The Temperature Dependence of the Adsorption of NO on Pt{211}: A RAIRS and DFT Investigation

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RAIRS experiments have been performed to investigate the adsorption of NO on Pt{211}. Results show that adsorption is complex and strongly temperature dependent. At 307 K, three bands are seen at saturation with frequencies of 1801, 1609, and 1576 cm^{-1}. However, at 120 K only two bands, at 1688 and 1620 cm^{-1}, are observed. To help with the assignment of these vibrational bands, DFT calculations were also performed. The calculations show that a bridged NO species, bonded to the step edge, is the most stable species on the surface and gives rise to the band observed at 1610−1620 cm^{-1}. The calculations also suggest that the temperature dependence of NO adsorption on Pt{211} can be assigned to NO dissociation which occurs at room temperature but not at 120 K. In particular, the RAIRS band observed at 1801 cm^{-1}, which is observed on adsorption at 307 K but not at 120 K, is tentatively assigned to the formation of an O−NO complex. This species forms when a NO molecule bonds on top of an O atom, which results from the dissociation of NO on the Pt{211} surface at room temperature.

Introduction

The chemistry of NO on Pt surfaces is of great scientific and technological interest. The catalytic reduction of NO_x to N_2 and O_2 is one of the most important reactions in the three-way car exhaust catalyst, of which Pt is an important component. The adsorption of NO on surfaces is also interesting to study from a basic chemical point of view because of the amphoteric bonding nature of NO to the surface. The result of this is that the chemistry of NO adsorption is generally more complex than that of CO adsorption, with an extensive range of vibrational frequencies being observed for NO species adsorbed on surfaces.[1] Here, we present the results of a reflection absorption infrared spectroscopy (RAIRS) study of the adsorption of NO on the stepped Pt{211} surface over the temperature range from 120 to 310 K. Several different N−O vibrational bands were observed for this system. To help with the assignments of the observed infrared bands, we have also performed a density functional theory (DFT) study of NO adsorption on Pt{211}. This is the first theoretical calculation of this adsorption system. Temperature-programmed desorption (TPD) data have also been recorded and these are reported in detail elsewhere.[2]

The Pt{211} surface consists of three atom wide terraces with {111} structure and one atom high steps of {100} character. Well-defined stepped surfaces are interesting to study as they provide a first step toward understanding the role of defects in adsorption and catalysis. In particular, it is expected that defect-covered surfaces are more active for the dissociation of NO, compared to flat surfaces.

There are very few previous experimental studies of the adsorption of NO on Pt{211}[3−7] and there are no previous theoretical studies of this adsorption system. Yates et al. performed investigations of electron[3,4] and photon[3] stimulated

desorption of NO from the step sites of Pt{211}. RAIRS was used as a probe of the surface species present before and after irradiation of the NO adlayer with electrons or photons. RAIR data recorded following NO adsorption on Pt{211} at 90 K, followed by annealing to 350 K, showed two absorption bands.[3] At low coverage, a band was observed at 1593 cm^{-1}, which was assigned to bridged or bent NO on the step edge.[3] At higher coverages, a second band at 1794 cm^{-1} grew into the spectrum.[3] This species was assigned to atop NO bonded to the step edge. At higher coverages, following adsorption at 90 K (without annealing to 350 K), bands at ∼1700 and 1440 cm^{-1}, assigned to atop and bridged NO on the Pt{211} terraces, were also observed.[3]

NO adsorption on Pt{211} has also been studied using TPD,[6,7] UPS,[6] and XPS.[6] Sugisawa and co-workers[6] used XPS and UPS to show that NO is adsorbed molecularly on Pt{211} at 95 K. At saturation coverage at this temperature, half of the molecules adsorbed at the step and half adsorbed on the terraces. TPD spectra following adsorption at 95 K[6] showed that NO molecules at the step sites decomposed on heating to give N_2 in the TPD spectrum. The TPD spectra also showed the presence of three peaks due to molecular NO desorption[6] at 303, 378, and 488 K. No desorption of molecular O_2 was seen in the TPD. TPD spectra following adsorption at 300 K[7] showed only two peaks for NO, at 370 and 500 K, and one peak for N_2 at 450−500 K. NO dissociation was assumed to take place on the step edges at $T \geq 400$ K.[7]

While there are no other studies of NO adsorption on Pt{211}, vibrational studies of NO adsorption on polycrystalline Pt[8−10] and on stepped Pt{111} surfaces[11] have been reported. In both cases, similar bands to those seen on Pt{211} were observed. RAIR spectra recorded following adsorption on polycrystalline Pt at 300 K[8] showed absorption bands at 1600−1610 cm^{-1} and 1625−1640 cm^{-1}. The peak at 1600−1610 cm^{-1} was assigned to a bridged or bent NO species at the step edge.

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However, the polycrystalline nature of the surface led to ambiguity in the assignment of the band at 1624−1640 cm⁻¹. It was believed that this peak was due either to NO on a terrace site, adjacent to a step edge, or to NO adsorbed on a {110} facet. A band at 1800 cm⁻¹ was assigned to a NO molecule at a step defect site. A small band seen at 1710 cm⁻¹, following preadsorption of atomic O, was assigned to atop NO bonded to {111} terraces.[8] The bands at 1600−1610 and 1800 cm⁻¹ were strongly attenuated by the preadsorption of O atoms.[8]

Agrawal and Trenary studied the adsorption of NO on a defect-rich Pt{111} surface.[11] Numerous infrared bands were observed in the range 1320−1840 cm⁻¹. Bands at 1820−1840 cm⁻¹ and at 1609−1634 cm⁻¹ were assigned to linear and bent NO species bonded to defect sites. The assignment of these bands was confirmed by blocking the defect sites with atomic O. Preadsorption of O had opposite effects on these two peaks at 300 K. The peak near 1620 cm⁻¹ was partially suppressed by the presence of O on the surface and the peak at 1820 cm⁻¹ was enhanced by the presence of preadsorbed O. A peak observed at 1591 cm⁻¹ was assigned to adsorption at kinks on the surface. Other observed bands at 1700−1720 cm⁻¹, 1475−1500, and 1367 cm⁻¹ were assigned to NO on atop, bridge, and three-fold hollow sites on the {111} terraces.

TPD studies have also been performed for NO adsorption on a stepped Pt{111} surface, thought to be close to a {211} surface.[12] NO was observed to adsorb molecularly on the step and the terrace at 300 K. These two species gave rise to two NO desorption peaks in the TPD. In addition, TPD peaks due to the desorption of N_2 and N_2O were observed.

In addition to the surfaces described above, NO adsorption has also been studied on other stepped and kinked Pt surfaces including Pt{533},[13−15] Pt{210},[16] and Pt{410}.[17−19] On Pt-{533}, following adsorption at 100 K,[13] NO was observed to dissociate during the TPD experiment. However, Pt{210} and {410}[16−19] have been reported to decompose NO at 300 K.

It is obvious from the information presented above that caution must be applied when assigning vibrational bands to NO. The various different vibrational studies on Pt{211}[3,4] and on polycrystalline[8−10] and defect-covered Pt{111} surfaces[11] have all assigned similar vibrational bands to different species. Studies of NO adsorbed on surfaces have been undertaken for many years and vibrational assignments have generally been made by comparison of surface vibrational data with NO group stretching frequencies in a wide range of nitrosyl complexes.[20] However, various studies have shown that such a simple comparison is not always valid. Examples where assignments from vibrational data do not agree with assignments based on structural studies and on theory include NO adsorption on Ni{111}[21−30] and Pt{111}.[31−34]

In light of these problems with the assignment of NO vibrational bands, we have compared our vibrational spectra with previous data for Pt{211},[3,4] polycrystalline Pt,[8−10] and defect-covered Pt{111}[11] surfaces. We have also undertaken a theoretical investigation of the adsorption of NO on Pt{211}. The results of these calculations proved to be essential in helping the assignment of the various NO vibrational bands observed in the RAIR spectra.

Methodology

The Pt{211} crystal was cleaned by repeated cycles of Ar ion sputtering at 300 K (drain current ∼2.2 μA), oxygen treatment at 900 K in 5 × 10⁻⁸ mbar O_2, and annealing at 1050 K. Sample cleanliness was confirmed by observation of the expected LEED pattern for Pt{211} and by the production of
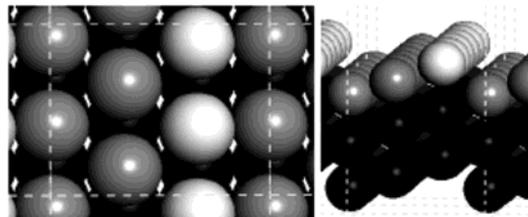
Figure 1. A schematic diagram showing the geometric structure of the modeled Pt{211} surface: a top view (left) and a side view (right). The dotted line shows the (1 × 2) unit cell of Pt{211}. The step-edge Pt atoms are indicated by white spheres.

CO TPD spectra in good agreement with those of Yates et al.[35,36] NO (99.5% purity, BOC Ltd.) was admitted into the chamber by means of a high precision leak valve. RAIRS data were recorded using a Mattson Instruments RS1 Research Series FTIR spectrometer coupled to a liquid nitrogen cooled narrow band MCT detector. All spectra were taken at a resolution of 4 cm⁻¹ and are the result of the co-addition of 256 scans. It took approximately 3 min to collect each spectrum. In RAIRS experiments where the sample was heated, it was annealed to a predetermined temperature, held at this temperature for 40 s, and then cooled back down to the original temperature before a spectrum was taken.

DFT calculations with the generalized gradient approximation[37] were performed using CASTEP.[38] The electronic wave functions were expanded in a plane wave basis set and the ion cores were described by ultra-soft pseudopotentials.[39] The vacuum region between slabs was 10 Å and a cutoff energy of 340 eV was used. Monkhurst-Pack **k**-point sampling with 0.07 Å⁻¹ spacing was used for all of the calculations. For example, for a (1 × 2) Pt{211} slab, 2 × 3 × 1 **k**-point sampling was used. The Pt{211} surface was modeled by (1 × 2) (1/6 ML) or (1 × 3) (1/9 ML) slabs with three effective layers (see Figure 1). In all of the calculations, the top layer of the slab was relaxed and the other layers were fixed at the bulk truncated structure.

To facilitate the characterization of the infrared spectra observed in the experiments, stretching frequencies for NO adsorbed in various configurations on Pt{211} were calculated. Previous work has shown that there is a systematic error in the N−O vibrational frequencies that result from our DFT pseudo-potential calculations. To evaluate the systematic error in the calculated NO stretching frequencies in a Pt surface−NO bonding environment, we first calculated a vibrational frequency for NO adsorbed on flat Pt{111} where the experimental value of the NO stretching frequency on the most stable site, the fcc hollow site, is available (1476−1498 cm⁻¹ [31,32]). Our calculated N−O vibrational frequency for NO at this site was 1608 cm⁻¹, which is ∼121 cm⁻¹ higher than the experimentally determined value. In light of this, we then subtracted 121 cm⁻¹ from each calculated NO stretching frequency on Pt{211} and the result is given as our predicted value.

Previous work[40−44] has demonstrated that the above set up for the DFT total energy calculations[40,41] and the vibrational frequency calculations[44] affords good accuracy. In particular, this method of correcting calculated vibrational frequencies is very effective. Previous results have shown that the systematic error in the calculated N−O vibrational frequencies is rather constant for many different systems. Table 1 shows a comparison between experimentally and theoretically determined N−O stretch frequencies for NO in the gas phase[45] and adsorbed on various surfaces.[31,32,46] It is clear from the table that the correction factor is fairly constant for both gas-phase NO and also for NO adsorbed in various sites on different metal surfaces.

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TABLE 1: Calculated N−O Vibrational Frequencies, v(calc), and Experimentally Determined N−O Vibrational Frequencies, v(expt), for Gas-Phase NO and for NO Adsorbed in Different Sites on Pt and Ir Metal Surfaces[a]

	gas-phase NO	NO on fcc hollow site on Pt{111}	NO on hcp hollow site on Ir{111}	NO on atop site on Ir{111}
v(expt)/cm^{-1}	1876[b]	1487[c]	1440[d]	1860[d]
v(calc)/cm^{-1}	2004	1608	1553	1971
Δv(calc − expt)/ cm^{-1}	128	121	113	111

[a] Also included in the table is a measure of the error, Δv(calc − expt), in the calculated frequencies which is given as the difference between the calculated and experimental vibrational frequencies. [b] Reference 45. [c] References 31 and 32. [d] Reference 46.
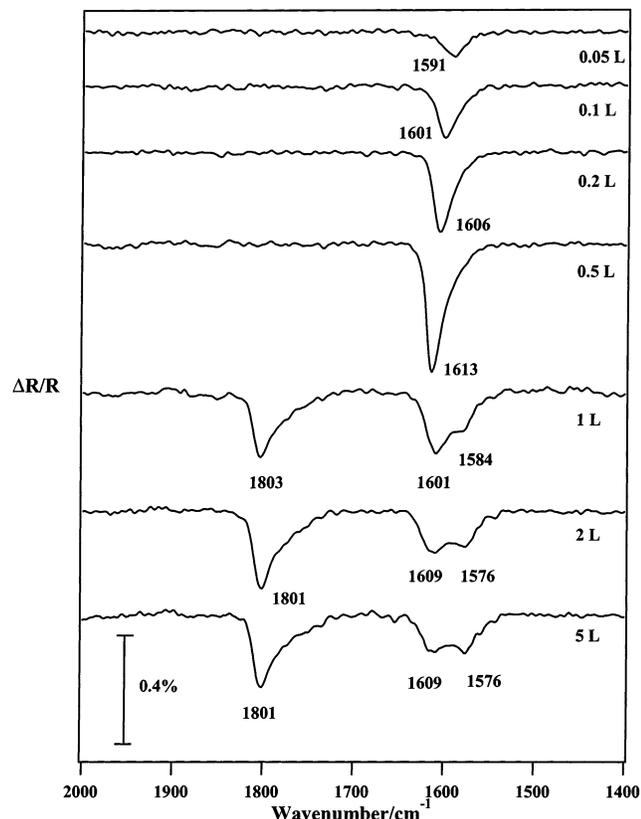
Figure 2. RAIR spectra following adsorption of NO on Pt{211} at 307 K. The NO exposures are marked on the figure.

It is therefore expected that, by applying a correction factor of 121 cm^{-1}, it is possible to predict the experimental N−O vibrational frequencies for NO adsorbed on Pt{211} with a good degree of accuracy.

Results

RAIRS Results. *A. Room-Temperature Adsorption.* Figure 2 shows RAIR data for the sequential adsorption of NO on Pt{211} at 307 K. Initially, a band is observed at 1591 cm^{-1}, following a NO exposure of 0.05 L. With increasing exposure, this peak grows in intensity and shifts up in frequency to 1613 cm^{-1}. A marked change then occurs in the spectrum between 0.5−1 L NO exposure. The peak initially observed at 1591−1613 cm^{-1} falls in intensity and shifts down in frequency to 1601 cm^{-1}. At the same time, a low frequency shoulder appears on this peak at 1584 cm^{-1}. A third band, at 1803 cm^{-1}, is also observed in the spectrum. The spectra then only change slightly with increasing exposure until at saturation three peaks are observed at 1801, 1609, and 1576 cm^{-1}.
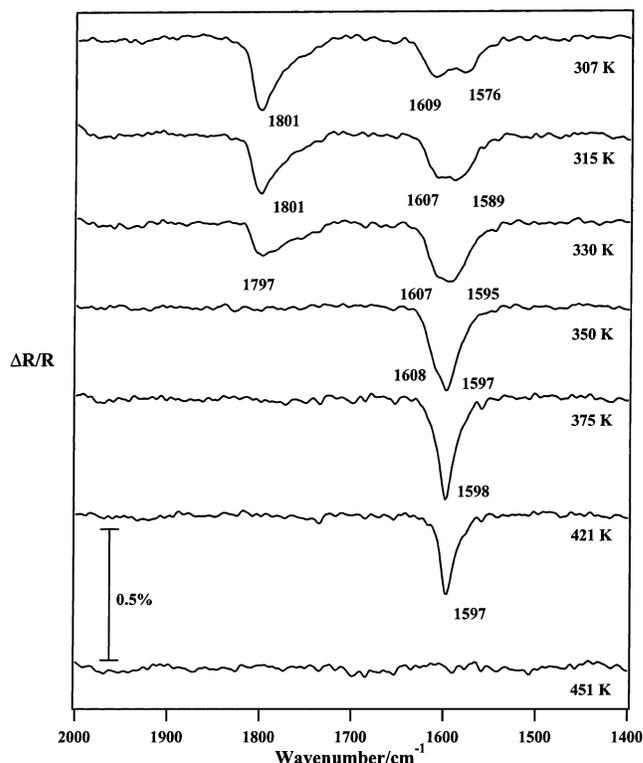
Figure 3. RAIR spectra following annealing of a Pt{211} sample saturated with NO at 307 K to various temperatures. The temperatures to which the sample was heated are marked on the figure.

RAIR spectra following saturation of Pt{211} at 307 K, and annealing to various temperatures, are shown in Figure 3. On initial heating to 315 K, the intensity of the peaks at 1609 and 1576 cm^{-1} increases slightly and the peak at 1801 cm^{-1} loses intensity. By 350 K, this species has disappeared from the spectrum completely. On further heating, the two peaks initially seen at 1609 and 1576 cm^{-1} merge into one peak at 1598 cm^{-1}. The new peak grows to a maximum intensity following annealing to 375 K, before disappearing from the spectrum by 451 K.

B. Low-Temperature Adsorption. RAIR spectra following NO adsorption on Pt{211} at 120 K are shown in Figure 4. These spectra are rather different to those observed following adsorption at 307 K (Figure 2). Initially, a peak is observed at 1612 cm^{-1}. With increasing exposure, this band first increases in frequency and intensity. Following a NO exposure of 1 L, this band then begins to decrease in intensity and frequency, reaching a frequency of 1620 cm^{-1} at saturation. At the same time as this band begins to decrease in intensity, an additional band at 1689 cm^{-1} grows into the spectrum. The frequency of this band remains relatively constant with increasing exposure. However, the intensity of this peak increases until it reaches a maximum at a NO exposure of 20 L. No other absorption features are seen in the infrared spectra at this temperature. In particular, bands observed at ~1800 and 1580 cm^{-1} following adsorption at 307 K are not observed.

Figure 5 shows a series of spectra following annealing of a Pt{211} surface saturated with NO at 120 K to various temperatures. Only very small changes are observed for annealing to temperatures ≤200 K. Following annealing to 230 K, a small peak at 1802 cm^{-1} grows into the spectrum. This band increases in intensity with increasing annealing temperature to reach a maximum intensity at 300 K. Further annealing then leads to the disappearance of this species until it has gone from
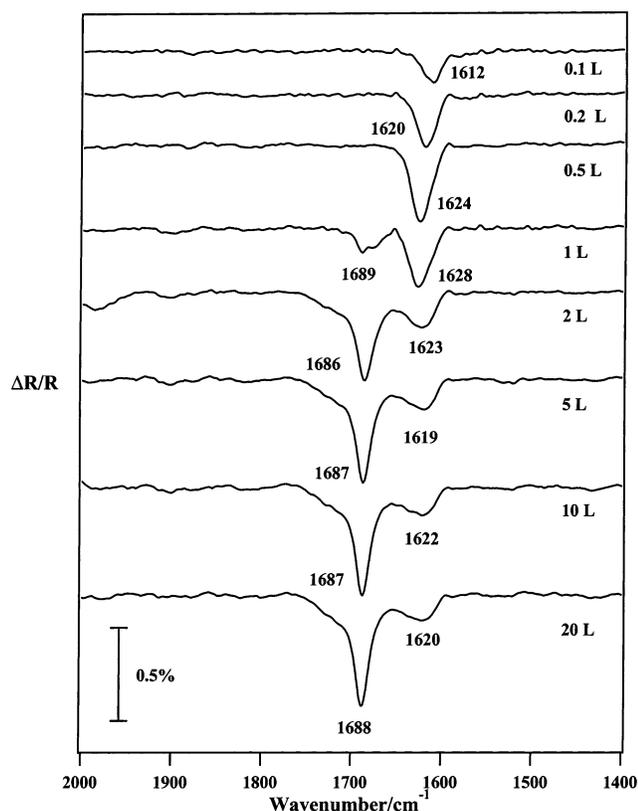
Figure 4. RAIR spectra following adsorption of NO on Pt{211} at 120 K. Note the marked difference between this series of spectra and those shown in Figure 2.

Figure 5. RAIR spectra following annealing of a Pt{211} sample saturated with NO at 120 K to the various temperatures marked on the figure.

the spectrum by 360 K. At the same time, the band at 1684 cm^{-1} decreases in intensity and has disappeared from the spectrum completely by 300 K. On further heating to 330 K, bands at 1615 and 1594 cm^{-1} appear in the spectrum. With further heating, these peaks merge to form one peak at 1606 cm^{-1}. This peak disappears from the spectrum by 450 K.

C. DFT Calculations. DFT calculations were performed to determine the adsorption energy, vibrational frequency, and N−O and Pt−NO bond lengths for NO adsorbed on various different sites on Pt{211}. The sites for which calculations were performed are shown in Figure 6. Table 2 shows the results of these calculations for the different sites shown in Figure 6. Note that, as described earlier, the predicted vibrational frequencies are obtained by subtracting 121 cm^{-1} from the calculated vibrational frequencies.

It is clear from the results shown in Table 2 that the most stable species on the Pt{211} surface is a bridged NO molecule bonded to the step edge, which has a predicted vibrational frequency of 1586 cm^{-1}. As expected, because of the unsaturated nature of the Pt{211} surface, the most stable species on the Pt{211} surface has a larger adsorption energy (228 kJ mol^{-1}) than the most stable species on the flat Pt{111} surface (198 kJ mol^{-1}). The next most stable species on Pt{211} is NO bonded to a three-fold hollow site, bonded to one step atom and two terrace atoms, which has an adsorption energy of 186 kJ mol^{-1} and a vibrational frequency of 1558 cm^{-1}. An atop NO molecule bonded to the step edge has a calculated adsorption energy of 178 kJ mol^{-1} and a predicted vibrational frequency of 1664 cm^{-1}. As expected, NO species on the terrace on Pt{211} are considerably less stable than NO species bonded to the step edge. The terrace top NO species (with the steps filled with bridged NO molecules) has an adsorption energy of 137 kJ mol^{-1} and a vibrational frequency of 1670 cm^{-1}. The terrace-
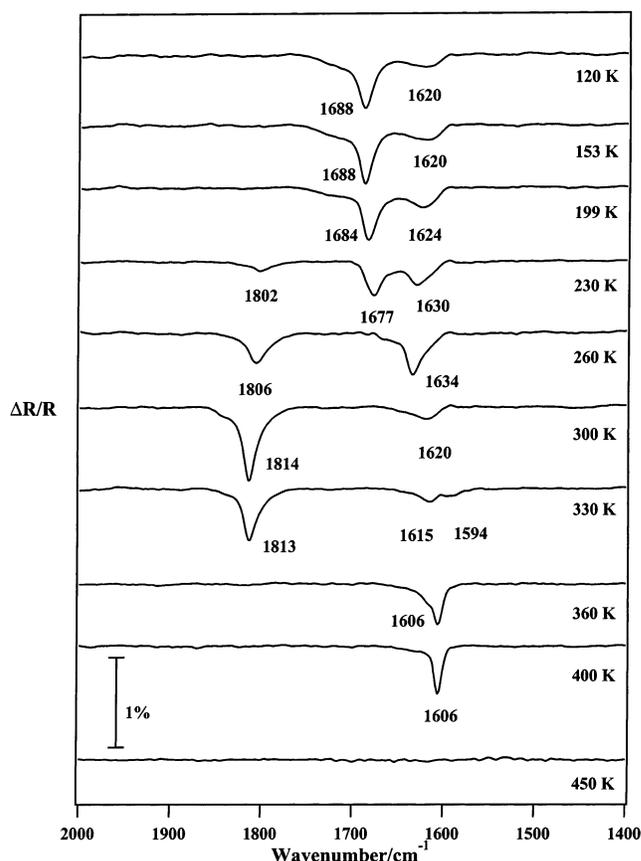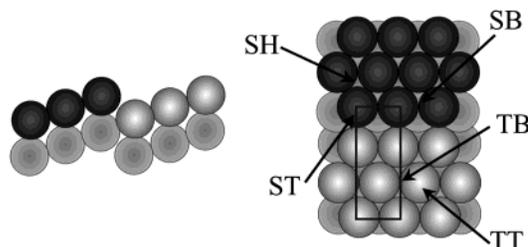
Figure 6. A schematic diagram of the Pt{211} surface, showing the sites for which NO adsorption was investigated theoretically. The sites labeled are a step-bridge site (SB), step-hcp-hollow site (SH), step-top site (ST), terrace-top site (TT), and a terrace-bridge site (TB).

TABLE 2: Theoretically Calculated Adsorption Energies, Bond Lengths, and Predicted Vibrational Frequencies for NO Adsorbed on Pt{211} in the Sites Shown in Figure 6

adsorption site	adsorption energy/ kJ mol^{-1}	predicted vibrational frequency/cm^{-1}	N−O bond length/ Å	Pt−NO bond length/Å
SB	228	1586	1.199	1.970, 1.968
SH	186	1558	1.203	2.027, 2.026, 2.333
ST	178	1664	1.181	1.887
TT[a]	137	1670	1.179	1.949
TB[a]	166	1586	1.198	2.012

[a] TT and TB: the adsorption energies and vibrational frequencies for the terrace-top and the terrace-bridge sites were calculated with the step-bridge sites already filled with NO molecules.

bridged NO species (again with the steps filled with bridged NO molecules) has an adsorption energy of 166 kJ mol^{-1} and a predicted vibrational frequency of 1586 cm^{-1}.

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Discussion

A. Room-Temperature Adsorption. It is obvious from the results shown above that the adsorption of NO on Pt{211} is strongly temperature dependent with completely different behavior observed for adsorption at 307 K (Figure 2) and 120 K (Figure 4). Adsorption of NO on Pt{211} at 307 K initially gives rise to a band at 1591 cm^{-1}. This band has a vibrational frequency that might be expected for a bridged NO species on a surface. In addition, the DFT calculations show that the most stable adsorption site for NO on Pt{211} is a step-bridge site with a predicted vibrational frequency of 1586 cm^{-1}. We therefore assign the band observed initially at 307 K to NO adsorbed in a bridge site on the step edge of Pt{211}. This assignment is in good agreement with that of Yates et al. for NO on Pt{211}[3,4] and with Agrawal and Trenary[11] for NO adsorbed on defect-covered Pt{111}. As the surface is further exposed to NO (Figure 2), the band assigned to bridged NO on the step edge increases in intensity and shifts up in frequency to reach a maximum intensity following a NO exposure of 0.5 L. This observed frequency shift may be due to dipole coupling resulting from increased amounts of NO on the surface. However, it is also possible that the frequency increase occurs partly because of the presence of O atoms, resulting from NO dissociation at the step edges. When NO is adsorbed on Pt{211} in the presence of pre-dosed O atoms,[47] the frequency of the band due to step-bridged NO increases as a function of increasing O pre-dose. Further evidence that NO dissociation may be occurring on the Pt{211} surface, even at 307 K, is given below.

As the surface is further exposed to NO, two additional bands, at 1803 and 1584 cm^{-1}, are observed in the spectrum (Figure 2). At the same time, the band assigned to the step-bridged NO decreases in frequency and intensity. The band at 1803 cm^{-1} has previously been observed by Yates et al.,[3] by Agrawal and Trenary,[11] and by Levouger and Nix.[8] In all of these cases, this band was assigned to atop NO bonded to step (or defect) sites. However, our calculations (see Table 1) show that the expected vibrational frequency for an atop NO molecule bonded to the Pt{211} step edge is 1664 cm^{-1}—considerably lower than the frequency of the band observed here. It is therefore suggested that this band is not due to NO bonded to a top site at the step edge as previously indicated.[3,8,11] The presence of this band in the RAIR spectrum is very temperature dependent—it is observed following adsorption at 307 K (Figure 2) but not following adsorption at 120 K (Figure 4). However, when a surface saturated with NO at 120 K is annealed to above 230 K, this band appears in the spectrum (Figure 5).

The presence of NO dissociation on the steps of the Pt{211} surface at 307 K, but not at 120 K, is a possible cause of the observed temperature dependence of this band. There is currently no real consensus in the literature concerning NO dissociation on Pt{211} at 300 K. Banholzer and co-workers[48] used symmetry considerations to show that Pt{111} surfaces with {100} steps, such as Pt{211}, should show high activity for NO dissociation at the step sites. However, Sugisawa and co-workers used TPD, XPS, and UPS to investigate NO adsorption on Pt{211} and found that NO dissociation was not observed until ~480 K.[6] Gohndrone and Masel[7] noted that Pt{211} dissociates NO with a very similar reactivity to that of Pt{411} and Pt{100}, which is known to dissociate NO at 300 K.[49] However, NO dissociation on Pt{211} was assumed to take place on the step edges at temperatures ≥400 K.[7] Yates et al.[3,4] did not look for NO dissociation on Pt{211}. Work on polycrystalline Pt[8] and defect-covered Pt{111}[11,12] showed that

TABLE 3: Predicted Vibrational Frequencies for Various NO Containing Species on Pt{211}

species	predicted vibrational frequency/cm^{-1}
(NO)$_2$ on the step edge	1607, 1680
N$_2$O on the step edge	1429
NO on O atom (O on step-bridge)	1829
NO on O atom (O on step-bridge) with N atom on terrace hcp site	1813

NO adsorption at 300 K was predominantly molecular. Gland and Sexton[32] reported some NO dissociation on Pt{111} in the temperature range 300−500 K.

To help determine the nature of the species giving rise to the band at 1803 cm^{-1}, further DFT calculations were performed. Calculations were initially performed to investigate the dissociation of NO on Pt{211}. The calculations showed that the transition state for NO dissociation at the Pt{211} step edge has an energy 64 kJ mol^{-1} lower than that of the gas-phase NO molecule, suggesting that dissociation may be possible on Pt{211}. However, the bridged NO molecule at the step edge has an adsorption energy of 228 kJ mol^{-1}. Hence, it is more likely that, initially, NO will adsorb molecularly on the surface. This is in agreement with our RAIRS data and with previous observations.[3,4,8,11,12] However, the products of dissociation, adsorbed N and O atoms, are expected to have a higher adsorption energy than molecular NO and therefore dissociation is overall an energetically favored process. Given that the transition state for NO dissociation on Pt{211} is favored with respect to the gas phase, it is expected that some dissociation may be observed on Pt{211}. This would particularly be expected at higher coverages when the adsorption of NO in the bridge site on the step edge becomes less favored because of surface crowding.

In light of these results, calculations were also performed for NO species which might form as the result of NO dissociation on the surface. The results of these calculations are shown in Table 3. Just as before, a correction factor of 121 cm^{-1} was applied to the calculation of the vibrational frequencies given in Table 3. Although the NO containing species in Table 3 do not all consist of NO directly bonded to the Pt surface, the same correction factor can be applied. As we have already shown (Table 1), the correction factor is the same for different NO−metal adsorption systems, and also for gas-phase NO, and hence, it is also expected to be valid for the species shown in Table 3.

The first species for which the vibrational frequency was calculated was an (NO)$_2$ dimer species. (NO)$_2$ dimers have previously been observed on Ag{111}[50,51] and Cu{110}[52] with vibrational frequencies of ~1860 cm^{-1} and ~1780 cm^{-1}. The presence of (NO)$_2$ dimers has also been speculated on Pt{111} at high coverage.[32] However, the predicted vibrational frequencies for the (NO)$_2$ species on Pt{211}, shown in Table 3, are rather low, suggesting that the band at 1803 cm^{-1} cannot be due to this species. The calculations also showed that the (NO)$_2$ dimer species was only bonded very weakly to the Pt{211} surface.

The predicted vibrational frequency for N$_2$O adsorbed on the step edge was also calculated. N$_2$O has been seen in TPD following NO adsorption on Pt{211}[2] and defect-covered Pt{111}[12] and could form on the surface as a result of the reaction of molecular NO with an adsorbed N atom. However, the predicted N−O vibrational frequency for N$_2$O, shown in Table 3, is too low. We also performed experiments where N$_2$O was adsorbed on the Pt{211} surface at 300 and 100 K, and in all cases no bands were seen in the RAIR spectrum, suggesting that N$_2$O does not adsorb on Pt{211} at these temperatures.

The only species for which the predicted vibrational frequency was close to the measured vibrational frequency of 1803 cm^{-1} was a species where NO was bonded on top of an O atom which was adsorbed on a step bridge site. The calculated vibrational frequency of this species is 1829 cm^{-1}. The only way that this species could form would be if NO dissociation was occurring on the surface at 307 K. In light of this assumption, the predicted vibrational frequency of this species was recalculated to include the presence of N atoms on the terrace sites. As can be seen from Table 3, the predicted vibrational frequency then reduces to 1813 cm^{-1}. Hence, the band observed at 1803 cm^{-1} is tentatively assigned to the N—O stretch of an O—NO complex which forms as the result of NO dissociation on Pt{211} at 307 K. The calculated energy of the bond between the NO and the O atom is 68 kJ mol^{-1}. Calculations were also performed to investigate the formation of a N—NO complex. However, in all cases, geometrical optimization of the N—NO complex on the Pt{211} surface leads either to the formation of N_2O in the gas phase or to the formation of gas-phase NO and adsorbed N atoms. Hence, the band at 1803 cm^{-1} cannot be due to the formation of an N—NO complex.

A similar band, at 1820 cm^{-1}, has previously been observed following NO adsorption on defect-covered Pt{111}.[11] It was speculated that this band may have arisen due to the formation of NO_2 on the surface. However, this assignment was rejected because NO_2 adsorbed on Pt{111} shows vibrational bands at 795, 1180, and 1550 cm^{-1},[53] not at 1820 cm^{-1}. In addition, O_2 preadsorption studies using isotopically labeled oxygen[11] were performed and did not lead to a shift of the band at 1820 cm^{-1} as would be expected if it were due to an NO_2 species. However, as our calculations show, the species giving rise to the band at 1803 cm^{-1} is not a NO_2 molecule; it is more like an O—NO complex, since the bond between the NO molecule and the O atom is very weak. The calculated NO bond lengths for this species are 1.180 Å for the N—O bond in the NO molecule and 1.776 Å for the bond between the NO and the O. Hence, the vibrational mode which gives rise to the band at 1803 cm^{-1} may be the N—O stretch of this complex.

It is perhaps surprising that this weakly bound complex is formed in preference to the more stable atop or bridge terrace species. However, the presence of NO dissociation on the surface means that the terraces may be covered with N atoms. It is known that when NO dissociates on a stepped surface, the O atoms remain bound at the step edges and the N atoms migrate to the terrace.[54] In this case, NO cannot adsorb on the terrace sites since they are already filled with N atoms. When adsorption occurs at 120 K, the atop terrace NO species is formed, in preference to the O—NO complex, as dissociation does not occur at this temperature (see later).

Further evidence for the assignment of the RAIR band observed at 1803 cm^{-1} to an O—NO complex comes from the observation that pre-dosing the surface with O atoms causes the intensity of this peak to increase with increasing O atom pre-dose.[47] Figure 7 shows the integrated intensity of the RAIR band observed at ~1800 cm^{-1} as a function of oxygen pre-dose and NO dose. For all NO doses above 0.5 L, the intensity of the band assigned to the O—NO complex increases with increasing oxygen pre-dose, to reach a maximum at 5 L oxygen pre-dose. This is as expected, as increased amounts of O atoms on the surface will allow more of the O—NO complex to be formed. However, at higher oxygen pre-doses, the intensity of the band, at a given NO dose, decreases again. This is most likely due to site blocking by the adsorbed O atoms. It is likely that the NO molecules bond to the Pt{211} surface before
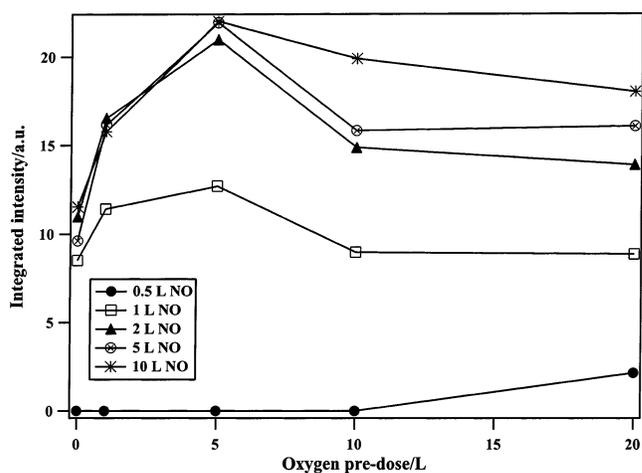
Figure 7. The integrated intensity of the ~1800 cm^{-1} RAIRS band, observed when NO is adsorbed on Pt{211} at room temperature, as a function of both O atom pre-dose and also NO dose.[47]

forming the O—NO complex. At high oxygen pre-doses, there are less sites available for NO adsorption and hence the intensity of the band due to the O—NO complex decreases for any given NO dose. However, at higher NO doses (≥2 L), the intensity of the band due to the O—NO complex, especially at high oxygen pre-doses, is still larger than the intensity of the band observed on a clean surface.

For low NO doses of 0.5 L, the ~1800 cm^{-1} band only increases in intensity following a 20 L oxygen pre-dose (Figure 7). This is not surprising since, as we have already shown, the most stable NO species on the Pt{211} surface is a step-bridged NO species. Hence, the O—NO complex will only be formed after all of the step sites are filled with bridged NO molecules. The fact that the band at ~1800 cm^{-1} is observed for NO doses of 0.5 L, following a 20 L oxygen pre-dose, is further evidence that this band is strongly influenced by the presence of O atoms on the Pt{211} surface. This is exactly what would be expected if this band is due to the formation of an O—NO complex.

In addition to the evidence provided by RAIR spectra, TPD experiments following NO dosing onto an O pre-dosed Pt{211} surface also show that the intensity of the TPD peak assigned to the desorption of NO from the O—NO complex[2,47] increases with increasing O atom pre-dose. Further details about the influence of pre-dosed O atoms on the adsorption of NO on Pt{211} can be found elsewhere.[47]

At the same time as the band at 1803 cm^{-1} appears in the spectrum, a band at 1584 cm^{-1} also grows in (Figure 2). This band shifts down to 1576 cm^{-1} with increasing NO exposure. This band was also observed by Agrawal and Trenary for adsorption of NO on defect-covered Pt{111}[11] and has a frequency which is very similar to that of the step-bridged NO, suggesting that this band is also due to a bridged NO molecule. This band was not observed by Yates et al.[3] although their saturation RAIR spectrum at 350 K showed a broad feature in the bridge region of the spectrum, which could have contributions from at least two species. Agrawal and Trenary[11] assigned this band to adsorption at kinks, which are present between the steps. It is unlikely that this band is due to the adsorption of NO in a bridge site on the terrace, although our calculations (Table 2) suggest that the terrace-bridged NO species has a similar frequency to the bridged NO on the step edge. However, experimental data for Pt{111} shows that the bridged NO species has a vibrational frequency in the range 1470—1500 cm^{-1}.[3,11,31,32] Yates et al.[3] also saw a peak at 1440 cm^{-1}, which they assigned to bridged NO on the terrace sites. This frequency

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is much lower than that observed here. In addition, as already mentioned, the terrace sites are expected to be filled with N atoms which will inhibit the adsorption of NO on the terraces.

Looking at the results of the DFT calculations (Table 2), it is possible that the band at 1584 cm^{-1} is due to NO adsorbed in a three-fold hollow site on the steps of Pt{211}. This is calculated to be the second most stable species on the surface. However, it is not clear why this species would be formed in preference to the step-bridge species, which is more stable. In addition, at the point where this band appears in the spectrum, it is likely that the steps are already saturated with bridged NO and hence there would be no room for NO to adsorb in a three-fold site at the step. We also note that the band at 1576−1584 cm^{-1} appears in the spectrum in Figure 2 at the same time as the 1803 cm^{-1} band. With this in mind, we tentatively assign the band observed at 1576−1584 cm^{-1} to a step-bridged NO molecule which is no longer influenced by the presence of O atoms. It has already been suggested that the observed frequency increase of the step-bridged NO vibrational band, seen in Figure 2, could be due both to dipole coupling and to the presence of O atoms on the surface. When the O−NO complex is formed, O atoms are no longer available to directly influence the step-bridged NO. In fact, the band at 1576−1584 cm^{-1} has a frequency very close to that calculated for bridged NO bonded to the step edge on the clean surface (Table 2). There will thus be a mixture of step-bridged NO molecules on the surface— some still bonded adjacent to O atoms, some bonded next to the O−NO complex, and some bonded next to other step-bridged NO molecules. These different environments for the bridged NO molecules could give rise to two bands in the RAIR spectrum.

Figure 3 shows the result of heating the saturated NO adlayer which is formed at 307 K. The first band to disappear from the spectrum is the band at 1801 cm^{-1}, assigned to the N−O vibration of an O−NO complex. This species disappears from the spectrum at temperatures above 330 K. This supports the assignment of this band, since the bond between the NO molecule and the O atom is calculated to be weak (68 kJ mol^{-1}) and hence it would be expected to disappear from the spectrum first.

At the same time as the band at ∼1800 cm^{-1} disappears from the spectrum, the two bands at 1609 and 1576 cm^{-1} merge into one peak at 1598 cm^{-1} (Figure 3). The bands at 1609 and 1576−1584 cm^{-1} have already been assigned to step-bridged NO species in different environments: either influenced by adjacent O atoms (higher frequency band) or not influenced by O atoms (lower frequency band). It is well known that heating the Pt-{211} surface causes adsorbed O atoms to dissolve into the surface.[6] In fact, peaks due to O$_2$ are not observed in TPD spectra from NO dosed Pt{211}.[2,6] Once the O atoms have gone subsurface, they are no longer available to influence the step-bridged NO species and hence the observed NO bridge bands revert to one species. In agreement with our suggested assignment that the lower frequency of these two bands is due to bridged NO not influenced by adsorbed O atoms, the merged band has a frequency closer to that of the lower of the two bands. The resulting band due to the step-bridged NO, at 1598 cm^{-1}, is the last to disappear from the spectrum and has gone by 451 K. This further confirms the assignment of this band to the step-bridged NO species, since it is the most stable species on the Pt{211} surface.

B. Low-Temperature Adsorption. Adsorption of NO at 120 K gives rise to two bands at 1612−1628 cm^{-1} and at ∼1688 cm^{-1} (Figure 4). At first sight, these two bands have very similar

frequencies to those calculated for the adsorption of the (NO)$_2$ dimer species on Pt{211} (Table 3). However, while the frequencies are very similar, calculations show that the (NO)$_2$ species is rather unstable on the Pt{211} surface. It is therefore not expected that it would form in preference to the more stable step-bridged NO species. Hence, the lower frequency of these two bands is assigned to the step-bridged NO species, as at 307 K. The calculations show that this is the most stable species on the surface. The frequency of this band is higher than that observed at 307 K (Figure 2) possibly because NO is not dissociating at this temperature and hence there is a larger coverage of NO on the surface, leading to more dipole coupling. The observed overall frequency shift at 120 K because of dipole coupling (16 cm^{-1}) is smaller than that observed at 307 K (22 cm^{-1}), which was assigned to both dipole coupling and to the influence of O atoms. With increasing exposure, a second band at ∼1688 cm^{-1} grows into the spectrum. This band is assigned to an atop NO species, most likely bonded to the terrace. This assignment is in agreement with that of Yates and co-workers.[3] The calculated vibrational frequency for this species (Table 2) is 1670 cm^{-1}, in good agreement with the observed vibrational frequency. This frequency is very close to that seen for atop NO on Pt{111},[31,32] again confirming this assignment. The band is assigned to a terrace atop species, rather than a step atop species, because the step sites are already filled with bridged NO molecules. This species is not seen when adsorption occurs at 307 K because of the presence of NO dissociation at the higher temperature. N atoms produced by dissociation diffuse to the terrace,[54] hence blocking the adsorption of molecular NO.

When the surface saturated with NO at 120 K is heated, no change in the spectrum is observed until 230 K (Figure 5). At this temperature, the band at 1688 cm^{-1} disappears from the spectrum and, at the same time, a peak at 1802 cm^{-1} begins to grow in. The species giving rise to the band at 1688 cm^{-1} does not desorb from the surface, as no NO desorption peaks are seen in the TPD until above 300 K.[2,6] Hence, this species must move to another adsorption site when the surface is heated. The observation of the band at 1802 cm^{-1} at temperatures above 230 K, assigned to the O−NO complex, suggests that this temperature is the onset of NO dissociation on Pt{211}. It is therefore likely that the atop terrace NO species is displaced by N atoms, formed during NO dissociation, which diffuse to the terrace. The atop terrace species therefore moves to the step where it bonds on top of an O atom to give the O−NO complex. It is most likely that it is the step-bridged NO which dissociates on heating, as it is expected that dissociation will occur at the step edges. This is supported by the fact that the band due to step-bridged NO, at 1620−1630 cm^{-1}, virtually disappears from the spectrum above 260 K. It is not clear why this band reappears at 360 K, although readsorption of NO from the NO−O complex may occur as the NO−O bond is broken and the O goes subsurface because of heating.[6] Just as in the spectra in Figure 3, the last band to disappear from the spectrum is that assigned to the bridged NO species on the step edge. As for the spectra in Figure 3, this species has gone by 450 K.

Summary and Conclusions

A combined RAIRS and DFT investigation of the adsorption of NO on the stepped Pt{211} surface has been performed for the first time. The RAIRS experiments show that very different adsorption behavior occurs at 120 and 307 K. At 307 K, three bands are seen at saturation with frequencies of 1801, 1609, and 1576 cm^{-1}. However, at 120 K only two bands, at 1688 and 1620 cm^{-1}, are observed. A full summary of all of the assignments of the observed RAIRS bands is given in Table 4.

TABLE 4: A Summary of the Observed RAIR Bands, and the Band Assignments, for NO Adsorbed on Pt{211}

band frequency/cm^{-1}	adsorption temperature/K	band assignment
1801	307	NO–O complex
1609	307	step-bridged NO affected by O atoms
1576	307	step-bridge NO
1688	120	top-terrace NO
1620	120	step-bridge NO

At all temperatures above 120 K, the most stable species on the surface is a bridged NO molecule, bonded to the step edge. This gives rise to the RAIRS band seen at 1610–1620 cm^{-1}. The band observed at 1801 cm^{-1} is very temperature dependent; it is observed following adsorption at 307 K but not following adsorption at 120 K. However, when a surface saturated with NO at 120 K is annealed to above 230 K, this band appears in the spectrum. DFT calculations suggest that the temperature dependence of NO adsorption on Pt{211}, and in particular of the 1801 cm^{-1} RAIRS band, can be assigned to the occurrence of NO dissociation on the Pt{211} surface. It is suggested that, at 307 K, NO dissociation occurs on Pt{211}. This allows the formation of N and O atoms at the surface. The O atoms remain bonded to the step edge and the N atoms are thought to migrate to the terraces of Pt{211}. As a result of this NO dissociation, it is speculated that, on further adsorption of NO at 307 K, an O–NO complex is formed between molecular NO and adsorbed O atoms. This complex is adsorbed at the step edge and is thought to give rise to the RAIRS band observed at 1801 cm^{-1}. The band at 1801 cm^{-1} is not observed when adsorption occurs at 120 K, as NO dissociation does not occur at this temperature. The onset of NO dissociation is thought to be ~230 K, as indicated by the appearance of the 1801 cm^{-1} band in the RAIR spectrum which results when a surface saturated with NO at 120 K is annealed to this temperature.

When adsorption occurs at 120 K, the formation of an atop NO molecule bonded to the terrace, which gives rise to a RAIRS band at 1688 cm^{-1}, is also observed. This species is not observed when adsorption occurs at 307 K, as dissociation of NO causes the terrace sites to be saturated with adsorbed N atoms, thus preventing the adsorption of NO on the terraces. This species disappears when the surface is heated above 230 K and it is thought that, rather than desorbing from the surface, it diffuses to the step sites where it forms the O–NO complex.

We have shown here that the combination of DFT and RAIRS experiments is extremely powerful and allows a deeper understanding of the NO/Pt{211} adsorption system than would be possible using either technique in isolation. However, it is clear that further investigations of this adsorption system are needed to allow a full understanding of the adsorption and reactions of NO that take place on this surface.

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