are generated by light doping of polyacetylene and these turn into polsons by further doping.[18—22] We also suppose that the transition from the charged soliton to the polson lattice from lightly- to heavily-doped state occurs at around $y=0.08$ in $(CH_y)_x$ described above.

In Fig. 5, we show the π electron density of states obtained by P–P–P method for these states by Na-doping, together with the results for undoped state.[20] The abscissa is binding energy relative to vacuum level. In the undoped state (Fig. 5(a)), the HOMO band is at the top of the C 2pπ band. In the lightly-doped state (Fig. 5(b)), a new band appears in the band gap region due to the charged soliton formation. The charged soliton band becomes the HOMO band, and E_F is raised by the formation of this band. In the heavily-doped state, a metallic state is generated by the polson formation with a finite density of states across E_F (Fig. 5(c)). At the same time, E_F is further raised from that of the charged soliton states.

The calculated trend is in accordance with the observed UPS spectra. In the case of light-doping, E_F is shifted closer to the vacuum level, and a new state (Fig. 3(d) and 3(e)) in the band gap region is observed for the case of K-doping. This is the first observation of the charged soliton state in the doped polyacetylene. On further doping, E_F is further shifted to the vacuum level, as seen in Figs. 3 and 4. From stage (e) to (f), the spectral shape changes drastically from those of lightly-doped ones. This transition occurs at $y=0.08$, where the Raman and the magnetic measurements also showed significant changes of electronic and molecular structures. In the heavily-doped polyacetylene, a finite density of states was calculated across the Fermi level by the polson chain. The observed spectra in Fig. 2(c) and Fig. 4(f) show occupied states extending close to E_F, which may be due to the metallic energy band of the polson chain.[18—22]

However, a finite density of states with a sharp Fermi step was not observed at E_F. This absence of the real finite density of states may arise from the sample treatment. A real metallic state may not be achieved by the present method of sample treatment. In the previous optical measurements on perchlorate-doped polyacetylene,[23] the real metallic state was achieved by stretching of polyacetylene film before doping. By stretching, the interchain interaction might be enhanced. In fact, in the case of perchlorate-doped polyacetylene, a finite density of states at E_F was actually observed by using the stretched film.[9] In the present experiment, thin films were not stretched to keep the surface clean. In this situation, the carriers might be localized because of insufficient interchain interaction.[23]

The shape of the spectral onset may originate in a characteristic property of the strongly electron correlated one-dimensional system appearing in UPS experiments of low-dimensional conductor.[24,25] Although the energy resolution of the present UPS system is lower than those of reported ones used for such examination,[24,25] the tendency of the spectral onset resembles that of other low-dimensional materials. In a one-dimensional conductor, a metallic Fermi-step has

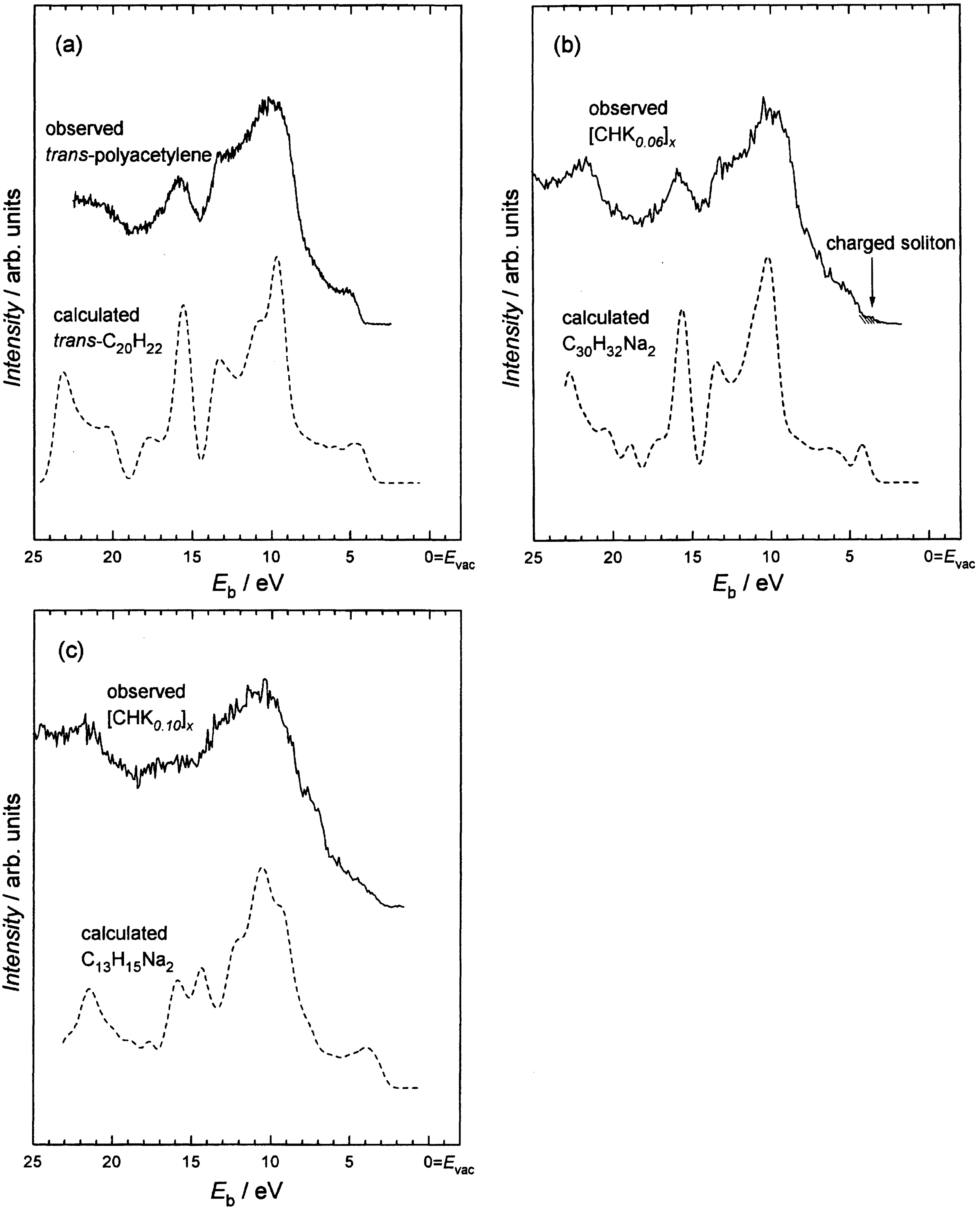

Fig. 6. The observed (solid line) and simulated (dotted line) UPS spectra of neutral and alkaline-metal doped polyacetylene; (a) *trans*-polyacetylene and isolated *trans*-$C_{20}H_{22}$,[22] (b) intermediately-doped polyacetylene, $[CHK_{0.06}]_x$, and the isolated charged soliton model compound ($C_{30}H_{32}Na_2$), and (c) heavily-doped polyacetylene, $[CHK_{0.10}]_x$ and the molecule of the polson structure ($C_{13}H_{15}Na_2$) put on the crystal lattice.

not been found on the E_F level; this result has been discussed as evidence for a Tomonaga–Luttinger (T–L) liquid.[25)] According to the T–L liquid theory of one-dimensional systems, the UPS spectra near the Fermi edge will exhibit a spectral shape of $\sim|\omega|^{\alpha}$, where ω is the energy measured from E_F and $\alpha > 1$. The observed spectra in Fig. 2(c), Fig. 4(f), and also the UPS spectrum of perchlorate-doped polyacetylene[9)] showed a large value of $\alpha = 1.0$, which suggests the effect of strong long-range repulsive interaction.[25)] This result is close to those of the other one-dimensional systems such as $(TMTSF)_2PF_6$,[26)] $K_{0.3}MoO_3$, and $(TaSe_4)_2I$.[27)]

The theoretical calculations of the P–P–P method give information only for the C 2pπ states, which compose the topmost part of the valence states. On the other hand, in the UPS spectra of metallic state (Fig. 1(c) or Fig. 3(f)), quite a different band shape was found in the 5—20 eV region of C 2pσ and C 2s bands compared with that of neutral *trans*- and lightly-doped polyacetylene (Fig. 6(a) and (b)). To analyze the spectra in this region, we performed ab initio molecular orbital calculations for the simplified model systems. For the lightly-doped polyacetylene, the energy levels of isolated charged soliton model compound ($C_{30}H_{32}Na_2$) were calculated, using the optimized geometry reported previously.[22)] In Fig. 6(b), the simulated UPS spectrum using these results is shown, with corresponding UPS spectrum of K-doped polyacetylene shown in Fig. 5(e) (y=0.06±0.01). For a better fit with the observed spectra, each molecular orbital was contracted along the energy scale by the factor of 1/1.3 and shifted to higher binding energies by 0.6 eV. The simulated spectra were obtained by convoluting with a Gaussian function of 0.5 eV FWHM without correction for any cross section effect. Correspondence between the calculated and observed curves in Fig. 6(b) is quite satisfactory, supporting the conclusion that the intermediately doped polyacetylene can be regarded as the charged soliton chain.

In contrast to the cases of undoped, lightly-, and intermediately-doped polyacetylene, the UPS spectra of heavily alkaline-metal doped films were difficult to explain by the calculations for the isolated model compounds. We found that the only way to explain the observed broad band is to consider the interaction between the doped chains.[22)] Considering the crystal structure studies of alkaline-metal doped polyacetylene by Fischer et al.[28)] and Saldi et al.,[29)] we have proposed the structural model of alkaline-metal doped polyacetylene as shown in Fig. 7 for Na-doped polyacetylene.[22,21)] The crystal structural model was obtained by putting the polson model compounds in the crystal lattice, where each polson chain is numbered as in Fig. 7. The energy levels are calculated for two types of $C_{13}H_{15}Na_2$ pairs composed of polson chain No. 1, one of the surrounding polson chains at positions No. 3 or 4, and two Na atoms. In Fig. 6(c), we show the simulated UPS spectrum as the overlap of the contribution from the two types of pairs. The molecular orbital was treated in the same manner as in the cases of lightly-doped polyacetylene. The interactions between the chains are effective to shift the energy bands in the C 2pσ region, leading to good correspondence between the simulated and observed UPS spectra. The interaction is also effective for the broadening of the topmost C 2pπ band. These results suggest the importance of the interchain interactions in the heavily alkaline-metal doped polyacetylene. In contrast to this, similar calculations for the charged soliton chains indicate only small effect of interchain interaction. This is consistent with our conclusions from optical[23)] and electrical conductivity measurements[30)] that a three-dimensional interaction in heavily-doped polyacetylene is important for the appearance of the metallic state.

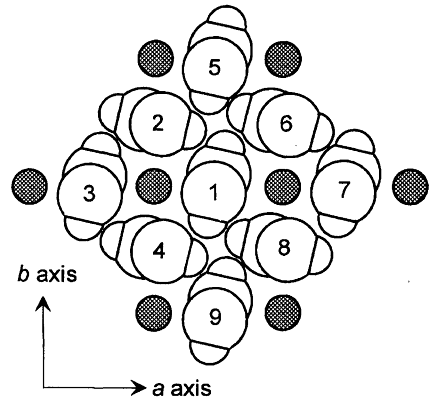

Fig. 7. Projection of the heavily Na-doped polyacetylene crystal onto *ab* plane.[22)] Polyacetylene chains are numbered from 1 to 9, and the Na columns are shown by hatched circles.

To summarize, the changes of the UPS spectra of polyacetylene were studied by stepwise in situ doping of sodium and potassium. Upon doping, a new state appears in the originally empty energy gap region. This state was assigned to the charged soliton band by comparison with theoretical calculations. This is the first direct observation of the charged soliton state. At saturate doping level, the quasi-metallic finite density of states was found just below E_F. No finite density of states was observed at E_F in the present unoriented polyacetylene films. The shape of the spectral onset suggests a strong correlation effect characteristic of one-dimensional conductors. The energy band calculations for the polson and the charged soliton chain showed good correspondence with the shift of E_F and appearance of new states, indicating that the electronic structure is drastically changed by stepwise doping of polyacetylene. Three-dimensional interactions among the polson chains were important for explaining the change of UPS spectra in the C 2pσ valence band region.

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