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Adsorption and dissociation of N_2O on copper single-crystal surfaces

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The adsorption of nitrous oxide on copper surfaces is investigated by means of ultraviolet, x-ray photoemission, electron-energy-loss, and Auger electron spectroscopies, low-energy electron diffraction, and work-function measurements. Only on Cu(110) is adsorbed molecular N_2O found, whereas on Cu(100) and Cu(111) in the temperature range between 90 and 300 K no adsorption or dissociation of N_2O can be detected. On Cu(110) at 90 K nitrous oxide first adsorbs dissociatively, leaving atomic oxygen on the surface. For oxygen coverages above a quarter of a monolayer, molecular N_2O can stay undissociated on Cu(110). Its molecular axis is orientated essentially perpendicular to the surface.

I. INTRODUCTION

The adsorption and interaction of triatomic molecules is often investigated in order to get more insight into the bonding mechanism of more complex adsorbates. Among the studied molecules such as H_2O or CO_2, N_2O is an exception because of its less symmetric molecular structure. N_2O is linear with an atomic arrangement N—N—O. In the gas phase N_2O is fairly stable; it dissociates at temperatures higher than about 900 K into N_2 and O. This reaction is enhanced in the presence of metal oxides or metal surfaces; it can be used to study surface reactions with *in situ*—generated atomic oxygen. Based on this process the active area of copper catalysts can be determined by adsorbing atomic oxygen from N_2O dissociation and measuring the amount of desorbing molecular nitrogen.[1-3] Since up to now there is not much known about the surface specificity of this reaction, the adsorption and decomposition of N_2O on the low-index and polycrystalline copper surfaces is studied between 90 K and room temperature. For the interaction of N_2O with copper at temperatures above 270 K there are some data available.[4-8] Also on several other metals[9,10] the adsorption and dissociation of N_2O has been investigated. Among these there are only a few studies[9-15] with sample temperatures below 150 K. These temperatures are necessary to find adsorbed molecular nitrous oxide or intermediates in the decomposition.

II. EXPERIMENTAL

The study is performed by uv photoemission spectroscopy (UPS), x-ray photoemission spectroscopy (XPS), electron-energy-loss spectroscopy (EELS), Auger-electron spectroscopy (AES), low-energy electron diffraction (LEED), and work-function measurements. The experimental equipment is incorporated into a stainless-steel UHV chamber pumped by a turbomolecular and an ion pump; the base pressure is below 10^{-8} Pa. For UPS, XPS, EELS, and AES a hemispherical electron-energy analyzer with entrance optics is used. The analyzer energy resolution is adjusted to $\Delta E = 0.25$ eV for He II (40.8 eV) spectra, whereas He I (21.2 eV) spectra are recorded with a resolution of $\Delta E = 0.1$ eV. The work-function changes $\Delta\Phi$ are determined from the emission onset of the He I spectra; the accuracy is therefore limited to ± 0.02 eV. XPS measurements with the Al $K\alpha$ line are performed with an analyzer resolution of 0.75 eV.

In EELS (primary energies between 50 and 100 eV) the energetic resolution is determined by the energetic width of the primary beam, i.e., ~ 0.3 eV. The measurements are mainly performed in the constant resolution mode of the analyzer ($\Delta E = \text{const}$).

The Cu samples are cut from 99.999% pure copper single crystals. They are mechanically polished to optical quality before mounting to the sample holder. The final cleaning procedure consists of repeated short Ar bombardments and annealing to about 900 K. More details about the experimental setup are given in a previous publication.[16]

N_2O with a purity higher than 99% is further purified by two cycles of freezing, pumping, and warming up. By this procedure traces of oxygen, nitrogen, and carbon monoxide are removed. In this way the purity of the N_2O is improved by a factor of about 10. The entire process and the cleanliness of the N_2O are checked by mass spectrometry. N_2O exposures higher than 10 L (1 L = 1 langmuir = 10^{-6} Torr sec) are performed with the ion pump switched off and a cryopanel kept at liquid-nitrogen temperature. Then the system is pumped by the turbo-molecular pump. In this way exchange reactions are minimized.

III. RESULTS

A. Adsorption on Cu(110) and polycrystalline Cu

During adsorption of N_2O on Cu(110) at 90 K the UPS spectra [Fig. 1(b)] show additional emission bands near 6- and 1.5-eV binding energy (referred to Fermi level) up to exposures of 0.4 L. From previous work these structures are well known to be due to atomic oxygen. For dosages higher than 0.5 L four new structures develop with rela-

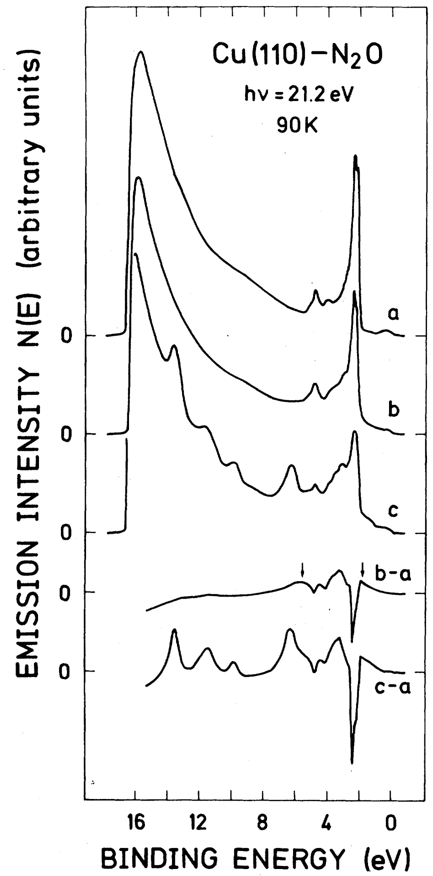

FIG. 1. He I UPS spectra [energy-distribution curves (EDC's)] with the sample at 90 K. *a*, clean Cu(110) surface; *b*, after a 0.4-L exposure to N_2O; and *c*, after a 1-L N_2O dosage. The difference curves are calculated with respect to the spectrum of the clean surface. In curve *b* — *a* the adsorbate-induced emission bands are indicated by arrows. The zero level of each spectrum is marked on the ordinate. All binding energies are referred to Fermi level.

tive positions resembling those of the vertical ionization energies of gaseous nitrous oxide (Figs. 1 and 2). These bands are saturated for dosages of about 0.8 L with relative intensities somewhat different in He I and He II spectra. For dosages higher than 1 L the four bands are uniformly shifted by 0.1 eV to higher binding energies.

The change of the work function $\Delta\Phi$ shows a corresponding behavior. For dosages up to 0.5 L the work function increases with a maximum near 0.5 L and decreases for higher exposures, reaching its final value slightly above 1 L (Fig. 3). In EELS in the range of electronic transitions the loss near 7 eV on the clean Cu(110) surface is shifted to 6.2 eV upon N_2O exposure. For dosages above 0.6 L new losses emerge at 9.3, 10.9, and 14.8 eV (Fig. 4). These structures are most pronounced for exposures around 1.5 L. On a polycrystalline copper surface the same sequence of EELS spectra as on Cu(110) is found. LEED measurements on the Cu(110) surface show no superstructures upon N_2O exposure. The LEED pattern of the clean surface only loses its contrast.

We also tried to get information about the adsorbed N_2O by XPS. Unfortunately, the N_2O adsorbed on Cu(110) at 90 K (1-L exposure) is not stable. It dissociates nearly completely into chemisorbed atomic oxygen and molecular nitrogen during the time necessary for recording an XPS spectrum. In the region of the O 1*s* core level the emission of chemisorbed atomic oxygen at 529.2-eV binding energy is detected. The peak area is almost the same as after a 20-L oxygen exposure at room temperature. It therefore corresponds to half a monolayer coverage.[16] Additionally, a very weak emission around 534.5-eV binding energy is seen. In the region of the N 1*s* core level no emission structures are detectable. Only

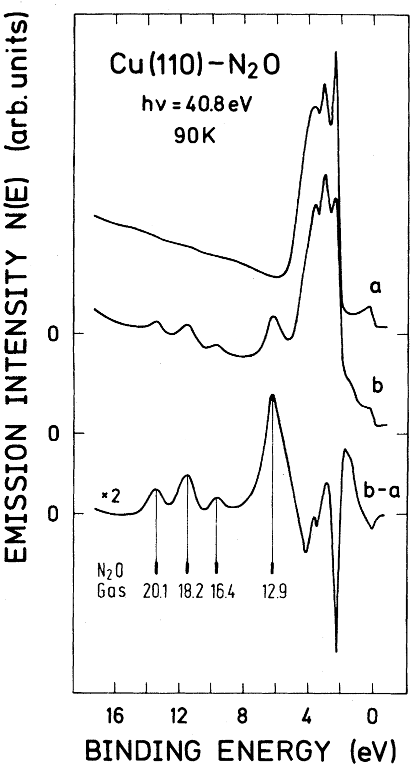

FIG. 2. He II UPS spectra of a clean Cu(110) surface at 90 K (*a*) and after a 1-L exposure to N_2O (*b*). Under the difference curve (scale enlarged by a factor of 2) the vertical ionization energies of gaseous N_2O (referred to vacuum level) are marked.

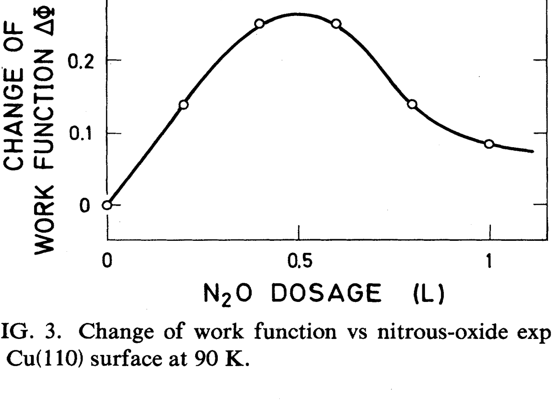

FIG. 3. Change of work function vs nitrous-oxide exposure of a Cu(110) surface at 90 K.

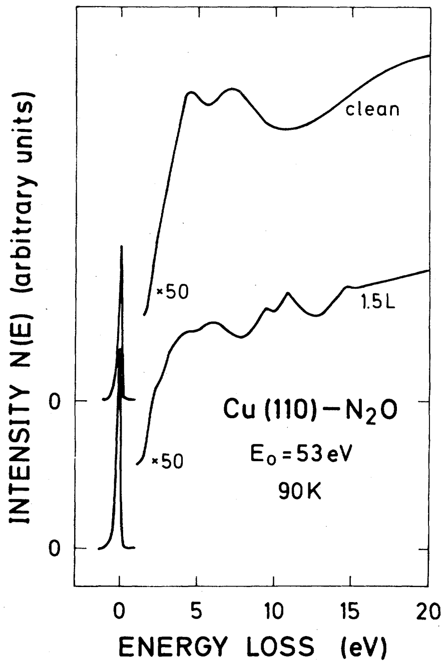

FIG. 4. Electron-energy-loss spectra of a clean Cu(110) surface and after exposure to N_2O at 90 K. E_0 is the primary energy; the factor indicates the amplification with respect to the elastic beam; the zero levels are marked on the ordinate.

traces of the N_2O emission bands can be found in the UPS spectra recorded after the XPS measurements.

During the warming up of a Cu(110) surface covered with N_2O (1 L at 90 K), the emission structures of molecular N_2O in UPS diminish and completely disappear at 115 K. No new structures due to intermediates can be found. For temperatures higher than 115 K, only the emission of chemisorbed atomic oxygen is seen. The work function increases monotonically during annealing; at 115 K it reaches a value of about 0.3 eV and remains unchanged up to room temperature. Then in AES and XPS the oxygen signals correspond to half a monolayer coverage, as is known from previous work.[16] In LEED the (2×1) superstructure has developed. On a polycrystalline copper surface exposures to nitrous oxide and subsequent annealing result also in an oxygen covered surface above 120 K.

In another series of experiments N_2O is adsorbed at 90 K on a Cu(110) surface precovered with atomic oxygen. After a 0.4-L oxygen exposure at 90 K and subsequent N_2O exposures the same sequence of spectra is found in UPS as if the surface were first exposed to 0.4-L N_2O instead of oxygen. The same is true for the change of the work function. In the annealing experiments the results are identical with those obtained after N_2O exposures of the clean surface. On a Cu(110) surface covered with half a monolayer of atomic oxygen a 0.2-L N_2O exposure induces four emission bands in the UPS spectra at the same binding energies as after a 2-L N_2O exposure of the clean surface. The work function decreases by about 0.15 eV. Further dosages of N_2O up to 2 L do not significantly change the intensities of the emission bands in UPS nor the work function. By annealing the surface all nitrous oxide is desorbed at 100 K and the surface appears as if it were covered with half a monolayer of atomic oxygen. This is concluded from Auger spectra taken at room temperature.

B. Adsorption on Cu(100) and Cu(111)

On Cu(100) or Cu(111) surfaces N_2O exposures up to 1000 L at 100 K do not give rise to new structures in the UPS spectra. Also the work function remains nearly unchanged for those N_2O dosages. No oxygen can be detected in AES after warming up the sample to room temperature.

Exposure of a Cu(100) or Cu(111) surface to 1000-L N_2O at room temperature does not result in new emission bands in UPS nor does the work function change. In AES no oxygen contamination is found.

The attempt to get adsorbed nitrous oxide on an oxygen precovered Cu(100) surface failed, too. The sample is first exposed to 1000-L oxygen at room temperature. Then the surface is characterized by an oxygen signal in AES and a week $(\sqrt{2}\times\sqrt{2})R45°$ superstructure in LEED. After cooling down this sample to 90 K no emission bands due to N_2O can be detected for dosages up to 100 L.

IV. DISCUSSION

In the following mainly the adsorbed species on Cu(110) are discussed because of the lack of adsorbates detected on the other single-crystal surfaces. In UPS additional emissions near 6 and 1.5 eV appear after a 0.4-L N_2O exposure of Cu(110) at 90 K (Fig. 1), and the work function increases (Fig. 3). It is therefore concluded that the first adsorption step of N_2O leads to dissociation with only atomic oxygen being chemisorbed on the surface. The same results are found for chemisorbed atomic oxygen in a previous study of the oxygen adsorption on Cu(110).[16] On the other hand, it is known that molecular nitrogen does not adsorb on copper surfaces above 70 K.[17–19] From AES measurements the oxygen coverage after a 0.5-L N_2O exposure is determined to be a quarter of a monolayer. The calibration procedure is described elsewhere.[16]

Further N_2O adsorption gives rise to four new photoemission bands with relative positions resembling those of the vertical ionization energies of gaseous nitrous oxide[20,21] (Figs. 1 and 2). The second adsorbate is therefore identified as molecular N_2O. The structure of the valence orbitals is nearly unaffected by the adsorption since no binding shifts of orbitals are detected within the experimental error. The nitrous oxide molecules are coadsorbed with the atomic oxygen since the emission at 6 eV from the atomic oxygen is clearly distinguished from the N_2O bands [Fig. 1(c)]. Also the oxygen emission near 1.5 eV still remains. This is also confirmed by the fact that the coadsorption of 0.4-L oxygen and nitrous oxide gives the same results as the adsorption of nitrous oxide only.

To get more information about the orientation of the adsorbed N_2O, the energy-loss spectrum of the N_2O covered surface (Fig. 4) is compared with that of free nitrous oxide molecules.[22–27] Beside losses related to the ionization of the molecule the gas-phase spectra show pronounced losses at 8.5 and 9.6 eV and weaker structures around 11 and 14.5 eV. There exist several theoretical assignments of the observed gas-phase bands to electronic transitions.[24,27–30] Most authors attribute the 8.5-eV loss to a $\sigma \rightarrow \pi^*$ and the 9.6-eV structure to a $\pi \rightarrow \pi^*$ transition.[24,27–29] This interpretation seems likely since in linear molecules the $\pi \rightarrow \pi^*$ transition should have the strongest dipole moment. It should therefore give rise to the most intense loss in the spectrum.[24] In the experimental spectra the 9.6-eV loss is the dominating structure. Concerning the other loss features, their assignment to Rydberg transitions is not unequivocal.

To analyze the orientation of the adsorbed N_2O molecules one concentrates on the two transitions $\sigma \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$. The $\sigma \rightarrow \pi^*$ transition has a dipole moment perpendicular to the molecular axis, whereas the dipole moment of the $\pi \rightarrow \pi^*$ transition is oriented parallel to the axis. In the loss spectrum of adsorbed N_2O a structure at 9.5 eV is seen which corresponds to the $\pi \rightarrow \pi^*$ transition in the gas phase. Therefore an orientation of the molecular axis parallel to the Cu(110) surface must be excluded since losses with a dipole moment parallel to the surface are suppressed according to the dipole selection rule for electronic transitions.[31] On the other hand, no loss around 8.5 eV can be detected for adsorbed N_2O. On the basis of the orientation selection rule, therefore, a nearly perpendicular orientation of the adsorbed nitrous oxide molecules is derived. For this adsorption geometry the $\sigma \rightarrow \pi^*$ transition is suppressed. Recently a similar vertical adsorption geometry of N_2O on Ru(001) has been reported.[15]

From the results obtained with the described techniques no information can be derived concerning the binding end of the N_2O molecule (oxygen or nitrogen nearest to the surface). In UPS no binding shift is found, which could give hints about an orbital being mostly involved in the chemisorption. The change of the work function after N_2O adsorption neither allows any conclusion since nothing is definitely known about the direction of the static dipole moment of nitrous oxide.[32]

In the desorption experiments the temperatures up to which any N_2O is detectable in the spectra are higher for adsorption of N_2O on the clean than on the oxygen precovered ($\Theta = \frac{1}{2}$) surface. This indicates that the N_2O molecules are more weakly bound on Cu(110) in the presence of coadsorbed oxygen. In accordance with this finding, the UPS spectra of molecular nitrous oxide on the oxygen precovered surface reveal the same relaxation and/or polarization shift as the multilayer spectra on the clean surface.

The dissociation of nitrous oxide on copper single-crystal surfaces is an activated process with activation energies significantly differing for the three low-index Cu surfaces. For Cu(110) the dissociation reaction is observed in this study already at 90 K. In contrast, on Cu(100) and on Cu(111) exposures in the 10^6-L range at temperatures higher than 300 and 500 K, respectively, are necessary to obtain adsorbed atomic oxygen from the dissociation of N_2O.[6,8] The reactivity of the three copper surfaces for the dissociation of molecular oxygen has the same order. A coverage of half a monolayer of atomic oxygen is most easily obtained on Cu(110) and higher oxygen dosages are necessary on Cu(100) and Cu(111). The mechanism for the dissociation of N_2O shows, therefore, some correspondence to the dissociation of molecular oxygen.

For the adsorption of N_2O molecules on Cu(110) the presence of chemisorbed oxygen atoms is necessary. The oxygen atoms are bound to the surface by accepting electronic charge from the metal whereas the adsorption bond to N_2O as a soft Lewis base might involve charge donation. An electron donor-acceptor interaction through the metal between oxygen and nitrous oxide therefore seems to stabilize the adsorbed N_2O molecule.

V. CONCLUSION

On Cu(110) at 90 K the first adsorption stage of N_2O is dissociative resulting in chemisorbed atomic oxygen. For oxygen coverages above a quarter of a monolayer N_2O can adsorb molecularly with an electronic structure similar to the gas phase. The molecular axis is oriented essentially perpendicular to the surface. For sample temperatures higher than 115 K N_2O exposure leads to an oxygen coverage of half a monolayer.

The catalytic activity of Cu(100) and Cu(111) for nitrous oxide dissociation is much lower than that of Cu(110). If one uses the dissociation reaction at room temperature to determine the active area of copper catalysts, one has to take into account that the (110) or other more open surfaces are favored over the closed-packed ones.

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