A Study of the Interaction of Nitric Oxide with Nickel and Oxidized Nickel Surfaces by X-Ray Photoelectron Spectroscopy

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The adsorption of nitric oxide by nickel and also nickel surfaces preexposed to oxygen has been studied by X-ray photoelectron spectroscopy in the temperature range 80 to 290°K. The surface reactivity to NO interaction has been controlled by varying the temperature and conditions of preexposure to oxygen. This has enabled three distinct states of NO adsorption to be delineated, a dissociative state and two molecular states. One of the molecular states is weakly adsorbed while the other, more strongly chemisorbed, is the precursor to dissociation. We suggest the latter is adsorbed in the "bent" form while the former is linearly bonded to the surface. N_2O is also observed within the adlayer at 80°K particularly with nickel surfaces preoxidized at 290°K. The N_2O is weakly adsorbed. There are strong analogies between the present data and previous studies with copper, iron, and aluminum, metals with very different electronic structures. It should be noted, however, that although in all cases a new surface phase is generated, the inherent reactivities of the clean metals differ only in degree rather than in kind.

INTRODUCTION

There has been considerable interest during the last decade in the catalytic chemistry of nitric oxide, which is to some extent due to effort to find catalysts which will remove efficiently noxious constituents from the exhaust gases of automobiles (1). Our own interest in the surface chemistry of nitric oxide stems partly from our earlier adsorption work with carbon monoxide (2) but also because we wish to explore whether X-ray photoelectron spectroscopy (XPS) can provide an insight into the catalytic aspects of the chemistry of nitric oxide.

More recently we have studied by photoelectron spectroscopy the interaction of nitric oxide with iron (3), copper (4, 5), and aluminum (6) surfaces; in the case of copper both polycrystalline and single crystal surfaces have been used. There are certain reactivity features common to all the metals even though copper and aluminium are typical sp metals whereas iron is a transition metal with "holes in the d-band." All the metals, for example, dissociatively chemisorb NO even at 80°K; with aluminum and copper dissociative chemisorption was shown to be accompanied by the catalytic formation of N_2O at 80°K. In the case of Cu(100) and Cu(111) surfaces X-ray photoelectron spectra obtained using the highest possible resolution conditions combined with ultraviolet photoelectron spectroscopy have been interpreted (7) in terms of two
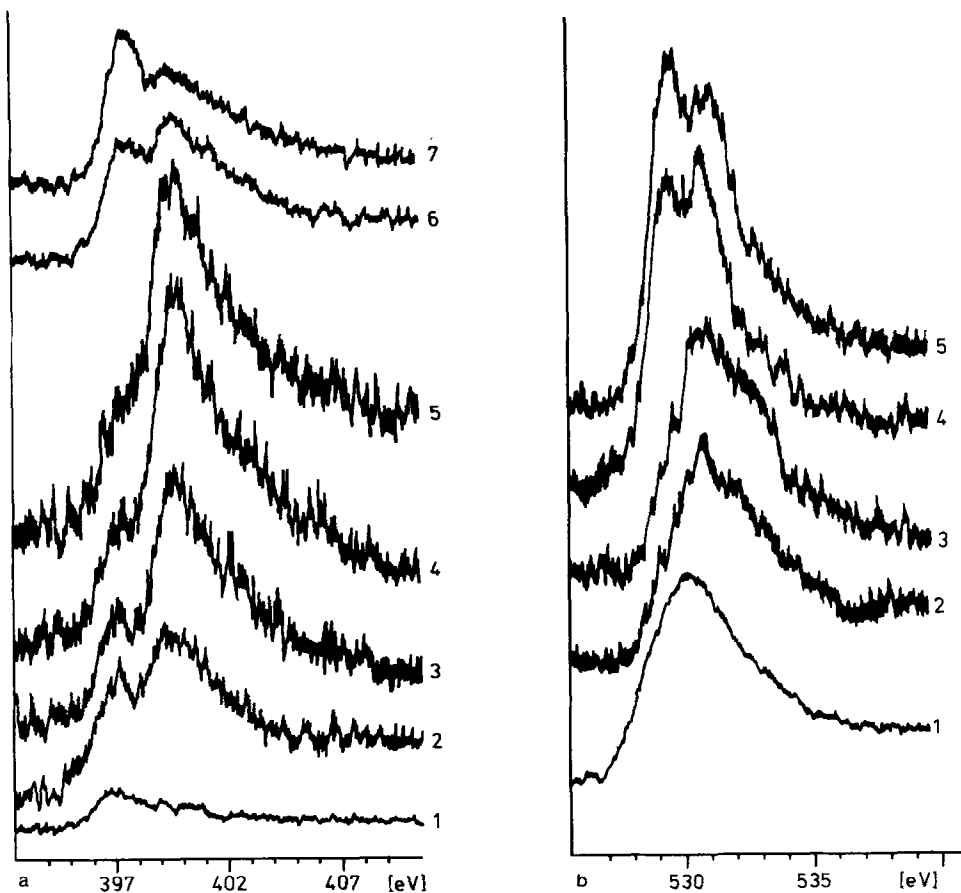
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FIG. 1. Adsorption of nitric oxide on nickel at 80°K. (a) N(1s) spectra: curve 1, nickel film (analyzing conditions: 100 eV, f.s.d. 10^4 cs^{-1}); curve 2, after exposure (3 L) of NO (100 eV, f.s.d. 3×10^3 cs^{-1}); curve 3, after exposure (6 L) of NO (50 eV, f.s.d. 10^3 cs^{-1}); curve 4, after exposure (1500 L) of NO (as for curve 3); curve 5, after warming adlayer to 115°K (as for curve 3); curve 6, after warming to 280°K (50 eV, f.s.d. 3×10^3 cs^{-1}); curve 7, after warming to 290°K (as for curve 6). (b) O(1s) spectra: curve 1, after exposure (3 L) of NO (100 eV, f.s.d. 10^4 cs^{-1}); curve 2, after exposure (1500 L) of NO (20 eV, f.s.d. 10^3 cs^{-1}); curve 3, after warming adlayer to 150°K; curve 4, after warming adlayer to 285°K; curve 5, after warming adlayer to 290°K. Analyzing conditions for curves 3–6 as for curve 2.

molecular states of NO, one assigned to a "bent" form that dissociates, the other a more weakly adsorbed linearly bonded species. The behavior of aluminum was somewhat similar to that of copper but due to overlapping peaks in the O(1s) and N(1s) spectral regions the analysis could not be as detailed as was possible with Cu(100) and Cu(111) surfaces.

In the present paper we report an XPS study of the interaction of nitric oxide with "atomically clean" polycrystalline nickel surfaces and also with nickel pre-exposed to oxygen. There have been reported two electron spectroscopic studies of the interaction of nitric oxide with nickel (8, 9) and one of the additional reasons for the present study was to determine whether nickel, which had been reported to adsorb nitric oxide in only a single molecular state at 77°K (8), was intrinsically different from iron, copper, and aluminum. At 290°K nickel dissociatively chemisorbed nitric oxide (8). A

further reason for the present work was to probe the idea that we might be able to control the surface reactivity of nickel in such a way, by, for example, preexposing the surface to oxygen, that distinct states of NO adsorption, two of them molecular as observed with copper and one dissociative, could be isolated one from the other. If this indeed is possible then it should provide a clearer picture of the reactive sites present at a nickel surface and in turn a better understanding of the catalytic chemistry of nitric oxide.

EXPERIMENTAL

The spectra were determined using a Vacuum Generators ESCA-3 instrument, details of which have been described (10). The electron binding energies are accurate to ±0.2 eV. Nickel films were evaporated on to the end of the probe at room temperature from a spec-pure filament at a pressure of ~10^{-9} Torr. The films were examined by X-ray photoelectron spectroscopy and shown to exhibit only small concentrations (≤10% of a monolayer) of impurities (usually carbon and oxygen). Nitric oxide was prepared as previously described (3) while oxygen was obtained in spec-pure form from British Oxygen Ltd. and used after passing through a trap maintained at 80°K. All the adsorption studies were carried out with NO and O_2 at pressures in the range 10^{-5} to 10^{-7} Torr.

RESULTS

Nitric Oxide Adsorption on Nickel at 80°K

In Fig. 1 are shown N(1s) and O(1s) spectra after exposing a "clean" nickel surface to 3, 6, and 1500 L (1L(Langmuir) ≡ 10^{-6} Torr·sec) of nitric oxide at 80°K. These N(1s) spectra are dominated by the peak centered at 399 eV; there is a small contribution at 397 eV (formed from traces of NO(g) in the ambient during cooling to 80°K) with a distinct asymmetry

extending over the range 402 to 406 eV. Obviously we could not assign individual binding energies to peaks that may exist in the 402 to 406 region but previous studies (4–6) have shown the presence of peaks at both about 402 and 406 eV.

At temperatures above about 240°K intensity is being clearly transferred into the N(1s) peak at 397 eV. At 290°K the 397 eV peak is dominant with an obvious second peak at 399.5 eV and probably some intensity at about 402 eV.

The O(1s) spectra at 80°K (Fig. 1b) are somewhat less informative; the initial peak after 3 L exposure is centered at ~530 eV but is very broad. With continued exposure the FWHM increases. On warming, the O(1s) profile clearly reveals the development of two distinct components and at 285°K they are seen to be centered at 529.5 and 530.7 eV (Fig. 1b, curve 5). The FWHM value of the combined peaks at 290°K is appreciably less than that of the broad peak at 80°K (curve 2).

Nitric Oxide Adsorption on Nickel at 290°K

Figure 2a shows the development of the N(1s) spectra after the exposure of an initially clean nickel surface to nitric oxide at 290°K. The spectrum is dominated by the growth of the peak centered at a binding energy of about 397.5 eV although at exposures grater than 6 L the emergence of a second peak at about 399 eV is evident. After 30 L exposure (Fig. 2a) this second peak is clearly to be seen together with the possibility of a small third component at about 401 eV. There is no increase in intensity above that of the background in the spectral region of 406 eV (Fig. 1a).

The O(1s) spectrum (Fig. 2b) shows after 15 L exposure to NO the appearance of two components, one at a binding energy of 529.5 eV and the second at 530.5 eV together with a shoulder at ~531.5 eV.
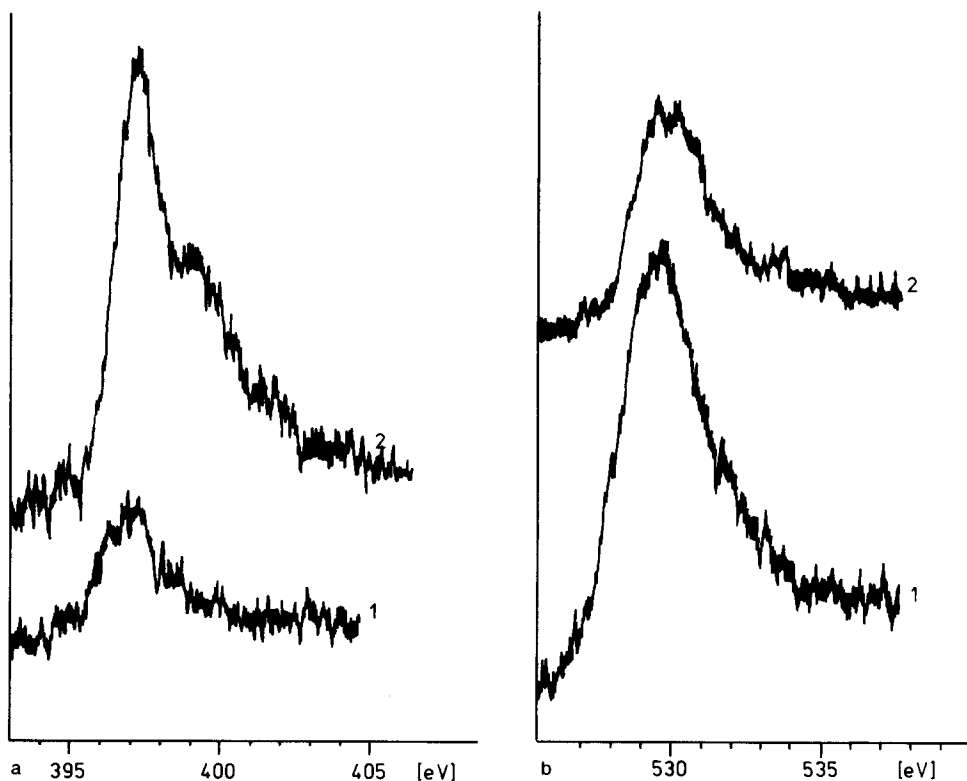
FIG. 2. Adsorption of nitric oxide on nickel at 290°K. (a) N(1s) spectra: curve 1, after exposure (3 L) of NO (analyzing conditions: 100 eV, f.s.d. 3×10^3 cs^{-1}); curve 2, after exposure (15 L) of NO (50 eV, f.s.d. 10^3 cs^{-1}). (b) O(1s) spectra: exposures of NO as in (a), analyzing conditions: curve 1, as in (a); curve 2, 20 eV, f.s.d. 10^3 cs^{-1}.

Nitric Oxide Adsorption at 80°K on Nickel Preexposed to Oxygen

Oxygen exposure at 290°K. The Ni 2p$_{\frac{3}{2}}$ spectral region of the clean nickel surface is shown in Fig. 3a; after exposure (300 L) to óxygen at 290°K (Fig. 3b) there was considerable attenuation of the metal peak intensity and the development of broad structure at high binding energy together with a shift in the binding energy of the shake-up satellite. This is undoubtedly evidence for the formation of a surface oxide. Similar behavior has been reported by Norton and Tapping (11a) in their study of the interaction of oxygen with nickel but we report our data since it is diagnostic of the electronic state of the nickel surface (see also Ref. 11b). When this surface was exposed to nitric oxide

(9 and 50 L) at 80°K, the N(1s) spectral region was as shown in Fig. 4. The main peak is centered at about 402.5 eV and the second peak is at about 405.5 eV. It should be noted that there is no extra intensity (i.e., above the background) in the 397.5 to 400 eV region. On warming to 290°K the overall intensity diminishes although when the feature centered at about 405.5 eV has disappeared (~190°K) the intensity of the 402 eV component has apparently diminished by only about a third. At 290°K there is only one significant peak present, that with a binding energy of about 402 eV, although a small increase in intensity has occurred at about 397 eV. The intensity of the 402 eV peak is about half of its intensity at 80°K.

Oxygen preexposure at 80°K. In order to

characterize the clean nickel surface the Ni 2p$_{\frac{3}{2}}$ spectral region was scanned at 80°K and also after exposure to oxygen at the same temperature. Figure 3c shows that there was little change after exposure to oxygen, contrasting with the gross perturbation observed after oxygen exposure at 290°K (Fig. 3a). This agrees with Norton and Tapping's observations (11). The O(1s) peak area after oxygen exposure was one-quarter of that after exposure to oxygen at 290°K (see above); in this case the oxygen is confined to the adlayer.

When nitric oxide was adsorbed on this oxygen preexposed surface at 80°K the N(1s) spectral region was as shown in Fig. 5a. There is a broad peak straddling the 399 eV to 407 eV region. Apparently the spectrum is composed of the individual peaks observed with clean nickel and preoxidized nickel (Figs. 1 and 2), i.e.,
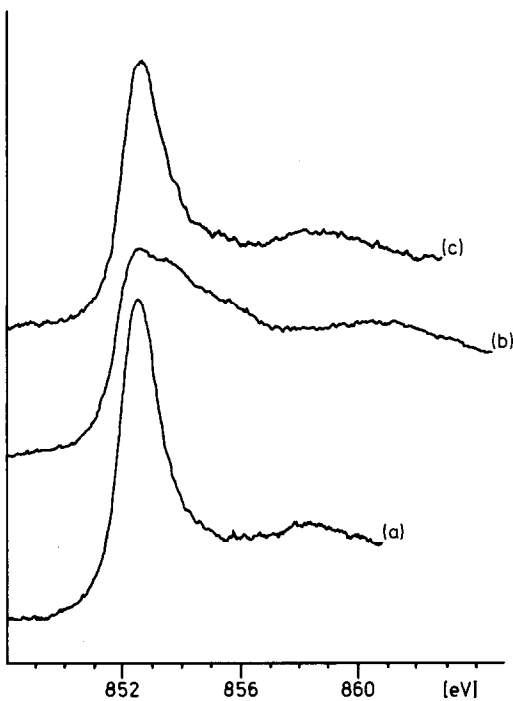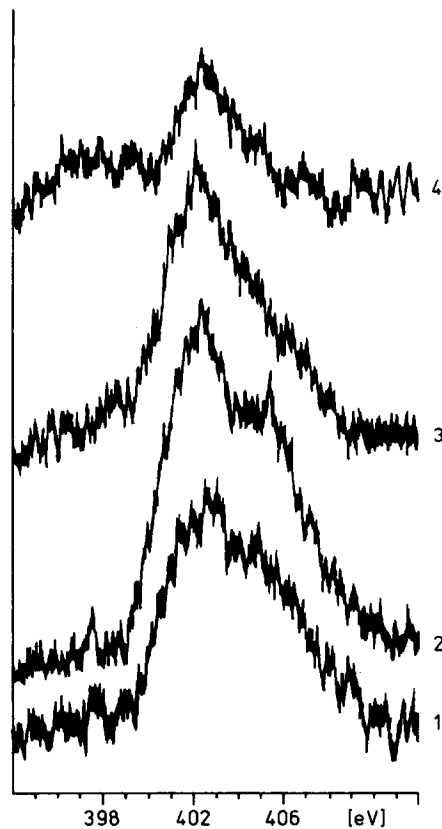

FIG. 4. Adsorption of NO at 80°K on nickel which has been preexposed (300 L) to oxygen at 290°K. N(1s) spectra: curve 1, after exposure (9 L) of NO; curve 2, after exposure (50 L) of NO; curve 3, after warming adlayer to 190°K; curve 4, after warming adlayer to 290°K. Analyzing conditions: 100 eV, f.s.d. 3 × 10³ cs⁻¹.

FIG. 3. Ni 2p$_{\frac{3}{2}}$ spectra (a) for clean nickel, (b) after exposure (300 L) to oxygen at 290°K, (c) after exposure to oxygen (1000 L) at 80°K.

peaks recognized to be centered at binding energies of about 399.5, 402.5, and 405.5 eV. On warming to 190°K the component at 405.5 eV has disappeared, intensity begins to develop at 397.4 eV, and at 245°K there are two distinct peaks with binding energies of about 399.5 and 402.5 eV. At 275°K the intensity of the 397.4 eV peak has now developed well. When we consider the corresponding O(1s) spectra (Fig. 5b) we can observe the development with increasing temperature of two distinct peaks at binding energies of about 529
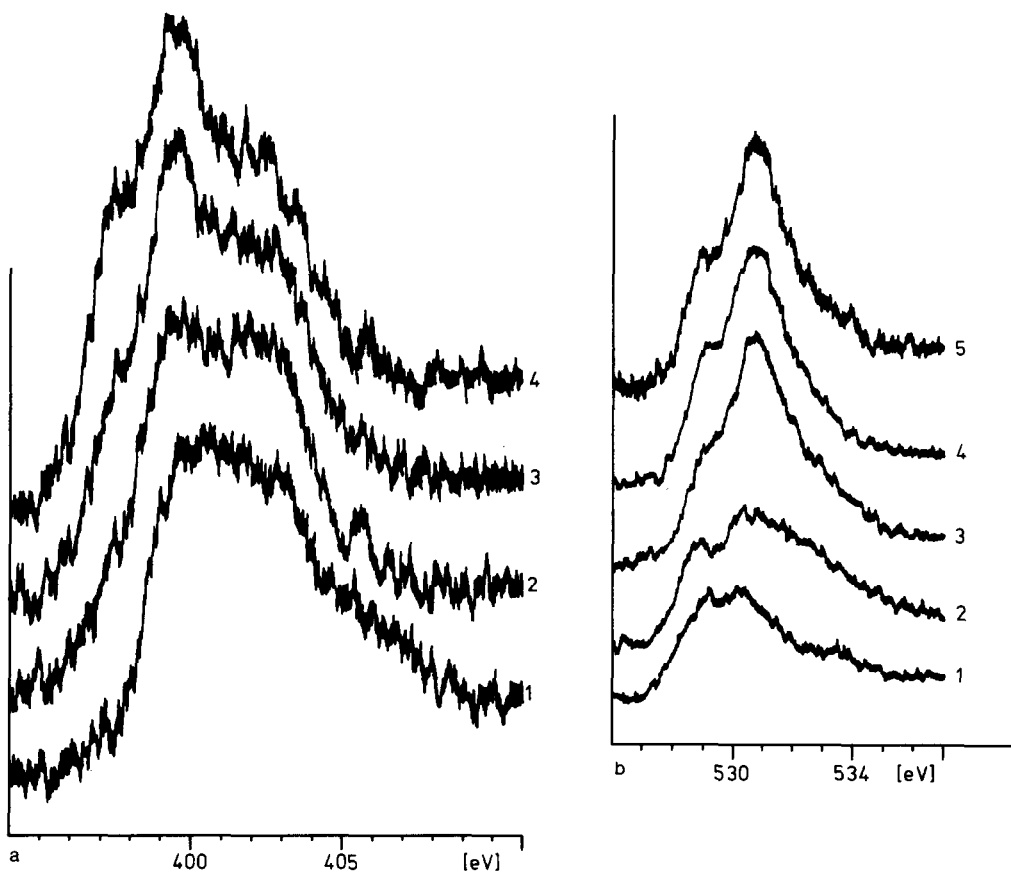
FIG. 5. Adsorption of NO at 80°K on nickel which as been preexposed to oxygen at 80°K. The oxygen coverage based on the observed O(1s) intensity is 0.25 of that at 290°K (see Fig. 4). (a) N(1s) spectra: curve 1, after exposure (2500 L) of NO; curves 2, 3, 4, after warming adlayer to 190, 245, and 275°K, respectively. Analyzing conditions: 50 eV, f.s.d. 10^3 cs^{-1}. (b) O(1s) spectra: curve 1, after exposure (1200 L) to oxygen at 80°K; curve 2, after exposure (2500 L) of NO at 80°K; curves 3, 4, and 5, after warming adlayer to 220, 260, and 270°K, respectively, in vacuo. Analyzing conditions: curves 1–4, 20 eV, f.s.d. 3×10^3 cs^{-1}; curve 5, 10 eV, f.s.d. 10^3 cs^{-1}.

and 531 eV together with a smaller third peak at about 532.5 eV. Therefore, whether we rely on N(1s) or O(1s) spectra the conclusions are similar.

DISCUSSION

In Fig. 6 we bring together the final N(1s) spectra (see Figs. 1, 2, 4, and 5) observed after the interaction of "clean" nickel with nitric oxide at 80 and 290°K and also nickel preexposed to oxygen with nitric oxide at 80°K. There are four distinct peaks in the N(1s) spectral region: 397.5, 399.5, 402.5, and 405.5 eV. The N(1s)

binding energy value characteristic of the most stable surface species formed after the adsorption of nitric oxide is that at about 397.5 eV and we are certain that this reflects nitrogen adatoms formed by dissociative chemisorption (3–6). Previous studies with nitric oxide, nitrogen, and ammonia support this assignment (12). The O(1s) spectra indicating a peak at about 529.5 eV, characteristic of chemisorbed oxygen adatoms, also support this assignment.

The surface species characterized by the N(1s) peak at 399.5 eV we assign to molecularly adsorbed nitric oxide. It is

clearly the precursor to the dissociative state, the 399.5 eV peak observed with clean nickel at 80°K transforming into the 397.5 eV peak on thermal activation (Fig. 1a). At 290°K, the N(1s) region is dominated by the 397.5 eV peak (Fig. 2a), the 399.5 eV feature only developing with increasing surface coverage. In other words there is sufficient thermal energy at 290°K to overcome the activation energy for dissociation, but with increasing coverage of nitrogen and oxygen adatoms the activation energy increases and we see the onset of the 399.5 eV peak. A similar observation has been made on the Ni(111) surface (9).

The third N(1s) peak at about 402 eV

(Fig. 6) is the least intense of the three peaks present at 290°K. It is however the most significant peak present when the nickel surface has been preexposed to oxygen at 290°K and then exposed to NO at 80°K (see also Fig. 4). This would suggest that the surface species is weakly adsorbed and desorbs rapidly in the temperature range 80 to 290°K. At 290°K the FWHM value is about 2.2 eV, suggestive of only a single surface species being present. At 80°K the peak is composite, one component disappearing at 190°K. The other, and by far the smallest in intensity, is still present at 290°K (Figs. 4 and 5). The N(1s) peak at 405.5 eV also disappears on warming to 190°K. By analogy with our studies of NO interaction with aluminum (6), and making use of the fact that $N(1)$ peaks at ~402 and 406 eV are observed for nitrous oxide adsorbed at 80°K on copper (5), aluminum (6), and nickel (8), we assign the major part of the 402.5 eV peak and all of the 405.5 eV peak to emission from adsorbed nitrous oxide formed from NO at 80°K.

The remaining more strongly held species with an N(1s) binding energy at ~402 eV we ascribe to a second molecularly adsorbed NO species. This species we observe only after the surface has "reacted" with NO, i.e., when the surface is appreciably covered by oxygen and/or nitrogen adatoms. A parallel exists in the case of nitric oxide adsorption on a preoxidized ion surface where an $N(1s)$ peak at 401.5 eV is observed (3). That this adspecies was molecularly adsorbed NO was confirmed by He(I) valence level spectroscopy (3).

To summarize, therefore, we have present at 80°K two molecular states of nitric oxide, one of which is strongly adsorbed and is the precursor to dissociative chemisorption while the other is more weakly adsorbed. In addition N_2O is formed. We consider next the distinguishing features of the two molecular species.
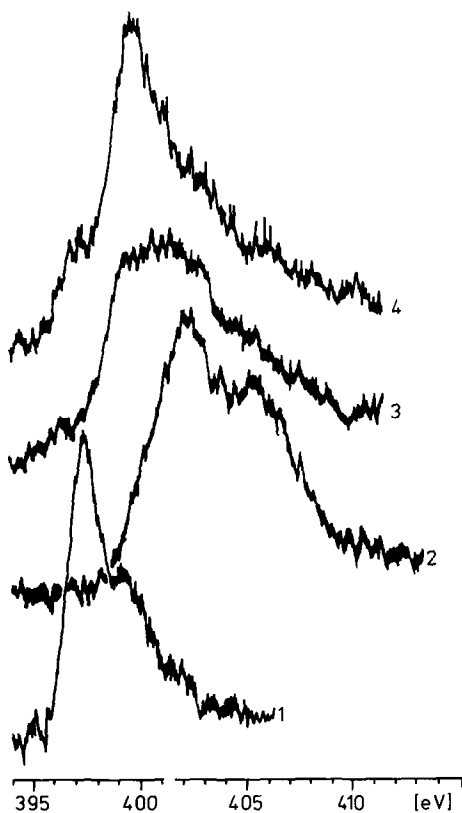

Fig. 6. Comparison of N(1s) spectra observed after NO adsorption: curve 1, clean nickel at 290°K; curve 2, nickel preoxidized at 290°K, NO adsorbed at 80°K; curve 3, nickel with chemisorbed oxygen adlayer present (formed at 80°K), NO adsorbed at 80°K; curve 4, clean nickel at 80°K.

In view of the fact that the NO species characterized by an N(1s) value of 399.5 eV dissociates, it is reasonable to suggest that in the process of dissociation the molecule goes through various stages of "tilting" until eventually the oxygen atom becomes strongly chemisorbed. Recently Plummer and Gustafsson (13) have interpreted angle-resolved photoemission data for nitric oxide adsorbed on a Ni(100) surface at 170°K in terms of a species tilted at 30° with respect to the surface normal. We can consider the molecule in this configuration to be in a state of incipient dissociation and possibly simulating the strongly chemisorbed NO species observed in the present study. When we next consider the structure of metal nitrosyl complexes (14) we find that the M–N–O bond angle is between 120 and 180°, i.e., the molecule's orientation with respect to the surface ranges from the linear form to one with a tilt of about 60° from the surface normal. By assuming only a "single bond" between the metal atom and the NO ligand, three limiting cases involving sp, sp², and sp³ hybridization with formal charges of +1 (sp hybridized), −1 (sp² hybridized), and −3 (sp³ hybridized) can be associated with the NO ligand. There are, of course, well-established relationships (15) between formal charge or oxidation state and the experimentally observed binding energy; the more negatively charged is the ligand, the smaller is the binding energy. We therefore suggest that the surface species characterized by the N(1s) peak at about 399.5 eV is adsorbed in the bent or tilted form. On the other hand the species with the higher N(1s) binding energy (between 401 and 402 eV) we suggest is in a linearly bonded or sp hybridized form. Further support for the assignment to bent and linear forms of adsorbed nitric oxide comes from the recent calculations of Clark et al. (16) who have examined theoretically linear and bent NiCO as a prototype molecule. Both core levels, C(1s) and O(1s),

are shifted to lower binding energy in the bent compared with the linear form. We therefore have evidence for the following surface species present in the temperature range 80 to 290°K; N, O, NO(b), NO(l), and N_2O.

There have recently been a number of studies of the interaction of nitric oxide with metal surfaces (17–19). In the case of iridium (19) an asymmetric N(1s) profile observed after exposure to nitric oxide at 170°K was resolved into two peaks at ~400 and 402 eV, and interpreted as arising from paramagnetic splitting in the final state of a single molecularly adsorbed species. Our interpretation of the spectra from nickel in the present study in terms of two molecular states of adsorbed NO raises a possible question regarding the assignment of the spectra observed with iridium (19).

The spectra observed with aluminum (6) and copper (4, 5) are most similar to those reported in this paper. We should emphasize, however, that only when spectra were taken at the highest possible resolution did sufficient detail become available for a proper interpretation. This was not available in our earlier studies with copper (4). Furthermore in the studies with iridium and the earlier studies with nickel (8) the spectra were not recorded at high resolution and we suspect that, as in our initial work with copper (4), overlapping peaks were not resolved.

As for the formation of N_2O this has been discussed previously only in connection with the spectra observed with aluminium (6) and copper (4, 5) although Eley and Wilkinson (20) had reported in a combined mass-spectrometric and kinetic study the formation of $N_2O(g)$ during NO interaction with aluminium at low temperature. With nickel the most active surface for N_2O formation at 80°K is clearly the "oxide" while "clean" nickel is least active. It is interesting to note that aluminium (6) first dissociated NO at

80°K, and having formed the surface oxide and nitride, only then did N_2O appear on the surface. At this stage at least a monolayer of "oxide" and "nitride" had formed. The analogy with nickel preoxidized at 290°K is clear; oxygen has penetrated into the subsurface with aluminium (oxidation) even at 80°K while with nickel this only occurs to any appreciable extent at 290°K. More detailed aspects of the mechanism of N_2O formation are being pursued.

We have no evidence for dimer formation although Ibach and Lehwold (21) have recently interpreted their electron-energy-loss spectra in terms of the formation of $(NO)_2$. Only one desorption peak is, however, observed in their thermal desorption spectra; the peak is coverage dependent and shifts from 405 to 360°K with increasing coverage. During heating, part of the NO dissociates, so that from this point of view there is some similarity between platinum, nickel, and copper. Ibach and Lehwold's view is that although NO adsorbs initially as a single molecular state, with increasing coverage at low temperature increasing Coulombic repulsion leads to dimerization. There is a reversible change-over between the two states which is coverage dependent. No analogous process has been observed by X-ray photoelectron spectroscopy with nickel although we should emphasize that we suspect that core-level shifts between, say, what we have assigned as NO(1) and a possible dimer $(NO)_2$ might not be significant. We hope to pursue this question by studying the adsorption of nitric oxide in the presence of NO(g) at pressures up to 1 Torr.

ACKNOWLEDGMENT

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