



Electronic structure near the Fermi level of the organic semiconductor copper phthalocyanine

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Abstract

The electronic structure of thin films of the prototypical organic semiconductor copper phthalocyanine (CuPc) has been measured using resonant soft X-ray emission spectroscopy. We report the observation of two discrete states near E_F . This differs from published photoemission results, but is in excellent agreement with density functional calculations. The implications of this result for the use of resonant soft X-ray emission (SXE) in the study of organic semiconductors are discussed. We also compare our data to published X-ray emission results, and show that the latter display clear evidence of beam damage.

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Organic semiconductors are the subject of intense study due to the challenge they pose to our understanding of the physical properties of complex solids and due to technological interest in developing carbon-based electronic devices [1,2]. Copper phthalocyanine (CuPc) is a prototypical organic semiconductor. The phthalocyanine ligand has a complex electronic structure which is further complicated by the introduction of a transition metal ion into the system, such as Cu^{2+} . The overlap of the metal 3d electronic states with ligand 2p states within the molecule produces a combination of both localized and delocalized states near the Fermi level (E_F). Accurate determination of this electronic structure near E_F is of general importance in understanding the properties of organic semiconductors. Many photoemission studies have been undertaken to measure this electronic structure, but it is important to appreciate that photoemission spectroscopy measures the electronic structure of an ionized system.

We report here a synchrotron radiation-excited resonant soft X-ray emission (SXE) spectroscopy study of the electronic structure near E_F of thin films of CuPc. Our results are in excellent agreement with theory [3], but differ significantly from previously published X-ray emission and photoemission results [4,5]. The CuPc films were discovered to be highly susceptible to synchrotron radiation beam damage. We successfully circumvented this effect by continuous translation of the films during measurement. Resonant SXE spectra from undamaged samples show spectral features near E_F that have not been observed from damaged samples. These states are predicted to exist, but have not previously been observed by either photoemission spectroscopy or soft X-ray emission spectroscopy. Since it is the properties of the highest occupied molecular orbital (HOMO) states that are of most interest, the ability of resonant SXE to accurately measure these states is significant, as is our discovery that previously published SXE studies of organic semiconductors are dominated by beam damage effects. This application of resonant SXE has important consequences for the determination of band gap energies in organic molecular crystal systems, since it allows determination of the non-ionized electronic structure.

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CuPc thin films were grown in an ultra high vacuum organic molecular beam deposition (OMBD) system (base pressure 2×10^{-9} Torr), and transferred under vacuum into the spectrometer system (with identical base pressure). This is important if the intrinsic properties of CuPc are to be measured, since thin film samples can be strongly p-doped due to oxygen contamination [6]. Films were deposited on P:Si (100) substrates which were ultrasonically cleaned in acetone, then heated to 900 °C for 10 min in the OMBD chamber. 200 nm of CuPc was deposited from a well out-gassed source with the substrate at 150 °C. Film thickness was determined using a quartz microbalance. At this temperature it is expected that the films consist primarily of the α -polymorph. X-ray absorption spectra indicate that the CuPc molecular plane was approximately parallel to the substrate surface, as expected from previous studies [7,8].

SXE spectroscopy involves the measurement of the photon emitted when a valence electron makes a radiative transition into a hole on a localized core level created by excitation of a core electron with monochromatic synchrotron radiation. Since strong dipole selection rules associated with the core level govern the transition, SXE directly measures the orbital angular momentum resolved partial density of states (PDOS) [9,10]. Furthermore, since the core level is associated with a specific element in a compound, the element specific PDOS is measured [9,10]. Additional information can be extracted from emission spectra if the incident monochromatic synchrotron radiation is tuned to the energy close to a core absorption threshold. In this resonant case, the excited electron resides in a conduction band or lowest unoccupied molecular orbital (LUMO) state, and the system does not become ionized. Two additional phenomena can be observed with resonant excitation. First, if the system exhibits core level shifts due to different chemical bonding or site symmetry, holes can be resonantly created on each core level and the PDOS associated with a particular bond or chemical environment can be measured. For example, in a system with C–C, C–N, and C–O bonds, the C 2p PDOS of each can be measured by sequentially creating holes on the respective C 1s level. This variant is referred to as resonant SXE (RSXE). The second phenomenon that can appear with resonant excitation are features in the emission spectrum associated with excitations near E_F ; i.e. the incident photon, resonant with a core level, excites an electron hole pair around E_F , and scatters from the system with an energy shifted to lower values by the characteristic energy of the valence excitation. This variant of SXE is known as resonant inelastic X-ray scattering (RIXS) [11–13]. RIXS features are losses from the main excitation energy, and thus change their photon energy in step with changes in the incident photon energy. This is in contrast to PDOS features seen

in SXE or RSXE, which are fixed at the photon energy associated with the transition into the core hole. This makes the identification of PDOS and RIXS features in SXE spectra straightforward. Note also that at resonance, the excited core electron effectively screens the empty core-hole state in large delocalized molecular systems [14]. This reduces the effect that the core-hole has on the energies of the valence states and reduces the strength of final state effects in SXE spectra in comparison to photoemission measurements.

The experiments were performed at the soft X-ray undulator beamline X1B at the National Synchrotron Light Source, which is equipped with a spherical grating monochromator. The photon beam is focused to an approximately $60 \times 40 \mu\text{m}$ spot on the sample. SXE measurements were performed with a grazing incidence grating spectrometer [10]. The energy resolution for SXE spectra presented here was 0.3 and 0.6 eV for C K α and N K α emission, respectively. The energy resolution of the incident beam was set to 0.5 eV for RSXE spectra. Photoemission measurements were made using a 100 mm Scienta hemispherical analyzer.

High resolution SXE measurements require a small photon spot (circa $40 \mu\text{m}$) with a high photon flux (10^{13} ph/s) on the sample, and long collection times (30–60 min). This combination can lead to significant beam induced damage in organic systems [15]. We have solved this problem by continuously translating the films in front of the beam (at $40 \mu\text{m/s}$) as the spectra are being recorded. This technique has a dramatic effect on the measured SXE spectra. Fig. 1 shows the C K α SXE spectrum reflecting the C 2p PDOS from both a stationary and continuously translated CuPc film. The excitation energy was 294 eV, and is well above the absorption threshold for the C 1s states. The spectral feature marked ' α ' at 294 eV visible in both spectra is elastically scattered light. Significant differences in the measured electronic structure of identical films when

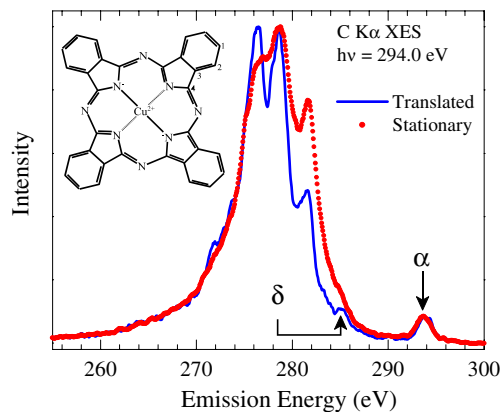


Fig. 1. Comparison of non-resonant C K α SXE spectra reflecting the C 2p PDOS for both stationary and translated films of CuPc. The inset shows a schematic of the CuPc molecule.

stationary or translated are visible in Fig. 1. We note that the spectrum obtained here for the damaged, stationary film is very similar to that recently published by Kurmaev et al. [5] for CuPc and by Tegeler et al. [4] for the related compounds PtPc and MgPc. In particular, the feature observed in our spectrum from the translated sample near the top of the valence band at 285 eV (marked ‘ δ ’) is missing from both the spectrum we obtained from a stationary film, and from the published spectrum [5]. The significance of this observation will be addressed below. The remainder of SXE spectra presented in this letter are from samples translated during data acquisition.

The left panel of Fig. 2 shows a series of C K α SXE spectra from CuPc recorded as a function of excitation energy. The right panel of Fig. 2 shows the results of a DFT calculation for the electronic structure of the valence band within approximately 3 eV of E_F [3]. Also shown are the binding energies for the ring and pyrrole C 1s core levels as measured using photoemission from our translated films. To first approximation, there are two distinct chemical environments for C atoms in CuPc: C bonded to other C in the exterior rings (for example, atoms 1, 2, 3 in the inset to Fig. 1) and C bonded to N in the pyrrole structure (for example, atom 4 in the inset of Fig. 1). The spectra in Fig. 2 show only the states near the top of the valence band and are presented with an expanded vertical scale; the spectrum in Fig. 1 corresponds to spectrum (viii) in the series of Fig. 2. Consider spectrum (i), excited with a photon energy of 284.6 eV. The feature marked ‘ α ’ in the series is the elastic emission feature, and is manually truncated

in the figure for clarity. At an excitation energy of 284.6 eV, only electrons from ring C atoms are excited into the conduction band states. Thus the emission spectrum reflects valence electron transitions into this hole. DFT calculations indicate that the uppermost occupied states in CuPc (D_{4h} point group) consist of a half filled HOMO state at E_F of b_{1g} symmetry, a filled state of a_{1u} symmetry 0.5 eV below E_F , and a manifold of states roughly 2 eV below E_F marking the onset of the main valence band [3]. The feature marked ‘ β ’ corresponds to transitions from the manifold of states at the top of the valence band into a hole on a ring C atom. As the excitation energy is increased to 285.9 eV (spectrum (iii)), two weak emission features now are visible between features ‘ α ’ and ‘ β ’. These features, labeled ‘ γ ’, are not RIXS loss structures since they do not move in energy as the excitation energy is increased to 286.3 eV, spectrum (iv). Although weak, these features are well above the noise, as can be seen in the inset to Fig. 2, which expands spectrum (iv). Based on comparison with the DFT calculations [3], we assign these features to transitions from the b_{1g} and a_{1u} states to a hole on a 1s level in a ring C. The higher energy feature is assigned to the half-filled b_{1g} symmetry HOMO state at E_F . The calculations indicate that this state is a result of the overlap of phthalocyanine 2p character states with Cu^{2+} 3d states [3]. Observation of emission from this state indicates that there must be significant overlap of the molecular orbital with a core-hole state excited in a ring position C, indicating that the ligand states hybridized with the Cu^{2+} 3d states are partially delocalized over the entire molecule. The second state, observed at 0.8 eV

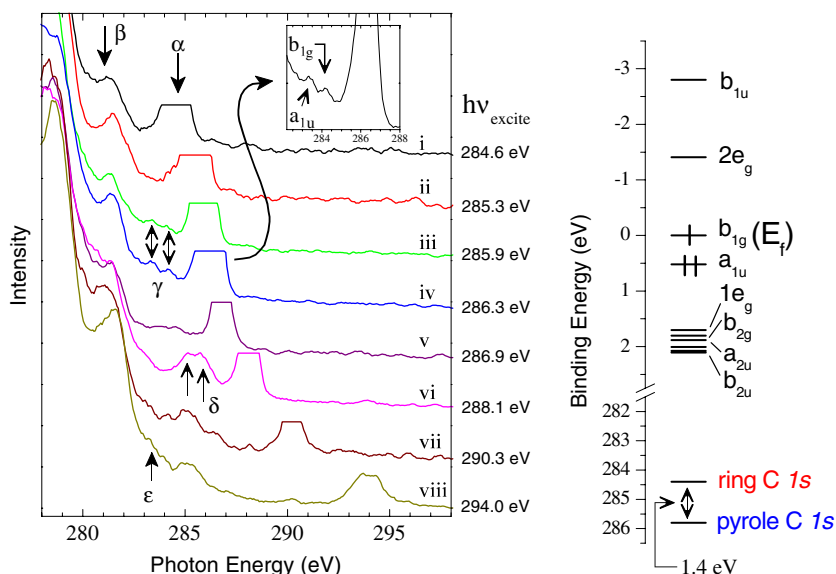


Fig. 2. Left panel: Series of SXE spectra from CuPc showing emission from states near E_F . Right panel: Electronic structure of CuPc near E_F as predicted by DFT calculations [3], with measured C 1s core level binding energies indicated. Note that the DFT calculation energies have been rigidly shifted such that the binding energy of the b_{1g} state at E_F is set to zero, allowing comparison to the measured XPS spectra and the excitation energies in the RSXE spectra.

lower in energy, is assigned to the a_{1u} symmetry state that is delocalized over the entire phthalocyanine ligand. The observation of this state is somewhat surprising as the parity conservation rule in RIXS indicates that emission by this state should be forbidden, as it involves a transition between a u parity core-hole state (produced by excitation into the empty $2e_g$ level) and a u parity molecular orbital state. That it is visible is attributed to a mixing of u and g parity states by excited vibrational modes [14,16,17]. Note that emission from these states is not visible from damaged films. The doublet is not observed in the threshold spectrum (i), since the excitation and emission involve the same half filled b_{1g} state, and thus the doublet lies in the elastic emission manifold. We note that the predicted doublet separation is 0.5 eV [3], and the observed separation is 0.8 eV.

As the excitation energy is increased above the threshold for creation of C 1s holes on the pyrrole C atoms, we expect to observe the same features (valence band emission ‘ β ’, and HOMO emission doublet ‘ γ ’) due to transitions to the pyrrole C 1s hole. However, since holes are still being created on the ring C 1s states, the emission features from transitions into both holes will overlap. Thus emission feature ‘ δ ’ corresponds to emission from the same pair of b_{1g} and a_{1u} states (‘ γ ’), but shifted by 1.4 eV to higher photon energies because of the chemical shift of the pyrrole C sites, and emission feature ‘ ε ’ corresponds to ‘ β ’, but again shifted by 1.4 eV. The intensity and spectral definition of emission feature ‘ δ ’ is quite different than that of ‘ γ ’. This is likely caused by two effects. As will be shown below, there is an energy loss feature associated with the N sites of the molecule. This leads to a resonant enhancement of both of the features. Secondly, this loss feature also resonantly populates a lower lying unoccupied level which in turn emits photons at a photon energy of 285.7 eV, partially filling the gap in spectral intensity between the b_{1g} and a_{1u} features. Off resonance, at higher incident photon energies, the features remain with reduced intensity.

SXE spectra were also recorded around the N $K\alpha$ edge, reflecting the N 2p PDOS. Fig. 3 presents, on a common binding energy scale, the N $K\alpha$ spectrum recorded just above threshold, the C $K\alpha$ spectrum (iv) from Fig. 2, and a published ultraviolet photoemission spectroscopy (UPS) spectrum for CuPc [18]. The UPS spectrum is similar to many in the literature, and as it was recorded using a lamp and not high intensity synchrotron radiation, it is likely to be from a film that is relatively free of beam damage. The SXE spectra are aligned via calibrated absorption energies, and the energy of the HOMO b_{1g} state is determined from Fig. 2. The fact that the b_{1g} state is half filled allows both emission and absorption from the same state, facilitating the alignment. Note that the elastic emission in the N $K\alpha$ spectra is very weak. The low energy asymmetric

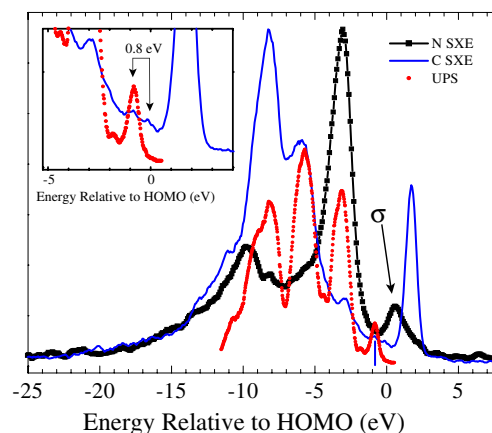


Fig. 3. Comparison of resonant C and N $K\alpha$ spectra and UPS spectra from CuPc. The SXE excitation energy corresponds primarily to the C/N $1s \rightarrow 2e_g$ resonance. The UPS spectrum is from Chasse et al. [18].

emission feature ‘ σ ’ visible in the N $K\alpha$ spectrum, is a RIXS energy loss feature. This feature lies approximately 1 eV below the excitation energy and remains at this constant loss energy as the excitation energy is varied. (The alignment of C and N states observed in this experiment agrees with the earlier measurements of Tegeler et al. [4], but differs from that of Kurmaev et al. [5].) Since the SXE spectra represent the C 2p and N 2p PDOS, the combination plotted in Fig. 3 represents the dominant fraction of the total density of states for CuPc, and can be compared to the UPS spectrum. Since the UPS spectrum represents the total DOS, it can be placed on a common binding energy scale with the SXE spectra by aligning the three prominent valence band features in the UPS spectrum with the equivalent features in the N and C 2p PDOS.

The inset in Fig. 3 shows the detailed electronic structure close to E_F , where the C $K\alpha$ and UPS spectra are plotted. (The N $K\alpha$ spectrum in this region is dominated by the RIXS loss feature, ‘ σ ’, and is not plotted in the inset.) As is clear, the lowest energy feature in the UPS spectrum aligns exactly with the second lowest, a_{1u} , feature in the SXE spectrum. i.e. the SXE spectrum reveals that the HOMO state at E_F in CuPc lies 0.8 eV higher in energy than measured by photoemission spectroscopy. The difference lies in the fact that while UPS is an ionizing spectroscopy, RSXE is not. Liao et al. [3] note that ionization of the CuPc molecule first occurs from the ligand a_{1u} state rather than the lower binding energy ligand-metal shared b_{1g} state. The ionization energy of the b_{1g} state is calculated to be 0.7 eV higher than that of the a_{1u} . This is ascribed to the large difference in the degree of localization of the two states. If an electron is removed from a delocalized orbital it has less of an effect on the energy of that level than if the orbital is localized. Thus, strong final state effects modify the binding energy of the b_{1g} state, as observed by UPS, and photoemission from this state

overlaps in energy that from the a_{1u} state producing a broad asymmetric photoemission feature that is identified in UPS spectra as the HOMO. The presence of the excited electron in the system in resonant SXE strongly screens the core-hole state and leaves the arrangement of states close to that of the neutral, ground state molecule.

In conclusion, it has been shown that resonant SXE can be used to successfully study the electronic structure near E_F in undamaged organic semiconductors. We have measured the properties of the prototypical organic semiconductor CuPc, and found excellent agreement with theory, in contrast to previous studies. Resonant SXE is thus an important tool to determine band gap energies in organic molecular crystal systems, since it allows determination of the non-ionized electronic structure.

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