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Study of the Interaction of Nitric Oxide with Cu(100) and Cu(111) Surfaces Using Low Energy Electron Diffraction and Electron Spectroscopy †

BY DAVID W. JOHNSON, MOHAMMED H. MATLOOB AND M. WYN ROBERTS*§

School of Chemistry, University of Bradford, Bradford BD7 1DP

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The adsorption of nitric oxide on Cu(100) and Cu(111) surfaces has been studied by combining X-ray and u.v. photoelectron spectroscopy with low energy electron diffraction. At 80 K two molecular states, characterised by N(1*s*) values of 399.5 and 401 eV, have been assigned to "bent" and "linear" configurations, respectively. The bent form dissociates slowly at 80 K while the linear species desorbs above ≈ 170 K. Assignments of the "bent" and "linear" forms were facilitated by recourse to the known sterochemistry of metal nitrosyl complexes where a correlation between formal charge on the ligand and sterochemistry has been established. Furthermore the results are compared with the adsorption of NO on both clean nickel and nickel whose surface reactivity has been controlled by pre-exposure to oxygen.

The N-adatoms arising from dissociation at 80 K are mobile and highly reactive forming N_2O which remains on the surface at this temperature. There is no evidence for dinitrogen desorption. The N_2O was characterised by both its X-ray and u.v. photoelectron spectra. Cu(100) and Cu(111) behave similarly, Cu(111) being less active than Cu(100) in dissociation. At 80 K with Cu(100) there is evidence from LEED for the formation of an ordered $(\sqrt{2}\times\sqrt{2})R45°$ structure superimposed on an increase in the background intensity of the scattered electrons. On warming the adlayer to 290 K well ordered $(\sqrt{2}\times\sqrt{2})R45°$–O structures are present. No ordered structures were observed with Cu(111) at either 80 or 290 K and this is compatible with previous studies of chemisorbed oxygen on Cu(111). At 290 K NO chemisorbed dissociatively on Cu(100) and Cu(111) both fragments being retained at the surface. With Cu(100) the symmetry of the adlayer conformed to a $(\sqrt{2}\times\sqrt{2})R45°$ structure.

From a curve fitting analysis of the O(1*s*) data for the adlayer formed on Cu(100) concentrations of the individual surface species O(a), NO(a) and N_2O(a) present at 80 K and on thermal activation to 110, 133 and 290 K were calculated.

A detailed understanding of the mechanism of inherently simple surface processes is essential for the development of models for more complex heterogeneously catalysed reactions. This is clear from the impact that the early studies of Langmuir (see Suits)[1] and J. K. Roberts [2] had on the future development of the subject. X-ray photoelectron spectroscopy (X.p.s.) offers a new dimension to the study of molecular processes occurring at solid surfaces in that it allows the chemical identification of all elements (other than hydrogen); furthermore, the measured core-electron binding energies are sensitive to the chemical environment of the atom in question. Ultraviolet photoelectron spectroscopy (u.p.s.) provides an important adjunct to X.p.s. in that it gives more direct information on the electron density of states close to the Fermi level of the substrate and also reflects changes in the latter after gas adsorption. By making direct comparison with the photoelectron spectrum of the gaseous molecule (the "finger print" approach) it is possible to decide whether or not the molecule

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§ Present address: Department of Chemistry, University College, Cardiff CF1 1XL.

is associatively or dissociatively adsorbed. This has been particularly helfpul in studying the adsorption of carbon monoxide on metal surfaces (see, for example, Bradshaw *et al.*,[3] Umbach *et al.*[4] and Roberts [5]).

We recently investigated the adsorption of nitric oxide with both polycrystalline iron [6] and copper surfaces [7] by means of photoelectron spectroscopy. In the case of iron unambiguous evidence was obtained for dissociation of the molecule at low coverage at 85 K but with increasing exposure, further adsorption was predominantly associative. However, thermal activation of the adlayer effected complete dissociation and at 295 K evidence for molecular adsorption was only observed at " high " (10^{-3} Pa) pressure of nitric oxide. In order to explore the molecular behaviour of adsorbed nitric oxide it was important that we choose a system where the adsorbent's anticipated activity for inducing dissociation of molecular nitric oxide was appreciably less than that of iron. We chose copper in view of its known low activity in the chemisorption of such diatomic molecules as hydrogen, carbon monoxide, nitrogen *etc.* Furthermore, Brodén *et al.*[8] proposed that NO adsorption on copper should be molecular at room temperature. However, results with polycrystalline copper were surprising in that what we interpreted [7] as a molecular adlayer formed at 80 K, and consisting of two distinct surface species, transformed into an adlayer at 295 K which was exclusively chemisorbed oxygen. No nitrogen was present. A clean copper surface at 295 K dissociatively chemisorbed nitric oxide, both the nitrogen and oxygen adatoms being retained at the surface in an approximately 1 : 1 ratio. A number of interesting issues are, therefore, raised by our results which require more detailed study involving well defined single crystal surfaces.

In the present paper nitric oxide interaction with both Cu(100) and Cu(111) surfaces has been studied in the temperature range 80-295 K by combining surface structural studies using low energy electron diffraction (LEED) with high resolution X.p.s. and also u.p.s. High resolution facilities were not available in our previous work [7] and in view of the wide profile of the core-level spectra observed at 85 K the possibility that unresolved overlapping peaks were responsible required investigation. As well as of intrinsic fundamental interest the results will also be relevant to the catalytic chemistry of nitric oxide, whether in the context of automotive exhaust problems or the ammoxidation of olefins to nitriles.

EXPERIMENTAL

Details of the photoelectron spectrometer-low energy electron diffraction system used in this work have already been described [9] except that a windowless helium discharge lamp, providing He(I) and He(II) radiation, has been added.

The copper single crystals of (100) and (111) orientation were cut by spark erosion from larger crystals obtained from Metals Research, and oriented to within 1° of that stated. Before insertion in the spectrometer the crystal was polished to a mirror finish using the procedure of Ahern *et al.*[10] Clean surfaces were generated as described previously.[9] Low energy electron diffraction (LEED) patterns expected of the clean unreconstructed surface were observed (see later) before adsorption studies were started.

Nitric oxide supplied by Matheson in " lecture " cylinders was further purified by a sequence of freeze–evacuation–thaw cycles and passed through a trap cooled in liquid nitrogen before use. The pressures used in the adsorption experiments were usually in the range 10^{-6} to 10^{-3} Pa.

The spectra were recorded on a conventional X–Y recorder and simultaneously stored in a Digico M16V microcomputer. Data analysis consists of removing inelastic background, following a method due to Shirley,[11] smoothing of raw data, calculation of peak areas, peak heights and full-width at half-maxima (f.w.h.m.) values and the generation of "difference" spectra. Electron binding energies are quoted relative to the Fermi level and calibrated

against the Au($4f_{\frac{7}{2}}$) level at 83.8 eV which gives a Cu($2p_{\frac{3}{2}}$) peak at 932.8 eV. We estimate that the binding energies are accurate to about ± 0.2 eV. A broad feature in the 403-405 eV electron binding energy region, only obvious when the spectrometer is operated at high sensitivity, is observed with the clean copper surface. We have no firm view as to its origin but its presence does not influence the interpretation of the spectra observed in the N(1*s*) region.

Adatom surface concentrations (σ) were estimated using eqn (1) which is a modified form of that originally used by Madey *et al.*[12] making use of the recent data of Schofield [12] and Penn [14] for ionisation cross-sections and escape depths, respectively.

$$\frac{Y_m}{Y_s} = \frac{\mu_m M \sigma}{\mu_s N \rho \lambda \cos \phi}. \quad (1)$$

Y_m is the photoelectron yield from either the N(1*s*) or O(1*s*) peaks; Y_s is the intensity of the "clean" Cu($2p_{\frac{3}{2}}$) peak; $\mu_{m,s}$ the ionisation cross-sections of the O(1*s*)/N(1*s*) and Cu($2p_{\frac{3}{2}}$) orbitals; λ the electron escape depth; ϕ = angle between collected electrons and normal to the substrate; ρ = density of Cu; N = Avogadro's number and M = atomic weight of Cu. These terms have been discussed elsewhere.[7]

RESULTS AND DISCUSSION

INTERACTION AT 290 AND 80 K; X-RAY PHOTOELECTRON SPECTRA

Fig. 1 shows the N(1*s*) and O(1*s*) spectra regions for a Cu(100) surface before and after exposure to nitric oxide at 290 K. The total exposure was $\approx$900 L (1 Langmuir $\equiv 10^{-6}$ Torr s; 1 Torr $\equiv$ 133.3 Pa) at a pressure of $\approx 10^{-3}$ Pa. The N(1*s*) spectrum shows a distinct peak centred at 397.3 eV; associated with this is an O(1*s*) peak at $\approx$530.2 eV. These binding energies are now well established as being due to nitrogen and oxygen adatoms (*e.g.*, Kishi and Roberts;[6] Mason and Textor [15] and Matloob and Roberts [7]) and indicate dissociative chemisorption of nitric oxide on Cu(100) at 290 K. Both peaks are, however, broad so that NO(a) may also be present. More detailed studies of the development of peak intensities with exposure indicate that a plateau is reached after an exposure of $\approx$300 L which suggests an overall average sticking probability of $\approx 3 \times 10^{-3}$.

Also shown in fig. 1 are the spectra for a similar experiment with a Cu(111) surface and again we observe an N(1*s*) peak centred at a binding energy of $\approx$397 eV and an O(1*s*) peak at 530 eV.

Both Cu(100) and Cu(111) surfaces, therefore, chemisorb nitric oxide dissociatively at 290 K. When the N(1*s*) and O(1*s*) peak areas are compared and stoichiometries calculated the ratio of nitrogen to oxygen adatoms present on the Cu(100) surface is close to 1.0. For Cu(111) the ratio is significantly less than unity ($\approx$0.6) which indicates that the surface is enriched in oxygen presumably by nitrogen adatom recombination and desorption.

We can therefore summarise NO interaction with both Cu(100) and Cu(111) surfaces at 290 K as follows:

$$NO(g) \rightarrow NO(a) \quad (2)$$

$$NO(a) \rightarrow N(a) + O(a) \quad (3)$$

$$N(a) + N(a) \rightarrow N_2(g). \quad (4)$$

Reaction (4), nitrogen desorption, is invoked to account for N : O ratios of less than unity with the Cu(111) surface. It is, however, not the only process possible since the formation of $N_2O(g)$ *via* a surface reaction involving N(a) + NO(a) could also account for the N : O ratio observed.

Fig. 2 shows the O(1*s*) spectra observed after the exposure of a Cu(100) surface to nitric oxide at 80 K followed by warming the adlayer in stages to 290 K. After an exposure of 24 L at 80 K (which saturates the adlayer) three distinct O(1*s*) peaks (↑) are observed : at 529.8, 531 and 534.5 eV.

The 529.8 eV peak is clearly due to chemisorbed oxygen and so we have evidence for dissociative chemisorption of nitric oxide occurring on a Cu(100) surface at 80 K and exposures <20 L. These results, therefore, throw into question the conclusions from our earlier studies with polycrystalline copper [7] where only two O(1*s*) peaks were resolved, one at about 531 eV and the second at 534.5 eV.

After warming this adlayer to 110 K the intensity of the O(1*s*) peak at 534.5 eV had almost disappeared while at 170 K there is no apparent intensity left in this spectral region. The peak formerly at 531 eV is at 170 K only a shoulder on the peak centred at 529.8 eV while at 290 K only a single narrow O(1*s*) peak, with a binding energy of 529.8 eV, is apparent.

We next examine the corresponding N(1*s*) spectra (fig. 3). At 80 K there are two peaks, one with a binding energy of ≈402 eV and the second ≈406 eV. On warming the adlayer to 110 K, the higher binding energy feature has disappeared and the profile of the 402 eV peak has changed, the peak maximum having moved ≈0.5 eV to lower binding energy : this being accompanied by narrowing of the peak.

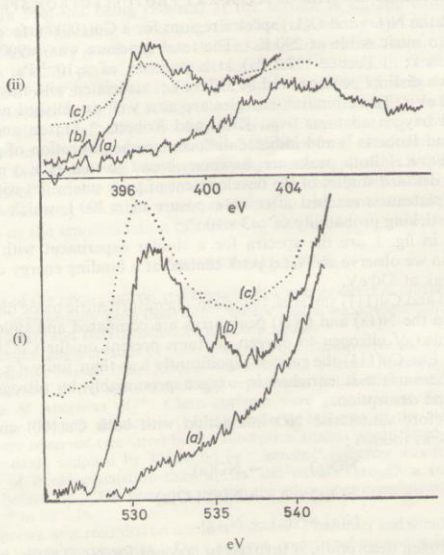


FIG. 1.—(i) O(1*s*) spectra of Cu(100) (solid line) and Cu(111) (broken line) at 290 K : (*a*) before exposure to nitric oxide, (*b*), (*c*) after exposure of 360 L. (ii) N(1*s*) spectra as for (i). (Analysing conditions : f.s.d. 3×10^3 count s^{-1}, 50 eV pass energy.)

The intensity of the N(1*s*) peak at 401 eV remained almost unchanged up to a temperature of about 160 K but above this it diminished rapidly with no evidence of it at 290 K (fig. 3).

If we accept that the O(1*s*) peak at 529.8 eV is due to chemisorbed oxygen and formed by a dissociative chemisorption process [eqn (3)], then from the spectra observed at 290 K we would anticipate the presence of nitrogen adatoms characterised by an N(1*s*) binding energy value of about 397 eV. Clearly no such species is present at 80 K (fig. 3). There are two possibilities, either dissociative chemisorption is followed by a fast nitrogen adatom recombination and desorption as dinitrogen or the nitrogen atom is retained within the adlayer but in a form other than chemisorbed nitrogen. Nitrogen desorption [eqn (4)] is ruled out since the overall composition of the adlayer at 80 K indicates a nitrogen to oxygen ratio of close to unity. This stoichiometric relationship was also observed in our earlier studies [7] with polycrystalline copper films.

Changes in the O(1*s*) spectra indicate that the peak observed at 80 K at a binding energy of 534.5 eV disappears at the same temperature as the N(1*s*) peak at 406 eV and also when what is obviously a composite N(1*s*) peak at ≈402 eV narrows.

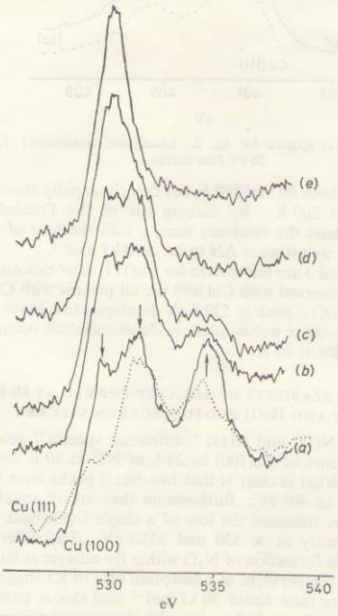


FIG. 2.—O(1*s*) spectra for NO adsorption on Cu(100) at 80 K and thermal activation of adlayer; (– – –) Cu(111) at 80 K. Exposure ≈24 L. (Analysing conditions: f.s.d. 3×10^3 count s^{-1}, 20 eV pass energy.) (*a*) 80, (*b*) 100, (*c*) 133, (*d*) 170 and (*e*) 290 K.

This suggests strongly that the change in the O(1*s*) and N(1*s*) spectra between 80 K and 110 K is due to the desorption of a single surface species containing two spectroscopically distinguishable nitrogen atoms and an oxygen atom. We return to this point later.

Above 140 K, the O(1*s*) peak at 531 eV diminishes in intensity as also does the N(1*s*) peak at 401 eV. At 290 K there is no evidence for any nitrogen species in the N(1*s*) spectra and only a single narrow O(1*s*) peak at a binding energy of 529.8 eV remains. We associate the N(1*s*) peak with a binding energy of ≈401 eV with the O(1*s*) peak at 531 eV and reflecting a molecularly adsorbed nitric oxide species.

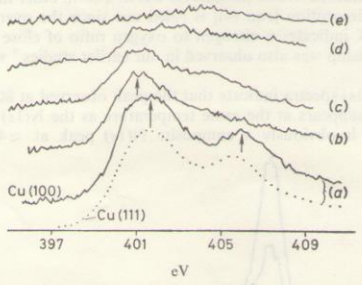


FIG. 3.—Corresponding N(1*s*) spectra for fig. 2. (Analysing conditions: f.s.d. 10^4 count s^{-1}, 50 eV pass energy.)

This species is present at both 80 and 140 K but desorbs rapidly above 170 K. There is no evidence for it at 290 K. By making use of the Frenkel equation, $\tau = \tau_0 \exp \Delta H/RT$, which relates the residence time, τ, with the heat of adsorption, ΔH, and taking $\tau_0 \approx 10^{-13}$ s, we estimate ΔH to be ≈70 kJ mol^{-1}.

Also shown in fig. 2 and 3 are the spectra for Cu(111) after exposure to nitric oxide at 80 K. The features observed with Cu(100) are all present with Cu(111), the main difference being that the O(1*s*) peak at 529.8 eV developed to a lesser extent than with the Cu(100) surface. In other words nitric oxide dissociation occurred slower with Cu(111) than with Cu(100) at 80 K.

THERMAL STABILITY OF ADLAYER FORMED AT 80 K; X-RAY AND He(I) PHOTOELECTRON SPECTRA

Fig. 4(*a*) shows the N(1*s*) and O(1*s*) "difference spectra" generated from the adlayer formed on exposure of Cu(100) to 24 L of NO at 80 K and after warming the adlayer to 110 K. What is clear is that two N(1*s*) peaks have been lost, one at ≈402 eV and the other at 406 eV; furthermore they are of equal intensity. The O(1*s*) difference spectrum indicates the loss of a single O(1*s*) peak at 534.7 eV and some small gain in intensity at ≈ 530 and 531.8 eV. The difference-spectra are therefore suggestive of the formation of N_2O within the adlayer at 80 K; this desorbs below 110 K. The low temperature of adsorption (≲110 K) suggests that the heat of adsorption is no more than about 30 kJ mol^{-1} and this is compatible with the participation of dispersion forces in keeping with the vapour pressure of N_2O being only ≈10^{-5} Pa at 80 K. The molecule once formed therefore remains within the adlayer in the physically adsorbed state.

The N(1*s*) and O(1*s*) spectra of N_2O adsorbed on both Cu(111) [fig. 4(*b*)] and gold at 80 K (Carley and Roberts, unpublished data) indicate the presence of N(1*s*) peaks at 402 and 406 eV and a single O(1*s*) peak at 535 eV providing strong corroborative evidence for the catalytic formation of N_2O at 80 K. In addition to the 535 eV peak a second one of low intensity developed slowly on Cu(111) at 529.5 eV [fig. 4(*b*)]; this is due to a slow dissociation of N_2O at 80 K. The small gain in intensity at 530 and 531.8 eV [fig. 4(*a*)] we attribute to an increase in the concentration of chemisorbed oxygen and molecularly adsorbed nitric oxide.

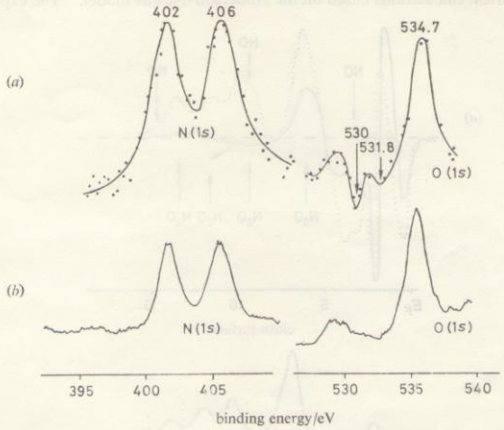


FIG. 4.—(*a*) N(1*s*) and O(1*s*) difference spectra for NO adlayers on Cu(100) at 80 and 110 K. (*b*) N(1*s*) and O(1*s*) spectra for N_2O adsorption on Cu(111) surface at 80 K. (Analysing conditions: f.s.d. 3×10^3 count s^{-1}, 20 eV pass energy.)

We examine next further evidence for the catalytic formation of N_2O at 80 K from our He(I) spectra. Fig. 5(*a*) shows the difference spectrum of the adlayer formed on exposing a Cu(100) surface to 20 L of nitric oxide at 80 K and also after warming this layer to 250 K. Both difference spectra are with respect to the clean metal density of states curve. For weak interaction with the substrate there should be little perturbation of the metal wave functions so that the difference spectrum should show positive spectral structure which can be correlated (but shifted in energy) with the gas phase spectrum. On the other hand, for strong adsorbate–substrate interaction we anticipate gross perturbation of the surface density of states due to shifting of charge density in bond formation and reflected in the occurrence of negative regions in the difference curve. We see clear evidence for both " positive " and " negative " contributions to the difference curves at 80 K and 290 K [fig. 5(*a*)]. In view of our X.p.s. data providing strong evidence for the formation of N_2O within the adlayer at 80 K we determined the He(I) difference curve for N_2O adsorption on Cu(111) at this temperature [fig. 5(*b*)]. There are in the 5 to 15 eV spectral region four obvious " positive peaks " at 6, 9.5, 11.5 and 13.3 eV. In the *d*-band region, *i.e.*, below 5 eV, there is a strong " negative peak " (antiresonance) at about 2 eV and

two components, one negative and the other positive, close to E_F. The similarity between the " N_2O " difference spectrum at 80 K and that observed with nitric oxide at the same temperature is striking, the only distinguishing feature in the 5 to 15 eV region being the shoulder on the low energy side of the peak at about 9.5 eV [fig. 5(*a*)] and additional intensity near 14 eV.

The assignment of peaks in the He(I) spectrum of molecularly adsorbed nitric oxide present on Pd(111) has been discussed previously by Conrad *et al.*,[16] their experimental data being compared with both cluster calculations for Ni—NO and semi-empirical calculations based on the Anderson–Newns model. The experimental

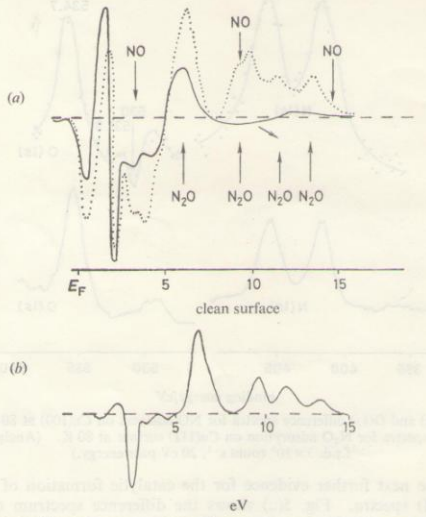


FIG. 5.—(*a*) He(I) difference spectra for NO adlayer on Cu(100) at 80 and 290 K. (*b*) He(I) difference spectrum for N_2O adlayer at 80 K.

data of Conrad *et al.*[16] with peaks at 9.2 and 14.6 eV were identified with chemisorption levels derived from the $(5\sigma + \mu\pi)$ and 4σ molecular orbitals of NO, respectively, and correspond to our assignments of peaks observed for NO adsorption on iron [6] at 80 K. We therefore assign the low binding energy feature associated with the peak at 9.5 eV to the presence of molecularly adsorbed NO. This also agrees with both theory and experimental observations [17, 18] for NO adsorbed on Ni(111). All the other peaks in the 5 to 15 eV range [fig. 5(*a*)] can be ascribed to nitrous oxide [fig. 5(*b*)]; the expected 4σ peak at 14.6 eV from nitric oxide is not obvious since it overlaps with that for N_2O.

Below 5 eV, *i.e.*, in the *s–p* and *d*-band regions, changes in the emission intensity are complex showing both positive and negative peaks. There is an ehhancement of intensity at $\approx$1.5 eV followed by a deep minimum at the *d*-band edge of $\approx$2 eV, while at the Fermi level there is considerable attenuation of intensity. Similar data

were obtained by Doyen and Ertl [18] with Ni(111)+NO; they predict that the occupied 2π-level should be close to E_F and that the peaks seen at 2.3 eV [Ni(111)] and 3.2 eV [Pd(111)] are due to the isolated *d*-band state which is split off below the band. Analogous behaviour has also been observed recently in the adsorption of oxygen, acetylene and carbon monoxide on polycrystalline copper [19] and was interpreted as hybridization of the metallic orbitals involved in bonding. The pattern of behaviour observed by Spicer *et al.*[19] below 5 eV was very dependent on the nature of the molecular interaction. We are unable to decide as to whether the data observed close to E_F conform to either the Doyen–Ertl or Spicer models.

The He(I) spectra observed after NO interaction with Cu(100) at 80 K are therefore compatible with a model based on the presence of molecularly adsorbed nitrous oxide, molecularly adsorbed nitric oxide together with oxygen adatoms arising from the dissociative chemisorption of nitric oxide. The particularly complex behaviour below 5 eV [fig. 5(*a*)] we associate with dissociative chemisorption leading to oxygen chemisorption and it is similar to the observations [19] for oxygen interaction with copper. These characteristics are also present to some extent with N_2O at 80 K which is compatible with our observations by X-ray photoelectron spectroscopy [fig. 5(*b*)] that, although molecular adsorption is predominant, there is evidence for some dissociation as reflected by the slow development of an O(1*s*) peak with a binding energy of 530 eV [fig. 4(*b*)].

THERMAL ACTIVATION OF PARTIALLY FORMED NO ADLAYER ON Cu(100)

Fig. 6 shows the N(1*s*) spectra for clean Cu(100) at 80 K, after exposure ($\approx$6 L) to nitric oxide at the same temperature and on warming this adlayer to 290 K. We estimate the total coverage at 80 K to be $\approx$40 % of the "saturated adlayer" (fig. 2) at the same temperature. At 80 K two N(1*s*) peaks are present, one rather broad peak centred at 401 eV and the second at 406 eV. These are identical to those described earlier (fig. 3). On warming the adlayer to 290 K these two peaks are replaced by one of appreciably lower intensity and shifted to a lower binding energy, 397 eV. The emergence of an N(1*s*) peak at 397 eV contrasts with the behaviour of a "saturated adlayer" (fig. 3) and is clear evidence for the presence of nitrogen adatoms on the Cu(100) surface at 290 K. Associated with this is the oxygen chemisorption peak at 529.5 eV, the only surface species found present on thermal activation of a saturated adlayer (fig. 2). The N(1*s*) peak is unusually wide (*cf.* fig. 1) and may reflect the presence of a second species. We discuss further evidence for this later.

We conclude that the absence of nitrogen adatoms at 290 K after thermal activation of the saturated adlayer (fig. 3) is not a consequence of the surface being incapable of bonding nitrogen atoms arising from NO dissociation but to the preferential chemisorption of the oxygen fragment thus excluding nitrogen from the surface. We suggest therefore that both nitrogen and oxygen adatoms are bonded at similar sites; from our LEED studies discussed below these are likely to be the four-fold coordination sites.

LOW ENERGY ELECTRON DIFFRACTION (LEED)

The clean Cu(100) and Cu(111) surfaces showed the expected (1×1) diffraction pattern [fig. 7(*a*) and (*b*)]. After exposure (20 L) of the Cu(100) surface to nitric oxide at 80 K there was evidence for extra spots being present in the $(\frac{1}{2}, \frac{1}{2})$ positions. They were, however, of rather weak intensity and accompanied by an enhanced background intensity.

On warming the adlayer to 290 K the intensity of the extra diffraction spots increased [fig. 7(*c*) and (*d*)] and the unit cell could be assigned to the $(\sqrt{2}\times\sqrt{2})R45°$–O structure; the diffraction pattern is shown at two electron voltages, 125 and 39 eV. This is compatible with both our electron spectroscopic results which indicated the presence of only chemisorbed oxygen and previous LEED studies which have shown that oxygen chemisorbed on Cu(100) gives rise to the $(\sqrt{2}\times\sqrt{2})R45°$ structure (Braithwaite *et al.*[9] and references therein). We suggest that this symmetry is most likely to arise from oxygen adatoms present at the four-fold coordination sites, *i.e.*, sites of maximum ligancy. We know from our electron spectroscopic results that nitric oxide, nitrous oxide and chemisorbed oxygen are all present at 80 K. Enhanced background intensity is therefore to be expected and we presume that the weak $(\sqrt{2}\times\sqrt{2})R45°$ structure observed at 80 K arises from chemisorbed oxygen.

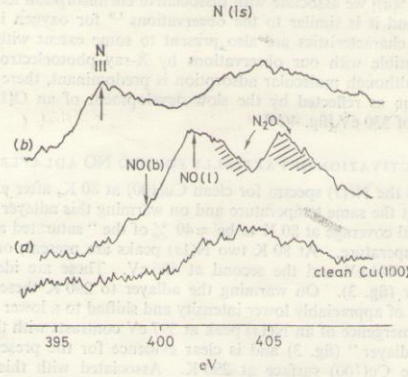
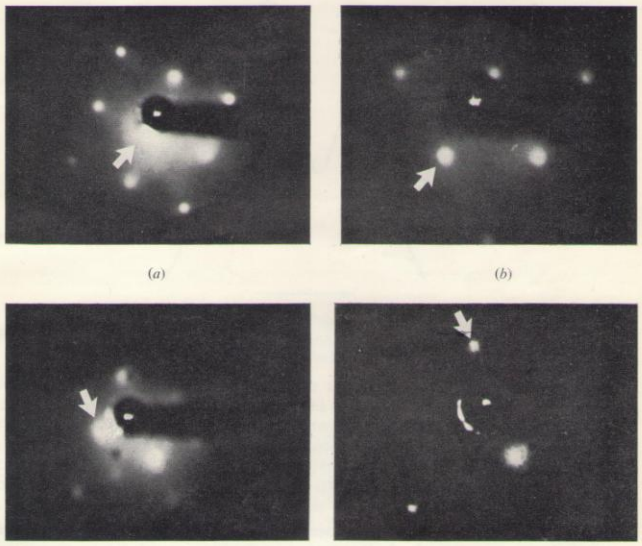


FIG. 6.—Thermal activation of partially covered NO adlayer at 80 K on Cu(100); N(1*s*) spectra (Analysing conditions: f.s.d. 10^4 count s^{-1}, 50 eV pass energy.) (*a*) 80, (*b*) 290 K.

When the Cu(111) clean surface [fig. 7(*b*)] was exposed to nitric oxide at both 80 and 290 K there was no evidence for ordered structures, the background intensity being merely enhanced. This observation is compatible with both our conclusions that nitric oxide is dissociatively chemisorbed on Cu(111) and also previous LEED studies for oxygen interaction, summarised by McDonnell and Woodruff [20] indicating the formation of a disordered adlayer.

CONCENTRATION OF SURFACE SPECIES

When we examine, for example, the O(1*s*) spectral region after the exposure of Cu(100) to nitric oxide at 80 K it is obvious that to estimate the contributions made by individual surface species a further analysis of the data is essential. Spectra stored in the computer were therefore fitted by a series of Gaussian functions, having first removed the background and using three parameters, peak height, peak position and peak width, following the curve-fitting programme devised by Fraser and Suzuki.[21] The success or otherwise of the curve-fitting procedure was tested by minimizing the



(*a*) (*b*)

(*c*) (*d*)

FIG. 7.—LEED patterns for : (*a*) Clean Cu(100) surface (126 eV) (*b*) Clean Cu(111) surface (118 eV) (*c*) Cu(100) surface after exposure to NO at 80 K and warming to 290 K (125 eV) (*d*) as for (*c*) (39 eV) ↑ indicates the (0, 0) spot.

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root mean square deviation between the calculated and the experimental observed peak intensities. Fig. 8 shows the "calculated" and experimental data for the change in the O(1*s*) spectral region observed when Cu(100) was exposed (24 L) to nitric oxide at 80 K. This is known to give a saturated adlayer. Table 1 gives the concentrations, σ, calculated using eqn (1), of the species associated with the three O(1*s*) peaks observed at binding energies of about 529.5, 531 and 535 eV (*cf.* fig. 2) and their respective f.w.h.m. values.

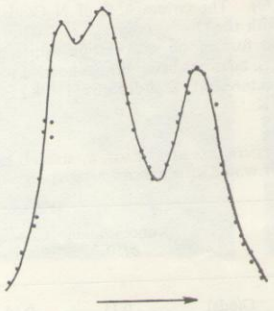

FIG. 8.—Curve fitting of experimental O(1*s*) data (solid line) for NO adlayer on Cu(100) at 80 K (points: computer generated envlope.)

We have good evidence for assigning the three peaks to chemisorbed oxygen, molecularly adsorbed nitric oxide and adsorbed nitrous oxide. In estimating surface coverages (θ) both NO and N_2O are assumed to be linearly bonded to a single copper atom while for chemisorbed oxygen there is good experimental evidence from both our LEED and previous data [7] for two copper atoms being bonded to an oxygen adatom. The atom density of the clean Cu(100) plane is 1.53×10^{15} cm^{-2}. There are a number of points which emerge from this analysis.

(*a*) When saturation of the adlayer is reached at 80 K, *i.e.*, when neither the concentrations of O(ads) nor NO(ads) increase with further exposure to NO, the total coverage (θ) is between 70 and 80 % of the estimated monolayer value. After a total exposure of 12 L, θ is 67 % (table 1), *i.e.*, it is close to the value at saturation.

(*b*) After an exposure of 6 L at 80 K the estimated concentration of N_2O formed conforms exactly to the stoichiometry implied by:

$$NO(g) \rightarrow N(ads) + O(ads),$$

the mobile nitrogen adatoms reacting further with adsorbed NO to give N_2O(ads):

$$N(ads) + NO(ads) \rightarrow N_2O(ads),$$

i.e., every nitrogen atom formed by dissociative chemisorption reacts with a further molecule of nitric oxide. There is, therefore, no evidence for any significant nitrogen adatom recombination followed by nitrogen desorption at 80 K. The concentration of molecularly adsorbed NO is therefore sufficiently high at 80 K and the NO pressure used ($\approx 10^{-4}$ Pa) to ensure the formation of N_2O at the expense of dinitrogen desorption.

(*c*) The f.w.h.m. value (≈3 eV) of the O(1*s*) peak observed at ≈ 531 eV at 80 K is approximately twice the natural O(1*s*) line width. This suggests that there are at least two NO species present at 80 K. We discuss further evidence for this suggestion later.

(*d*) With increased exposure (above 12 L) at 80 K the O(1*s*) peak at 534.9 eV intensifies slowly but with virtually no change in either the NO(ads) or O(ads) concentrations. We believe this is evidence for the accumulation of surface contaminants (*e.g.*, H_2O, CO). The coverage, θ, of N_2O(ads) formed at 80 K (0.08) is compatible (table 1) with the O(ads) coverage of 0.20 at the same exposure, nearly every nitrogen adatom formed on dissociation apparently giving rise to linearly bonded N_2O, the oxygen adatoms being bridge-bonded to two copper surface atoms. With increasing temperature N_2O first desorbs (110 K) followed by the contaminant which is absent at 170 K.

TABLE 1.—SURFACE CONCENTRATION, COVERAGE, θ, BINDING ENERGIES AND FULL WIDTH AT HALF MAXIMA VALUES (F.W.H.M.) FOR SPECIES PRESENT ON Cu(100) AT 80 K AND 290 K

exposure /L	temperature /K		concentration $\sigma/10^{15}$	coverage θ	f.w.h.m. /eV	binding /eV
		O(ads)	0.11	0.14	1.35	529.5
6	80	NO(ads)	0.23	0.15	3.1	531.0
		N_2O(ads)	0.11	0.07	1.94	534.9
		O(ads)	0.15	0.20	1.28	529.6
12	80	NO(ads)	0.60	0.39	2.9	531.3
		N_2O(ads)	0.12	0.08	1.98	534.9
After " saturation " (24 L) at 80 K the adlayer was warmed in stages to :						
	110	O(ads)	0.28	0.36	1.54	529.8
		NO(ads)	0.48	0.32	2.27	531.6
		impurity	0.16	0.12	2.30	534.6
	133	O(ads)	0.29	0.38	1.52	529.8
		NO(ads)	0.50	0.34	2.23	531.6
		impurity	0.12	0.09	2.3	534.5
	290	O(ads)	0.56	0.74	1.7	530.0

(*e*) When we compare the coverages of NO(ads) at 110 and 80 K we see that there has been a decrease of 0.07 in the fractional coverage after warming. This is almost exactly balanced by the increase (0.16) in the surface coverage of bridge-bonded chemisorbed oxygen.

(*f*) The total coverage (0.74) of bridge-bonded chemisorbed oxygen at 290 K compared with that present at 110 and 133 K (≈0.36) indicates that approximately half of the NO(ads) present at the lower temperature dissociated on warming.

One of the conclusions we have drawn from table 1 is that there are possibly two molecularly adsorbed nitric oxide species present on Cu(100) at 80 K [(*c*) above]. This led us to search carefully for any direct experimental evidence for this and in

view of our observation (fig. 2) that Cu(111) is less active in the dissociation of nitric oxide than Cu(100) we chose to study this plane in detail.

Fig. 9 shows the development of the N(1*s*) spectra as a function of the exposure of Cu(111) to nitric oxide at 80 K. In these experiments it should be noted that the spectra were recorded at higher resolution than used elsewhere in this work and hence the lower signal to noise ratio. At low exposure (2 L) there is only one obvious peak and this is at a binding energy of 399.5 eV ; after 6 L there are three N(1*s*) peaks

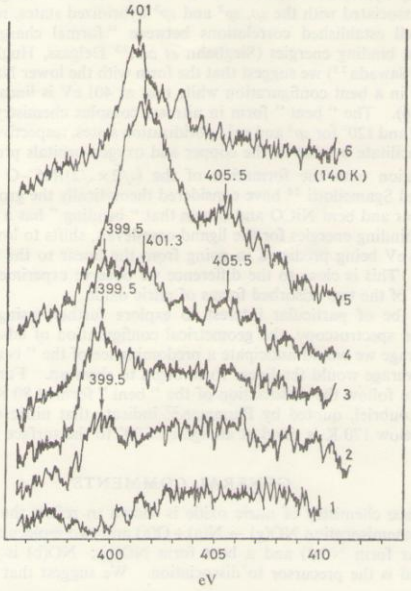

FIG. 9.—N(1*s*) spectra during the exposure of Cu(111) to nitric oxide at 80 K and after warming the adlayer to 140 K. Curve 1, clean Cu(111) surface ; 2, +2 L of NO(g) ; 3, +4 L of NO(g) ; 4, +6 L of NO(g) ; 5, +12 L of NO(g) ; 6, after warming the adlayer to 140 K. (Analysing conditions : 10^3 count s^{-1}, 20 eV pass energy, 3000 s scanning time).

with binding energies of ≈399.5, 401 and 406 eV. We have therefore evidence for two distinct NO species at 80 K. The lower binding energy peak diminishes in intensity as the 401.4 eV peak increases at higher exposure. On warming the adlayer to 140 K just one peak, that at 401 eV, remains. This disappears, by desorption of the surface species, above 170 K.

We have, therefore, direct experimental evidence for two molecularly adsorbed NO species at 80 K, one which dissociates and the other which remains adsorbed up to about 170 K. That dissociation occurs is reflected by a decrease in the intensity of the N(1*s*) peak at 399.5 eV and a concomitant increase in the O(1*s*) peak at 529.8 eV.

These results provide direct evidence for the suggestion based on the curve-fitting analysis (table 1) of the spectral data for the more reactive Cu(100) surface.

BENT AND LINEAR FORMS OF ADSORBED NITRIC OXIDE

In nitrosyl complex chemistry the sterochemistry of the nitrosyl ligand can be correlated with the charge on the ligand (McGinnety),[22] a negative charge being associated with either sp^2 or sp^3 hybridization (the " bent " form) and a positive charge with sp hybridization (the " linear " form). Formal charges of $+1$, -1 and -3 can be associated with the sp, sp^2 and sp^3 hybridized states, respectively. Since there are well established correlations between " formal charges " or " electron density " and binding energies (Siegbahn *et al.*;[23] Delgass, Hughes and Fadley;[24] Yashida and Sawada[25]) we suggest that the form with the lower N(1*s*) binding energy (399.5 eV) is in a bent configuration while that at 401 eV is linearly bonded (fig. 9, see also fig. 6). The " bent " form in nitrosyl complex chemistry has metal–ligand angles of 109 and 120° for sp^3 and sp^2 hybridization states, respectively, a configuration which will facilitate overlap of the copper and oxygen orbitals providing a route for NO dissociation with the formation of the $(\sqrt{2}\times\sqrt{2})R45°$–O structure. Clark, Cromarty and Sgamellotti [26] have considered theoretically the ground and core hold states of linear and bent NiCO and shown that " bending " has a dramatic influence on the core binding energies for the ligand core-levels, shifts to lower binding energy of about 1.5 eV being predicted in going from the linear to the bent configuration of CO(ads). This is close to the difference we observe experimentally between the N(1*s*) values of the two adsorbed forms of nitric oxide.

It would be of particular interest to explore further, using angular resolved photoelectron spectroscopy, the geometrical configuration of adsorbed nitric oxide. At low coverage we would anticipate a predominance of the " bent " form and only at higher coverage would the linear form begin to show up. Furthermore it should be possible to follow the dissociation of the " bent " form at 80 K. Recent angular studies by Loubriel, quoted by Plummer [27] indicate that nitric oxide adsorbed on Ni(100) at below 170 K is tilted at an agnle of 30° to the surface normal.

GENERAL COMMENTS

The surface chemistry of nitric oxide is shown to reflect the interplay between dissociative chemisorption NO(g) → N(a)+O(a) and two molecular states of adsorption, a linear form NO(l) and a bent form NO(b); NO(b) is the more strongly adsorbed and is the precursor to dissociation. We suggest that N_2O is formed as follows:

$$\mathrm{NO(b)} \rightarrow \mathrm{N(a)+O(a)}$$

$$\mathrm{NO(l)+N(a)} \rightarrow \mathrm{N_2O(a)}$$

i.e., both linear and bent forms of adsorbed NO are involved, linearly adsorbed NO being a highly efficient scavenger at 80 K of nitrogen adatoms. For NO adsorption at 290 K NO(l) is not present (it desorbs above 170 K) so that we observe only N(a) and NO(b). Evidence for the presence of NO(b) at 290 K is based on the larger width of the O(1*s*) peak at 290 K compared with that observed on warming the saturated adlayer formed at 80 K to 290 K (when no " nitrogen " remains on the surface) and also the overlap of the N(1*s*) peak at 397 eV with the binding energy ($\approx$399 eV) expected for NO(b). This is also apparent in the N(1*s*) spectra for a partially covered layer at 80 K and also after thermal activation of this adlayer.

Further evidence for three distinct forms of adsorbed nitric oxide has been obtained in a recent study [28] of " clean " nickel and also nickel surfaces whose reactivity has been controlled by pre-exposure to oxygen after adsorption of nitric oxide at 290 K. The evidence from our nickel work is unambiguous and lends support to the conclusions we have drawn from our studies with copper. At 290 K the catalytic activity of nickel is such that dissociation of NO occurs readily giving rise to an N(1*s*) peak at 397 eV, a second surface species has a binding energy of ≈399 eV and there is some evidence for a third species with an N(1*s*) value of ≈401 eV. When we examine the less active surface, *i.e.*, nickel pre-treated with oxygen at 290 K, there is no evidence for N(1*s*) peaks at 397 and 399 eV and on warming the adlayer from 80

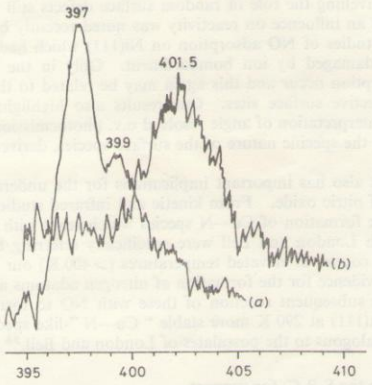

FIG. 10.—N(1*s*) spectra: curve (*a*), clean Ni after exposure to NO at 290 K (30 L exposure); curve (*b*), nickel pre-exposed to oxygen at 290 K (300 L, 10^{-5} Torr) and subsequently to NO at 80 K; spectrum taken after warming the adlayer to 240 K. (Analysing conditions: curve (*a*): f.s.d. 10^3 count s^{-1}, 50 eV pass energy; curve (*b*): f.s.d. 3×10^3 count s^{-1}, 100 eV pass energy.)

to 290 K a single peak whose intensity decreases with increasing temperature is present. The spectrum (fig. 10, curve *b*) was taken at a temperature of ≈ 240 K and shows this peak at a binding energy of between 401 and 402 eV. The NO species responsible is weakly adsorbed ($\Delta H \lesssim 80$ kJ mol^{-1}) which is compatible with our assignment of the N(1*s*) peak at about 401 eV observed with Cu(111) (fig. 9) to " a linearly bonded weakly held species ". A similar conclusion was arrived at in a study [6] of the adsorption of nitric oxide by oxidized iron surfaces where only a single N(1*s*) peak at 401 eV was also observed. Furthermore, the N(1*s*) peak at ≈ 399 eV (fig. 10) would reflect those nitric oxide molecules which are in an incipient state of dissociation and assigned to the " bent-form " of adsorbed NO (*cf.* fig. 9). At smaller exposures (and therefore lower coverage) the activation energy of dissociative chemisorption is negligible so that N(ads) forms readily.

We have no evidence from our studies for a strong electronic factor (*cf.* Brodén *et al.*)[8] in the surface chemistry of nitric oxide, aluminium (Carley and Roberts)[29] and copper (both *sp* metals) being very active in dissociative chemisorption at 80 K

and for this reason can be coupled with iron (Kishi and Roberts)[6] rather than with palladium (Conrad *et al.*[16] and Kishi and Ikeda [30]) or platinum (Bonzel and Fisher)[31] both of which are reported to adsorb NO molecularly at 290 K. In the case of nickel both associative and dissociative states exist at room temperature (fig. 10, see also Brundle and Carley [32] and Conrad *et al.*[33]). It may well be that the formation of the " bent " form of adsorbed nitric oxide is a pre-requisite for dissociation. Surface structure obviously has some influence on the reactivity of the NO molecule, Cu(100) being more reactive than Cu(111), but we have no information on the possible role of random topographical defects which LEED is incapable of monitoring. The studies of Somorjai [34] and Mason *et al.*[15] have clearly demonstrated the role of ordered surface steps and kink sites in inducing chemical reactivity; the challenge of unravelling the role of random surface defects still remains. That random defects have an influence on reactivity was noted recently by Eastman and Demuth [35] in their studies of NO adsorption on Ni(111) which had first been well annealed and then damaged by ion bombardment. Only in the latter case did dissociative chemisorption occur and this again may be related to the formation of " bent " NO at defective surface sites. Our results also highlight the problems associated with the interpretation of angle resolved u.v. photoemission studies where no regard is given to the specific nature of the surface species, derived, for example, from X.p.s. data.

The present work also has important implications for the understanding of the catalytic chemistry of nitric oxide. From kinetic and infrared studies, London and Bell [36] postulated the formation of Cu—N species which react with nitric oxide to give N_2O. Although London and Bell were specifically referring to the catalytic reaction of NO with copper at elevated temperatures (>400 K) our results provide direct experimental evidence for the formation of nitrogen adatoms at low temperatures (80 K) and the subsequent reaction of these with NO to form N_2O. With both Cu(100) and Cu(111) at 290 K more stable " Cu—N "-like species are formed which are directly analogous to the postulates of London and Bell.[36]

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