# Activation of Carbon Dioxide leading to a Chemisorbed Carbamate Species at a Cu(100) Surface

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The formation of a strongly chemisorbed copper carbamate complex, tilted with respect to the surface, is shown to occur during the coadsorption of $CO_2$ and $NH_3$ at a Cu(100) surface at low temperatures; a mechanism is suggested involving the nucleophilic attack of ammonia at the positively polarised carbon atom of a transient $CO_2^-$(s) species.

The present work extends our studies of the activation of carbon dioxide at metal surfaces.[1] With a number of sp-metals (magnesium and aluminium) reactive chemisorption involving dissociation and reduction has been observed at very low temperatures (100—200 K) while with atomically rough Cu(211) surfaces the formation of $CO_2^-$ is suggested. In this communication we report experimental evidence for the formation of a strongly chemisorbed copper carbamate complex at a Cu(100) surface from combined *in situ* high resolution electron energy loss (HREELS) and *X*-ray photoelectron (XPS) spectroscopies using a specially designed spectrometer. The latter enables the reactivity of atomically clean surfaces to be studied by a combination of techniques including in addition to XPS and HREELS, ultraviolet photoelectron spectroscopy (UPS) and low energy electron diffraction (LEED). The spectrometer was designed and built through the co-operation of VG Scientific (XPS, UPS, and LEED) and VSW (HREELS). The electron energy loss spectrometer was operated at a primary beam of 5 eV and a typical resolution of 60 $cm^{-1}$. The Cu(100) single crystal was cleaned by successive cycles of $Ar^+$ bombardment and annealing at 500 K.

Both ammonia and carbon dioxide, when studied separately, are physically adsorbed at a Cu(100) surface at low temperatures (80 K) but on warming desorption is complete leaving in both cases an atomically clean surface at 295 K whether judged by HREELS or XPS; $CO_2$(s) is completely desorbed at 120 K and $NH_3$(s) at about 200 K. Cu(100) is therefore inherently chemically unreactive to both carbon dioxide and ammonia under these conditions.

If the molecules are coadsorbed at 80 K and the adlayer warmed to 295 K the *X*-ray photoelectron spectra show intensities in the C(1s), O(1s), and N(1s) regions (Figure 1). The peak intensities at 295 K are at binding energies of 289, 531, and 400.4 eV which, based on earlier studies, we would assign to chemisorbed $CO_2^-$(a) species and a surface amide species $NH_2$(a). Further support for these assignments comes from the work of Kishi and Ehara[3] who have reported C(1s) and N(1s) values of 287 and 400.3 eV respectively for $H_2N-CH_2-CH_2-NH_2$. Quantitative analysis of the spectra[2] using the appropriate relative photoionisation cross-section and electron escape depth data gave the following atom concentrations: carbon $2.7 \times 10^{14}$ $cm^{-2}$; oxygen $5.8 \times 10^{14}$ $cm^{-2}$; nitrogen $2.8 \times 10^{14}$ $cm^{-2}$, *i.e.* a C : O : N ratio of 1 : 2 : 1. Clearly a species compatible with this stoicheiometry is $O_2CNH_2$(a). It should be emphasised that extensive exposure of a Cu(100) surface to a $CO_2$–$NH_3$ gas mixture at 295 K at the same pressure ($10^{-6}$ torr) provided no evidence for any surface species being formed.

In Figure 2 are shown the corresponding HREELS data: there are six loss peaks at 280, 680, 790, 1400, 1600, and 3480 $cm^{-1}$. We assign the 680 and 790 $cm^{-1}$ peaks to the δ(OCO) in-plane bend vibration and the ω(OCN) out-of-plane bend. The two peaks at 1400 and 1600 $cm^{-1}$ we assign to the

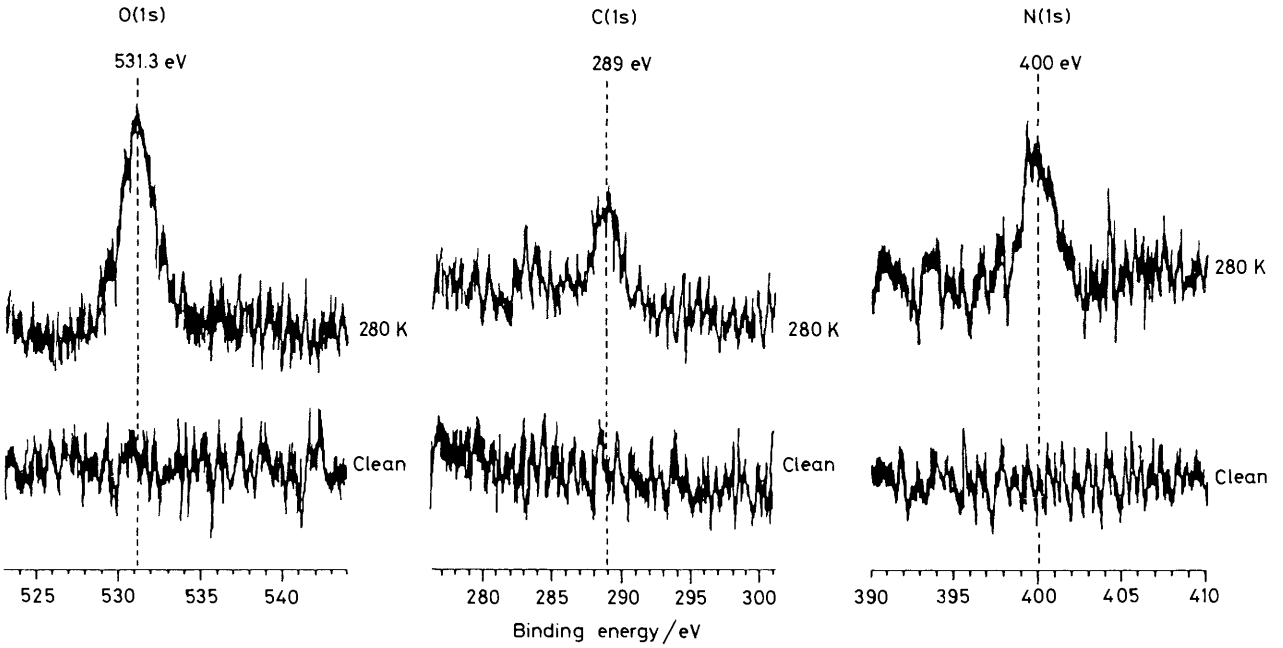

**Figure 1.** O(1s), N(1s), and C(1s) photoelectron spectra after warming an adlayer of physically coadsorbed ammonia and carbon dioxide at a Cu(100) surface from 80 to 280 K.

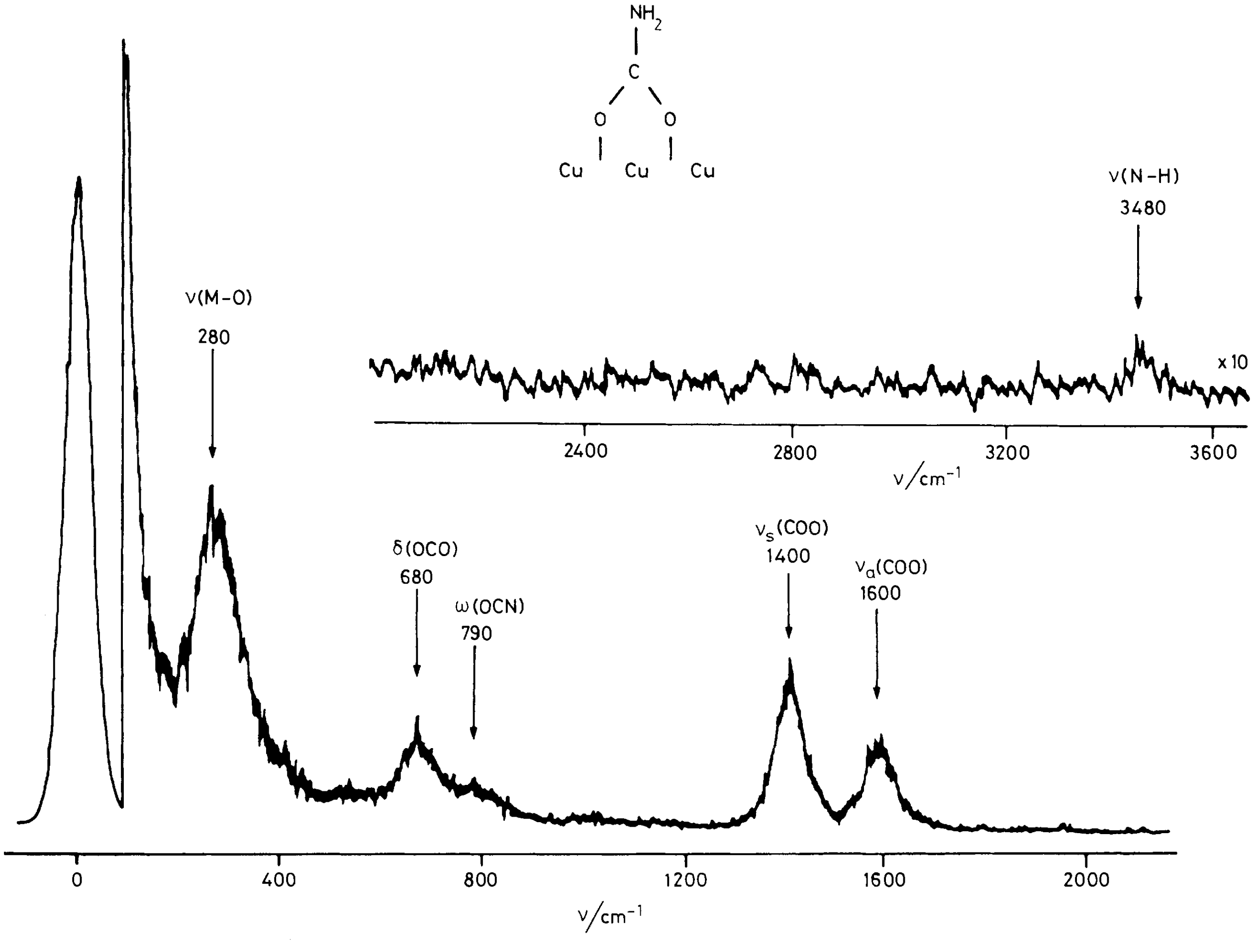

**Figure 2.** Electron energy loss spectra corresponding to the photoelectron spectra in Figure 1.

symmetric COO stretching mode $\nu_s(COO)$ and the asymmetric $\nu_a(COO)$ respectively. These assignments are compatible with those attributed to the formate species and reported by Sexton[3] to occur at 1360 and 1540 $cm^{-1}$ for formic acid interaction with a Cu(100) surface. Separate EELS studies in this laboratory of oxygen chemisorption at Cu(100) exhibited a loss peak at 300 $cm^{-1}$ assigned to the $\nu$(Cu–O) vibration. This is close to the peak at 280 $cm^{-1}$ observed in the present study (Figure 2) and which we assign to the copper–oxygen vibration associated with the bidendate bonding of the carboxylate type complex to the surface copper atoms. This is similar to the value (340 $cm^{-1}$) reported by Sexton[4] for the $\nu$(Cu–O) vibration associated with the Cu(100)–formate complex. A single sharp peak is observed at 3480 $cm^{-1}$ probably due to the symmetric N–H stretch. We correlate this with the N(1s) photoelectron peak at 400.4 eV and assign it to an amide species, $NH_2$. There is no evidence in the EEL spectra for any molecularly adsorbed ammonia at 295 K.

The surface species is therefore suggested to be a bidendate carbamate species bonded to surface copper atoms (Figure 2). The presence of the $\nu_a$(CO–O) vibration at 1600 $cm^{-1}$ suggests that the carbamate species is tilted with respect to the surface plane so that the two oxygen atoms of the complex are non-equivalent, *i.e.* the symmetry of the chemisorbed complex is lower than $C_{2v}$. Ito and Suetaka[5] have reported $\nu_s(COO)$ and $\nu_a(COO)$ i.r. bands for surface formate at copper but which were variable in their relative intensities with different copper substrates. These authors suggested a symmetric bidentate bonding model with different orientations of the formate species as the reason for the variation in the relative intensities of the two peaks.

The steps in reactions (1)—(3) are therefore suggested to be involved in the formation of the chemisorbed carbamate species from the phsyically coadsorbed carbon dioxide and ammonia adlayer.

$$CO_2(g) \leftrightarrows CO_2^-(s) \quad (1)$$

$$NH_3(g) \leftrightarrows NH_3(s) \quad (2)$$

$$CO_2^-(s) + NH_3(s) \rightarrow H_2N\text{–}CO_2(a) \quad (3)$$

We use (s) to designate low-temperature, weakly adsorbed species which are absent at 295 K either when the molecules interact individually or when they are coadsorbed, whereas (a) designates a strongly chemisorbed stable species. The central step in the mechanism involves a nucleophilic attack at the positively polarised carbon atoms of the transient $CO_2^-(s)$ species by weakly physisorbed ammonia, $NH_3(s)$, undergoing surface diffusive hops. Elimination of a hydrogen atom occurs, the fate of which we are uncertain. In effect activation can be thought of as resulting in the insertion of $CO_2$ into a copper–nitrogen bond.

These results illustrate not only the specific surface chemistry that can be revealed by XPS–EELS studies at low temperatures, including further evidence for the presence of a $CO^-_2$ surface species with copper, but also the very facile nature of the molecular events involved in surface complex formation. At these low temperatures the surface lifetimes of the transition states are sufficiently long for the co-operative electronic interactions involving surface copper atoms, $CO_2^-(s)$ and $NH_3(s)$ to result in the formation of the stable chemisorbed carbamate complex. At 295 K, where no reactive chemisorption is observed, the surface residence times of both carbon dioxide and ammonia are many orders of magnitude smaller and unlikely to be greater than $10^{-10}$ s.

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