

INFLUENCE OF MULTI-ELECTRON EFFECTS ON BANDDISPERSION IN TWO DIMENSIONAL
 ADSORBATE SYSTEMS: CO on Cu (111)¹

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In some cases, of which Ni is the most prominent one, one-particle band structure fails to explain the band widths in d-electron metals as determined by photoemission². It has been shown that this is a many-body effect associated with the localization of the hole³. As another consequence of this localization satellite structure is observed and it is believed that its intensity is connected with the degree of localization of the wave functions in the initial state.

These qualitative arguments 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 molecular orbitals. However, all of the published literature on dispersion from ordered CO overlayers, for example, has been interpreted quite successfully in terms of single-particle band structure⁴.

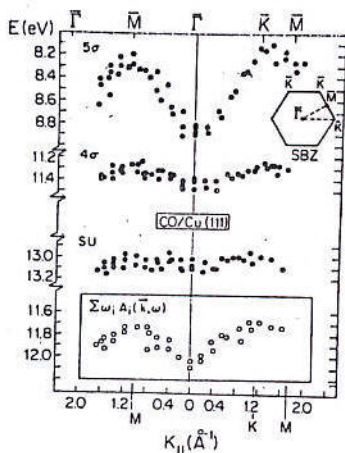
The system CO on Cu is distinctly different from other CO overlayers examined so far, in that the valence band spectra for Cu displays an intense satellite line. This line has been identified as a shake-up associated with ionization of the 4s level^{5,6}. Fig. 1 plots the binding energy of the CO peaks as a function of the two dimensional crystal momentum $k_{||}$ in the two high symmetry directions of the Cu surface¹. The high symmetry points for this 1.39 x 1.39 structure (according to the LEED pattern⁷) are indicated in Fig. 1. The important observations are the following:

- i) The 4s band has much smaller dispersion than expected from a CO-CO spacing of 3.61 Å;
- ii) the 5s band dispersion is normal;
- iii) there is a strong satellite line associated with the 4s level.

Therefore we come to the conclusion that the presence of a satellite line causes a

reduction in the measured band dispersion. The difference to other, e.g. three dimensional metal systems, 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 rules⁸ on intensity and energy of multi electron excitations. The most important sum rule states that the first moment of the frequency distribution is equal to the single-particle Hartree-Fock eigenenergy.

Figure 1.



The CO on Cu(111)-system furnishes in principal a test of this sum rule. However, because of the nature of the first-moment conserving sum rule it is important, as we have shown for gas phase molecules⁹, to include a sufficient frequency range to determine correctly the first moment of the spectral function. Fortunately most of the higher-energy low-intensity satellites are due to intra-molecular CO excitations, while the intense low-energy satellites are due to inter adsorbate substrate excitations. 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. 1 are the first moments of the 4σ level and its intense satellite. This curve exhibits the correct dispersion, both in magnitude and periodicity, expected from a single-particle picture.

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