ELECTRONIC EFFECTS OF SURFACE OXYGEN ON THE BONDING OF NO TO Pt(111)

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Changes in the bonding of NO on Pt(111) induced by the coadsorption of high coverages of oxygen atoms have been studied with temperature programmed desorption (TPD), vibrational spectroscopy using high resolution electron energy loss spectroscopy (HREELS), and ultraviolet photoelectron spectroscopy (UPS). Modification of the electronic structure of surface Pt atoms by the strongly electron-withdrawing adsorbed oxygen atoms alters the relative stabilities of NO adsorption sites and the nature of the Pt–NO bond. Coadsorption of 0.25 ML of O(a) destabilizes the two-fold bridge site for NO adsorption that is energetically preferred on clean Pt(111) and causes preferential NO adsorption in the atop site initially. For this oxygen coverage, some population of the bridge site occurs at the highest NO coverages, but occupation of this site can be eliminated completely by preadsorption of 0.75 ML of oxygen. This high coverage of coadsorbed oxygen now induces a further change in the nature of the NO chemisorption bond for NO adsorbed in atop sites, forming bent NO rather than the linear NO species formed on clean Pt(111). The saturation coverage of bent NO is 0.15 ML on this 0.75 ML oxygen-precovered surface and the heat of adsorption is only 1–2 kcal/mol less than linear NO adsorbed in atop sites on clean Pt(111). By using the HREELS and UPS data to identify these three chemically distinct forms of NO(a), we are able to rationalize their formation (and subsequent properties) in different electronic environments by correlating bonding configurations with the charge-transfer capabilities of the Pt substrate. Finally, we note that despite the presence of large excesses of O(a), NO is never oxidized to form NO₂, unlike the analogous facile oxidation of CO on Pt. This contrast in oxidation energetics is readily explained in terms of the measured relative barrier heights for oxidation versus desorption.

1. Introduction

A recent study has probed the effect of coadsorbed oxygen atoms at coverages as high as 0.75 monolayers (ML) on the adsorption of NO₂ on...
Pt(111) [1]. The adsorption of NO$_2$ is partially irreversible at oxygen coverages less than 0.75 ML, with adsorbed NO$_2$ decomposing to coadsorbed NO and oxygen atoms when heated to 170 K. At the time of this study, no information concerning the coadsorption of NO and oxygen atoms on Pt(111) for oxygen coverages greater than 0.25 ML was available. The need for understanding the interaction between oxygen atoms and NO on Pt surfaces in our NO$_2$ studies and also for a wide range of NO$_2$ catalytic reduction studies has prompted this report. In this paper, we have extended a previous study of the coadsorption of NO and oxygen atoms for $\theta_O \leq 0.25$ ML [2] to include oxygen coverages up to $\theta_O = 0.75$ ML (produced by NO$_2$ exposures at 400 K [3,4]). Temperature programmed desorption (TPD), high resolution electron energy loss spectroscopy (HREELS), and ultraviolet photoelectron spectroscopy (UPS) are used to characterize electronically induced changes in the binding of NO to Pt(111) due to the coadsorption of varying amounts of oxygen.

2. Experimental

The experiments were performed in a UHV chamber that has been described previously [5,6]. The system contains the instrumentation necessary to perform TPD, HREELS, UPS, Auger electron spectroscopy (AES) and low energy electron diffraction (LEED). Experiments were performed as a function of oxygen atom precoverage obtained by exposing the crystal to NO$_2$ at 400 K [3]. The chemical state of these high coverages of atomic oxygen has been studied in detail [3]. This oxygen atom precovered surface was then exposed to NO at 100 K. The heating rate in TPD was 15 K/s. No signals above background effects were detected upon heating the crystal except for 14, 16, 30 (NO) and 32 amu (O$_2$). For the exposures of NO necessary for the experiments reported here, no desorption of NO from the crystal supports could be detected (although this did occur when extremely large NO exposures were used in other work not reported here). No desorption of N$_2$ nor O$_2$ due to decomposition of NO was observed under any condition, clearly showing that NO dissociation observed in previous studies on Pt(111) crystals was due to defects [2,7–9]. The O$_2$ thermal desorption spectra for large oxygen atom coverages were identical to those observed previously [3].

HREELS spectra were obtained for specular scattering with $\theta_{\text{in}} = \theta_{\text{out}} = 65^\circ$ from the sample surface normal using an incident beam energy of 6 eV. UPS spectra were taken with a double-pass cylindrical mirror analyzer using a pass energy of 15 eV ($\Delta E = 0.25$ eV) and 25 eV ($\Delta E = 0.40$ eV) for He I and He II, respectively. The incidence angle for the UV light was 72$^\circ$ from the surface normal and the photoelectron collection angle was 42$^\circ$ from the surface normal.
Further information on the cleaning and characterization of the Pt(111) crystal, as well as the methods used to purify the NO and NO₂ is available [5].

3. Results

3.1. Thermal desorption of NO on Pt(111) + O(a)

Three NO thermal desorption spectra are shown in fig. 1. On the clean Pt(111) surface at 100 K, two high temperature desorption states (denoted as β₁ and β₂) and a low temperature desorption state can be populated by a saturation exposure of NO. This notation is different from that used by Campbell et al. [7], who labeled the defect site desorption state (centered about 450 K) as β₂ and the entire peak centered about 350 K as β₁. We
separate this latter peak characteristic of perfect Pt(111) sites into two components labeled $\beta_1$ and $\beta_2$ due to NO desorption from atop and two-fold bridge sites, respectively. The suggestion of a direct relationship between the desorption state and the adsorption site for NO on Pt(111) was first made by Gland and Sexton [2], who studied NO as a function of coverage using TPD and HREELS. We have independently confirmed these results, agree with their interpretation, and provide additional support for this assignment (vida infra).

Precovering the surface with 0.25 ML of oxygen atoms causes a large attenuation of the $\beta_1$ state, which is now present only as a high temperature shoulder on the $\beta_1$ state. This oxygen coverage has little effect on the $\beta_1$ population, since the $\beta_1$ desorption peak temperature is not shifted. The desorption of NO from the low temperature state shifts from 200 K down to 165 K and a small, new NO desorption state appears at 230 K. These observations are in agreement with the work of Gland and Sexton [2]. We find that the saturation coverage of NO is 70% of that found for the clean surface, based on the relative areas of the integrated NO TPD spectra.

When NO is coadsorbed with 0.75 ML of oxygen, the $\beta_1$ desorption peak temperature is lowered by only 15 K compared to clean Pt (or for 0.25 ML of oxygen on Pt), while the $\beta_2$ state has disappeared completely (as shown in the vibrational spectra of fig. 2). There are also two low temperature desorption states present, however these are different from the two low temperature desorption states observed for $\theta_O = 0.25$ ML. The population of the $\beta_1$ state is significantly decreased and the saturation coverage of NO is reduced further to 30% of the saturation coverage of NO on clean Pt(111). However, the activation energy for desorption (calculated using a pre-exponential factor of $10^{13}$) of the $\beta_1$ state of NO from the oxygen saturated surface is only slightly lower (18.9 kcal/mol) from that found on clean Pt(111) (19.9 kcal/mol).

The effect of oxygen preadsorption on the saturation coverage of NO on Pt(111) at 100 K is essentially a linear attenuation of $\theta_{NO}$ by $\theta_O$ (a plot of $\theta_{NO}$ versus $\theta_O$ yields a slope of $-1/2$), with two oxygen atoms required to block the adsorption of an NO molecule. Previous studies involving the coadsorption of NO$_2$, NO, and oxygen atoms on Pt(111) have shown that a total surface coverage of 0.9 ML can be achieved regardless of the relative coverages of the individual adsorbates [1,5]. This leads us to suggest that the NO saturation coverage is 0.15 ML when $\theta_O = 0.75$ ML. This allows the NO saturation coverage on clean Pt(111) at 100 K to be estimated at 0.5 ML, in close agreement with a coverage between 0.55 and 0.7 ML proposed by Gorte et al. [8], but substantially more than the 0.25 ML estimated by Hayden [9].

3.2. Vibrational spectroscopy of NO on Pt(111) + O$_{(\alpha)}$

On clean Pt(111), NO initially adsorbs in two-fold bridge sites at 100 K [2]. At higher coverages, NO occupies both two-fold bridge and atop sites. At
saturation NO coverage, the vibrational frequencies of NO adsorbed in an atop site are 290 and 1710 cm$^{-1}$ for the Pt–NO and the N–O stretching modes, respectively. For NO adsorbed in the two-fold bridge site, the vibrational frequencies of the same respective modes are 450 and 1490 cm$^{-1}$. Fig. 2 presents HREELS spectra of NO adsorbed at 100 K on Pt(111) precovered with oxygen atoms ($\theta_O = 0.25$ ML). A loss peak due to the Pt–O stretching mode of preadsorbed oxygen atoms occurs at 460 cm$^{-1}$. This peak is in good agreement with previous work [3,10]. It has also been shown that the position of this peak is essentially invariant with $\theta_O$ over this range ($\Delta \nu = 9$ cm$^{-1}$ for $\theta_O = 0.25–0.75$ ML) [3]. A small NO exposure of 0.15 L following preadsorption of 0.25 ML of oxygen yields an HREELS spectrum with an energy loss peak at 1740 cm$^{-1}$ due to the N–O stretching mode. This shows that NO initially prefers to occupy atop sites when $\theta_O = 0.25$ ML, in contrast to the site preference on clean Pt(111). The Pt–NO stretch peak of atop site NO at 280 cm$^{-1}$ is very weak at this low coverage of NO. This peak becomes more intense when the surface containing $\theta_O = 0.25$ ML is given a saturation exposure of NO. For this case, the loss peak at 1740 cm$^{-1}$ becomes more intense and a new energy loss peak is observed at 1520 cm$^{-1}$, corresponding to
NO adsorbed in a two-fold bridge site. The associated Pt–NO stretching frequency for this site is expected to be close to that found for bridge-bonded NO on clean Pt(111). Since the intensity of this mode relative to that of the NO stretching mode on the clean surface is quite low and we observe similar intensities at 450 and 1520 cm$^{-1}$, this indicates that the loss peak at 450 cm$^{-1}$ has contributions from both the Pt–NO stretch mode at $\approx 450$ cm$^{-1}$ and the Pt–O stretching mode at 460 cm$^{-1}$.

When the oxygen precovered surface with $\theta_O = 0.75$ ML is given a saturation exposure of NO, no loss peaks for NO bonded in a two-fold bridge site are observed, with NO found only in atop sites. Furthermore, no population of the two-fold bridge site occurs for lower coverages of NO at $\theta_O = 0.75$ ML. The NO stretching frequency is shifted up to 1775 cm$^{-1}$ and the Pt–NO stretching mode is shifted down to 265 cm$^{-1}$, while the Pt–O stretch is still present at 460 cm$^{-1}$. However, a new loss peak is seen as a distinctive shoulder at 510 cm$^{-1}$. The significance of this loss peak is discussed in detail below. The simplicity of this vibrational spectrum suggests that the three-peak desorption profile of NO when it is coadsorbed with 0.75 ML of oxygen atoms is due to NO bonded in atop sites that have different local environments with respect to the geometry of nearest-neighbor oxygen atoms, rather than NO possessing three different binding sites. This is similar to the explanation offered for the observed states of NO when it is coadsorbed with smaller coverages of oxygen [2].

The singleton N–O stretching frequencies obtained by extrapolation to the zero NO coverage limit are 1476 and 1698 cm$^{-1}$ for the respective two-fold bridge and atop site NO species on clean Pt(111) at 100 K [9]. We observe an upward frequency shift of approximately 43 cm$^{-1}$ for both adsorption sites of NO in the presence of $\theta_O = 0.25$ ML. This is in agreement with past work [2] indicating a 30 cm$^{-1}$ shift in the presence of $O_{(a)}$. In addition, we observe that for $\theta_O = 0.75$ ML, the atop site NO stretching frequency is shifted 65 cm$^{-1}$ higher than that for a saturation coverage of NO on the clean surface and 77 cm$^{-1}$ higher than the singleton atop site NO stretching frequency. Furthermore, as the oxygen coverage increases, the frequency of the Pt–NO stretch decreases. These changes are similar to those seen when NO is coadsorbed with oxygen atoms on Ru(001) and Rh(111) [11–13]. The presence of segregated O and NO islands (i.e., regions on the surface containing high local concentrations of NO) is unlikely, since there is no evidence of NO adsorbed in two-fold bridge sites nor is an ordered LEED pattern obtained when $\theta_O = 0.75$ ML. As island formation has been ruled out and since only low coverages of NO are present when $\theta_O = 0.75$ ML, we conclude that the upward frequency shifts observed with coadsorbed oxygen are not due to increased dipole coupling between adsorbed NO molecules, but rather due to a chemical effect of coadsorbed oxygen acting to increase the NO bond order.

At the highest oxygen coverage examined, coadsorbed oxygen not only
changes the adsorption site, but also the NO bonding geometry. The loss at 510 cm\(^{-1}\) in the top spectrum of fig. 2 must be assigned to a Pt–NO bending mode, since the Pt–O stretching mode is invariant with oxygen coverage in the absence of coadsorbed NO [3] and since coadsorbed NO is expected to have a minimal effect on the potential well of the strongly adsorbed oxygen adatoms. The observation of a Pt–NO bending mode in specular scattering in HREELS means that NO is adsorbed in a low symmetry "bent" configuration, such that the bending mode exhibits a large dipole moment perpendicular to the surface (required by the dipole selection rule for specular scattering [14]). This assignment is consistent with studies of several Pt nitrosyl complexes [15] identifying Pt–NO stretching frequencies of 283–291 cm\(^{-1}\), Pt–N–O bending frequencies of 540–569 cm\(^{-1}\), and N–O stretching frequencies of 1680–1730 cm\(^{-1}\), as well as with similar results for Fe and Co nitrosyls [16]. We point out that the frequencies of the NO stretching mode in bent nitrosyl complexes have been known to be as low as 1525 cm\(^{-1}\) and as high as 1844 cm\(^{-1}\) [17–19]. Furthermore, we can compare this assignment with that of bent NO species identified on other metal surfaces. On reconstructed Pt(100)-5 \( \times \) 20, Pirug et al. [20] assigned HREELS loss peaks of 310, 465, and 1690 cm\(^{-1}\) to the Pt–NO stretch, Pt–N–O bend, and N–O stretch vibrations, respectively. Assignments of bent NO have also been made on Ni(111) [21] and on Cu(100) [22].

3.3. Ultraviolet photoelectron spectroscopy of NO on Pt(111) + O\(_{\text{ad}}\)

The HREELS data indicate that NO bonds in three chemically distinct modes: (i) two-fold bridge bonding on clean Pt(111) and for saturation coverages of NO when \( \theta_0 = 0.25 \text{ ML} \); (ii) linear atop bonding for high \( \theta_\text{NO} \) on clean Pt(111) and for any \( \theta_\text{NO} \) on Pt(111) with \( \theta_0 = 0.25 \text{ ML} \); and (iii) bent atop bonding for \( \theta_0 = 0.75 \text{ ML} \) on Pt(111). In order to probe the electronic structure (and hence the molecular geometry) more directly, we have obtained the valence electronic spectra for NO chemisorbed on these surfaces using UPS. In figs. 3–6 are shown the HeII and HeI UPS spectra for NO\(_{\text{(a)}}\) on Pt(111) in the presence of varying amounts of chemisorbed oxygen. Fig. 3 shows the UPS spectra for bridging NO on clean Pt(111), obtained by heating a saturation coverage of NO on Pt(111) to 340 K to remove all linear atop NO. Fig. 4b shows the UPS spectra for a saturation coverage of NO on clean Pt(111) at 100 K. Subtraction of the UPS spectra for bridging NO (fig. 4a) from these spectra yields the UPS difference spectra (fig. 4c) for linear atop NO on clear Pt(111). Fig. 5 also shows the UPS spectra for linear atop NO, obtained by producing nearly a saturation coverage of NO on Pt(111) + 0.25 ML O\(_{\text{(a)}}\), in order to ensure a high coverage of linear atop NO exists without any bridging NO. Fig. 6 shows UPS spectra of bent atop NO, obtained by forming a saturation coverage of NO on Pt(111) + 0.75 ML O\(_{\text{(a)}}\).
Fig. 3. UPS spectra for both HeII (top panel) and HeI (bottom panel) photon energies for (a) clean Pt(111), (b) saturation coverage of NO on Pt(111) which was heated to 340 K, and (c) difference spectra of two-fold bridging NO chemisorbed on Pt(111). Spectra were obtained from the same surfaces immediately following the UPS measurements to verify the identity of the adsorbed NO species.

Fig. 7 summarizes these data and compares the energy levels of gas-phase NO with NO chemisorbed in different bonding modes. In the UPS spectrum of gas-phase NO, binding energies of ≈ 9.3, ≈ 16.9, ≈ 17.4, and ≈ 21.0 eV (referenced to the vacuum level, $E_{\text{vac}}$) are ascribed to the $2\pi$, $1\pi$, $5\sigma$, and $4\sigma$
Fig. 4. UPS spectra for both HeII (top panel) and HeI (bottom panel) photon energies for (a) saturation coverage of NO on Pt(111) which was heated to 340 K (bridging NO), (b) saturation coverage of NO on Pt(111) at 100 K (bridging and linear atop NO), and (c) difference spectra of linear atop NO chemisorbed on Pt(111).

energy levels of NO, respectively [23]. The photoelectron spectrum of NO$_{\text{g}}$ is comparatively complicated due to overlapping vibrational manifolds of the several electronic final states caused by the unpaired electron in the 2$\pi$ orbital. This causes two spin-split states of the $\sigma$ levels and a multiplet of terms for the 1$\pi$ level, which heavily overlaps the 5$\sigma$ levels, as shown in fig. 7.
In order to assign the UPS peaks in figs. 3–6 to energy levels in chemisorbed NO, we rely on comparisons to NO\textsubscript{(g)} and to UPS spectra of CO\textsubscript{(a)} on Pt(111) [24]. The final-state relaxation shifts that occur upon adsorption are approximately the same for each level and can be accounted for reasonably by a rigid shift of the gas-phase energy levels to align an orbital not involved in the chemisorption bonding with the corresponding orbital in the adsorbate. In
Fig. 6. UPS spectra for both He II (top panel) and He I (bottom panel) photon energies for (a) 0.75 ML O\(_\text{ad}\) on Pt(111), (b) saturation coverage of NO on Pt(111) + 0.75 ML O\(_\text{ad}\), and (c) difference spectra of bent atop NO chemisorbed on Pt(111) + 0.75 ML O\(_\text{ad}\).

fig. 7, we have aligned the centroid of the NO\(_\text{(g)}\) 4\(\sigma\) level with the 4\(\sigma\) level of bent atop bond NO since this 4\(\sigma\) level is not expected to be involved in the Pt–NO bond (vida infra). Since the separation of the 2\(\pi\), 1\(\pi + 5\sigma\), and 4\(\sigma\) levels in NO\(_\text{(g)}\) is so large, we expect that the relative ordering of the valence levels to remain unchanged upon adsorption and that we will observe three distinct peaks in the UPS spectra of NO\(_\text{(g)}\). The He II difference spectra in figs.
3–6 indicate binding energies of ≈ 3, ≈ 10, and ≈ 14 eV for the $2\pi$, $1\pi + 5\sigma$, and $4\sigma$ levels of NO adsorbed on Pt(111). The He I difference spectra in figs. 3–6 support our assignment of the peaks near 3 and 10 eV as due to the $2\pi$ and $1\pi$ levels, respectively. Two observations lead us to conclude that the large peak in both He II and He I spectra is essentially due to the $1\pi$ level of NO$_{(a)}$. It is well known that using a He I photon energy (21.2 eV) gives a relative enhancement in photoemission sensitivity of adsorbate-derived $\pi$ levels over $\sigma$ levels compared to using a He II photon energy (40.8 eV) (see, for example, ref. [25]). This leads, for instance, to a relatively clean resolution of $5\sigma$ and $1\pi$ derived levels for CO$_{(a)}$ on Pt(111) [26]. However, no shift occurs in the large peak near 10 eV upon changing from He II to He I excitation. This indicates
primarily a $1\pi$ contribution to the peak in both spectra. Also, we observe that the $4\sigma$ level of NO$_{(a)}$ has a much lower cross-section in HeII spectra than the $4\sigma$ level of CO$_{(a)}$, consistent with other synchrotron radiation studies of NO$_{(a)}$ [25]. Another indication that the large peak near 10 eV is primarily due to the $1\pi$ level comes from assuming that the $5\sigma$ level has a similar cross-section to the $4\sigma$ level of NO$_{(a)}$ and hence is also very weak even at HeII excitation energies. Due to the near overlap of the much stronger $1\pi$ emission with that from the $5\sigma$ level, it is very difficult to identify the $5\sigma$ binding energy except in fig. 3, where the binding energies are different enough to observe emission from the $5\sigma$ level. In fig. 3, the $4\sigma$ and $5\sigma$ peaks have similar (very weak) intensities. In the other figures, we propose that the $5\sigma$ peak shifts to lower binding energy and is not resolved from the more intense $1\pi$ peak. However, a predicted binding energy of the $5\sigma$ level of bent NO is given in parentheses in fig. 7. A rationale for all of the UPS assignments is given in the discussion (section 4).

In the course of obtaining the photoemission spectra, work function measurements were made using the low kinetic energy onsets of the energy distribution curves. The work function changes observed are consistent with the existence of three chemically distinct NO$_{(a)}$ species, since both the signs and magnitudes of the adsorbate–surface dipoles are unique for each case. Clean Pt(111) has a work function of $\phi = 5.70$ eV. Addition of $= 0.25$ ML of bridging NO increases $\phi$ to 5.78 eV, with $\Delta\phi = +0.08$ eV. Pt(111) at 100 K with a saturation coverage of NO (bridging and linear atop) has $\phi = 5.50$ eV, with $\Delta\phi = -0.20$ eV. This indicates that addition of $= 0.25$ ML of linear atop NO causes $\Delta\phi = -0.28$ eV. Adsorption of $\theta_O = 0.25$ ML on clean Pt(111) increases $\phi$ to 5.84 eV. Subsequent adsorption of $\sim 0.25$ ML of linear atop NO decreases $\phi$ to 5.45 eV, with $\Delta\phi = -0.39$ eV. Adsorption of $\theta_O = 0.75$ ML on clean Pt(111) increases $\phi$ to 6.2 eV. Subsequent adsorption of $\sim 0.15$ ML of bent atop NO decreases $\phi$ to 5.5 eV, with $\Delta\phi = -0.7$ eV.

Given the work function information and these general UPS assignments for the four valence molecular orbitals of NO$_{(a)}$, a logical rationalization of the location of the energy levels for NO adsorbed in each of the three bonding geometries (induced by varying amounts of adsorbed oxygen) may be constructed and is given in the next section.

4. Discussion

4.1. Bonding in the Pt(111)–NO surface complex

The changes that occur in the chemisorption bonding of NO due to coadsorbed oxygen atoms on Pt(111) can be explained as follows. A first-order description for the bonding of NO to a metal surface is obtained by analogy
with the bonding found in transition-metal–nitrosyl complexes [27]. Thus, adsorbed NO may bond to the surface in three ways:

(a) **terminally bonded (atop), linear** NO, where the nitrosyl is bound to the metal via a donor $\sigma$ bond, comprised of the $N$ lone pair (primarily $N\ 2s$) delocalizing into an empty metal $\sigma$ orbital, and a covalent $\pi$ bond, formed from the unpaired $2\pi$ electron (primarily $N\ 2p$) and a metal $d\pi$ electron; (b) **terminally bonded (atop), bent** NO, where the nitrosyl utilizes the $NO\ 2\pi$ unpaired electron and a metal $\sigma$ electron to form a covalent $\sigma$ bond (leaving the $5\sigma$ or $N\ 2s$ lone pair non-bonding); and (c) **bridging** NO, where the $5\sigma$ lone pair and unpaired $2\pi$ electron are used respectively to form a donor $\sigma$ bond to one metal atom and a covalent $\sigma$ bond to another metal atom (of course, the actual bonds are a linear combination of two resonance structures).

This bonding description leads to the prediction of a splitting of the once doubly-degenerate $2\pi$ level (in the gas-phase diatomic molecule) into a level at high binding energy corresponding to the Pt–N covalent $\sigma$ bond (comprised of the $2\pi$ electron and Pt $d\pi$ electron) and a level at low binding energy corresponding to the empty $NO\ 2\pi$ antibonding orbital which acts as an acceptor for Pt $d\pi$ backbonding.

Two of these three adsorbed species are good $\pi$-acceptor ligands: terminally bonded, linear NO and bridging NO. In these cases, the interaction of the partially unoccupied $2\pi$ orbital with a filled metal $d\pi$ orbital results in a delocalization of electron density from the metal onto the nitrosyl ligand (i.e. $\pi$-backbonding). This $\pi$-backbonding contribution to the bonding can be significant, resulting in a decreased N–O bond order upon adsorption. However, adsorbed oxygen atoms withdraw considerable amounts of charge from nearby Pt atoms, modifying the surface electronic structure, as evidenced by the increase in the work function. The work function increases linearly as the oxygen coverage is increased on Pt(111), with a work function change of $+0.60\ eV$ at $\theta_0 = 0.75\ ML$ [3]. The reduction in electron density at each Pt surface atom decreases the amount of electron donation into the $2\pi$ orbital of adsorbed NO. This leads to a change in the relative stabilities of NO adsorption geometries, an increase in the NO bond order, and a decrease in the Pt–NO bond order. Evidently, NO adsorbed in the two-fold bridge site has the strongest component of backbonding in its chemisorption bond, since this configuration is destabilized immediately upon adding oxygen adatoms.
By contrast, the heat of adsorption of NO adsorbed in atop sites is essentially unaffected, as evidenced by the absence of a shift in the TPD peak temperature. At the highest coverages of coadsorbed oxygen, the capacity of surface Pt atoms to transfer charge into the NO2\pi orbital is severely reduced. Since it is terminally bonded, bent NO is bound primarily via a covalent Pt–N bond, with \pi-backbonding contributing negligibly to the Pt–NO bond (by symmetry arguments it is obvious that there is poor overlap of the Pt d\pi orbital with the NO2\pi orbital). Thus, unlike the other NO species which would like to accept \pi-electron density from Pt, bent NO should readily coadsorb with high coverages of oxygen adatoms. It is interesting that the heats of adsorption are very similar for all three NO species (within a few kcal/mol). This situation will make it challenging for theoretical calculations to correctly identify the favored bonding site and geometry for NO on Pt, and also points to the possibility that all three species could play important roles in catalytic reactions involving NO.

4.2. Electronic structure of chemisorbed NO

Identification of bent, linear, and bridging NO from HREELS data allows greater insight into the valence electronic energy levels observed in the UV photoelectron spectra (figs. 3–6) of NO\(_{(a)}\) on clean and oxygen-precovered Pt(111). In particular, given the \pi-accepting capabilities of each NO species (a)–(c) above, we predict a priori the relative positions of each of the valence molecular orbitals in adsorbed NO. These predictions and subsequent assignments of the UPS peaks are summarized in the energy level diagram shown in fig. 7. As discussed above, bridging NO appears to be the best \pi-acceptor, which is not surprising since bridging NO interacts with more than one Pt atom and is aligned such that good overlap may be obtained between the 2\pi orbital of NO and more than one set of Pt d\pi orbitals. Linear NO must be the next best \pi-acceptor, since its 2\pi orbital is aligned to obtain good overlap with the d\pi orbitals of one Pt atom. Bent NO is clearly the worst \pi-acceptor since its 2\pi orbital is not aligned to achieve high overlap with any of the d\pi orbitals of Pt. The general trend of the change in work function induced by NO adsorption is consistent with decreasing backbonding in the order outlined above.

When oxygen is coadsorbed with NO, the effect is to reduce \pi-backbonding and to enhance \sigma-donation from NO to Pt, since the Pt atoms at the surface are now more electrophilic. Thus, in the presence of oxygen, we expect the 5\sigma level (N 2s lone pair) to increase in binding energy due to more extensive delocalization of the 5\sigma electrons on to the metal. Similarly, we expect the 2\pi level to increase in binding energy due to less charge transfer from Pt to NO, while the 1\pi and 4\sigma levels are expected to remain essentially unchanged from NO adsorbed on clean Pt(111), due to their nonbonding nature with respect to
the surface. The extent to which each of the species (a)–(c) respond is dependent on their σ-donation and π-acceptor capabilities. Thus, we expect the UPS of bridging NO to be the most affected, linear NO to be moderately perturbed, with bent NO remaining largely unaffected by the presence of added oxygen.

Although we should keep the above points in mind, the major influence by far that oxygen has over the nature of the UPS spectra is simply to dictate which NO species predominates for a given set of laboratory conditions. Consider the 2π level of adsorbed NO. We have assigned (fig. 7) peaks for bridging, linear, and bent NO at 2.1, 2.9, and 3.3 eV to be due to the 2π level. The other once-degenerate 2π level (in gas-phase NO) corresponding to the Pt–N covalent σ bond is expected to appear at significantly higher binding energies. Due to the poor cross-section in He I and He II UPS spectra for σ levels in adsorbed NO and due to the presence of the Pt d-band, this level is not resolved. Thus, the following discussion refers only to trends in the 4σ, 5σ, 1π, and 2π-derived levels in adsorbed NO. We expect that bridging NO will have the smallest 2π binding energy, followed by linear NO, with bent NO possessing the largest binding energy for the 2π level, since the greater the π-accepting capabilities of the adsorbate, the more electron density is transferred to the NO 2π orbital, thereby decreasing its binding energy.

The other level expected to show a large shift depending upon the adsorption geometry is the 5σ orbital. Since both linear atop and bridging NO donate charge to the surface while bent NO does not, we expect the 5σ levels for bridging and linear atop NO to be seen at larger binding energies than for bent NO. Furthermore, we expect the 1π levels of NO to shift according to their degree of destabilization, which is proportional to the amount of π-back-donation. Thus, the 1π level of bridging NO should be least bound, followed by linear atop NO, with the 1π level of bent NO having the greatest binding energy.

Since the 1π level is greatly broadened and potentially overlaps the 5σ level, it is difficult to test these predictions from the data in figs. 3–6. However, the 1π level is expected to decrease in binding energy in the order bent, linear, and bridging, consistent with our assignment of the peaks at 10.0, 9.5 and 9.4, and 9.1 eV to the 1π level of NO(a) in each of those respective species. Since the 5σ level is involved in forming a donor σ bond to the metal for bridging and linear NO, we expect that this level would be stabilized relative to the 1π and 4σ levels upon adsorption. For example, the 5σ level in CO(a) on Pt(111) relative to gas-phase CO is shifted ~ 3 eV to higher binding energy [21], leading to the well-known change in the ordering of the 5σ and 1π energy levels compared to the gas phase. The 5σ level is predicted to have a higher binding energy for bridging and linear NO than for bent NO. Thus, assignment of the large peaks near 10 eV in both the He II and He I spectra to the 5σ level would be inconsistent with the expected shift from the gas phase
upon adsorption to form bridging NO and also the expected shift as the adsorption geometry changes from bridging to linear atop to bent NO. Therefore we tentatively assign the weak peak at 12.2 eV for bridging NO to be due to $5\sigma$-derived transitions, and predict that this peak shifts to 10.7 eV for bent NO. This predicted shift to lower binding energy is consistent with our UPS data.

By contrast, the $4\sigma$ levels are broadened, but all are close in energy, consistent with the nonbonding nature of the $4\sigma$ molecular orbital. Since both the $4\sigma$ and $5\sigma$ levels are nonbonding for bent NO, one would expect that the $(4\sigma-5\sigma)$ separation in this species would be similar to the gas-phase $(4\sigma-5\sigma)$ separation of 3.6 eV. The $(4\sigma-1\pi)$ separation of \( \approx 4.1 \) eV in the gas phase should be slightly smaller than the $(4\sigma-1\pi)$ separation of NO$_{(a)}$ due to slight destabilization of the $1\pi$ level due to backbonding. We observe a $(4\sigma-1\pi)$ separation of 4.3-4.5 eV for both linear atop and bent NO$_{(a)}$ and 5.8 eV for bridging NO$_{(a)}$. It also appears that the $4\sigma$ level of bridging NO is relatively stabilized, possibly due to some involvement in the stronger $\sigma$ donor bond of that species.

As expected, the valence level shifts observed in UPS as a function of adsorbate geometry are the most dramatic for the bonding $2\pi$ level (1.2 eV) (and we predict a shift of the bonding $5\sigma$ level of 1.5 eV), whereas the nonbonding $1\pi$ and $4\sigma$ levels vary by 0.9-1.0 eV. Utilizing simple ideas of charge transfer to and from the various molecular orbitals of NO, we have been able to provide logical assignments for the valence levels of NO on clean and oxygen-precovered Pt(111). Unfortunately, we cannot determine the binding energy of the Pt–NO covalent $\sigma$ bond that is the dominant contribution to the NO chemisorption bond. However, the binding energy of this level is not expected to shift much as a function of adsorbate geometry, since the Pt–N covalent $\sigma$ bond is present in each of the three isomers.

Perhaps the most important conclusion of this work is that the covalent $\sigma$ or $\pi$ bonds formed to the platinum surface using the $2\pi$ electron in NO dominate the strength of the Pt–NO bond. This conclusion stems from the fact that surface oxygen has little effect on the heat of adsorption of NO on Pt(111), but O$_{(a)}$ has a dramatic influence on the nature of the chemisorption bond. In particular, since bent NO has neither $\sigma$-donor nor any $\pi$-backbonding capability, yet has essentially the same heat of adsorption as those species with $\pi$ backbonding and $5\sigma$ donation, the covalent $\sigma$ bond for bent atop and bridging NO and the covalent $\pi$ bond of linear atop NO must dominate the chemisorption. Furthermore, contributions to the chemisorption bond strength from $5\sigma$ donation and $2\pi$ backbonding are not very important. This is in stark contrast to the usual bonding description given for CO adsorbed on metal surfaces.
4.3. NO adsorption sites and desorption states

On the clean Pt(111) surface, two NO desorption states, $\beta_1$ and $\beta_2$, are populated by a saturation coverage of NO. HREELS annealing experiments provide evidence that the respective $\beta_1$ and $\beta_2$ desorption states correspond specifically to NO bonded in atop and two-fold bridge sites [2]. Our work shows that at low oxygen coverages ($\theta_O = 0.25$ ML), the population of the $\beta_2$ desorption state and the amount of NO bonded in two-fold bridge sites is greatly attenuated. When the surface is saturated with oxygen at $\theta_O = 0.75$ ML, the opportunity for NO to bond in a two-fold bridge site is completely removed and NO no longer desorbs from the $\beta_2$ state. Instead, on the oxygen-saturated surface, NO adsorbs exclusively in atop sites, concomitant with a reduction in the population of the $\beta_1$ desorption state. NO$_2$ adsorption studies on Pt(111) [15] have shown that the oxygen adatoms derived from NO$_2$ decomposition also dictate the adsorption site preference for the NO formed from NO$_2$ decomposition. Specifically, NO is adsorbed in two-fold bridge sites when $\theta_O < 0.25$ ML, and NO desorbs from the $\beta_2$ state. The activation energy for NO desorption from this state is very sensitive to the oxygen atom coverage and decreases as $\theta_O$ increases. When $\theta_O > 0.25$ ML, NO is adsorbed in atop sites and NO desorbs from the $\beta_1$ state. The activation energy for NO desorption from this state is insensitive to the oxygen atom coverage, which can go as high as $\theta_O = 0.4$ ML from the partial decomposition of NO$_2$.

These collective observations provide strong evidence for a 1:1 correspondence between the desorption state and the adsorption site for NO on Pt(111), as suggested earlier [2]; the $\beta_2$ state is the result of the desorption of NO from a two-fold bridge site and the $\beta_1$ state is the result of the desorption of NO from an atop site. HREELS spectra taken at temperatures corresponding to the $\beta_1$ NO desorption state (when $\theta_O = 0.75$ ML) would be expected to confirm that only atop site NO is present at the time of desorption. This approach would unambiguously discriminate against reversible changes in the NO adsorption geometry (for which HREELS annealing experiments are insensitive).

4.4. Comparison of NO and CO oxidation on Pt(111)

A final surprising result is that NO$_2$ is not formed for any coverage of oxygen atoms coadsorbed with NO on Pt(111). The $\mu$-N–O-nitro (side-bonded NO$_2$) and the nitro (N-bonded NO$_2$) adsorption isomers, which have been identified with HREELS in the presence of oxygen atoms on Pt(111) at 100 K [1], would have been identified easily. Also, mass 46 was not detected during TPD, showing that NO$_2$ did not desorb upon raising the crystal temperature.

The lack of NO oxidation is an interesting contrast to the facile reaction between coadsorbed CO and oxygen atoms to produce CO$_2$ on Pt(111) [28].
The energetic differences between the two distinct reaction pathways of NO(a) – O(g) and CO(a) + O(g) are shown in fig. 8 to be the relative barrier heights to NO or CO desorption as compared with the barriers to formation of adsorbed NO2 or CO2. The potential energy diagram in fig. 8 shows adiabatic curves for these reactions with energies calculated using heats of formation (∆Hf) for the various species. The energy zero is the heat of formation of the elements in their standard states, i.e. ∆Hf,298(No(g)) = ∆Hf,298(N2(g)) = 0. Heats of formation of adsorbates, ∆Hf(No), are calculated using the heats of formation of the corresponding gas-phase species and the surface–adsorbate bond energies, D(M–X), according to ∆Hf(No) = ∆Hf,298(X) – D(M–X). The heats of formation of the gas-phase species were taken directly from Benson's compilation [29]: ∆Hf,298(NO(g)) = 21.6 kcal/mol, ∆Hf,298(NO2(g)) = 7.9 kcal/mol, ∆Hf,298(CO(g)) = −26.4 kcal/mol, ∆Hf,298(CO2(g)) = −94.05 kcal/mol, and ∆Hf,298(O(g)) = 59.6 kcal/mol using D(O–O)(g) = 119 kcal/mol. Heats of formation of the molecularly adsorbed species were obtained as described above using the measured heats of adsorption as the surface–adsorbate bond energy. We used ∆Hads(NO) = 19 kcal/mol (independent of θO) [this work], ∆Hads(NO2) = 19 kcal/mol (θO = 0.25) and 11 kcal/mol (θO = 0.75) [1,5], ∆Hads(CO) = 32 kcal/mol (θO = 0) [30], and ∆Hads(CO2) = 2 kcal/mol (θO = 0) [31]. The resulting heats of formation of the molecularly adsorbed species are ∆Hf(NO(g)) = 2.6 kcal/mol (independent of θO), ∆Hf(NO2(g)) = −11 kcal/mol (θO = 0.25) and −3.1 kcal/mol (θO = 0.75), ∆Hf(CO(g)) = −58.4 kcal/mol (θO = 0), and ∆Hf(CO2(g)) = −96.1 kcal/mol (θO = 0). Recent data on the thermal desorption of O2 from Pt(111) for θO = 0.25–0.75 [3], where D(Pt–O) was determined to be 85 kcal/mol (θO = 0) and estimated to be 77 kcal/mol (θO = 0.25) and 60 kcal/mol (θO = 0.75) was used to determine the heats of formation of adsorbed oxygen atoms as ∆Hf(O(g)) = −25.4 kcal/mol (θO = 0) and −17.4 kcal/mol (θO = 0.25) and 0 kcal/mol (θO = 0.75). Heats of formation for coadsorbed species were taken as the simple sum of the heats of formation of the separately adsorbed species, but as determined for the proper chemical state of the surface.

At oxygen coverages of 0.25 ML (solid curve in fig. 8a), formation of NO2(g) from NO(g) + O(g) is endothermic by 3.7 kcal/mol. Thus, warming a coadsorbed NO(a) + O(a) layer leads to desorption of NO2(g) rather than NO2(g). Formation of NO2(a) from NO(g) + O(g) is exothermic by 15.3 kcal/mol, but the presence of a large barrier separating the NO(a) + O(a) well from the NO2(a) accounts for our lack of observation of NO2(a). If one starts with NO(a) + O(a), the activation energy associated with desorbing NO is 19 kcal/mol, as measured from the desorption spectra presented in fig. 1. Previous measurements [1,5] of NO2 decomposition have shown that NO2 decomposition competes effectively with NO2 decomposition for θO ≥ 0.25 ML. This indicates that the barrier for side-bonded NO2 to decompose to NO(a) + O(a) is about 19 kcal/mol for θO = 0.25 ML. Formation of side-bonded NO2(a) from NO(a) +
Fig. 8. Reaction coordinates comparing the energetics of the oxidation and desorption of (a) NO and (b) CO when coadsorbed with oxygen atoms on Pt(111). The solid and hatched curves in (a) refer to $\theta_O = 0.25$ ML and $\theta_O = 0.75$ ML, respectively.
O\(_{(a)}\) is endothermic by 3.7 kcal/mol. Therefore, the barrier to producing side-bonded NO\(_{2(a)}\) from NO\(_{(a)}\) + O\(_{(a)}\) is estimated to be 23 kcal/mol.

Due to the decrease in the Pt–O bond strength at \(\theta_O = 0.75\) ML [3] (hatched curve in fig. 8a), formation of NO\(_{2(g)}\) from NO\(_{(g)}\) + O\(_{(a)}\) is exothermic by 13.7 kcal/mol. Only a large (> 19 kcal/mol) barrier to the oxidation of NO\(_{(a)}\) prohibits the formation of NO\(_{2(g)}\) and instead leads to desorption of NO\(_{(g)}\) upon warming the coadsorbed NO\(_{(a)}\) + O\(_{(a)}\) layer. The barrier to producing the nitro adsorption isomer of NO\(_{2(a)}\) from NO\(_{(a)}\) + O\(_{(a)}\) is estimated to be also about 23 kcal/mol and shows that the formation of this species is clearly the rate-determining step in producing NO\(_{2(g)}\). This is also consistent with our previous measurements [1] that show that no decomposition of nitro-bonded NO\(_{2(a)}\) occurs, since the barrier at \(\theta_O = 0.75\) ML to NO\(_{2(a)}\) decomposition is estimated to be larger than 19 kcal/mol. For any oxygen coverage, the barriers to NO oxidation are larger than the barrier to NO desorption, explaining our lack of observation of NO\(_2\) formation.

Since CO\(_{2(a)}\) is only weakly bonded to Pt(111), its formation is also the rate-limiting step in the CO oxidation process. An \(E_a = 11\) kcal/mol has been measured for the reaction between CO\(_{(a)}\) + O\(_{(a)}\) to form CO\(_{2(g)}\) when \(\theta_O = 0.25\) ML [28]. Kinetic measurements in our laboratory indicate that the barrier for this reaction is even lower when \(\theta_O = 0.75\) ML [32]. Due to the facile formation of CO\(_2\) upon heating, the effect of coadsorbed oxygen on the CO binding energy is not measured easily using TPD. However, if one assumes that the adsorption energy for CO is not a strong function of oxygen atom coverage, as we have determined in this study for NO (although we expect a stronger effect of oxygen adatoms on CO), then the barrier for CO desorption is close to 32 kcal/mol (the activation energy for CO desorption on clean Pt(111)). Thus, the barrier to CO\(_2\) formation is much less than that for CO desorption. This leads to CO oxidation upon warming the coadsorbed layer rather than desorption of CO.

5. Conclusion

We have presented a comprehensive picture of the effect of added oxygen on the interaction of NO with Pt(111), using three independent surface structural probes: TPD, HREELS, and UPS. The data clearly indicate the presence of three unique adsorption geometries for NO on a metal surface: bridging, linear atop, and bent atop NO. The relative stabilities of these three distinct species is dramatically affected by the amount of oxygen present. The HREELS and UPS data can be understood readily by using simple concepts of charge transfer (dictated by \(\theta_O\)) from and to the 5\(\pi\) and 2\(\pi\) levels of NO. Combining these results with the TPD data allows an unambiguous assignment of the \(\beta_1\) and \(\beta_2\) peaks for NO in the TPD spectrum to linear atop and
bridging NO, respectively. Since the heats of adsorption of all three species are very similar, we conclude that the dominant contribution to the Pt–NO bond is a covalent $\sigma$ or $\pi$ interaction ($\sigma$ for bent atop and bridging NO, $\pi$ for linear atop NO) between the 2$\pi$ electron of NO and a Pt$d$ electron. Finally, extraction of the barrier to desorption versus oxidation has been used to explain the lack of NO oxidation and the facile oxidation of CO on the same Pt surface.

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References


[26] In HeI spectra of CO$_{ads}$ on Pt(111) at 100 K [24], the 4σ peak has a very low intensity (almost not observable) and the 1π + 5σ peak has a maximum at 8.4 eV. In HeII spectra, the 4σ peak has a large intensity at 11.8 eV and the 1π + 5σ peak has a maximum at 9.3 eV. Thus, the 1π + 5σ peak in each spectrum can be deconvoluted into two peaks very nicely with the 5σ level at 9.3 eV and the 1π level at 8.4 eV.
