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Short Note

Electronic Structure of the Organic Superconductor κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ Studied by Angle-Resolved Photoemission Spectroscopy

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In the photoemission spectra of the κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ surface, two characteristic structures were observed at the binding energies of ~ -7.5 eV and ~ -11.5 eV, which were attributed to the π- and σ-bonding states, respectively, in comparison with the results of the molecular orbital (MO) calculations. Polarization dependence appearing in the spectra was comprehensively interpreted by the electronic structures calculated for those states, which is in good agreement with the results previously obtained using a scanning tunneling microscope.

KEYWORDS: organic superconductor, κ-(BEDT-TTF)$_2$Cu(NCS)$_2$, angle-resolved photoemission spectroscopy, molecular orbital calculation

BEDT-TTF-based organic materials are very attractive because of their intriguing physical properties: the electronic structure varies from insulating to superconducting in accordance with their crystal structure, especially in the molecular arrangement of BEDT-TTF molecules. Attempts have been made to understand these properties through molecular orbital (MO) calculations, and recently, some of the electronic structures of those materials have been examined on an atomic scale by scanning tunneling microscopy.[1,2] In order to confirm these results, we performed angle-resolved photoemission spectroscopy (ARPES) on κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ (where BEDT-TTF is bis(ethylenedithio)tetrathiafulvalene), an organic superconductor with one of the highest T_c's.

Measurements were performed using the Photon Factory BL-11D of the National Laboratory for High Energy Physics in Tsukuba. Single crystals of κ-(BEDT-TTF)$_2$Cu(NCS)$_2$, the surface conditions of which were examined by STM observation, were attached to Ta plates by means of conductive epoxy, with their bc-plane parallel to the substrate. Molecular and electronic structures of this material are described in ref. 2. Pressure of the chamber was below 1×10^{-8} Torr during the experiment.

Figure 1 shows the normal emission spectra for the κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ surface as a function of the incident beam angle measured in the Γ-Y, Γ-Z and Γ-M directions. The incident photon energy was 40 eV. Two dominant structures were similarly observed in the spectra obtained for all directions at the binding energies of ~ -7.5 eV and ~ -11.5 eV, which are labeled A and B in the figures. The intensity of "A" decreased with the increase in the incident beam angle (measured from the normal axis of the surface), while that of "B" was unchanged.

Figure 2 shows the electronic structure calculated by the extended Hückel method. The two shallow peaks appearing at ~ 4 eV and ~ 8 eV below Fermi energy correspond to the π- and σ-bonds, respectively. The molecular orbitals of the π-bonds expand from the BEDT-TTF molecules almost parallel to the sample surface and are almost isotropic in the bc-plane layers, while the σ-bonds are almost spherical in the crystal. Previously, the electronic structure of the π-bonds was partially examined using scanning tunneling microscopy (STM).[2]

Comparing the energy distribution and the polariza-

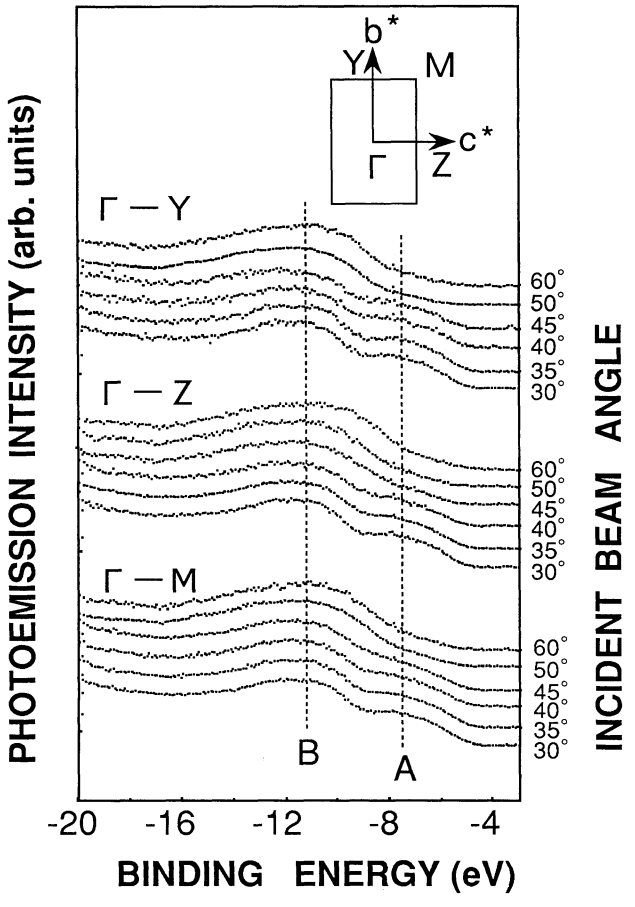

Fig. 1. Normal emission spectra of the κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ surface as a function of the incident beam angle.

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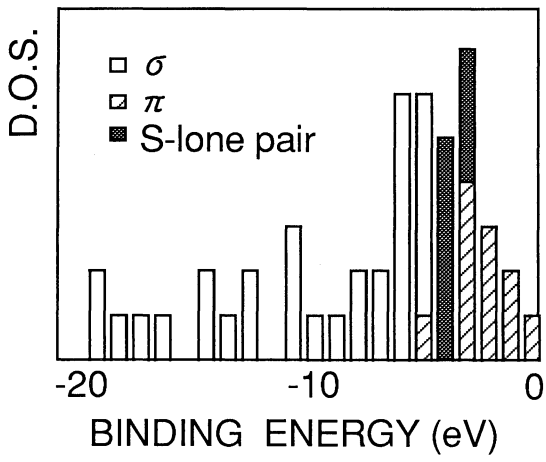

Fig. 2. Electronic structure of κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ calculated by the extended Hückel Method. The value of the horizontal axis is relative to the Fermi level.

tion dependence between experimental and theoretical results, peaks "A" and "B" in Fig. 1 are satisfactorily attributed to π- and σ-bonding states, respectively. Results obtained by ARPES, together with the results by STM,[2] support the validity of the analysis for the electronic structure of the BEDT-TTF-based organic conductors through MO calculations.[3]

In summary, structure of the π- and σ-bonding states of the κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ observed by angle-resolved photoemission spectroscopy shows satisfactory agreement with theoretical electronic structures based on the molecular orbital calculation.

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