

Electron Spectroscopic Study of Nitric Oxide Adsorbed on Copper

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Abstract

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The interaction of NO with copper has been investigated by electron spectroscopy. Nitric oxide is shown to be molecularly adsorbed in a linearly bonded configuration at 85 K; this adlayer is unstable above 120 K, resulting in an exclusively oxygen adlayer at 295 K, the nitrogen being desorbed. At 85 K N(1s) peaks observed at 401 and 406 eV are associated with two different surface species. We suggest that the former dissociates while the latter desorbs at a binding energy of 406 eV on thermal activation of the adlayer.

Interaction of nitric oxide with Cu at 295 K results in dissociative chemisorption with both oxygen and nitrogen retained at the surface. The surface concentration suggests that each nitrogen and oxygen adatom is bridge-bonded to two surface copper atoms. Estimates of absolute surface coverages are made by comparing the intensities of the N(1s) and O(1s) peaks with the Cu2p_{1/2} substrate intensity, while valence level spectroscopy (HeI and HeII radiation) supplements core-level spectroscopy for discriminating between molecular and dissociated surface species.

1. Introduction

Electron spectroscopic (u.v. and X-ray) studies [1] of the interaction of nitric oxide with iron surfaces have shown clearly the subtle molecular changes that can occur in the temperature range 85-290 K. The essential feature was the instability of the nitric oxide adlayer resulting, even at 85 K, in some dissociative chemisorption and nitrogen desorption. Other adsorption states including molecularly adsorbed species were also observed and their electron spectroscopic features characterized. These results were in many ways analogous to what we had observed in an earlier study of the interaction of carbon monoxide with iron, [2] the main difference being that dissociation of NO was more facile, occurring at much lower substrate temperature. The present investigation is a natural development of our earlier studies [1]. Copper, which is known to adsorb carbon monoxide only weakly seemed, by analogy, to be an ideal substrate on which to study molecularly adsorbed NO. The results were however more complex than anticipated.

We have also studied (to be published) the adsorption of hydrazine on copper and also of ammonia on both copper and oxidized copper. The data observed with hydrazine adsorption on copper are also compared with those obtained with iron. In the former case we anticipate that the N-N bond will be retained but with iron there is a distinct possibility for N-N bond scission occurring. The N(1s) binding energies associated with those distinct surface bonding configurations are relevant to definitive assignments of surface nitrogen species, and, therefore, to a more complete understanding of the nitrogen surface chemistry of copper.

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2. Experimental

The spectroscopic data were obtained using Vacuum Generators' ESCA-3 instrument, which has already been described [3]. The binding energies are given with reference to the Au(4f_{7/2}) line at 83.8 eV. Copper films were evaporated on to the ESCA-3 probe from a molten bead of copper supported on a molybdenum filament. The films were formed at a pressure of about 10⁻⁹ Torr with the probe nominally at room temperature; after evaporation the pressure decreased to about 4 × 10⁻¹⁰ Torr. Nitric oxide, ammonia and hydrazine were obtained in "lecture cylinders" from the Matheson Co. and were all purified further before use by vacuum distillation.

2.1. Concentration of surface species

The approach we have used to estimate the concentration of surface species is a modification of the method due to Madey, Yates and Erickson [4] (eq. (1)) making use of the recent data of Schofield [5] and Penn [6].

$$\frac{Y_m}{Y_s} = \frac{\mu_m M \sigma}{\mu_s N \lambda \cos \theta p} \quad (1)$$

σ is the surface concentration; Y_m is the photoelectron yield from the adlayer, i.e. either the O(1s) or N(1s) peaks; Y_s the intensity of the "clean" copper 2p_{1/2} peak; N - Avogadro's number; μ_s - ionization cross-section for Cu2p_{1/2} and μ_m the ionization cross-section for the O(1s) or N(1s) orbitals; λ - electron attenuation length in Cu substrate; ρ - density of Cu; M - molecular weight of substrate; θ - angle between collected electrons and the normal to substrate (45°). We also report *relative* concentrations obtained by comparing directly the corrected intensities of the O(1s) or N(1s) adsorbate peaks. Ionization cross-section data have been taken from the work of Schofield [5]; the escape depth ($\lambda \approx 8 \text{ \AA}$) is based on Penn's calculations [6]. The photoyields have been corrected for the known transmission factor of the electron-energy analyzer ($\propto 1/\text{KE}$) and the relative ionization cross-sections.

A number of studies [4, 7] have shown that the approach inherent in eq. (1) is fully justified. Surface concentrations of xenon and oxygen on W(111) and nitrogen and nitric oxide on polycrystalline examples estimated from photoyields being in good agreement (within 10%) with independent flash-desorption methods. It should however be emphasised that errors in estimating λ would lead to appreciable errors in σ .

3. Results and Discussion

3.1. Adsorption of nitric oxide

The O(1s) and N(1s) spectral regions of copper films after evaporation and just prior to the adsorption of nitric oxide showed no evidence for oxygen and nitrogen but the C(1s) regions

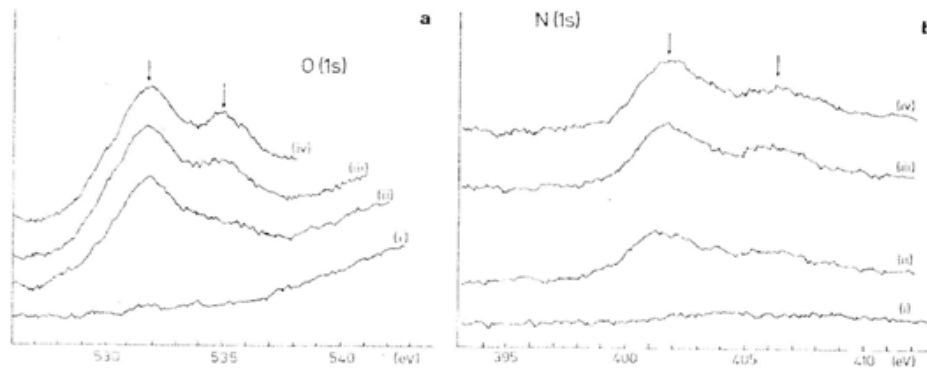


Fig. 1. (a) O(1s) spectral region at 85 K for (i) copper film (ii) after exposure to 150 L of NO(g) (iii) 300 L of NO(g) (iv) 450 L of NO(g). (b) N(1s) spectral region as for (a).

occasionally showed a very small peak centred at 286.2 eV. Fig. 1a shows the O(1s) spectrum after copper has been exposed to nitric oxide at 85 K. After an exposure of 150 L¹ a peak has developed centred at 531.6 eV but with a distinct high binding energy tail. With continued exposure to nitric oxide the "tail" develops into a definite peak centred at 534.5 eV. Associated with these O(1s) spectra are the N(1s) spectra shown in Fig. 1b, an N(1s) peak at 401 eV at low exposures (150 L) but with a second broad peak, centred at 406 eV, emerging with increased exposure to nitric oxide. Fig. 2a and b shows the X-ray induced O(1s) and N(1s) spectra observed when nitric oxide is adsorbed on copper at 85 K and also during warming slowly to 295 K. A diminution occurs in the intensity of the high binding energy O(1s) and N(1s) peaks at 534.5 and 406 eV respectively. At 143 K no evidence for either of these peaks is present. The O(1s) peak at 531.5 eV remains essentially unchanged in the temperature range 85 to 143 K other than some slight evidence for intensity developing on the low binding energy side of the peak. At 295 K

¹ 1 L = 10⁻⁶ Torr s.

the shift in the O(1s) binding energy to lower values is very obvious, the peak being now centred at 530 eV, representing a shift of nearly 2 eV. The N(1s) peak at about 401 eV also diminishes in intensity above 143 K until at 295 K no evidence for any nitrogen surface species is present.

The obvious conclusions are that two different molecular adsorption states of nitric oxide are formed on copper at 85 K, thermal activation leads to desorption of all the nitrogen but, prior to desorption, dissociation of nitric oxide also occurs since at 295 K we have evidence for an O(1s) peak characteristic of chemisorbed oxygen (530 eV). This is further supported by the absence of any surface nitrogen at this stage. When (Fig. 3) a clean copper surface at 295 K was exposed to nitric oxide the X-ray spectra showed, after an exposure of 6×10^3 L, the anticipated O(1s) peak at 530 eV but, in addition and rather surprisingly, an N(1s) peak at 397 eV which intensified only slightly after further exposure (6×10^4 L). The N(1s) intensity was shown in other experiments not to change appreciably in the exposure range 600 to 6×10^4 L. This low binding energy peak at 397 eV is assigned to chemisorbed nitrogen adatoms on the basis of

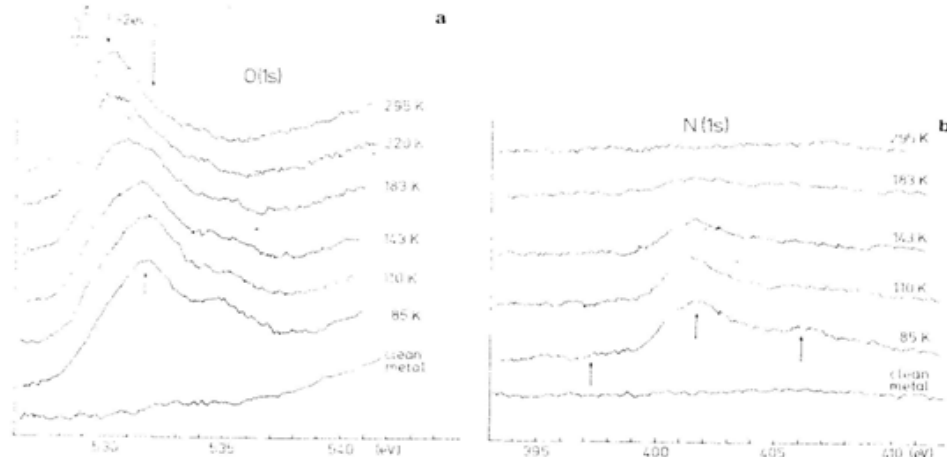


Fig. 2. (a) O(1s) spectral region for clean metal and after adsorption of NO at 85 K, followed by warming adlayer to 295 K. (b) N(1s) spectral region as for (a) above.

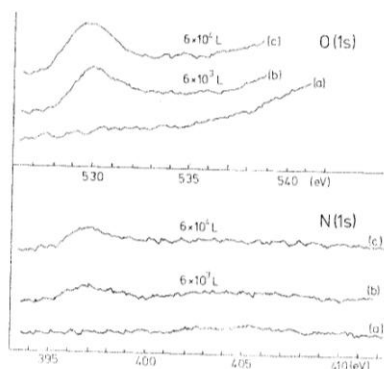


Fig. 3. O(1s) and N(1s) spectral regions after exposure of clean copper (a) to 6×10^2 L of NO (b) and 6×10^4 L of NO (c) at 295 K.

previous studies of dinitrogen, ammonia and nitric oxide and also of atomic nitrogen with copper, where a similar value was observed. Table I summarises the N(1s) and O(1s) binding energies and the O(1s):N(1s) ratios. We draw particular attention to the decrease in the FWHM values with increasing temperature.

We next examine the evidence from the u.v. (He I and II spectra). Fig. 4a shows He(I) spectra for clean copper at 85 K (curve 1) and after adsorbing NO at this temperature (curve 2). Peaks are seen to be present at about 6, 9 and 13 eV below the Fermi level with some "filling in" of states within about 1 eV of E_F . On warming the adlayer the peaks diminish in intensity with no evidence for them at 295 K. The He(I) spectrum is, however, now very different from that of the clean metal, distinct structure being present within 0.5 eV of E_F , attenuation of the *d*-band, i.e. within 2 eV of E_F and some evidence of enhanced intensity in the 6 eV region. The He(II) spectrum at 85 K (Fig. 4b) substantiates the He(I) peaks observed at 6 eV, the broad band

at 9 eV (separate peaks at 9.5 and 11 eV in the He(II) spectrum) and 13 eV. On warming to 295 K the peaks at 9.5, 11 and 13 eV disappear, but clear evidence for a peak at about 5.8 eV is present. Interaction at 295 K gave only a peak at 5.8 eV in the He(II) spectrum. This is in accord with the molecule being dissociated at 295 K. Table II summarises the peaks observed with both He(I) and He(II) radiation together with the known peaks in NO(g).

We have, therefore, evidence for two molecularly adsorbed NO species at 85 K. Examination of the spectra suggests that thermal activation of the adlayer at 85 K leads to desorption of the high binding energy molecule and dissociation of the lower binding energy molecule followed by chemisorption of oxygen and recombination of the nitrogen adatoms followed by desorption of dinitrogen. No nitrogen remains on the surface at 295 K. On the other hand, when copper is exposed to NO at 295 K dissociative chemisorption occurs, resulting in strongly chemisorbed nitrogen and oxygen adatoms. We consider next how surface stoichiometry provides further information on the molecular events.

3.2. Surface stoichiometry and reaction scheme

Using a sensitivity factor of 1.7 for the O(1s):N(1s) intensity ratio we find that at 85 K the ratio of oxygen to nitrogen present on the surface is close to 1:1. This is substantiated further by comparing N(1s):Cu(2p) and O(1s):Cu(2p) ratios. At 85 K the N(1s):Cu(2p) ratio is 0.22 while the O(1s):Cu(2p) ratio is 0.24. Therefore, we conclude that within the limits of error there is no evidence for nitrogen desorption from the surface at 85 K; the stoichiometry is consistent with our conclusion from both X-ray and u.v. data that nitric oxide is adsorbed molecularly. After warming the adlayer from 85 to 295 K no surface nitrogen was detectable at 295 K; about 40% of the "oxygen" present at 85 K is desorbed (as NO) while the rest has been transferred by thermally induced dissociation of nitric oxide into chemisorbed oxygen. For the interaction of NO at 295 K the O(1s):Cu(2p) ratios are identical at about 0.05, which indicates equal concentrations of surface nitrogen and oxygen adatoms.

A schematic representation of the molecular processes occurring

Table I. The N(1s) and O(1s) binding energies and FWHM values for species formed during the adsorption of nitric oxide on copper at 85 K followed by warming the adlayer to 295 K in vacuo

The O(1s):N(1s) ratios are also given

Interaction at 85 K	O(1s)		N(1s)		O(1s):N(1s) ratio by peak area
	B.E./eV	FWHM	B.E./eV	FWHM	
Exposure to NO at 5×10^{-7} Torr for 5 min	531.7	4.3	401.4 406.3	3.8	1.0
Further exposure to NO at 10^{-7} Torr for 5 min	531.7 534.9	5.9	401.8 406.3	4.0	1.1
Further exposure to NO at 10^{-6} Torr for 5 min	531.6 534.8	3.8	401.5 406.6	4.0	0.8
Further exposure to NO at 10^{-6} Torr for 15 min	531.6 534.8	4.0	401.8 406.3	4.3	1.0
Warmed in vacuo to: 110 K	530.2 531.7 534.7	4.0	401.5 405.8	3.0	1.3
143 K	530.2 531.4 534.5 (weak broad peak)	3.9	401.6 406 Very weak	3.0	1.5
183 K	530.3	3.6	Weak and broad	—	Very large
220 K	530.3	3.0	—	—	∞
295 K	530.0	2.5	—	—	∞

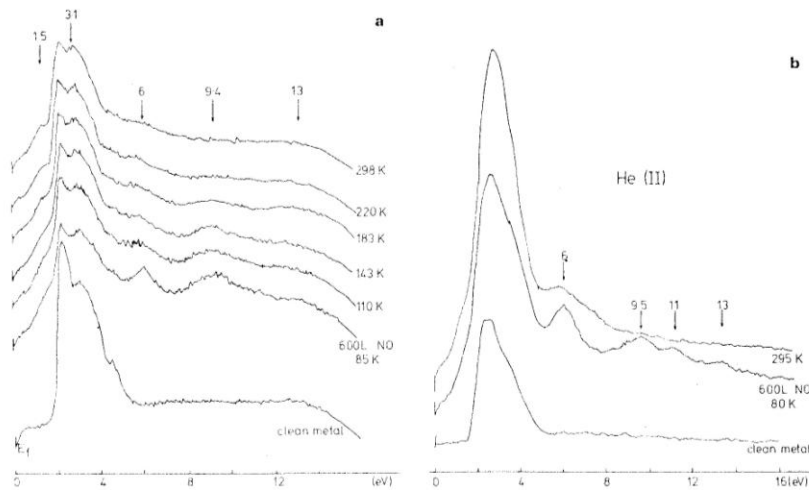
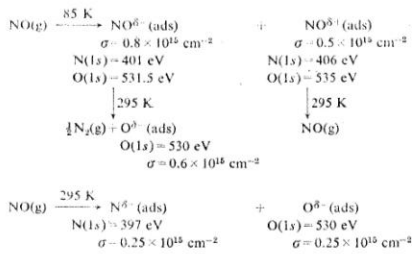


Fig. 4. (a) He(I) spectra for clean Cu, NO adsorbed on Cu at 85 K and during warming the adlayer to 295 K. (b) He(I) spectra for copper, copper + 600 L NO(g) at 85 K and on warming adlayer to 295 K.

at 85 K and on warming the adlayer to 295 K is given below, together with the surface coverages (σ eq. (1)) and the molecular assignments of the N(1s) and O(1s) binding energies. It is clear from the temperature dependence of the N(1s) peaks that the most weakly held species is that of highest binding energy (406 eV, Fig. 2a) desorption being complete at 142 K. This species is obviously associated with the O(1s) peak at 535 eV (Fig. 2a) which also has a substantially diminished intensity at 142 K, and with no evidence of it being present at 183 K. In contrast the N(1s) peak at 401 eV is still clearly present at 183 K. We assign the 406 eV peak to $\text{NO}^{\delta+}$ (ads) species in keeping with the charge-binding energy relationship, (i.e. the higher the N(1s) binding energy the smaller is the electron density associated with the species), the known electron-donor character of nitric oxide and the infra-red evidence for such species in the chemistry of nitric oxide. Furthermore, recent work on the interaction of nitric oxide



Reaction scheme. Scheme for adsorption and thermally induced dissociation of nitric oxide adsorbed on copper in the temperature range 85 to 295 K. N(1s) and O(1s) binding energies as well as estimated surface coverages (σ) calculated using eq. (1). The adlayer is warmed under a dynamic vacuum (10^{-9} Torr).

Note: The coverages quoted are for a particular experiment but in five separate studies the values did not deviate more than $\pm 8\%$.

with aluminium [8] has shown that the surface species characterised by an N(1s) value at 406 eV is desorbed specifically by water, leaving the "species" with an N(1s) at 401 eV largely unaffected. Water, like NO, is also a strong electron donor and will be adsorbed at similar surface sites to the $\text{NO}^{\delta+}$. In the He(I) spectra (Fig. 4a) the orbitals observed at 6 and 9.5 eV at 85 K diminish in intensity with increasing temperature until at 220 K there is no evidence for them. Since these orbitals can be correlated with peaks in NO(g), the spectra provide unambiguous evidence for desorption of molecular NO. The spectrum at 220 K (Fig. 4a, curve 6) is of course not typical of clean copper, the *d*-band being greatly attenuated with some additional structure present in both the *d* and *s*-bands. The latter are due to strongly chemisorbed oxygen species formed by the dissociation of $\text{NO}^{\delta-}$ (ads) and characterised by an O(1s) value of 530 eV. It is important to note that almost all the $\text{NO}^{\delta-}$ (ads) species dissociate but no nitrogen is retained by the surface above a temperature of 200 K (Fig. 2b). At 295 K nitric oxide is dissociatively chemisorbed (Fig. 3) giving an equal concentration ($2.5 \times 10^{14} \text{ cm}^{-2}$) of N(ads) and O(ads) species. There is no evidence for molecular NO at this temperature; these concentrations therefore represent the maximum possible at nitric oxide pressures of up to about 10^{-1} Torr, although exposure to $\text{O}_2(\text{g})$ at 295 K produced an increase in the O(1s) peak height. The total oxygen surface concentration after exposure of copper first to nitric oxide and then oxygen (5×10^{-6} Torr, 10 min) was about 4×10^{14} atoms cm^{-2} and the nitrogen 2.5×10^{14} atoms cm^{-2} .

The total surface concentration ($\text{NO}^{\delta-} + \text{NO}^{\delta+}$) at 85 K is 1.3×10^{15} molecules cm^{-2} . This is close to the density of copper atoms if we assume equal proportions of (111), (110) and (100) planes to be present in the polycrystalline film surface. We suggest, therefore, that both $\text{NO}^{\delta-}$ and $\text{NO}^{\delta+}$ species are each bonded linearly to a single copper atom, the former dominating at low coverage, and the latter at high coverage (Fig. 1a). On the other hand, during interaction at 295 K the total concentration of

Table II. He(I) and He(II) peaks for adsorption of NO on copper at 85 and 295 K together with those reported for NO(g)

NO(g)	He(I)	9.26	15.65	16.84	17.55	18.39	19.2
NO/Cu 5×10^{-7} Torr NO for 10 min, 85 K	He(I)	1.48	5.94	8.35	9.35	11.18	13.10
NO/Cu 5×10^{-7} Torr 10 min, 85 K	He(II)	5.98		9.51		10.98	13.10
NO/Cu after warming adlayer formed at 85-295 K	He(I)	1.48	5.84	—	—	—	—
NO/Cu interaction at 295 K (6000 L)	He(II)	5.83	—	—	—	—	—

nitrogen and oxygen adatoms is $0.5 \times 10^5 \text{ cm}^{-2}$ ($P_{\text{NO}} \approx 10^{-5}$ Torr). However, if each adatom is bridge-bonded to two surface copper atoms, then the number of copper atoms involved in bonding is 10^{15} cm^{-2} , which approaches the theoretical maximum. This point is further exemplified by exposure of this surface to $\text{O}_2(\text{g})$ where the final concentration at the surface was 6.5×10^{11} atoms cm^{-2} . Assuming bridge-bonding this is equivalent to all the surface copper atoms ($1.3 \times 10^{15} \text{ cm}^{-2}$) being involved.

This model further explains the absence of nitrogen adatoms after warming the adlayer from 85 to 295 K, since the oxygen adatoms ($0.6 \times 10^{15} \text{ cm}^{-2}$) present at 295 K would occupy nearly all the surface copper sites since $1.2 \times 10^{15} \text{ cm}^{-2}$ would be involved in bonding. Evidence for nitrogen and oxygen being bridge-bonded on copper is available from LEED studies where with Cu(100) the chemisorbed layer has the $\sqrt{2} \times \sqrt{2} \text{ R}45^\circ$ structure. The details of the transformation of the nitric oxide molecule from a linearly bonded configuration to a bridge-bonded form, with total exclusion of the nitrogen adatom from the adlayer, must await further studies combining LEED with electron spectroscopy.

4. General comments

By combining core and valence level spectroscopies, various molecular processes have been recognised; Table III summarises the O(1s) and N(1s) binding energies for the surface species involved. The surface chemistry is ascribed to a two-way electron transfer process, and the linearly bonded species we have designated $\text{NO}^{\delta+}$ is clearly analogous to the nitrosonium ion (NO^+) which is iso-electronic with CO. We, therefore, would expect the nitrogen-oxygen bond in $\text{NO}^{\delta+}$ to be appreciably stronger than in $\text{NO}(\text{g})$, 700 kJ mol^{-1} , probably approaching that in $\text{CO}(\text{g})$, 1000 kJ mol^{-1} . It is, therefore, reasonable that thermal activation would lead to desorption of the $\text{NO}^{\delta+}(\text{ads})$ species rather than dissociation; this view is supported by our data. We estimate from the temperature at which $\text{NO}^{\delta+}(\text{ads})$ desorbs (150 K) a heat of adsorption of about 50 kJ mol^{-1} .

Similarly the nitrogen-oxygen bond in $\text{NO}^{\delta}(\text{ads})$ will be weakened by what is suggestive of back bonding of electrons into the antibonding orbital; this agrees with our experimental evidence for $\text{NO}^{\delta}(\text{ads})$ being a precursor to dissociation. The process of dissociation, although activated, has an activation energy of no

more than a few kJ mol^{-1} since dissociation is observed at 120 K. The analogy with CO is very clear [9]. Although we intuitively expect that the molecule is bonded to the surface at 85 K via the nitrogen atom, nitrogen elimination, leaving only oxygen adatoms, is easier to visualise for a Cu-ON configuration [1]. Such details as how the linearly bonded molecular form is transformed into an adlayer which consists exclusively of bridge-bonded oxygen atoms, and whether surface crystallography has any influence on the formation of what we have tentatively assigned as $\text{NO}^{\delta+}$ and NO^{δ} , must await further work involving combined LEED and electron spectroscopy. The contrast with our observations at 295 K, where nitric oxide is dissociatively chemisorbed to give both bridge-bonded oxygen and nitrogen adatoms, is clearly intriguing.

Note added in proof: Recent high resolution X-ray photoelectron spectroscopic studies (Johnson, Matloob and Roberts, Chem. Commun., in press) with single crystals of copper indicate that what we have assigned in this paper as $\text{NO}^{\delta+}$ is in fact due to $\text{N}_2\text{O}(\text{ads})$. We therefore have evidence for the formation of $\text{O}(\text{ads})$, $\text{NO}^{\delta}(\text{ads})$ and $\text{N}_2\text{O}(\text{ads})$ at 85 K, the latter arising from the interaction of N(ads) with NO(ads).

Acknowledgement

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Table III. Assignment of binding energies (eV) to surface species

	$\text{NO}^{\delta+}(\text{ads})$	$\text{NO}^{\delta}(\text{ads})$	N(ads)	O(ads)
N(1s)	406	401	397	~
O(1s)	535	531.7	~	530