INTERACTION OF INTROUS OXIDE WITH SINGLE
CRYSTAL SURFACES OF Cu (100) AND Cu (111)

BY

Saadoon Aziz Isa

Department of Chemistry, College of Education, University of Baghdad

Baghdad-IRAQ

And

Mohammad Hashim Matloob

Department of Chemistry, College of Science, University of Baghdad

Baghdad- IRAQ

تتضمن الدراسة أستخدام تقنية ال PES و LEED في جهاز واحد . أن كلا مــــــن

(Cu(100) وCu(111) لم يبدصـا N_2O عند درجة حرارة الغرفة أن التحلل الانـدصاصي علــــــى

السطحين حـدثــــــــــــا بوجـــــــبو N_2O (ads) ⟶ N_2 (g) +O (ads)

تكونــت ثـلاثـة أسـطح على Cu(100) هي : $0 - 45$ R ($\sqrt{2}$ X $\sqrt{2}$)

عند درجـة حـرارة الغـرفـة ، ($0 - 45$ R ($\sqrt{2}$ X $2\sqrt{2}$) عنـد تسخيـــن

البلورات الى 800 K في N_2O ،وتركيب معقد ثالث هو ($0 - 45$ R ($\underline{a}$ X $\sqrt{2}$)

حيـث $\underline{a}$ لـه عدد صحيح ذو علاقة بأبعاد بلورة النحاس وتتكون نتيجـة التداخل الحراري مع N_2O

التحلل . أن أنـدصاص N_2O على سطح (111) Cu عند درجة حرارة الغرفة لم يغير التركـــــيب

الاصلي (1x1) للنحاس (Cu(111 ،حدث أنـدصاص ل N_2O جزيئيا في 77 K . والجزئيات المدصه

تحللت بعد تركيا للسطح في الفراغ وتسخينها الى درجـــــ حـــــــــــــــراره الغرفـــــــــــــ

This study was carried out using a combination of PES and LEED tech-
niques in one instrument. Both Cu(100) and Cu(111) surfaces did not show
high tendency to adsorb N_2O at room temperature. Dissociative adsorption
was found to occur on the two surfaces: $N_2O(ads) \rightarrow N_2(g)+O(ads)$.

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Three surface structures were developed on Cu(100): $(\sqrt{2} \times \sqrt{2})$ R45°-O at room temperature; $(\sqrt{2} \times 2\sqrt{2})$R45°- O after heating the crystal at 800 K in N_2O and a complex structure denoted as $(\sqrt{2} \times \underline{a})$ R45°- O, where $\underline{a}$ is not integrally related to copper lattice parameter, as a result of the interaction with thermally dissociated N_2O. N_2O adsorption on Cu(111) surface at room temperature did not change the primitive (1 x 1) structure of Cu(111) surface. N_2O was molecularly adsorbed at 77 K. The adsorbed molecules were dissociated as a con - sequence of leaving the adsorbed phase in vacuum or during warming from 77 K to room temperature.

INTRODUCTION

The study of metal oxidation is important and interesting for both academic and technological purposes. Oxygen interaction with single crystal surfaces of copper has been extensively studied using modern techniques in surface chemistry. Despite some disagreement in the published data of oxygen interaction with copper single crystal sur- faces, an intense information is available (1 - 34).

It is aimed in the present study to investigate the problem of interaction and/or oxidation of Cu(100) and Cu(111) single crystal sur- faces by nitrous oxide. Such a study has received little attention in the literature (19, 35). The relatively low N-O bond energy in N_2O (163 kJ mole^{-1}) as compared to that in NO might suggest a possible dis- sociation of the molecule upon adsorption, particularly, at high temperatures. The published data of metal films oxidation by nitrous oxide showed similarity when N_2O or oxygen is used in the oxidation process (36. 37).

A combination of photoelectron spectroscopic study (XPS and UPS) and low energy electron diffraction (LEED) were employed in this investigation.

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EXPERIMENTAL

The apparatus used in a UHV stainless steel system built by Vacuum Generators Ltd. A pressure of 6×10^{-11} torr can be obtained after bakeout at 450 K for 10 hrs. The techniques of XPS, UPS and LEED are incorporated in one instrument which enable us to perform analytical , chemical and surface structural studies. A schematic diagram of the apparatus is shown in Fig. 1. The X-ray source is a twin Al K_α /Mg K_α and the UV light source is a helium dc discharge lamp which produces both HeI and HeII resonance lines at 21.21 and 40.8 eV respectively. The LEED optics involves retarding potential grids mounted close in front of a fluorescent screen maintained at a positive potential (7 kV) where bright spots of diffraction patterns can be observed through a glass window in the UHV chamber. Cu(100) and Cu(111) single crystals were obtained from Metals Research Ltd; a slice of 1 mm thickness of each crystal was cut by a spark erosion machine. The crystals, prior to insertion into the chamber, were planed and chemically polished (38) . Cleaning of the crystals was performed by following the procedure of simultaneous heating and argon ion bombardment (800 eV and 2 uA). The crystals were thereafter annealed at 450 K and finally examined by XPS for surface cleanliness before starting experiments. The specimens could be resistively heated up to ~820 K or cooled down to liquid nitrogen temperature. The gases used were spectroscopically pure and obtained from BOC.

RESULTS

A. Adsorption on Cu(100)

The interaction of N_2O with Cu(100) surface was examined in the temperature range 295 – 800 K . Molecular and thermally dissociated N_2O
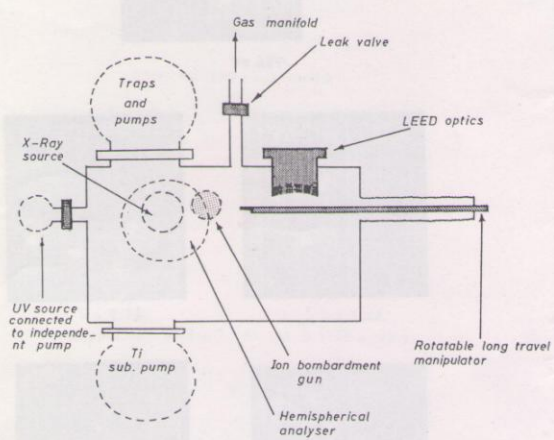
Fig. (1) The combination of LEED−XPS −UPS (ESCA 4) .

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were used in this study. The clean Cu(100) surface (as shown by XPS) did not tend to adsorb N_2O in low exposures at room temperature. As a result of exposing the crystal to 1500 L of the gas at 295 K, diffraction patterns of $(\sqrt{2} \times \sqrt{2})$ R45° mesh were observed. XPS results showed an oxygen uptake of 0.55×10^{15} adsorbed species/cm^2 but no nitrogen was retained by the surface. The Ols binding energy was 530.1 eV with FWHM = 2.4 eV. A second surface structure, $(\sqrt{2} \times 2\sqrt{2})$ R45° appeared after exposing the clean surface to 2000 L of N_2O at 800 K then cooling the crystal to room temperature in an atmosphere of N_2O. The oxygen uptake was 0.74×10^{15} adsorbed species/cm^2 with Ols binding energy = 530.5 eV and FWHM = 2.5 eV. Identical surface

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@ The concentration of the adsorbed species mentioned above was estimated on the basis of the following modified equation (39, 40) after smoothing the data and removing the background:

$$Y_m / Y_s = \mu_m M \sigma / \mu_s N n t \cos \Theta$$

σ = surface concentration;

Y_m = photoelectron yield from the adlayer, i.e., either the Ols or Nls peaks;

Y_s = the intensity of the clean Cu 2 P 3/2 peak;

N = Avogadro's number;

μ_s = ionization cross section for Cu 2 P 3/2;

μ_m = ionization cross section for the Ols or Nls orbitals;

t = electron attenuation length in the Cu substrate;

p = density of copper;

M = molecular weight of substrate;

Θ = angle between collected electrons and the normal to substrate (45°).

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structures were developed when Cu(100) is exposed to oxygen at room tempe-
rature as shown in Fig.2 (41). The third stage of N_2O interaction with
the Cu(100) surface was the use of thermally dissociated N_2O. Dissocia-
ted gas molecules were prepared by circulating N_2O at a pressure of 1 x
10^{-6} torr over a heated tungsten filament. The crystal was mounted fac-
ing the filament (at 800 K) and exposed to N_2O for 30 minutes. The
crystal was then cooled down to room temperature in N_2O and examined by
LEED and XPS. The diffraction patterns were quite different from those
noticed previously; they were complex but well ordered and contained
many extra spots along the edges of the $(\sqrt{2} \times 2\sqrt{2})R45^{\circ}$ mesh. Very
similar diffraction patterns were noticed after heating the crystal in
oxygen at temperatures $\geqslant 373$ K (41). Fig.3 shows typical examples of
these patterns at a range of electron beam energy. The fractional extra
spots were found to move along the edges of the $(\sqrt{2} \times 2\sqrt{2})R45^{\circ}$
mesh with changing the beam energy. The movement was neither towards
the 00 spot nor to any other fixed direction. The complex surface struc-
ture was examined and found to be stable even after heating the crystal
in vacuum at 800 K. The oxygen uptake was 1.5 x 10^{15} adsorbed species/
cm^2 with O1s binding energy = 530.7 eV and FWHM = 2.4 eV. These values
are also identical to those reported previously (41).


B. Adsorption on Cu(111)

The clean Cu(111) surface, as examined by XPS, was exposed to
nitrous oxide at room temperature. Initially, no N_2O adsorption occured
upon exposing the crystal to 800 L of the gas. Increasing the exposure
to 1800 L resulted in a weak O1s peak at 530.1 eV but no sign of N1s
peak was noticed in the spectrum. Further exposure to 4500 L of N_2O
did not lead to a significant change in the spectra (Fig.4). The surface
concentration of the adsorbed species was only 0.14 x 10^{15} per cm^2. Our
LEED results showed the absence of any extra spots. The primitive struc-
ture of Cu(111)-(1 x 1) was only seen. This result confirms the

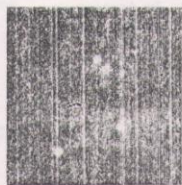S. A. Isa and M. H. Matloob
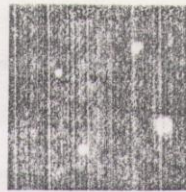
786 eV
Clean Cu(100) Surface
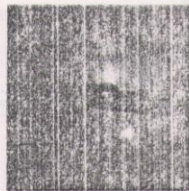
32.3 eV
$(\sqrt{2} \times \sqrt{2}) R$-45-O Surface Structure
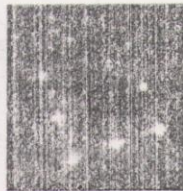
61.2 eV

31.2 eV
$(\sqrt{2} \times 2\sqrt{2}) R$-45-O Surface Structure
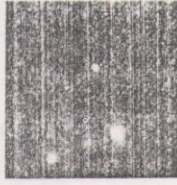
FIG. 2

51.3 eV

a

54·5 eV

b

60·5 eV

c
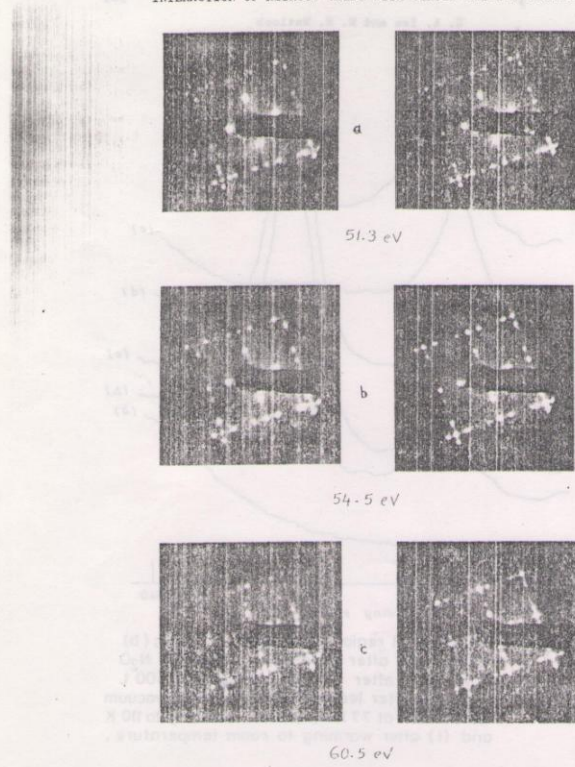
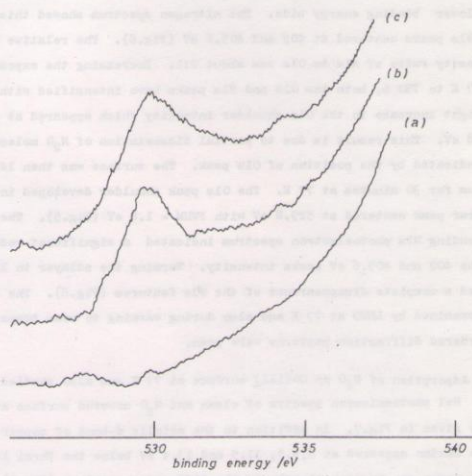FIG. 3. The Complex Structure of $(\sqrt{2} \times a)R-45-0$

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Fig. (4) O1s spectral region at 298 K for (a) clean Cu(III)
surface;(b) and (c) the surface after exposure
to 1800 L and 4500 L of N_2O.

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published work of Ertl (19) who did not see extra spots in LEED patterns during N_2O adsorption on Cu(111) surface at room temperature.

The interaction of N_2O with Cu(111) surface was also studied at low temperatures to investigate whether there is dissociative adsorption or not. The clean Cu(111) surface was exposed to 150 L of N_2O at 77 K. A single O1s peak emerged at 535.4 eV. (Fig.5) with a broad shoulder at the lower binding energy side. The nitrogen spectrum showed this time two N1s peaks centered at 402 and 405.6 eV (Fig.6). The relative peak intensity ratio of N1s to O1s was about 2:1. Increasing the exposure at 77 K to 750 L, both the O1s and N1s peaks have intensified with a slight increase in the O1s shoulder intensity which appeared at about 529.8 eV. This result is due to partial dissociation of N_2O molecules as indicated by the position of O1s peak. The surface was then left in vacuum for 30 minutes at 77 K. The O1s peak shoulder developed into a clear peak centered at 529.8 eV with FWHM = 1.8 eV (Fig.5). The corresponding N1s photoelectron spectrum indicated a significant reduction in the 402 and 405.6 eV peaks intensity. Warming the adlayer to 110 K caused a complete disappearance of the N1s features (Fig.6). The surface was examined by LEED at 77 K and also during warming to room temperature. No ordered diffraction patterns were seen.

Adsorption of N_2O on Cu(111) surface at 77 K was also studied by UPS. HeI photoemission spectra of clean and N_2O covered surface at 77 K are given in Fig.7. In addition to the metalic d-band of copper, four extra maxima appeared at 6,9.5, 11.5 and 13.4 eV below the Fermi level. These peaks can be seen clearly in the difference spectrum (Fig.7). Within the range of the d-band an enhanced emission at 1.8 eV and a marked decrease in the d-band intensity were observed. The published results of N_2O adsorption on Ni and Au films at 77 K (42,43) showed almost the same positions of the extra peaks observed in HeI spectrum (Table 1).
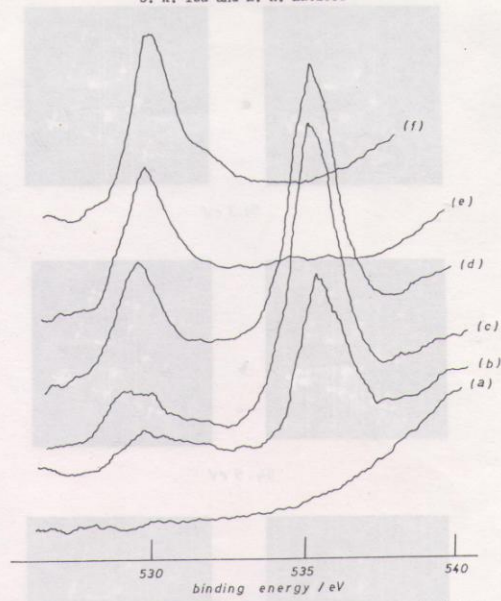
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Fig. (5) O1s spectral region of (a) clean Cu (III); (b)
the surface after exposure to 150 L of N_2O
at 77 K; (c) after further exposure to 600 L
N_2O; (d) after leaving the adlayer in vacuum
for 30 min. at 77 K; (e) after warming to 110 K
and (f) after warming to room temperature.
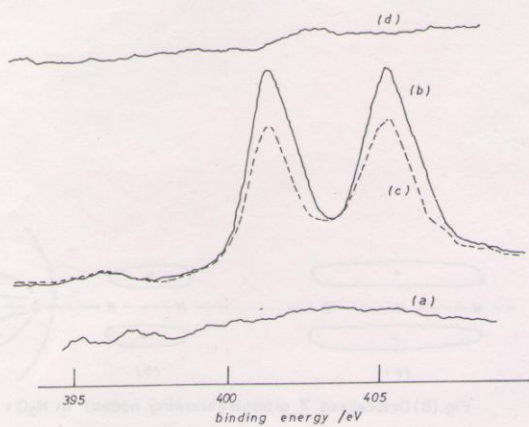
Fig.(6) NIs spectral region for (a) clean Cu(III) surface;
(b) the surface after exposure to 750 L of N_2O at
77 K; (c) the adlayer (b) after leaving it in vacuum
for 30 min. at 77 K and (d) the adlayer after warming
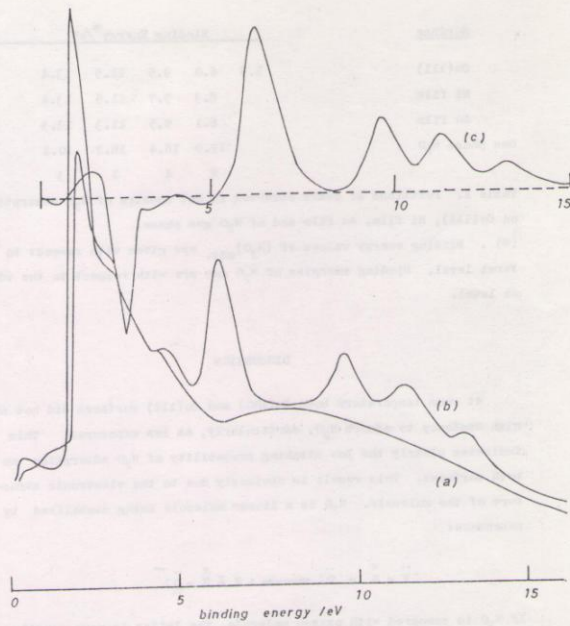to 110 K.

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Fig.(7) He I spectra of (a) clean Cu(Ⅲ) surface; (b) Cu(Ⅲ) surface after exposure to 750 L of N_2O at 7K and (c) the difference uv-spectra (b −a).

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Surface		Binding Energy[@]/eV				
Cu(111)	1.8	6.0	9.5	11.5	13.4	
Ni film		6.3	9.7	11.5	13.4	
Au film		6.1	9.5	11.3	13.3	
Gas phase N$_2$O		12.9	16.4	18.2	20.1	
		2	4	1	3	

Table 1. Positions of peaks observed in HeI spectra of N$_2$O adsorption
on Cu(111), Ni film, Au film and of N$_2$O gas phase.

(@) . Binding energy values of (N$_2$O)$_{ads}$ are given with respect to the
Fermi level. Binding energies of N$_2$O gas are with respect to the vacu-
um level.

DISCUSSION

At room temperature both Cu(100) and Cu(111) surfaces did not show
high tendency to adsorb N$_2$O, particularly, at low exposures. This
indicates clearly the low sticking probability of N$_2$O adsorption on
both surfaces. This result is obviously due to the electronic struc-
ture of the molecule. N$_2$O is a linear molecule being stabilized by
resonance:

$$: \overset{..}{N} = \overset{+}{N} = \overset{..}{O} : \longleftrightarrow : N \equiv \overset{+}{N} - \overset{..}{O} : {}^{-}$$

If N$_2$O is compared with oxygen molecule, the latter is more reactive
owing to its pseudo radical character caused by the presence of two
unpaired electrons in different p levels. The electronic structure of
N$_2$O molecule can be explained in terms of two σ bonds and two pairs
of non localized π orbitals extending over all three centers as shown
in Fig.8 (44). Each bond in the molecule well have a triple bond charac-
ter which appears greater in the N-N link. This explains the ease of
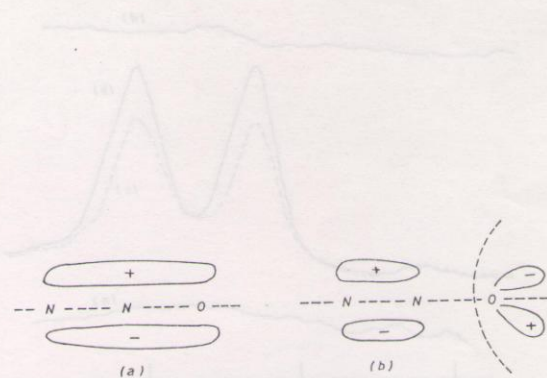
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Fig.(8) Delocalized π orbitals (showing nodes) in N_2O :

(a) bonding in both regions, N−N and N−O .
(b) weakly bonding in N−N, weakly anti bonding in N−O .

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N_2O dissociation through N-O bond and not the N-N bond. At high exposures of the gas at room temperature, the two surfaces adsorbed N_2O but Cu(100) was relatively more active than Cu(111). This result is expected due to the close packed structure of Cu(111) surface. It is evident from XPS results that N_2O adsorption on both surfaces at room temperature was dissociative (O1s peak at 530.2 eV and absence of any nitrogen species). This means that for each N_2O molecule adsorbed, one nitrogen molecule desorbed,

$$N_2O_{(ads)} \xrightarrow{\quad} {}^{\delta-}O_{(ads)} + N_{2(g)}$$
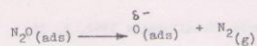
Adsorption of N_2O on Cu(111) surface did not change the primitive (1 x 1) structure while the adsorbed phase of Cu(100) showed a $(\sqrt{2} \times \sqrt{2})$ R45° structure. The similarity in surface structures when N_2O or oxygen is used for adsorption on Cu(100) (41) supports the conclusion mentioned above of N_2O dissociative adsorption. The structure of $(\sqrt{2} \times \sqrt{2})R45°$-O was discussed in many publications of Cu(100) oxidation studies (23, 24, 45, 46). This structure was considered as a consequence of strongly adsorbed oxygen adatoms in four fold coordination on top of the unconstructed copper (100) surface (24). The structure of $(\sqrt{2} \times 2\sqrt{2})R45°$ was observed by LEED after heating Cu(100) surface at 800 K in N_2O. This structure was also seen in oxygen adsorption with an exposure of 1000 L at room temperature (41). The transformation of surface structure from $(\sqrt{2} \times \sqrt{2})R45°$-O to $(\sqrt{2} \times \sqrt{2})R45°$-O was accompanied by an increase in the O1s binding energy of 0.4 eV which could be due to some oxygen incorporation into the metal lattice. Braithwaite et al (24) have suggested that surface reconstruction occurs only when the mesh changes to $(\sqrt{2} \times \sqrt{2})R45°$-O.

The complex structure which emerged as a consequence of Cu(100)
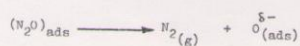
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oxidation by thermally dissociated N_2O is suggested to be due to a co-incidence lattice as a result of double diffraction. The dimentions of this structure are $Cu(100)-(\sqrt{2} \times \underline{a})R45°$ -O where $\underline{a}$ is not integrally related to copper lattice parameter.

The N_2O adlayer on $Cu(100)$ surface showed by LEED - in all stages of N_2O adsorption - no evidence of formation of mix fold symmetry which was noticed in two previous studies (19, 35).

Adsorption of N_2O on $Cu(111)$ surface at 77 K has shown two Nls peaks in X-ray photoelectron spectrum reflecting two non-equivalent nitrogen atoms in N_2O. This conclusion indicates the existence of the adsorbed N_2O in its molecular form. The relative intensity ratio of Nls to Ols (2:1) suggests also the molecular form of the adsorbed phase.

UPS data obtained at this stage confirm the XPS results. The co-mare UV induced spectra of the adsorbed phase with that of the gas phase, two factors have to be taken into consideration (47, 48). The first is the work function correction and the second is the relaxation effect . In our work, 5 eV as a work function correction and 2 eV for the relaxa-tion effect have been added to match the spectra of the gaseous and ad-sorbed phases (42, 43, 49). In such a case we find N_2O adsorption at 77 K is mainly molecular.

The weak emission in the UV induced spectrum at 1.8 eV may be at-tributed to a d-band splitting which arises from the prsence of small $O^{\delta-}$(ads) concentration. The changes occurred in both XPS and UPS results as a consequence of leaving the adsorbed phase at 77 K in vacuum or warming to room temperature reflect $(N_2O)_{ads}$ dissociation:

$$(N_2O)_{ads} \longrightarrow N_{2(g)} + O^{\delta-}_{(ads)}$$

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It is interesting to note that the concentration of oxygen species formed at 77 K after leaving the adlayer in vacuum for 30 minutes was four times greater than that formed when $Cu(111)$ surface is exposed to 1800 L of N_2O at room temperature. This result is unexpected since thermal energy should facilitate the dissociation process of N_2O. To understand such a behaviour, information concerning the geometry and the electronic state of N_2O species is required at 77 K. Within the frame work of our XPS and UPS data, such information can not be extracted. However, two points can possibly be considered; first, $N_2O_{(ads)}$ species at 77 K play a precursor role for dissociation and second, due to low heat of N_2O adsorption (~ 30 k J $mole^{-1}$) a very low concentration of these precursors is formed at room temperature compared to that at 77 K. Similar observation was reported by Kishi and Roberts (50) upon N_2 adsorption on iron.

ACKNOWLEDGEMENT

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