Adsorption of Carbon Monoxide on Copper (100) at 295 K, Characterized by Photoelectron Spectroscopy

By Saadoon A. Isa, Richard W. Joyner, and M. Wyn Roberts*
(*School of Chemistry, University of Bradford, Bradford* BD7 1DP)

Summary Carbon monoxide is shown to adsorb in the molecular form on copper (100) at 295 K, with a low sticking probability; u.v. and *X*-ray photoelectron spectra resemble those reported for CO adsorption on transition metals and it is suggested that, at 295 K, carbon monoxide acts more as an electron acceptor, $CO^{\delta-}$, than at 80 K.

In 1971 we reported[1] the adsorption of CO on Cu (100), using low energy electron diffraction, (LEED), and Auger electron spectroscopy. Subsequently, Tracy[2] and Chesters and Pritchard[3] suggested that our results were influenced by impurities or electron beam effects and that Cu (100) did not adsorb CO at room temperature. We have re-examined this system using u.v. (UPS) and *X*-ray induced photoelectron spectroscopy (XPS) in addition to LEED.

The apparatus, combining XPS and LEED in a single chamber with a base pressure of 3×10^{-9} Pa,† has been described previously, as has the preparation of single crystals.[4] A Vacuum Generators windowless discharge lamp has been added allowing the observations of He I and He II spectra. After ion bombardment ($1\,\mu A\,cm^{-2}$, 800 eV, 16 h) XPS showed no impurities at the limits of detectability (1—2% of a monolayer) and the u.v. induced spectra were those expected from clean copper (Figure, curve 1). The LEED pattern was well ordered with low background intensity.

After an exposure to CO at 10^{-2} Pa for 1 h at 295 K no change was observed in the photoelectron spectra or diffraction pattern, but on increasing the pressure to 1 Pa for 10 min peaks developed in the He II spectra at 8·0 and 11·1 eV binding energy (Figure 1, curve 2). These are due to molecular adsorbed CO (see ref. 5 and references therein). Also, an increase in intensity occurred in the *s*-band region of the spectrum, 1·5 eV below the Fermi level. The He I spectrum exhibits peaks at 7 and 11 eV as observed with nickel. XPS showed a carbon 1*s* peak centred at 286·6 eV [full width at half maximum (FWHM) = 2·6 eV] and an oxygen 1*s* peak at 532·8 eV, (FWHM = 2·8 eV). The oxygen 1*s*: carbon 1*s* peak area ratio, 2·2 ± 0·4 : 1, was that expected from adsorbed CO. No change was observed in the metal core-level binding energies or peak shape. The LEED pattern was $(\sqrt{2} \times \sqrt{2})\ R45°$, the extra spots being diffuse, and the O 1*s* : Cu $2p_{3/2}$ area ratio was indicative

---

† 133 Pa ≡ 1 Torr.

of a maximum coverage of *ca.* 0·3 monolayer. The clean surface was regenerated by heating *in vacuo* ($P < 10^{-7}$ Pa) to 360 K.

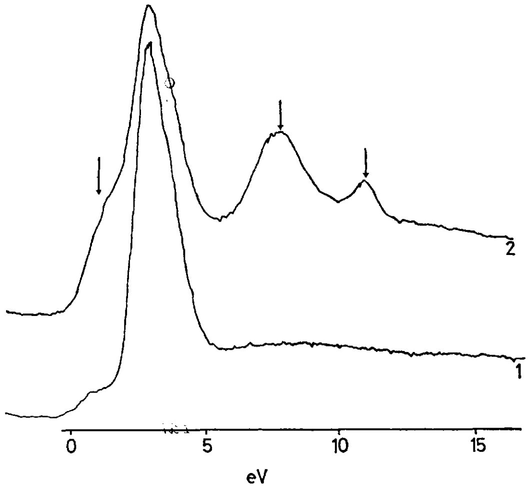

FIGURE. He II spectra. Curve 1: Cu (100) clean surface at 295 K. Curve 2: Cu (100) after exposure at 295 K to CO at 1 Pa for 10 min.

At 80 K the photoelectron spectra and LEED patterns resulting from CO adsorption were in good agreement with those reported previously.[2,3,6] However, changes in the He II spectra with increasing CO coverage, which have been associated with the presence of two adsorbed CO phases,[7] coincided with the onset of the well known LEED compression structures.[2,3] Warming from 80 K *in vacuo* resulted in desorption of the adlayer rather than conversion into the room temperature adsorbed state.

At 295 K the u.v. induced spectra are similar to those noted for molecular CO adsorption on transition metals.[5,8] Our correlation[9] indicates that an oxygen 1*s* binding energy of 532·8 eV corresponds to a heat of adsorption of *ca.* 100 kJ mol^{-1}, which is compatible with the observed desorption temperature of 360 K. When the adsorbed state formed at 295 K is compared with that at 80 K the following points are noted: (a) Substantially lower oxygen and carbon core electron binding energies at 295 K, which can be correlated with a higher heat of adsorption at the higher temperature. (b) The binding energies and profiles of the adsorbate valence orbitals are different at the two temperatures. (c) At 295 K a chemisorption level is present close to the Fermi edge. (d) Adsorption at 295 K is very slow (average sticking probability of *ca.* 10^{-6}) but is very rapid at 80 K. (e) The maximum observed coverage at 295 K is only *ca.* 0·3 monolayer.

We therefore suggest that at 295 K Cu (100) behaves as a transition metal with the CO molecule acting as an electron acceptor, 'CO$^{\delta-}$,' through enhanced back bonding into the π^* adsorbate orbitals. At 80 K σ bonding predominates and CO behaves more as an electron donor, 'CO$^{\delta+}$.' There are strong analogies between this two-way electron transfer process and recent studies[10] of NO adsorption on Cu.

(*Received*, 11*th March* 1977; *Com.* 234.)

[1] R. W. Joyner, C. S. McKee, and M. W. Roberts, *Surface Sci.*, 1971, **26**, 303.

[2] J. C. Tracy, *J. Chem. Phys.*, 1972, **56**, 2748.

[3] M. A. Chesters and J. Pritchard, *Surface Sci.*, 1971, **28**, 460.

[4] M. J. Braithwaite, R. W. Joyner, and M. W. Roberts, *Faraday Discuss. Chem. Soc.*, 1975, **60**, 89.

[5] R. W. Joyner and M. W. Roberts, *J.C.S. Faraday*, 1974, **70**, 1819.

[6] H. Conrad, G. Ertl, J. Küppers, and E. E. Latta, *Solid State Comm.*, 1975, **17**, 613; P. R. Norton and R. L. Tapping, *Chem. Phys. Letters*, 1976, **38**, 207; C. R. Brundle, *J. Electron Spectroscopy*, 1975, **7**, 484.

[7] J. E. Demuth and D. E. Eastman, *Solid State Comm.*, 1976, **18**, 1497.

[8] P. Biloen and A. A. Holscher, *Faraday Discuss. Chem. Soc.*, 1974, **58**, 106; H. Conrad, G. Ertl, J. Küppers, and E. E. Latta, *ibid.*, p. 116; J. C. Fuggle and D. Menzel, *Surface Sci.*, 1975, **53**, 21; K. Kishi and M. W. Roberts, *J.C.S. Faraday I*, 1975, **71**, 1721.

[9] R. W. Joyner and M. W. Roberts, *Chem. Phys. Letters*, 1974, **29**, 447.

[10] M. H. Matloob and M. W. Roberts, *J.C.S. Faraday I*, in the press.