

Site Adsorption in the Incommensurate Compression Structure of Chemisorbed CO on Cu(111)

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Isotopically decoupled i.r. spectra reveal distinct adsorption sites in the incommensurate (1.39 × 1.39) saturation structure of CO chemisorbed on Cu(111).

Simple ordered overlayer structures are formed first when CO is chemisorbed on copper single crystal surfaces. With increasing coverage the overlayer unit mesh appears to be compressed and incommensurate with the metal surface structure. All molecules cannot then occupy equivalent sites.¹ However, it is uncertain whether the CO molecules are uniformly spaced, and therefore not restricted to certain specific sites, or whether the diffraction patterns reflect a long range average order within which local adjustments allow the molecules to occupy specific sites. We present i.r. evidence for molecules occupying two distinct sets of sites on Cu(111).

A particular problem has been that vibrational spectra, both i.r.²⁻⁴ and electron energy loss spectra (e.e.l.s.),⁵⁻⁷ have shown only one ν_{C-O} band for the compression structures on Cu(100) and Cu(111). The simple structures are compatible with all molecules occupying identical sites, and the vibrational frequencies, near 2080 cm^{-1} on both surfaces, together with i.e.e.d. evidence⁸ point to linear carbonyl-like configurations of CO molecules adsorbed vertically above copper atoms. The ν_{C-O} bands change slightly as the compression structures form, but there is no obvious evidence for a variety of C-O stretching frequencies reflecting a variety of local bonding environments as expected for a uniformly spaced layer.

This problem has been discussed recently, and alternative site-adsorption models have been proposed. One approach¹ is based on relaxation of the uniformly compressed layer to allow molecules to move to the nearest linear sites or, if that is prevented by steric limitations to the crowding of molecules on contiguous linear sites, to two-fold bridging sites. A more recent model⁹ for the Cu(100) surface is similar but permits crowding in order to accommodate all molecules on linear sites. Either model divides the CO molecules into two inequivalent sets. The first model was proposed before e.e.l.s. had shown conclusively that there is no band in the usual bridging region below 2000 cm^{-1} . Nevertheless, the same e.e.l.s. study⁶ showed the appearance of an additional band

in the ν_{M-CO} region at 274 cm^{-1} in addition to the 347 cm^{-1} band of linear CO. This result is compatible with a bridging species although it leaves the corresponding value of ν_{C-O} very uncertain.

The failure to observe a second ν_{C-O} band could be due to very strong vibrational coupling in the densely packed compression layer, as previously suggested.¹⁰ Coupling is greater the smaller the frequency difference of the coupled species. It is characterised by transfer of intensity from the low frequency mode to the high frequency mode of the coupled system, and if strong enough it may practically eliminate the low frequency band.¹¹ Spectra of adsorbed mixtures of ¹²CO and ¹³CO (which separately give bands differing by 47 cm^{-1}) show that coupling is already quite strong in the simple overlayer structures.^{3,4} Intensity transfer effects are very clear. With increasing coverage, the spectrum of a mixture dilute in ¹³CO shows a loss of relative intensity of the lower frequency (¹³CO) band, while mixtures dilute in ¹²CO show an enhancement of the higher frequency band.³ The latter effect is particularly useful as it aids the observation of the high frequency minority species under conditions where, because of their dilution, they do not couple very strongly with each other. These are therefore the conditions where there should be the best chance to observe the separate bands corresponding to molecules bound at distinct types of sites, as the coupling between diluted ¹²CO molecules might be sufficiently weakened even in the compression structure. Unfortunately, the chemical effect of surrounding CO molecules also causes a frequency change with coverage. This effect is offset by the coupling interaction for the major (¹³CO) species but not for the almost uncoupled ¹²CO molecules. It is sufficient to cause the bands to merge and interact at saturation.³

In order to overcome this limitation we have used a mixture of 10% of ¹²C¹⁶O (99%) with ¹³C¹⁸O. The latter was not commercially available with sufficient isotopic purity, so it was prepared in the gas dosing system by combustion of ¹³C

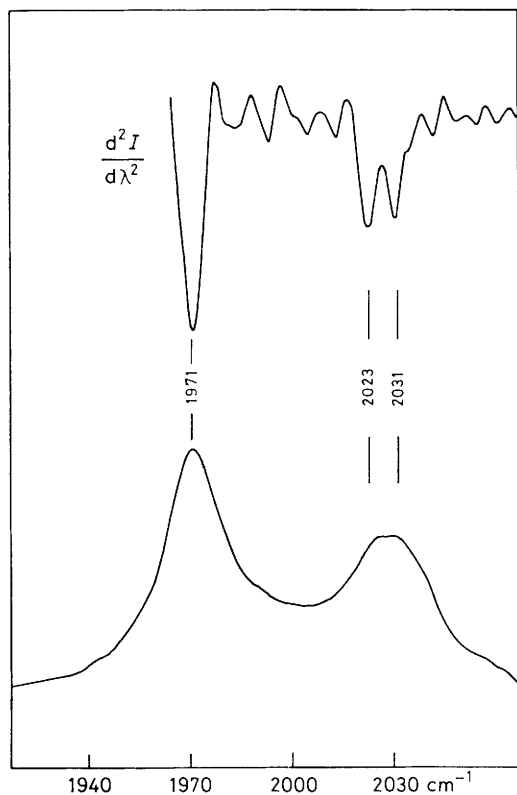


Figure 1. I.r. reflection spectra of mixed $^{12}\text{C}^{16}\text{O}$ and $^{13}\text{C}^{18}\text{O}$ at saturation coverage on Cu(111) at 82 K. Lower curve shows ordinary absorption spectrum; upper curve shows directly recorded second derivative spectrum in wavelength modulation.

(99.3%) in $^{18}\text{O}_2$ (99.86%). The much larger frequency difference for the separate $^{12}\text{C}^{16}\text{O}$ and $^{13}\text{C}^{18}\text{O}$ molecules results in a saturation coverage spectrum of the adsorbed mixture in which the main $^{13}\text{C}^{18}\text{O}$ band at 1971 cm^{-1} is well separated from the strong $^{12}\text{C}^{16}\text{O}$ band at about 2027 cm^{-1} with small amounts of $^{12}\text{C}^{18}\text{O}$ and $^{13}\text{C}^{16}\text{O}$ contributing to absorption between these bands. The spectrum is shown in Figure 1 (lower curve), and the significant feature, which is now apparent for the first time, is the shape of the $^{12}\text{C}^{16}\text{O}$ band. Its broad peak has a shallow dip suggesting incipient resolu-

tion of two overlapping bands. The presence of two distinct components is made evident by the second derivative spectrum (top curve) which was obtained in wavelength modulation by recording the detector signal at twice the modulation frequency.

This result shows that the saturation structure really does contain two distinct sets of CO molecules. Whether two bands so similar in frequency represent linear and bridged CO groups or just two kinds of linear species distinguished by crowding effects cannot be decided without other evidence. In this connection we recall that the e.e.l.s. result for Cu(100)⁶ is compatible with a bridging species, and a similar result has recently been obtained for Cu(111).⁷ Furthermore CO adsorption on Cu(110) gives a doublet i.r. band even at low coverages where isotopic studies¹² show that adsorption is random. In this case it is difficult to account for two distinguishable linear species associated with top layer copper atoms, although a second linear species could be imagined above exposed second layer atoms. Whether such a species, which is in a site bridging first layer atoms, is to be regarded as linear or bridged is arguable. However, second layer atoms are not accessible on the (111) surface, and it seems possible that the bands are due to linear and bridged species differing only slightly in frequency, as suggested for CO on copper clusters in matrix isolation studies.¹³

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