

# Summary Abstract: Determination of bond orientation for CO on Mo(100) by using angle-resolved ultraviolet photoelectron spectroscopy and near-edge x-ray absorption fine-structure spectroscopy

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Recent high-resolution electron energy-loss spectroscopy (HREELS) results indicate that CO adsorbs on Mo(100) in a unique configuration,<sup>1</sup> with vibrational modes between 1000 and 1250  $\text{cm}^{-1}$  below 230 K and half-saturation. Further CO chemisorption occurs on a top site and with the axis perpendicular to the surface, as seen in many other cases. Thermal desorption spectroscopy (TDS) experiments indicate that the low-coverage states are responsible for CO dissociation, and this has been explained by proposing a tilted CO chemisorption geometry, as also seen on Cr(110)<sup>2</sup> and on Fe(100).<sup>3,4</sup> Here we present near-edge x-ray absorption fine-structure spectroscopy (NEXAFS) and angle-resolved ultraviolet photoelectron spectroscopy (ARUPS) data confirming that indeed the low-coverage CO bonds on the Mo(100) surface with the molecular axis tilted  $40 \pm 5^\circ$  from the surface normal and with considerable rehybridization of the molecular orbitals.

The experiments were performed at the National Synchrotron Light Source of Brookhaven National Laboratory, on beamline U14A. This beamline was equipped with a planar grating monochromator and an ion pumped stainless-steel vacuum chamber containing a cylindrical mirror analyzer for Auger and NEXAFS and a rotatable angle-resolving hemispherical analyzer for ARUPS.

NEXAFS spectra for the carbon and oxygen 1s edges were obtained as a function of incidence angle after CO saturation at 120 K on Mo(100) (Fig. 1). Sharp  $\pi$ -resonance peaks

were seen at 529.3 and 283.8 eV for the O and C edges, respectively. Knowing that about one-half of the CO is bonded in the well-known perpendicular configuration,<sup>1</sup> we used the  $\pi$ -resonance angular dependence to estimate that the remaining CO is bonded at  $40 \pm 10^\circ$  from the surface normal.<sup>5</sup> Additionally, the peak position for the  $\sigma$  resonance (not shown) indicates that the tilted CO has a bond about  $0.25 \pm 0.05 \text{ \AA}$  longer than the perpendicular CO.<sup>6</sup>

Photoelectron spectra obtained for saturation CO were dominated by a narrow peak at 11.9 eV and a broader peak at 8.7 eV below the Fermi level. These peaks have been assigned to the  $4\sigma$  and  $1\pi + 5\sigma$  orbitals of CO, respectively, and their angular dependence follow the behavior expected for perpendicular CO.<sup>7</sup> Data taken for the low-coverage CO display a broad signal between 8 and 14 eV (Fig. 2). We deconvoluted three Lorentzian peaks from each spectrum and assigned them to the  $4\sigma$  (13.0 eV),  $1\pi$  (10.9 eV), and  $5\sigma$  (9.0 eV) orbitals. The  $1\pi$  orbital has clearly shifted to higher binding energies, indicating its strong interaction with the surface.

The variation in intensity of photoemission peaks as a function of photon incidence angle was used to confirm the

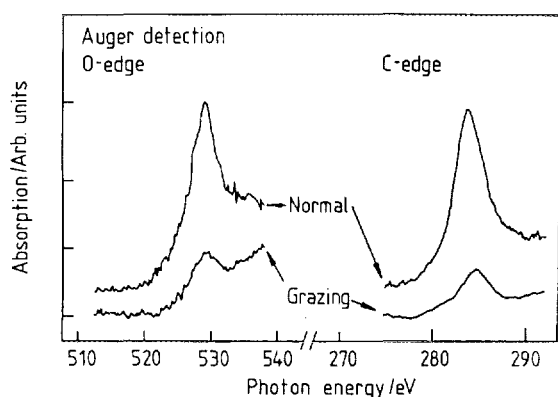


FIG. 1. Near-edge x-ray absorption fine-structure spectra showing  $\pi$  resonances at the oxygen and carbon edges for a Mo(100) surface saturated with CO.

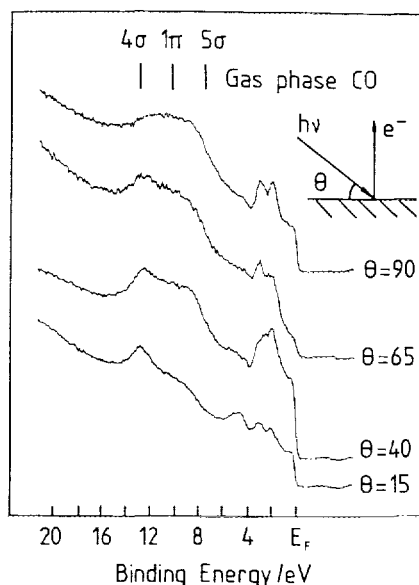


FIG. 2. Photoelectron spectra of 0.5 L of CO on Mo(100) taken at normal emission as a function of photon incidence angle. Photon energy was 40 eV.