

Site Switching and Surface Restructuring Induced by NO Adsorption on Pt{110}

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Received: February 11, 1998; In Final Form: April 17, 1998

We present the first infrared vibrational study of the adsorption of NO on Pt{110} over a wide range of temperatures. Adsorption is strongly dependent on both temperature and coverage, with many different species being formed on the surface. Under all conditions, site switching is observed during NO adsorption: at low coverages bridge-bonded species are formed on the surface, and at very high coverage NO switches to on-top sites. Other species, not previously reported, are also observed, depending on both adsorption temperature and coverage. The clean Pt{110} surface exhibits a (1×2) surface reconstruction which can be lifted by the adsorption of NO (or CO), depending on surface temperature and adsorbate coverage. In contrast to CO adsorption, the on-top surface species shows different frequencies on the (1×2) and (1×1) surface phases, and this is deployed to identify the temperature at which the reconstruction begins to lift.

Introduction

The adsorption and reaction of NO on transition-metal surfaces are of great scientific and technological interest. The reduction of NO_x products to N₂ and O₂ is one of the important reactions in the three-way car exhaust catalyst, and yet the mechanism of this reaction is not at all well understood. Pt is an important component of this catalyst. In addition, the adsorption of NO is particularly interesting due to its amphoteric bonding nature to a surface, arising from the presence of a single unpaired electron in the antibonding $2\pi^*$ orbital of NO. The molecule can either donate electron density to the surface or accept electron density from the surface. The result is that the chemistry of NO is much more complex than that of CO, with an extensive range of vibrational frequencies being observed for NO species adsorbed on surfaces. Here we present a reflection–absorption infrared spectroscopy (RAIRS) study of the adsorption of NO on Pt{110} over the temperature range 90–300 K. Pt{110} is the most open of the low-index Pt surfaces and provides a range of different sites for adsorption. The surface is also prone to restructuring, which adds another dimension of complexity to the study.

Clean Pt{110} exhibits a (1×2) missing row reconstruction, with every other row missing in the [001] direction.^{1,2} Adsorption of various molecules, such as CO and NO, leads to a lifting of this reconstruction back to the (1×1) bulk truncated surface phase, which is dependent both on surface temperature and on coverage. For the adsorption of CO on Pt{110} no lifting of the reconstruction occurs below ~250 K or below 0.2 ML coverage of adsorbate.³ Similar effects may be expected for NO adsorption.

There are relatively few previous studies of the adsorption of NO on Pt{110}^{4–12} and only one vibrational study:⁴ an electron energy loss spectroscopy (EELS) study which showed that the adsorption of NO on Pt{110} is always molecular. Two species were seen on the surface⁴ that gave rise to losses at ~1610 and 1760 cm⁻¹. These were assigned to bridged and on-top species, respectively. The presence or absence of these species on the surface depended on both surface temperature and coverage. Adsorption at 100 K produced a broad band in the EELS spectrum centered at 1690 cm⁻¹ which split into two

bands at 1620 and 1750 cm⁻¹ upon heating to 200 K. For overlayers that contained less than 30% of the total saturation coverage, only the band at 1610 cm⁻¹ was observed over the entire temperature range from 100 to 300 K. The results showed that initially NO is adsorbed in a bridge-bonded geometry, and with increasing coverage NO is forced into on-top sites, with only a small amount of bridged NO remaining at saturation coverage. Temperature-programmed desorption experiments showed only a single desorption peak at 470 K up to coverages of 30% of saturation. Above this coverage, various low-temperature states appeared in the temperature range from 300 to 400 K. No desorption was observed below 300 K. Only very small amounts of NO dissociation were observed.

Similar results were obtained by other groups.^{5,7–11} However, a recent reflection high-energy electron diffraction (RHEED) study⁶ of the adsorption of NO on Pt{110} at 300 K, in contradiction with other work, suggested that NO was adsorbed in many different sites, depending on coverage. On the (1×2) surface, bridged NO on the top layer was postulated as well as NO adsorbed on hollow sites of the {111} microfacets. On the (1×1) surface, on-top sites on the first layer were also said to be occupied, in addition to the sites present on the (1×2) surface. During the lifting of the reconstruction, they postulated that on-top and bridge sites were also occupied on the second layer of Pt atoms. However, the number of fitting parameters involved suggests that there is a problem in this work with underdetermination. The work is in contradiction to all other studies where, in agreement with the EELS data of Gorte and Gland,⁴ only on-top and bridge sites in the top layer were seen to be occupied. A photoemission, low-energy electron diffraction (LEED) and work-function study,⁵ while showing similar adsorption sites to the EELS data, implied that these bridged and on-top sites were occupied over the whole coverage range. It was, however, not completely obvious that two species were present on the surface over the entire adsorption regime due to the large amount of noise in the data which led to an ambiguous fit.

Various LEED patterns have been observed^{4,5,7,10,12} during NO adsorption on Pt{110}. At 300 K, the (1×2) LEED pattern for the clean Pt{110} surface is replaced by a (1×1) pattern at saturation coverage as the reconstruction is lifted. At lower temperatures (less than 250 K) several authors agree that a

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$c(8 \times 4)$ LEED pattern develops with increasing coverage,^{4,10,12} but there is some dispute as to the nature of this structure on the surface. It has been speculated¹² that the $c(8 \times 4)$ LEED pattern is actually due to the structure of the substrate atoms and not the overlayer and therefore involves a partial rearrangement of the substrate. It has been suggested that it would require the displacement of one monolayer (ML) of Pt atoms to form this structure.

Experimental Section

The infrared studies described here were performed with the novel RAIRS setup described elsewhere.¹³ The UHV chamber was designed for sensitive low-temperature infrared emission experiments,¹⁴ and a few minor modifications were made to allow RAIRS experiments to be performed. The UHV chamber has a base pressure of $\leq 2 \times 10^{-10}$ mbar. Dosing of NO (>99% pure, Air Products plc) was achieved by the use of a precision leak valve mounted on the chamber. Pressures were measured without correction of the ion gauge sensitivity to NO. All exposures are quoted in langmuirs where 1 langmuir = 1×10^{-6} mbar·s exposure. The sample was mounted on a continuous flow liquid helium cryostat and could be cooled to 90 K by filling this coldfinger with liquid nitrogen. During heating sequences, the sample was heated to the appropriate temperature, held there for ~ 30 s, and cooled to the appropriate adsorption temperature before recording an infrared spectrum.

The Pt{110} crystal was cleaned by repeated cycles of Ar ion sputtering at 500 K, O₂ treatment at 600 K in 2×10^{-7} mbar of O₂, and annealing at 1100 K in a vacuum until a good (1×2) LEED pattern could be observed and RAIR spectra were totally repeatable. The RAIR spectra were taken with a Mattson Instruments RS100 series FTIR spectrometer. All spectra were taken at a resolution of 4 cm^{-1} and are the result of the co-addition of 400 scans. A narrow-band MCT detector was used to detect the infrared signal.

Assignment of Infrared Bands for Chemisorbed NO

There is some controversy about band assignments for NO adsorbed on surfaces, with NO adsorption on Ni{111} being a particularly good example. Here, it was originally concluded from infrared data that NO occupied different adsorption sites as a function of coverage, but photoelectron diffraction¹⁵ and LEED¹⁶ measurements showed that this was not the case. Infrared spectroscopic investigations showed two NO stretching bands: 1507 cm^{-1} at low coverage and 1581 cm^{-1} at 0.5 ML coverage. Both of these NO species were assigned to bridge sites. However, the structural studies showed that NO occupies 3-fold hollow sites over the whole coverage range. This example illustrates that great care has to be exercised when assigning vibrational modes for NO; in particular, care should be taken when using nitrosyl frequencies to assign vibrational modes on metal surfaces. The reason for this is the amphoteric bonding nature of NO on metal surfaces which leads to the existence of a wide range of vibrational frequencies for each adsorption site.

Another example where initial assignments from vibrational spectroscopy were shown to be incorrect is in the adsorption of NO on Ag{111}. An EELS study¹⁷ showed species with vibrational frequencies of 1282 cm^{-1} (assigned to 3-fold NO), 1862 cm^{-1} (on-top NO), 2241 cm^{-1} (assigned to the N–N stretch of N₂O), and 1749 cm^{-1} (on-top NO). In a more recent infrared study¹⁸ it was shown that these assignments were incorrect: the bands at 1749 and 1862 cm^{-1} were due to the formation of submonolayer adsorbed (NO)₂, and the bands at 2241 and 1282 cm^{-1} were due to the presence of N₂O. The

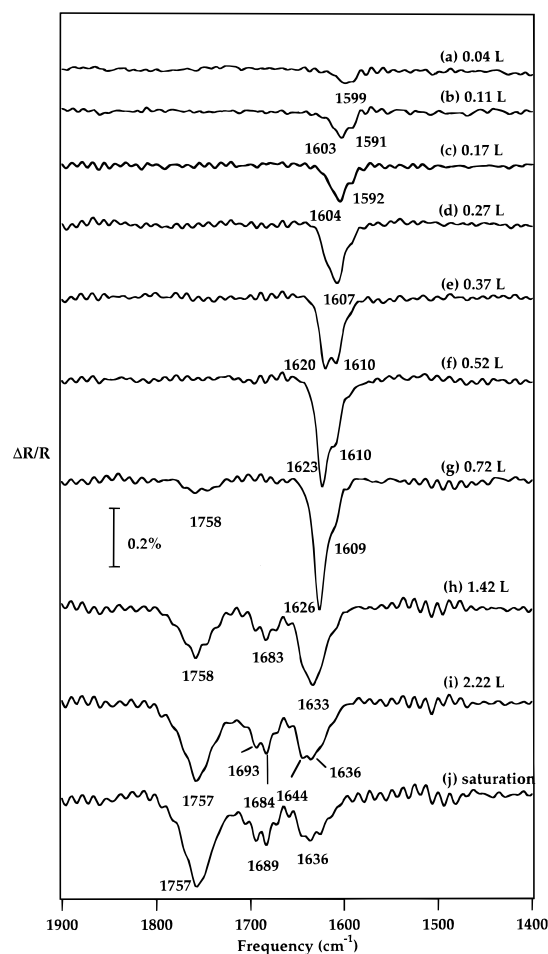


Figure 1. RAIR spectra resulting from the exposure of a Pt{110} surface held at 90 K to various exposures of NO.

reactivity of NO is therefore also very important in assigning bands observed for NO adsorption, since decomposition products such as N₂O can be formed. It is therefore very important to consider all of the evidence when assigning NO bands. The most definitive way to assign vibrational modes is in conjunction with structural studies or calculations. Recent density functional theory calculations¹⁹ for NO on Pd{110} showed frequencies of 1719 cm^{-1} (on-top species), $1672\text{--}1707 \text{ cm}^{-1}$ (bridged species), and 1456 cm^{-1} (3-fold species). For the adsorption of NO on Pt{110} assignments are based on the following band ranges: $\geq 1720 \text{ cm}^{-1}$, on top NO; $1600\text{--}1720 \text{ cm}^{-1}$, bridged NO; $< 1600 \text{ cm}^{-1}$, 3-fold NO, which are fully consistent with all available data. We note that recent structural^{15,16} and theoretical^{19,20} studies show no evidence for bent NO species.

Results and Discussion

The adsorption of NO on Pt{110} was investigated at surface temperatures of 300, 230, and 90 K to allow the observation of the contribution of the (1×2) to (1×1) reconstruction to the adsorption. Different results were observed at each substrate temperature. A further detailed study at 30 K showed the occupation of local potential energy minima, giving information relevant to adsorption dynamics, described in detail elsewhere.²¹

Adsorption of NO at 90 K on the (1×2) Surface Phase. Adsorption of NO was first studied at 90 K, where lifting of the (1×2) to (1×1) reconstruction is completely inhibited. Figure 1 shows a series of infrared spectra for the adsorption of NO on the Pt{110} surface at 90 K. Initial adsorption leads to the formation of a single band at 1599 cm^{-1} which shifts up

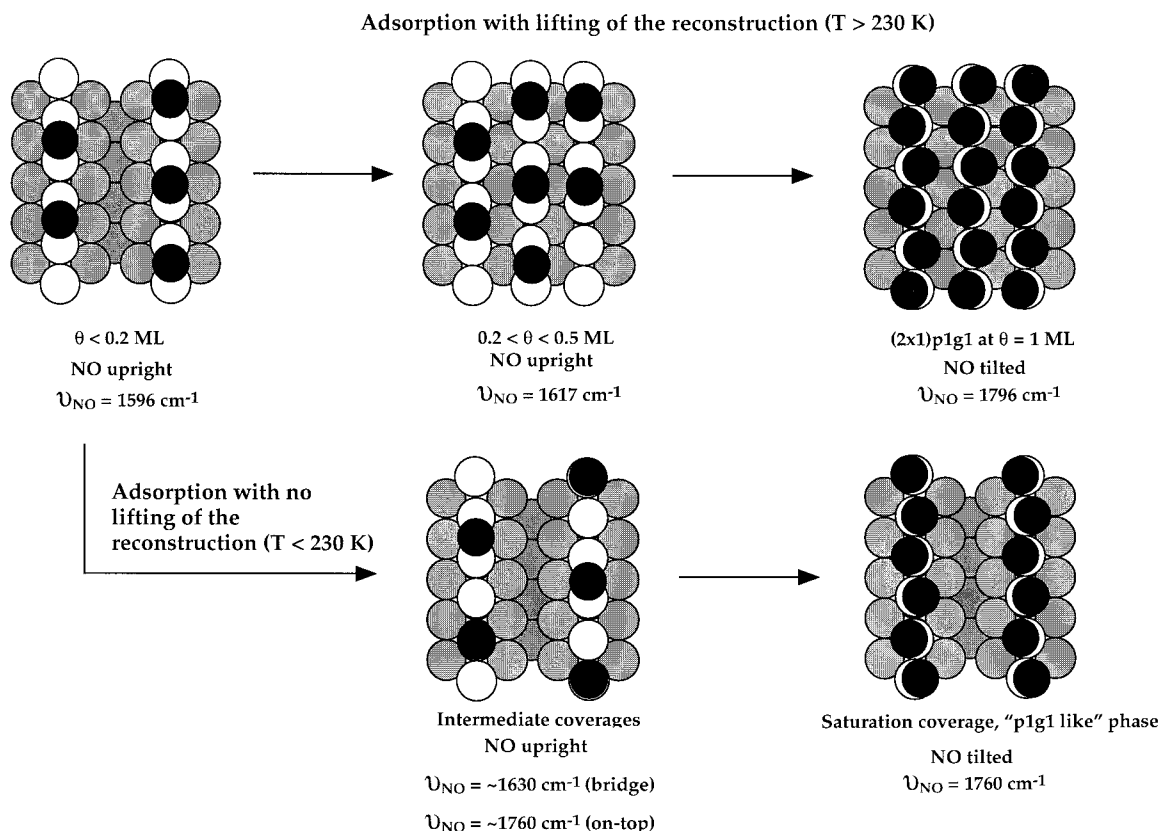


Figure 2. A schematic diagram showing the various structures that are formed on the Pt{110} surface with increasing coverage of NO. The exact nature of the structure depends on whether the (1×2) to (1×1) reconstruction is lifted. These structures are idealized and do not include the two minority species observed at 1710 cm^{-1} for the 300 K adsorption and at 1690 cm^{-1} for the 90 K adsorption. The NO molecules are indicated in the figure by filled black circles.

to 1610 cm^{-1} with increasing coverage. After an exposure of 0.37 langmuir, a second peak develops at 1620 cm^{-1} , which grows in intensity and shifts up to 1626 cm^{-1} before starting to decrease again at high exposure. As the bands in the $1610\text{--}1635\text{ cm}^{-1}$ region decrease in intensity, a broad band grows in at 1758 cm^{-1} . In addition, a further band, at $\sim 1690\text{ cm}^{-1}$, grows in at saturation coverage.

In agreement with previous EELS data,⁴ the bands at $1610\text{--}1630\text{ cm}^{-1}$ are assigned to bridged species bonded to the top layer of Pt atoms on the (1×2) surface phase. The two bands in this frequency region probably arise due to isolated NO (1610 cm^{-1}) and NO in islands, with the higher frequency being due to dipole coupling in the islands. At high coverages the bridged species disappears and is replaced by an on-top species with a frequency of $\sim 1760\text{ cm}^{-1}$, which is assigned to an on-top species along the $[110]$ rows of the surface. Occupation of every site on the rows causes tilting due to Pauli repulsion between neighboring NO molecules, as in the $p1g1$ structure formed at 300 K for CO (and NO) on Pt{110}.²² The proposed structural sequence is shown in Figure 2.

The on-top species is only occupied at high coverages, and a high coverage site switch is observed where most of the bridged NO molecules are converted into on-top NO molecules. It is somewhat surprising that NO should occupy on-top sites at all, since our own investigations at 30 K²¹ show that there is no minimum in the potential energy surface for the adsorption of NO into the on-top site on Pt{110} at low coverages. This is in agreement with recent density functional theory calculations for the adsorption of NO on Pt{111}²⁰ and NO on Pd{110}¹⁹ where, in both cases, the on-top site was found to be the least stable adsorption site for NO. The way in which the site switch is postulated to occur is illustrated schematically in Figure 3.

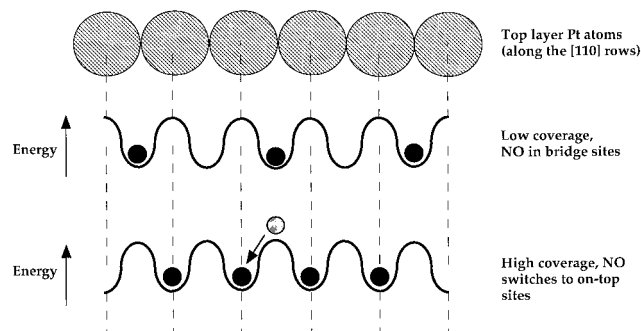


Figure 3. Schematic diagram showing how the site switching of the NO molecule from the bridge to the on-top site can occur with zero activation barrier. At low coverage, the on-top site is at a maximum in potential energy and the bridge site is at a minimum. At high coverages, repulsions between adjacent NO molecules mean that the bridge site becomes a maximum and the on-top site is now the minimum. Hence, the NO molecule switches to the bridge site without any input of energy. The dark circles represent stable NO molecules, and the shaded circles represent the unstable NO molecule at high coverage.

We suggest that the destabilization of bridge sites at high coverage produces a local maximum in the lateral potential energy surface at the bridge position so that there is no activation energy barrier to the switching process.

This site switch is also seen at higher adsorption temperatures (see later) and must be caused by the greater repulsive interactions between neighboring bridged NO molecules than between on-top-bonded NO molecules. This may be due to the amphoteric bonding nature of the NO molecule. In the bridge-bonded site NO accepts electron density into its partially filled $2\pi^*$ orbital,²⁰ but in the on-top site bonding is dominated by the donation of electron density to the Pt surface. The

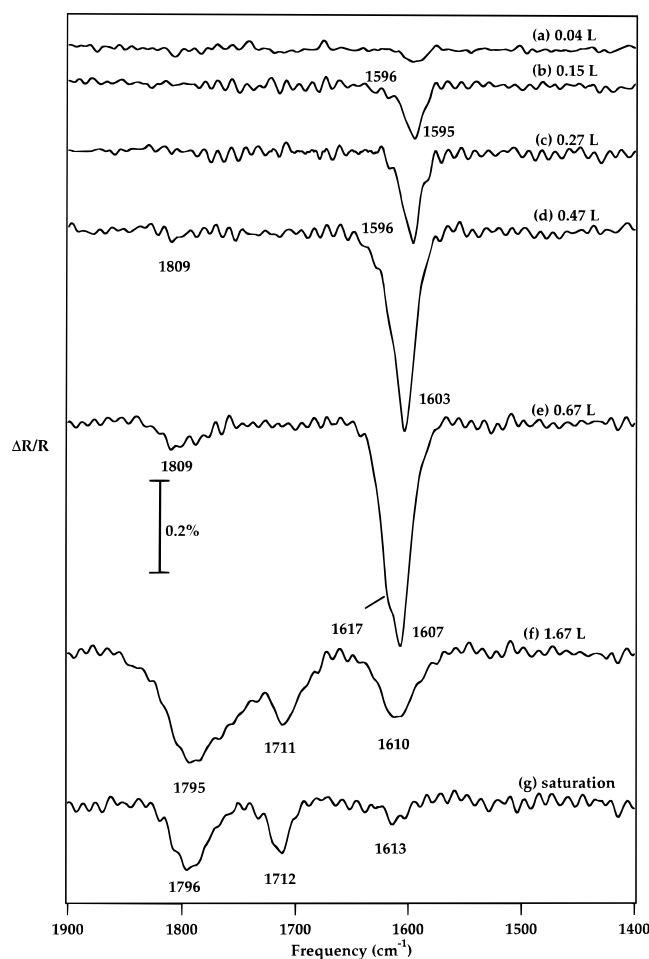


Figure 4. RAIR spectra resulting from the adsorption of NO on Pt{110} at 300 K. The NO exposures are marked in the figure.

repulsion between filled NO $2\pi^*$ states in the bridged site leads to the molecule switching to the inherently less stable on-top site. A calculation of the adsorption of O adatoms on Pt{100}-(1×1)²³ demonstrated low-coverage switching of O adatoms from a 4-fold hollow site to a bridged site with increasing coverage. Here, repulsive interactions between the atoms in the 4-fold hollow sites, due to the occupation of the oxygen p_x and p_y orbitals, led to a shift to a less stable bridge-bonded site at increased coverage. The site switching observed here for NO was not seen with NO on the similar Pd{110} surface²⁴ which also undergoes substantial reconstruction upon adsorption of NO, and there is no evidence for this phenomenon with CO on Pt{110}.²⁵

At saturation coverage, the bridge species is not completely replaced by the on-top species, and a new band appears in the spectrum at 1690 cm^{-1} , which we assign to a bridged NO species, possibly bonded between the first- and second-layer Pt atoms or to two second-layer Pt atoms. This species may play a role in preventing all of the bridged species at 1630 cm^{-1} converting to on-top species. The band was not previously reported, but in our work this same species is seen at 30 K.²¹

Adsorption of NO at 300 K: the (1×2) to (1×1) Surface Reconstruction. Infrared spectra for the adsorption of NO at 300 K are shown in Figure 4. At this adsorption temperature we expect the (1×2) to (1×1) reconstruction to occur with increasing coverage. Initially a band is seen at 1596 cm^{-1} which shifts up in frequency to 1603 cm^{-1} with increasing coverage after an exposure of 0.47 langmuir (spectrum d). Above this exposure an additional very broad band grows in at 1809 cm^{-1}

and shifts to 1796 cm^{-1} at saturation coverage. In addition, the band at 1603 cm^{-1} first of all develops into two bands (1607 and 1617 cm^{-1}) and then decreases in intensity until it has virtually disappeared at saturation. Another band, intermediate in frequency between these two bands, also grows into the spectrum at high coverage, at a frequency of 1712 cm^{-1} .

It is well-known that the Pt{110} (1×2) surface reconstruction is lifted upon adsorption of NO.⁴⁻¹² The reconstruction begins to be lifted above a coverage of $\sim 0.2\text{ ML}$ on the surface. The surface therefore reconstructs during the adsorption sequence shown in Figure 4. Again, we assign the infrared vibrational modes observed for NO on the surface of Pt{110} at 300 K to an on-top species ($\sim 1800\text{ cm}^{-1}$) and a bridged species ($\sim 1600\text{ cm}^{-1}$), in agreement with the EELS data of Gorte and Gland.⁴ Again a site switch is observed, with nearly all of the bridged NO species being converted to on-top NO species at high coverage. Since the (1×2) to (1×1) reconstruction occurs at this adsorption temperature, it is clear that site switching is not exclusive to adsorption on the frozen-in (1×2) surface.

The frequency we attribute to the on-top species ($\sim 1800\text{ cm}^{-1}$) is characteristic of adsorption on the Pt{110}-(1×1) surface since for adsorption on the frozen-in (1×2) surface at 90 K, the on-top species appears at a lower frequency ($\sim 1760\text{ cm}^{-1}$) and only shifts to $\sim 1800\text{ cm}^{-1}$ when the reconstruction is lifted (induced by heating of the saturated adlayer above $\sim 230\text{ K}$), as shown later. In general, the frequency of this species is higher on the (1×1) surface than on the (1×2) surface, which we attribute to larger dipole coupling in the more compact adlayer on the (1×1) surface, where the top layer site density is twice that on the (1×2) surface. At high NO coverage at 300 K, a (2×1)p1g1 NO structure is formed,²² which we therefore associate with the band at 1795 cm^{-1} . The structure is shown in Figure 2. In this structure, the NO molecules are again tilted in alternate directions to reduce the repulsions between them.

The band at 1712 cm^{-1} , observed here at high exposures, was not seen by Gorte and Gland with EELS,⁴ but the very broad loss peak, from 1610 to 1740 cm^{-1} , in their spectra could well have contained this band. The species that gives rise to this band only exists on the (1×1), and not on the (1×2), surface since it is only observed at temperatures or coverages where the lifting of the reconstruction occurs, and it always appears when a low-temperature saturated surface is heated to a temperature where the reconstruction is lifted (see below). However, the structural assignment of this band is not clear. Since the only site present on the (1×1) surface that is not available on the (1×2) surface is the long bridge site across the top layer rows, and the frequency of the observed mode is intermediate between that for the bridged species and that for the on-top species, it is possible that it resembles an asymmetric long bridge or bridge species. However, it is more likely that the (1×2) to (1×1) transformation induced by NO is incomplete and that the 1712 cm^{-1} band is due to adsorption on defect sites on the (1×1) surface, created by the incomplete lifting of the reconstruction. The presence of this species on the surface may well be associated with the incomplete conversion of bridged species into on-top species at saturation coverage on the (1×1) surface.

Adsorption of NO at 230 K. NO adsorption was studied at 230 K as this temperature is just below that reported to be the threshold for lifting the (1×2) reconstruction by CO.³ Figure 5 shows the adsorption at 230 K. The spectra are in many ways very similar to those observed at 300 K, with similar species

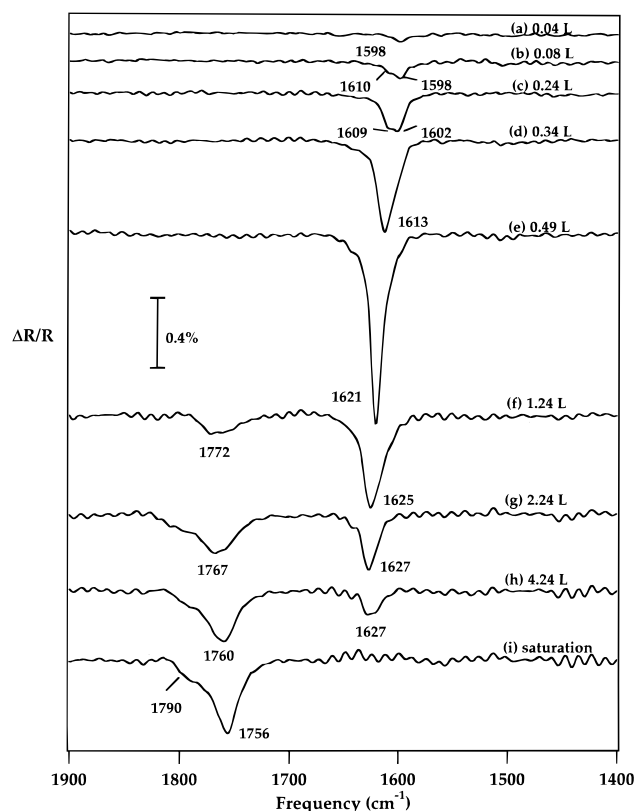


Figure 5. RAIR spectra due to the adsorption of NO onto a Pt{110} surface held at 230 K. This temperature is just below that reported to be threshold for lifting of the (1×2) clean surface reconstruction back to the (1×1) phase. The exposures given are marked in the figure.

present on the surface as a function of coverage. Initial adsorption again leads to the formation of a band at 1598 cm^{-1} at low coverage which shifts up in frequency before decreasing in intensity and then disappearing completely by saturation coverage. At the same time, a species at $\sim 1770 \text{ cm}^{-1}$ grows into the spectrum at the expense of the 1627 cm^{-1} band; this is at a lower frequency than observed at 300 K for the on-top species. The 1770 cm^{-1} band is therefore assigned to the on-top species on the (1×2) Pt{110} surface, as seen at 90 K.

The band at $\sim 1620 \text{ cm}^{-1}$ is again assigned to a bridged NO species on the (1×2) surface, consistent with the 90 K observations. This species shifts to a higher frequency than that observed at 300 K since a higher coverage is achieved on the (1×2) surface as at 90 K. At high coverage there is again a site switch favoring the on-top species which, at this adsorption temperature, goes to completion. Assuming no lifting of the reconstruction and adsorption on only the top layer Pt atoms, the maximum possible coverage at 230 K is half that possible at 300 K when the (1×1) surface is formed. However, at saturation coverage (spectrum i) a small, high-frequency shoulder is seen at 1790 cm^{-1} which is associated with the on-top species on the (1×1) surface. This implies that a small amount of lifting of the reconstruction occurs at high coverages at 230 K. This is a somewhat lower temperature than that stated for the lifting of the reconstruction by CO on Pt{110} (250 K).³ We note that in the present case RAIRS is a more sensitive probe of the reconstructing process since there is a significant frequency difference between on-top NO on the (1×2) and the (1×1) surfaces. Furthermore, reasonably long-range order is required for techniques such as LEED to detect changes in the surface structure. At this adsorption temperature, the band at $\sim 1710 \text{ cm}^{-1}$ is not observed. We attribute this to the fact that the (1×2) to (1×1) surface structure conversion is only

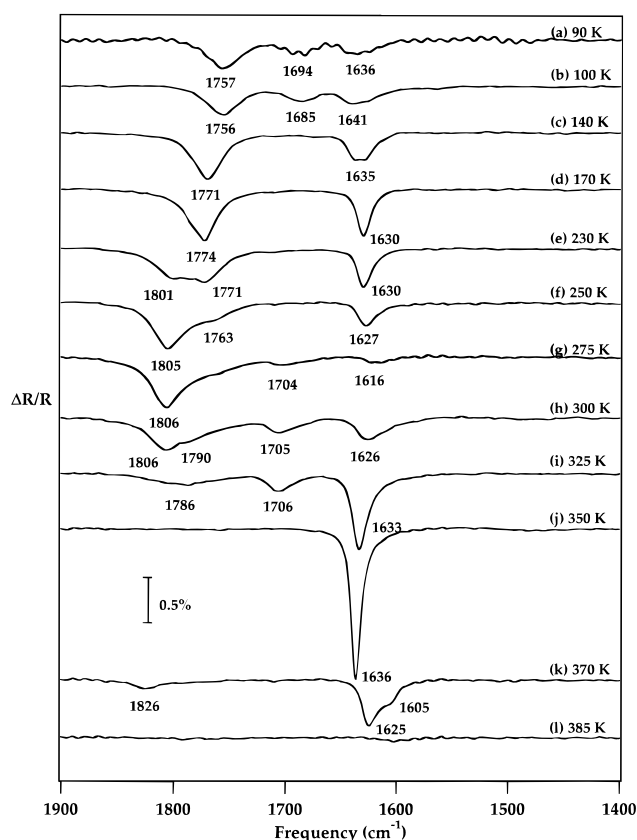


Figure 6. RAIR spectra resulting from the heating of the saturated adlayer formed at 90 K to the various temperatures marked in the figure. Again, the substantial lifting of the reconstruction is shown by the appearance of the $\sim 1800 \text{ cm}^{-1}$ on-top band after annealing the surface to 250 K.

very weakly initiated at this temperature. Since we have found that this adsorption temperature (230 K) is slightly above the threshold for lifting the reconstruction, it was necessary to determine the exact temperature at which the reconstruction lifted. This was performed by heating the adlayer formed after adsorption at 90 K to elevated temperatures.

Heating Sequences for NO-Saturated Adlayers. Figure 6 shows the results of annealing the 90 K NO-saturated surface to the various temperatures indicated. Using the shift in frequency of the on-top band from $\sim 1774 \text{ cm}^{-1}$ on the (1×2) surface to 1805 cm^{-1} on the (1×1) surface as a monitor of the (1×2) to (1×1) transition, the reconstruction starts at $\sim 230 \text{ K}$ (spectrum 6e), as suggested previously, and is completely lifted by $\sim 300 \text{ K}$ when the band at 1705 cm^{-1} (only observed on the (1×1) surface) appears. The on-top species disappears from the surface by 350 K, and the decrease in coverage is accompanied by the switch back to the bridged species. The species at 1705 cm^{-1} , which only appears upon lifting of the reconstruction, has also desorbed by this temperature. If this is due to adsorption on defects created by the incomplete lifting of the reconstruction, then we expect it to desorb as the underlying Pt atoms become more ordered with heating. With increasing temperature, the 1630 cm^{-1} band intensity first increases, with a loss of the 1690 cm^{-1} band, at about 170 K and then, at 250–275 K, it decreases again as the (1×2) to (1×1) conversion occurs; the adlayer is almost completely converted to the on-top species. It is most likely that the species giving rise to the 1690 cm^{-1} band converts into the first layer bridge species with heating, thus giving the observed increase in the 1630 cm^{-1} band intensity. It is not clear why the subsequent decrease in intensity occurs; we would

expect the intensity of this band to increase as the reconstruction lifts since more sites are available on the surface. At 300–350 K, the 1630 cm^{-1} band sharpens and increases in intensity and frequency, consistent with annealing and ordering of the underlying Pt surface. Once the surface is well ordered, increased dipole coupling leads to the observed frequency and intensity increase in the band at 1620 cm^{-1} . Heating beyond 350 K leads to desorption, which causes reconstruction back to the (1×2) surface phase. As this occurs, the NO bridge band decreases in intensity, and bands at 1625 and 1602 cm^{-1} are observed. These were observed during adsorption at 90 K (Figure 1) and are characteristic of the bridge-bonded species on the (1×2) surface. All of the adsorbate species are desorbed by 385 K. This temperature is lower than that for desorption of species from saturated adlayers formed by adsorption at 300 or 230 K, but consistent with the desorption temperature observed for adlayers formed after adsorption at 30 K.²¹

Heating the saturated adlayers formed at 230 and 300 K leads to somewhat similar observations. For the 230 K adlayer, initial heating leads to further lifting of the (1×2) to (1×1) reconstruction followed by the desorption of the on-top NO species by 350 K. As observed after heating the 90 K adlayer to ~ 230 K, and during the 300 K adsorption, the lifting of the reconstruction is characterized by the appearance of an infrared band at ~ 1710 cm^{-1} which disappears after heating to 370–390 K. This confirms the suggestion that this species may be due to incomplete lifting of the reconstruction since heating of the adlayer creates an ordering of the underlying Pt atoms and therefore leads to a disappearance of this species. Further heating to 375 K causes an increase in frequency and intensity of the band due to the bridge-bonded species as before. The bridged species desorbs by 410 K, a higher temperature than that observed after heating the 90 K saturated adlayer. The heating of the 300 K saturated adlayer results in disappearance of the infrared bands at exactly the same temperatures as for the 230 K saturated surface.

Summary

The behavior of NO on the Pt{110} surface is observed to be complex, partly due to site switching and partly due to restructuring. The observed species are dependent on a number of factors such as coverage, temperature, and the phase of the surface. There is no evidence for the formation of species such as N_2O on the surface which are formed during the adsorption of NO on metals such as Ag{111}¹⁸ and Cu{110}.²⁶ However, NO is observed to desorb at a higher temperature after adsorption at 300 and 230 K than at 90 K, and one possible reason for this difference could be that a small amount of NO dissociation takes place at the higher adsorption temperatures, thus leading to the presence of O adatoms on the surface which influence the NO desorption temperature.

At all temperatures, bridged NO is formed at low coverages, and then site switching occurs to an on-top NO species with increasing coverage. This is in agreement with other studies^{4–12} but is rather surprising since on-top NO is shown by both cluster and slab calculations to be the least stable species on the Pt{111} and Pd{110} surfaces.^{19,20} On-top NO is also not seen upon adsorption at 30 K²¹ when thermal diffusion is suppressed, implying that the on-top site is actually at a potential energy maximum. The site switching is attributed to larger repulsions between bridge-bonded molecules than between on-top molecules, which destabilizes the bridged in favor of the on-top at higher coverages. Two new species have also been observed on the surface. One with a vibrational frequency of ~ 1710 cm^{-1} , is only present on the (1×1) surface at high NO

coverage. This species may be due to adsorption on defect sites, created by incomplete lifting of the (1×2) to (1×1) reconstruction. The other, seen on adsorption at 90 K only, may be due to a bridged species that forms between the first- and second-layer Pt atoms on the (1×2) Pt surface at high coverages and has a vibrational frequency of 1690 cm^{-1} .

The on-top NO species has a frequency that is very sensitive to the surface structure, being higher on the (1×1) than the (1×2) surface. This is not observed with CO on Pt{110}, where the frequency simply shows a steady upward shift with increasing coverage.²⁵ The $2\pi^*$ orbital in NO is closer to the Fermi level of Pt than that of CO, thus making NO more sensitive to changes in the electronic structure of the Pt{110} surface. These frequency differences were used as a sensitive indicator to determine the temperature at which the lifting of the (1×2) reconstruction is initiated. The lowest temperature at which the reconstruction could be observed was 230 K, somewhat lower than previously suggested by other authors.³ It seems, however, that annealing to 370 K is required to yield a reasonably well-ordered (1×1) surface, since it is only after this treatment that the most intense infrared bands are observed, whatever the original adsorption temperature.

Acknowledgment. W.A.B. acknowledges Peterhouse Cambridge for a Research Fellowship, and R.K.S. acknowledges the EPSRC and the Newton Trust for a Studentship. The EPSRC is also acknowledged for an equipment grant.

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