

An Angle-Resolved Photoelectron Spectroscopy and Near-Edge X-ray Absorption Fine Structure Study of the Bonding and Orientation of NO on a Mo(100) Surface

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The nature of the surface formed by a saturated layer ($\theta(\text{NO}) = 1.0$) of NO on a Mo(100) surface at 150 K has been determined by using both angle-resolved ultraviolet photoelectron spectroscopy and the angular variation of near-edge X-ray absorption fine structure (NEXAFS). Photoelectron spectroscopy indicates that NO can adsorb molecularly at this temperature but that a portion of the NO is also dissociated, even at 150 K. The orientation of the molecular species is measured by using both photoelectron spectroscopy and NEXAFS. Both techniques yield identical geometries, indicating that chemisorbed NO has a molecular axis that is tilted at $35^\circ \pm 5^\circ$ with respect to the surface normal. In addition, measurement of the σ - π spacing in NEXAFS suggests that the NO bond in chemisorbed NO is up to 0.03 Å longer than in the gas phase. Heating this surface to 720 K causes the intensity of photoelectron peaks due to chemisorbed molecular NO to decrease by 50%. This temperature range corresponds to the desorption of molecular NO. Further heating of the surface to 1090 K causes the majority of the remaining NO to dissociate into chemisorbed nitrogen and oxygen. However, small NO photoemission peaks remain in the photoelectron spectrum after annealing the surface to 1090 K, suggesting the presence of a small amount of chemisorbed molecular NO, even after annealing to this temperature.

Introduction

Investigations of the chemisorption of NO have received significantly less attention than CO on transition-metal surfaces. This observation is borne out in the case of molybdenum surfaces, where significant attention has focused on the chemisorption of CO whereas only scant data for NO adsorption are available.¹ The chemistry of CO on the Mo(100) surface is of particular interest since two distinct CO binding sites have been identified.² The fourfold hollow site bonds CO molecularly at low temperatures in a fairly unique configuration in which the molecular axis is tilted with respect to the surface. The CO adsorbed in this state reacts on warming the surface to form chemisorbed carbon and oxygen atoms which recombine to desorb as CO at high temperature (1200 K). CO can also adsorb molecularly at an atop site with its molecular axis perpendicular to the metal surface; CO desorbs from this site as an intact molecule in a manner akin to that observed on the noble metals. The reactivity of NO on transition-metal surfaces is expected to be rather similar to that of CO, except that the extra electron in the $2\pi^*$ orbital of NO leads to a weakening of the N-O bond compared to the C-O bond and a concomitant increase in dissociation probability.

It has been shown in a previous publication by use of thermal desorption and Auger spectroscopies that NO dissociates so that the four-fold hollow sites are occupied following NO adsorption at room temperature below NO

coverages of 0.5.³ Further molecular nitric oxide desorption is observed following adsorption of NO to yield a saturation coverage, $\theta_{\text{sat}}(\text{NO}) = 0.75$. Thermal desorption results following adsorption of NO at 150 K suggest that at this temperature a portion of the NO adsorbs molecularly and on heating can either dissociate to form chemisorbed nitrogen and oxygen or alternatively desorb molecularly. The branching ratio of these two reactions depends on the heating rate. $\theta_{\text{sat}}(\text{NO})$ in this case is 1.0 and decreases to 0.7 following desorption of molecular NO. These observations are confirmed in the data presented in the following, where both molecular and dissociated NO are detected following NO adsorption at 150 K. Both angle-resolved photoelectron spectroscopy and near-edge X-ray absorption fine structure (NEXAFS) data suggest that NO is tilted at $35^\circ \pm 5^\circ$ with respect to the surface normal. Measurement of the σ - π spacing in NEXAFS suggests that the NO bond length is increased by 0.03 Å.

Experimental Section

The angle-resolved photoelectron spectra (ARUPS) and NEXAFS experiments were carried out at the Brookhaven National Laboratories using the National Synchrotron light source on beam-line U14A. The apparatus that was used for these experiments has been described in detail elsewhere.²

The Mo(100) single crystal was prepared by using standard metallographic techniques and was spot-welded to the end of a sample manipulator. It could be resistively heated to 2000 K and cooled to 80 K via thermal contact to a liquid nitrogen reservoir. The sample was cleaned by a standard protocol that consisted of heating in a background of 2×10^{-7} Torr of oxygen to remove carbon and annealing to 2000 K to remove oxy-

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(1) Miki, H.; Kato, K.; Kawana, A.; Kioka, T.; Sugai, S.; Kawasaki, K. *Surf. Sci.* 1985, 161, 446.

(2) Fulmer, J. P.; Zaera, F.; Tysøe, W. T. *J. Chem. Phys.* 1987, 87, 7265.

(3) Fulmer, J. P.; Tysøe, W. T. *Surf. Sci.* to be published.

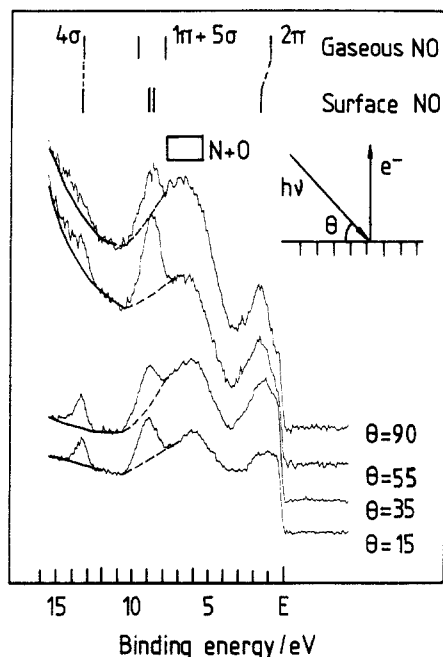


Figure 1. Plot of the angle-resolved photoelectron spectra following exposure of the Mo(100) surface to 5 langmuirs of NO at a sample temperature of 150 K ($\theta(\text{NO}) = 1.0$) as a function of incident radiation angle (θ) measured with respect to the surface. An estimated background has been drawn in to emphasize the peaks. The peak positions in the photoelectron spectrum of gas-phase NO are indicated as vertical lines. All energies are referenced to the Fermi level (E_F).

gen. The sample was judged clean when no signals due to contaminants (predominantly carbon and oxygen) were observed by Auger spectroscopy.

The NO used for these experiments was purified by distilling it several times in a vacuum line, and its purity was measured by using mass spectroscopy. After this process, the only detectable impurity was N_2O , which was present at concentrations less than 0.3% compared to the NO. The gas was stored in glass until use.

Results

A series of angle-resolved photoelectron spectra were taken with an incident photon energy of 30 eV following exposure of the Mo(100) surface to 5 langmuirs (1 langmuir = 1×10^{-6} Torr-s) of NO at a sample temperature of 150 K. It has been shown³ that this exposure corresponds to a surface saturated with NO at this temperature ($\theta(\text{NO}) = 1.0$). The 30-eV photon energy was chosen to optimize the adsorbate-induced signal relative to the background as well as the total signal intensity. A series of spectra were taken as a function of incident radiation angle measured with respect to the surface (that is, as a function of angle of the electric field to the surface normal) while detecting electrons emitted normal to the surface (Figure 1). These spectra have been normalized to the incident photon flux, which was measured by monitoring the total crystal current to ground. These spectra exhibit several adsorbate-induced peaks which vary in intensity as a function of incidence angle. They are a sharp peak at 13.5-eV binding energy (BE) and another sharp peak at 9.0-eV, BE which is superimposed on a broad peak centered at ~ 6.5 -eV BE. An estimated background profile for the 9-eV BE peak has been drawn in to emphasize these peaks. All energies are referred to the Fermi level (E_F).

A series of angle-resolved spectra were also taken in which the angle of incidence is kept constant (at normal, $\theta = 90^\circ$) while varying the detection angle of the emitted

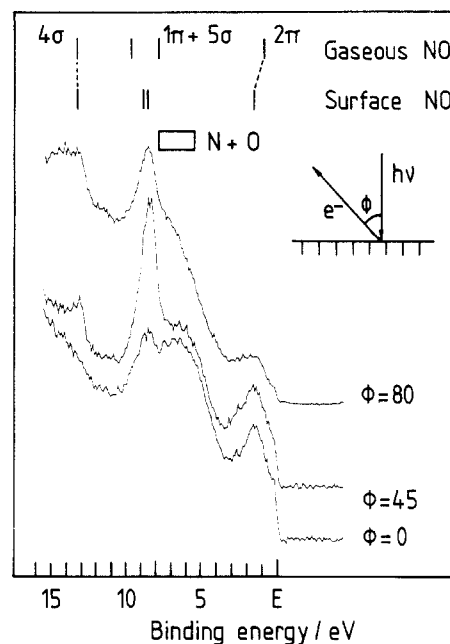


Figure 2. Plot of the angle-resolved photoelectron spectra taken by using 30-eV photons obtained following exposure of the Mo(100) surface to 5 langmuirs of NO at a sample temperature of 150 K ($\theta(\text{NO}) = 1.0$) as a function of detection angle (θ) of the emitted photoelectrons. The incident radiation angle was held constant (at normal, $\phi = 90^\circ$). The peak positions in the photoelectron spectrum of gas-phase NO are indicated as vertical lines. All energies are referenced to the Fermi level (E_F).

photoelectrons (ϕ , Figure 2). These spectra were again obtained by using 30-eV photons for a surface exposed to 5 langmuirs of NO at a sample temperature of 150 K. These spectra exhibit peaks at identical positions as shown in Figure 1, namely, the sharp peaks at 13.5- and 9.0-eV BE and a broad peak centered at 6.5 eV. Again, these peaks show significant variation in intensity as a function of detection angle. The peaks at 13.5- and 9.0-eV binding energy increase and then decrease in intensity as a function of ϕ .

A series of spectra were also taken as a function of sample temperature at a fixed detection geometry following NO adsorption at 150 K (Figure 3). These spectra were also taken after exposure of the surface to 5 langmuirs of NO at 150 K, followed by heating slowly to a particular temperature and annealing at that temperature for 10 s. The crystal was then allowed to cool to 150 K, at which temperature the spectra were recorded. These were taken at an incidence angle, θ , of 65° and detection angle, ϕ , of 15° . Note that θ is measured with respect to the surface and ϕ is measured with respect to the surface normal. This spectroscopic geometry was chosen so that no peaks would be symmetry forbidden. Warming the sample to 720 K reduces the intensities of the 13.5- and 9.0-eV BE peaks by identical factors of 2.0 ± 0.2 . This is accompanied by a slight increase in the intensity of the broad peak at 6.5-eV BE. In addition, there is a significant decrease in intensity in the region of 1.5-eV BE. Intensity in this region of the spectrum is normally assigned to photoemission from the substrate d-bands. However, d-band photoemission would be expected to increase upon heating the sample surface, as these peaks are generally attenuated by the presence of an adsorbate. At least a portion of the photoemission intensity at 1.5-eV BE must, therefore, be ascribed to the species that gives rise to the sharp peaks at 9.0- and 13.5-eV BE. Further heating of the surface to 1090 K results in a further diminution, but not the complete elimination, of the peaks at 13.5-, 9.0-, and 1.5-

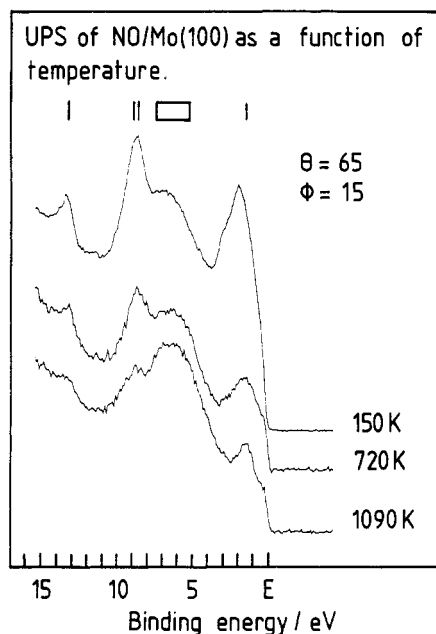


Figure 3. Plot of the photoelectron spectra taken by using 30-eV photons obtained following exposure of the Mo(100) surface to 5 langmuirs of NO at 150 K as a function of sample temperature. The spectroscopic geometry ($\theta = 65^\circ$, $\phi = 15^\circ$) was chosen so that no peaks would be symmetry forbidden. Shown adjacent to their respective spectra are the temperatures to which the sample was slowly heated and annealed for 10 s.

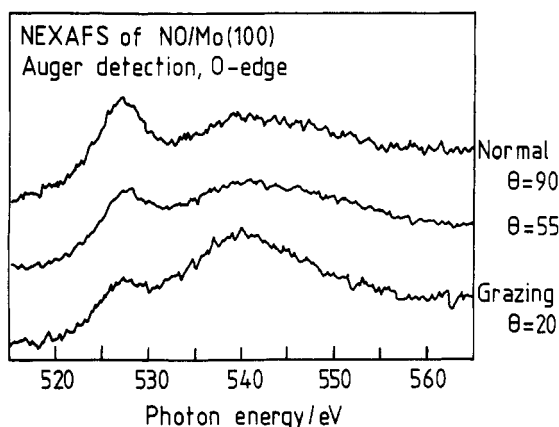


Figure 4. Plot of the near-edge X-ray absorption fine structure (NEXAFS) spectra obtained following exposure of the Mo(100) surface to 5 langmuirs of NO at 150 K as a function of incident radiation angle. These spectra were taken at the oxygen edge and show transitions from the O 1s core level.

eV BE and is accompanied by a substantial increase in the intensity of the broad 6.0-eV BE peak.

Finally, a series of NEXAFS were taken as a function of incidence angle following NO adsorption at 150 K. These are shown in Figure 4 for adsorption at the oxygen edge (that is, for transitions from the O 1s core level). The spectrum exhibits two peaks: one sharp peak at 527-eV photon energy and a broad peak centered at 540 eV. These peak positions remain constant as a function of incidence angle, but their intensities vary in an opposite manner, the 527-eV peak increasing in intensity as the incidence angle increases, the 540-eV peak decreasing. Finally, NEXAFS spectra were also taken at the nitrogen edge (using photon energies between 390 and 430 eV). However, the light intensity at these photon energies was significantly lower than at the oxygen edge (between 520 and 560 eV), resulting in spectra of significantly lower quality, which are therefore not presented. They do, however,

qualitatively reproduce the spectra obtained at the oxygen edge (Figure 4).

Discussion

The peaks in the photoemission spectra of Figures 1 and 2 can be assigned directly by comparison with the peak spacings in gas-phase NO,⁴ and the peak positions in the photoelectron spectrum of gas-phase NO are indicated as vertical lines in the figures. Note that these ionization energies are rigidly shifted from the gas-phase values to take account of the effects of chemisorption to the surface. Comparison with the gas-phase spectrum suggests that the peak at 13.5-eV BE is due to emission from the 4σ orbital of NO, and the peak at 9.0-eV BE is due to emission from both 1π and 5σ orbitals. These assignments are in accord with assignments of the photoelectron spectra of NO on other transition-metal surfaces.⁵ Comparison of the adsorbate-induced peaks with the gas-phase spectrum suggests that the peak at 1.5-eV BE, which is coincident with the substrate d-electrons, appears to be associated with molecular orbitals assigned to chemisorbed NO and is therefore assigned to emission from the $2\pi^*$ level of nitric oxide. Comparison of the peak in the adsorbate-induced spectrum at 1.5-eV BE with the gas phase spectrum of NO (Figures 1 and 2) suggests that the $2\pi^*$ level of NO is stabilized on chemisorption by ~ 1 eV compared to the gas-phase ionization energy. This shift is ascribed to surface bonding via an interaction of this level and the substrate orbitals. Note, however, that a transition from an oxygen 1s core level into an empty $2\pi^*$ orbital is observed in NEXAFS (Figure 4), so that the filled portion of this level observed in photoelectron spectroscopy does not necessarily reflect the true binding energy of this level.

The variation in intensity of photoemission peaks as a function of incidence angle taken at normal emission can be used to measure the orientation of chemisorbed NO with respect to the sample surface. We focus, for this purpose, on the peak at 13.5-eV BE, which has been assigned to emission from the 4σ level. The peak at 9.0-eV BE is not suitable for geometric measurements since it is due to emission from two levels, one of π symmetry and one of σ symmetry. Shown in Figure 5 is a plot of the theoretical variation in photoemission intensity from a molecular orbital with σ symmetry as a function of incidence angle for various molecular tilt angles (measured with respect to the surface normal). These curves have been calculated taking into account the complex dielectric constant of the surface⁶ for a photon energy of 30 eV. Also plotted on this graph are experimental points for the intensity of the 13.5-eV-BE peak taken from the spectra shown in Figure 1, along with error bars that take into account the errors associated with estimating the base line. These data indicate that the molecular axis of NO is tilted at $35^\circ \pm 5^\circ$ with respect to the surface normal following adsorption at 150 K.

The angular variation in absorption cross section in NEXAFS can also be used to measure molecular orientations. At the photon energies used for this experiments (~ 500 eV at the oxygen edge), no correction for the dielectric constant of the substrate is necessary. By comparison with the NEXAFS spectra of similar systems,⁷ the NEXAFS peak at 527-eV photon energy

(4) Turner, D. W.; Baker, C.; Baker, A. D.; Brundle, C. R. *Molecular Photoelectron Spectroscopy*; Wiley-Interscience: London, 1970; p 53.

(5) Steinrück, H.-P.; Schneider, C.; Heinmann, P. A.; Pache, T.; Umbach, E.; Menzel, D. *Surf. Sci.* 1989, 208, 136.

(6) Stratton, J. A. *Electromagnetic Theory*; Mc-Graw-Hill: New York, 1941.

(7) Stöhr, J.; Jaeger, R. *Phys. Rev. B.* 1982, 26, 4111.

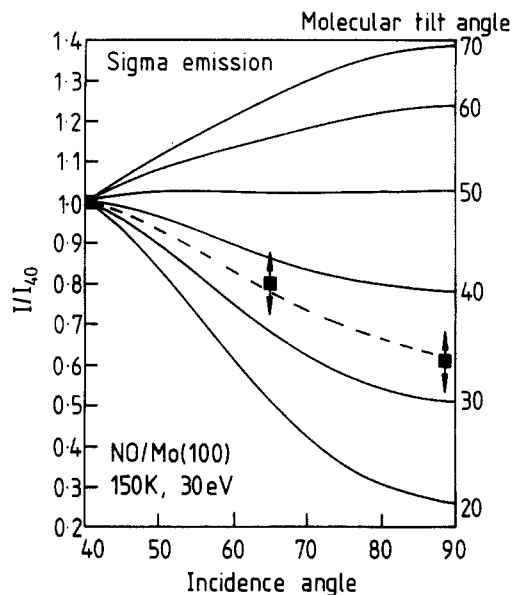


Figure 5. Plot of the theoretical variation in photoemission intensity from a molecular orbital with σ symmetry as a function of incidence angle for various tilt angles for an incident photon energy of 30 eV, which take into account the complex dielectric constant of the surface. Also plotted are experimental points for the intensity of the 13.5-eV-BE peak taken from the spectra in Figure 1. The data indicate that the molecular axis of NO is tilted at $35^\circ \pm 5^\circ$ with respect to the surface normal.

(Figure 4) is assigned to a π resonance, that is, to an O(1s) to NO($2\pi^*$) transition, and the peak at 540 eV to a σ resonance, that is, to an O(1s) to NO($6\sigma^*$) transition. In principle, variations in intensity of both the π and σ resonances can be used to determine molecular orientations. In addition to transitions into unoccupied molecular levels associated with these peaks, there are also transitions into free-electron states, corresponding to complete ionization of the core level. The increased signal at photon energies above 560 eV compared to the base line below 520 eV is due to this. These effects can be incorporated into a fitting procedure to allow the NEXAFS spectra to be synthesized.⁸ Since σ resonances in general occur at photon energies above the edge jump, this protocol is particularly useful in cases in which it is necessary to measure molecular geometries from these peaks. On the other hand, π resonances are generally at lower photon energies than the edge jump (that is, these energy levels are located between the Fermi level and the vacuum level), so that in this case no background subtraction procedure is necessary, and the intensities of the π^* resonances can be used directly. It can be shown⁹ that the 1s to π^* absorption cross section as a function of incidence angle, θ (measured with respect to the surface), and molecular tilt angle, t (measured with respect to the surface normal), is proportional to

$$4 - (3 \cos^2 \theta - 1)(3 \cos^2 t - 1)$$

This formula represents the square of the angular variation of the matrix element for a 1s to π^* transition, which is derived by calculating the component of the electric field perpendicular to the molecular axis as a function of θ (photon incidence angle), t (molecular tilt angle), and also the azimuthal angle of the chemisorbed molecule. The equation is then summed over all azimuthal angles. This latter procedure is valid for all adsorbate sites with higher than threefold symmetry.⁷ Finally, the analysis assumes

(8) Outka, D.; Stöhr, J. *J. Chem. Phys.* **1988**, *88*, 3539.

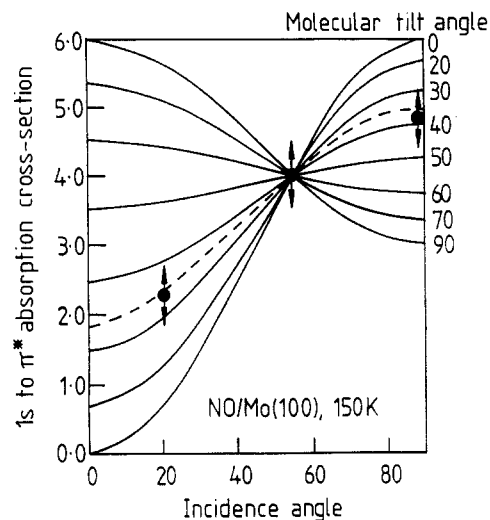


Figure 6. Plot of 1s to π^* absorption cross section as a function of incident radiation angle for various tilt angles. Also plotted are experimental points for the π^* resonance taken from the spectra in Figure 4. The data indicate that the molecular axis of NO is tilted at $35^\circ \pm 5^\circ$ with respect to the surface normal.

completely linearly polarized radiation, whereas, in fact, the radiation used for these experiments is only approximately 80% polarized. This deviation from perfect linear polarization, however, only results in a small error ($\sim 2^\circ$) in the final geometry and is included in the quoted error estimates.⁹

The equation is shown plotted in Figure 6 as a function of incidence angle for various tilt angles. Also plotted on this curve are data for the intensity of the π^* resonance taken from spectra in Figure 4, which shows that the molecular tilt angle measured by using NEXAFS for NO chemisorbed on Mo(100) at 150 K is $35^\circ \pm 5^\circ$. This value of molecular tilt angle is in striking agreement with that measured from the angular variation of the 4σ orbital in photoelectron spectroscopy. The agreement between the two values obtained by using two completely different techniques suggests that the presence of chemisorbed oxygen arising from NO dissociation (see below)^{10,11} has a minimal effect on the NEXAFS geometry measurements of NO. Also, the variation in intensity of the photoelectron peak at 1.5-eV BE (assigned to photoemission from the NO $2\pi^*$ level) as a function of incidence angle is also in accord with this assignment. Emission from an orbital of π symmetry should have its maximum intensity at $\theta = 90^\circ$ and decrease with θ , as is indeed the case in the spectra of Figure 1.

Further corroboration of the presence of tilted NO comes from the spectra of Figure 2, which show that the 13.5-eV-BE peak (assigned to emission from the 4σ level of NO) increases in intensity by a factor of 2 as the detection angle changes from 0° to 45° . Theoretical calculations for emission from the 4σ orbital of carbon monoxide suggest that the photoemission intensity from this peak should increase by a factor of ~ 2.1 as the detection angle increases from 0° to 45° using 41-eV photons for a tilted molecule.¹³ The experimental data of Figure 5 show that the intensity of the 4σ orbital of NO increases by a factor of ~ 2.2 as σ changes from 0° to 45° , providing further confirmation of the tilted geometry.

(9) Hoffmann, H.; Zaera, F.; Ormerod, R. M.; Lambert, R. M.; Wang, L. P.; Tysoe, W. T. *Surf. Sci.* In press.

(10) Stöhr, J.; Jaeger, R. *Phys. Rev. Lett.* **1982**, *49*, 142.

(11) Norman, D.; Stöhr, J.; Jaeger, R.; Durham, P. J.; Pendry, J. B. *Phys. Rev. Lett.* **1983**, *51*, 2052.

(12) Stöhr, J.; Outka, D. *Phys. Rev. B* **1987**, *36*, 7891.

(13) Reiger, D.; Schnell, R. D.; Steinmann, W. *Surf. Sci.* **1984**, *43*, 157.

Tilted NO has been previously observed on Al₂O₃-supported molybdenum oxide catalysts where the ON-NO dihedral angle was measured by using infrared spectroscopy.¹⁴ In a catalyst that had been reduced at ~1200 K (to form predominantly metallic molybdenum), a dihedral angle of $85^\circ \pm 3^\circ$ was measured, corresponding to a molecular tilt angle of $42^\circ \pm 2^\circ$; comparable with the molecular tilt angle of NO on Mo(100) at 150 K measured in this work by use of photoelectron spectroscopy and NEXAFS. Dimeric nitric oxide has also been detected following condensation of NO on copper at 19 K¹⁵ and was assigned to dimeric NO in the condensed multilayer. The N-N-O angle in the dimer is 99.6° , which would correspond to a molecular tilt angle of $\sim 10^\circ$ and is significantly less than the tilt angle measured in this work or on the catalytic surface. The photoelectron spectrum of the condensed dimer is very similar to that for molecular NO except for the presence of a small peak at a binding energy 3.4 eV above that due to emission from the $2\pi^*$ level. This region is obscured in the spectra of NO chemisorbed at 150 K by the broad peak centered at 6.5-eV BE, but there is no evidence of such a peak in these spectra, so a dimeric NO corresponding to that seen on copper can be ruled out.

The σ - π spacing in NEXAFS can be used to provide some indication of the N-O bond length.¹⁶ The gas-phase value for this spacing, $\Delta E(\sigma-\pi)$, measured at the oxygen edge is 13.6 eV.¹⁷ An increase in this value indicates a decrease in N-O bond length with an approximately linear correlation between $\Delta E(\pi-\sigma)$ and bond length with a proportionality constant of $0.03 \text{ \AA}/\text{eV}$. The π - σ spacing for NO on Mo(100) taken from the spectra of Figure 4 is $12.8 \pm 0.4 \text{ eV}$, suggesting that the N-O bond in chemisorbed NO is longer by $0.03 \pm 0.01 \text{ \AA}$ than in the gas-phase NO. The gas-phase bond length is 1.15 \AA , yielding a surface bond length of $1.18 \pm 0.01 \text{ \AA}$. This observation is in line with the position of the $2\pi^*$ level, which is visible in both photoemission and NEXAFS, suggesting that it interacts strongly with the substrate d-orbitals, causing a weakening of the N-O bond. It should be borne in mind in this analysis that the $2\pi^*$ orbital does interact with the substrate d-electrons, so that in addition to the shift in position of the $2\pi^*$ and 6σ orbitals due to a change in N-O bond length, there is likely to be an additional stabilizing shift in the $2\pi^*$ level due to surface bonding. In this case, the increased N-O bond length described above represents an upper limit to this value.

Consider now the photoelectron spectra for NO on Mo(100) taken as a function of temperature (Figure 3). Peaks at 13.5-, 9.0-, and 1.5-eV binding energies have been assigned to emission from orbitals associated with chemisorbed molecular NO, since they all decrease similarly in intensity as a function of sample temperature. This decrease in emission from peaks due to molecular NO is

(14) Millman, W. S.; Hall, W. K. *J. Phys. Chem.* **1979**, *83*, 427.

(15) Tonner, B. P.; Kao, C. M.; Plummer, E. W.; Caves, T. C.; Messmer, R. P.; Salaneck, W. R. *Phys. Rev. Lett.* **1983**, *51*, 1378.

(16) Stöhr, J.; Gland, J. L.; Eberhardt, W.; Outka, D.; Madix, R. J.; Sette, F.; Koestner, R. J.; Doebler, U. *Phys. Rev. Lett.* **1976**, *36*, 945.

(17) Huheey, J. E. *Inorganic Chemistry*, 3rd ed.; Harper International SI Edition: Cambridge, 1983; p 108.

accompanied by an increase in intensity in the broad peak centered at ~ 6 -eV-BE. Since thermal desorption experiments have shown that NO dissociates on Mo(100),³ the 6-eV peak is assigned to emission from dissociation products, that is, a combination of chemisorbed nitrogen and oxygen atoms. This implies that a portion of the NO has already dissociated at a sample temperature of 150 K.

Warming the surface from 150 to 720 K causes the peaks ascribed to molecular NO to decrease in intensity by a factor of approximately 2. Thermal desorption experiments show that molecular NO desorption is complete by 720 K, and Auger spectroscopy measurements indicate that this is accompanied by a decrease in NO coverage from $\theta(\text{NO}) = 1.0$ following NO adsorption at 150 K to $\theta(\text{NO}) = 0.7$ after desorbing all molecular NO (i.e., by annealing to above 700 K).³ Since the photoelectron peaks associated with molecular NO (at 13.5- and 9.0-eV BE) decrease by a factor of ~ 2 on heating to 720 K, this implies that following NO adsorption at 150 K, the molecular NO coverage, $\theta(\text{NO}) = 0.6$ and $\theta(\text{N})$ and $\theta(\text{O})$ (from dissociated NO) = 0.4. This coverage of chemisorbed nitrogen and oxygen is less than that formed following NO adsorption at room temperature. The photoelectron spectroscopic data indicate that further heating of the surface to 1090 K (which is a lower temperature than the onset of N₂ desorption in thermal desorption) results in additional NO dissociation without, however, any detectable NO desorption. It is of interest to note that small peaks still remain at 13.5- and 9.0-eV BE at this temperature, suggesting the presence of molecular NO at the surface, even after annealing the surface to 1090 K.

Conclusions

NO adsorbs both molecularly and dissociatively at 150 K. Both photoelectron spectroscopy and NEXAFS measurements indicate that the molecular axis of chemisorbed NO is tilted at $35^\circ \pm 5^\circ$ with respect to the surface normal. Heating the surface to 720 K results in a loss of intensity of the photoelectron peaks associated with molecular NO, and the desorption of molecular NO is detected over this temperature range in thermal desorption. Heating the sample to 1090 K causes a further decrease in intensity but not the complete elimination of peaks due to molecular NO and a concomitant increase in intensity of peaks due to dissociated NO, but without detection of any molecular desorption products. This implies the presence of a very strongly bound molecular state that has not completely dissociated even above 1000 K.

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