Influence of Multielectron Excitations on the Band Structure of Adsorbate Overlayers

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Photoelectron spectra from ordered CO on Cu(111) exhibit anomalously small 4σ band dispersion compared to all other CO adsorption systems previously studied. The bonding 5σ band displays normal one-electron dispersion. It is shown that the energy dependence of the 4σ band expected for a single-particle system is transferred into k-dependent intensity variations of the quasiparticle excitation and the intense satellite line ~2 eV lower in energy. The first moment of the spectral weight function over this energy range recovers the anticipated one-electron band dispersion.

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During recent years angle-resolved photoemission has been extensively used to study the band structure of pure metals as well as ordered overlayers.[1] Nearly all of these experiments have been interpreted with the aid of single-particle calculations, where the photoexcited conduction electron is represented as a Bloch state. In most cases single-particle band theory has been very successful in describing bandwidths and band dispersion.[2] There are, however, exceptions of which the most prominent is nickel.[3] The one-electron band theory fails to explain the observed d-band width.[4] Theoretically it has been shown that the band narrowing in Ni is a many-body effect associated with the localization of the hole. Another consequence of this localization is the satellite structure observed in the Ni spectra.[4] These satellites (called shake-ups) are due to particle-hole excitations in the presence of the one-particle–hole state. Generally it is assumed that the intensity of these satellites is connected with the degree of localization of the wave functions of the initial state.[4]

The qualitative arguments given above indicate that the single-particle picture for band dispersion could fail to explain the photoelectron spectra of ordered overlayers of molecules on a surface because of the relatively small overlap of the molecular orbitals. However, all of the published literature on dispersion from ordered overlayers has been interpreted quite successfully in terms of a single-particle band picture. For example the measured dispersion from the 4σ energy level of ordered overlayers of CO on various substrates agrees remarkably well with theoretical calculations containing only CO-CO interactions. Greuter *et al.*[5] have correlated the measured 4σ bandwidths and the CO-CO spacing for all previously studied systems. They found that the bandwidth is exponentially related to the CO-CO spacing, as expected from tight-binding calculations.[5]

The system of CO adsorbed on Cu is distinctly different from all of the systems examined by Greuter *et al.*[5] in that the valence-band spectra for Cu display an intense satellite line. This line has been identified experimentally[6] and theoretically[7] as a shake-up associated with the ionization from the 4σ level. Figure 1 shows a set of spectra taken at a photon energy of 40 eV as a function of collection angle or momentum parallel to the surface $\{k_{\parallel} = [(2m/\hbar^2)E_{\text{kinetic}}]^{1/2} \sin\theta\}$. These spectra consist of three CO-induced peaks. The peak at ~11 eV binding energy is the CO 4σ level which is not strongly involved in the substrate bond. The deepest peak is the satellite line on the 4σ parent line already mentioned. It is a many-body excitation caused by the readjustment of the valence electrons of the system to screening the photoinduced 4σ hole.[7] The peak near 8 eV binding energy is a composite of the CO 1π and 5σ levels, the latter of which drops in energy upon bonding to the substrate until it is nearly degenerate with the CO 1π levels. The nearly degenerate 5σ and 1π CO levels can mix together except at the high-symmetry points of the surface Brillouin zone (like $\bar{\Gamma}$ or normal emission).[5] Notice in Fig. 1 that the $5\sigma+1\pi$ peak disperses upwards in energy as the angle or $k_{\parallel}$ is increased while the 4σ or its shake-up peak hard-

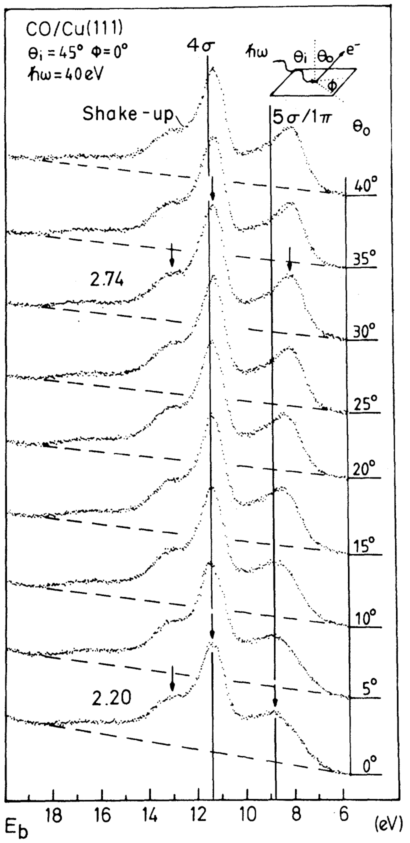

FIG. 1. Adsorbate-induced peaks as a function of polar angle θ_0 for a saturation layer of CO on Cu(111) at liquid-nitrogen temperatures. The two spectra marked with arrows represent an electron momentum at the center of the Brillouin zone (0°) and at the zone boundary (30°) (Ref. 8). For these k values the intensity ratio of satellite and main line is indicated. The spectra are in the $\bar{\Gamma}$-$\bar{K}$ direction of the Cu surface Brillouin zone. The energy scale is binding energy from the Fermi energy.

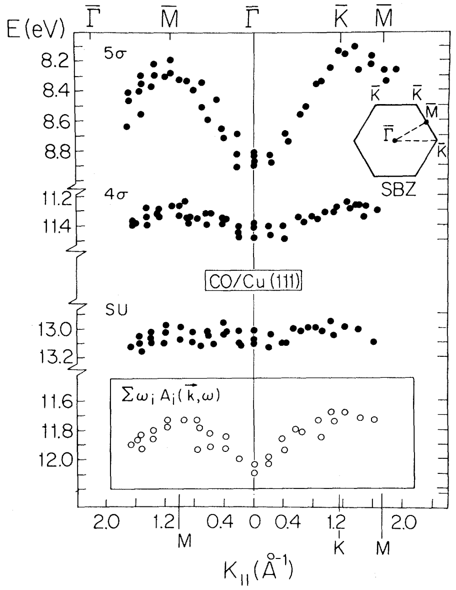

FIG. 2. Dispersion of adsorbate-induced peaks in CO/Cu(111) (solid circles) in two perpendicular directions on the Cu surface (Ref. 9). The open circles contained within the box are from the application of sum rule (ii) [Eq. (2)]. The data were accumulated at two different photon energies (40 and 50 eV) to eliminate effects of cross section.

ly moves at all. The relative intensity of the shake-up and the 4σ peaks does change with collection angle.

Figure 2 plots the binding energy of the CO peaks as a function of the two-dimensional crystal momentum in the two high-symmetry directions of the Cu surface. The low-energy electron-diffraction pattern for CO adsorbed on Cu(111) at liquid-nitrogen temperatures has been reported previously by Hollins and Pritchard[8] as a 1.39×1.39 structure. The high-symmetry points for this structure are indicated in Fig. 2, showing that the periodicity of the dispersion in the 5σ band agrees quite well with the structure observed in low-energy electron diffraction. This hexagonal CO overlayer has a CO-CO spacing of 3.61 A. All previous measurements or calculations for ordered CO layers predict that a CO layer with this spacing should have a 5σ dispersion of ~0.7 eV in excellent agreement with these data.[5] In contrast to the "normal" behavior seen in the 5σ band, the 4σ band has only ~0.15 eV disperison compared with a value of 0.36 eV predicted from a single-particle calculation[5] or from other CO overlayers with similar spacings.[5]

The important observations are the following: (1) The 4σ band has much smaller dispersion than expected from the CO-CO spacing[5,8]; (2) the 5σ-band dispersion is normal[5]; and (3) there is a strong satellite line associated with the 4σ level.[6,7] Therefore we come to the same conclusion as was deduced for bulk nickel; the presence of a satellite line causes a reduction in the measured band dispersion.[4] The difference in this system is that we have a satellite line associated with a single band which is separated in energy from any other band. Therefore we can investigate the validity of proposed sum rules on intensity and energy of the multielectron excitations.

In theoretical treatments of extended systems the effects of electron correlation are often discussed in terms of the spectral function $A(\vec{k}, \omega)$.[1,10]

A general theoretical treatment of the k dependence of the spectral function, including satellites, for the case of an electron gas has been presented by Lundqvist.[11] The following sum rules for valence excitations can be obtained from his work.[10] (i) For a given value of k the frequency integral is constant:

$$\int_{-\infty}^{\infty} A(\vec{k}, \omega) d\omega = 1. \tag{1}$$

(ii) The first moment of the frequency distribution is equal to the single-particle Hartree-Fock eigenenergy,

$$\int_{-\infty}^{\infty} \omega A(\vec{k}, \omega) d\omega = E_k^{\mathrm{HF}}. \tag{2}$$

In the gas phase there is no k dependence but the total intensity is conserved [Eq. (1)] and the first moment of the spectral weight function gives the Hartree-Fock eigenvalue. These sum rules have been tested for core ionization from small molecules and carbonyl complexes.[12] In this paper we are primarily concerned with the sum rule over the first moment of the spectral weight function [Eq. (2)] and its implications for the dispersion of individual peaks in the spectra.

In Fig. 3 we have tried to illustrate the consequences of the two sum rules on the observed photoelectron spectra from a periodic two-dimensional system. If there are no correlation effects associated with photoionization from the hypothetical level the spectral weight function $A(\vec{k}, \omega) = \delta(\epsilon_k - \omega)$, where ϵ_k is the single-particle eigenvalue. The solid bars in Fig. 3 show what this situation could look like. Now consider for simplicity an interacting system where there is only one dominant satellite line caused by correlation. If a two-particle–hole state is close in energy to the quasiparticle state, the self-energy couples the two states leading to the spectral distribution indicated by two Lorentzians. The intensity distribution depends on the coupling strength of the two states and their relative energy. As k changes so does the relative energy of the hole-state and the two-particle–hole state as well as the coupling matrix element between the states. Therefore the intensity and frequency distribution of the spectral function $A(\vec{k}, \omega)$ change. As a result we can find two band systems, both with only little dispersion but varying relative intensity (the Lorentzians in Fig. 3). The first moment of the spectral function produces the single-particle dispersion $\epsilon(k)$. The single-particle dispersion is transferred into an energy-dependent intensity.

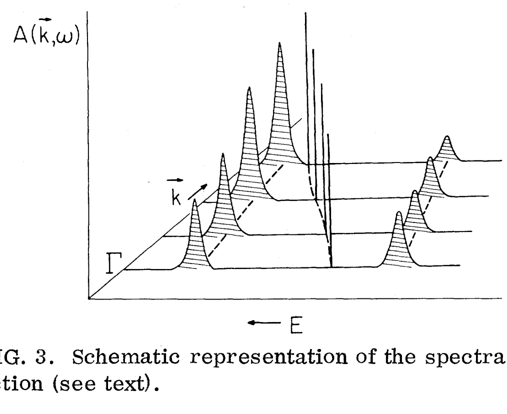

FIG. 3. Schematic representation of the spectral function (see text).

The CO on Cu(111) system furnishes in principle a test of the sum rule on the first moment of the spectral function and the simple model presented in Fig. 3. The implementation of the sum rule (ii) is more difficult than Fig. 3 would indicate. It is important, as we have shown for gas-phase molecules, to include a sufficient frequency range to determine correctly the first moment of the spectral function. Because of the nature of the sum rule (ii) low-intensity multielectron excitations at large excitation energies may contribute significantly to the first moment.[12] Fortunately most of the higher-energy low-intensity satellites are due to intramolecular CO excitations, while the intense low-energy satellites are due to interadsorbate-substrate excitations.[7,12] Therefore only the new satellite lines produced by bonding to the substrate should be important in the k dependence of the sum rule. The data plotted within the box in Fig. 2 are the first moment of the 4σ level and its intense satellite.[13] This curve exhibits the correct dispersion both in magnitude and periodicity expected from a single-particle picture.

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Raman Scattering from the Orthorhombic Charge-Density-Wave State of $2H$-TaSe$_2$

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Raman-scattering experiments from the commensurate charge-density-wave lattice modes of $2H$-TaSe$_2$ exhibited large relative intensity variations as the incident polarization was rotated in the basal plane of the crystal. The observations are consistent with orthorhombic symmetry and imply the existence of either large (≈ 1 mm), or smaller coherently ordered, orthorhombic domains. A microscopic theory incorporating intralayer interactions with orthorhombic symmetry, in conjunction with an explicit proposal for the electronically active commensurate charge-density-wave regions, is also presented.

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Since its initial characterization,[1] the triple-q commensurate charge-density-wave (CCDW) state occurring in the layered compound $2H$-TaSe$_2$ has been found to possess a structure of remarkable subtlety. Results obtained from both neutron-scattering[2] and Raman-scattering[3] experiments were found to be consistent with the assignment of the normal-state hexagonal symmetry ($D_{6h}{}^4$) to the CCDW. However, recent electron-diffraction studies indicate that the CCDW state of $2H$-TaSe$_2$ is of orthorhombic rather than hexagonal symmetry.[4,5] The discovery of orthorhombic symmetry has prompted a new series of investigations, both theoretical[6-8] and experimental.[9,10] In this Letter we present results of Raman scattering on the CCDW state of $2H$-TaSe$_2$ where a strong variation in the relative intensities of the CCDW modes is observed as the incident polarization is rotated in the basal plane. These relative intensity variations are consistent with a strong orthorhombic layer symmetry. We then present a microscopic Hamiltonian where orthorhombic layer symmetry, in conjunction with a two-phonon term enhanced by electronic coupling at twice the CCDW wave vector, generates a CCDW mode structure in good agreement with experimental results.

The crystal was glued to a copper disk and mounted in a Displex refrigerator, and measurements were made on freshly cleaved (0001) surfaces at 16 K utilizing a Spex double monochromator with an attached third monochromator and 200 mW of 514.5-nm laser excitation. The polarized incident beam was approximately normal to the basal plane of the crystal. The incident polarization angle θ_E was measured relative to one