THE MOLECULAR ADSORPTION OF NO₂ AND THE FORMATION OF N₂O₃ ON Au(111)

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Received 8 July 1988; accepted for publication 9 November 1988

The adsorption of NO₂ on Au(111) has been investigated using temperature programmed desorption (TPD) and high resolution electron energy loss spectroscopy (HREELS). At 100 K, NO₂ is adsorbed molecularly to form a Au(111) O,O'-nitrito surface chelate with C₂ᵥ symmetry. The saturation coverage of chemisorbed NO₂ is about 0.4 monolayers. The adsorption is reversible and NO₂ desorbs with first-order kinetics and an activation energy of 14 kcal/mol. When the chemisorbed state is saturated, an N₂O₄ multilayer can be formed at 100 K with greater NO₂ exposures. Also, when the chemisorbed NO₂ surface chelate is exposed to NO at 100 K, N₂O₃ is formed on the surface in an upright configuration. While it is not clear whether NO₂ chemisorbs on Au(111) as a radical, its reactivity towards gas-phase NO to produce adsorbed N₂O₃ shows that it is capable of undergoing radical-radical types of reactions. The reaction can be reversed by warming to 175 K implying that the N–N bond energy is approximately 10 kcal/mol. NO and N₂O do not adsorb on Au(111) at 95 K in ultrahigh vacuum.

1. Introduction

Recent investigations using high resolution electron energy loss spectroscopy (HREELS) and temperature programmed desorption (TPD) to study the adsorption of NO₂ on transition metals have provided detailed information about the adsorption geometries of NO₂ and the extent of NO₂ decomposition of Pt(111), Ru(001), and Ag(110) [1-5]. On clean Pt(111) at 100 K [1], NO₂ is chemisorbed to yield a Pt(111) µ-N₂O-nitrito surface complex. This NO₂ adsorption isomer has C₂ᵥ symmetry and is bonded to the surface via an oxygen atom and the nitrogen atom. The chemisorbed saturation coverage if θ(NO₂) = 0.5 monolayer (ML). When θ(NO₂) < 0.25 ML, all NO₂ is irreversibly adsorbed. But when θ(NO₂) ≥ 0.25 ML, some NO₂ does not decompose and desorbs with an activation energy (Eₐ) of 19 kcal/mol. On a Pt(111) surface that is precovered with 0.75 monolayers (ML) of oxygen atoms, NO₂ is bonded to the surface exclusively through the nitrogen atom to form a Pt(111) nitro surface complex [2]. At 100 K, the chemisorbed NO₂ saturation coverage
on this latter surface is reduced to 0.15 ML. NO$_2$ does not decompose when this surface is heated and desorbs with an $E_a = 11$ kcal/mol. The nitro adsorption isomer is also formed when NO$_2$ is coadsorbed with oxygen atoms on NO and Ru(001) at 80 K [3,5]. Desorption of this species occurs when $E_a = 8-10$ kcal/mol. In another report [4], NO$_2$ has been proposed to bond to Ag(110) with a symmetric bidentate geometry adsorbed via its oxygen atoms when coadsorbed with its decomposition products at 95 K. The chemisorption bond energy of this species is 18 kcal/mol.

The physisorption of NO$_2$ on gold has been studied previously with photoelectron spectroscopy [6]. It was determined that an NO$_2$ multilayer (N$_2$O$_4$) on a gold film at 77 K has the same spectral features as NO$_2$ in the gas-phase. The chemisorption of NO$_2$ on gold has not been studied previously. However, the novel reactivity of NO$_2$ in the presence of gold catalysts has been observed, suggesting that NO$_2$ chemisorption occurs on gold surfaces. NO$_2$ can efficiently oxidize CO to CO$_2$ with the aid of a gold catalyst [7]. Also, the selective oxidation of organic compounds by NO$_2$ can be achieved in the presence of gold [8,9].

This paper reports the first study of NO$_2$ chemisorbed on Au(111). HREELS and TPD have been used to establish that NO$_2$ adsorbs molecularly and is bonded to the surface exclusively through its oxygen atoms to form a bidentate surface chelate. Also, the first identification of N$_2$O$_3$ chemisorbed on a metal surface is reported. This compound is formed as a result of a reaction between the NO$_3$ surface chelate and gas-phase NO. In addition, the lack of adsorption of NO and N$_2$O on clean Au(111) at 95 K is noted. This study is one in a series that examines the adsorption of nitrogen oxides on metal surfaces [1,2,10–14].

2. Experimental

The experiments were carried out in a stainless steel UHV system that has been described previously [1,15]. The system contains the instrumentation necessary to perform Auger electron spectroscopy (AES), low energy electron diffraction (LEED), ultraviolet photoemission spectroscopy (UPS), HREELS, and TPD. The crystal is heated resistively and is cooled by direct contact between the crystal holder and a liquid nitrogen reservoir. All data-acquisition is accomplished under computer control except for the LEED observations.

The Au(111) crystal was cleaned by heating in $2 \times 10^{-10}$ Torr of NO$_2$ at 600 K to remove carbon from the surface. Only gold and oxygen were detected by AES after this treatment even after heating the crystal to 1000 K. The presence of oxygen on gold surfaces at high temperatures is known to be due to the presence of stable oxides formed from the reaction between oxygen and
impurities such as calcium and silicon [16–18]. Ozone adsorption experiments have shown that the peak temperatures for \( \text{O}_2 \) desorption from Au(111) occurs at 540 K [19]. However, Auger transitions for calcium or silicon or any other element except for gold, oxygen, and carbon could not be detected even after leaving the crystal at high temperatures for extended periods of time. The oxide was removed by argon ion sputtering at 800 K [20]. Oxidation of carbon by \( \text{NO}_2 \), followed by argon ion sputtering, was repeated until the high-temperature oxide could no longer be formed from \( \text{NO}_2 \) exposures.

The crystal was annealed at 800 K after the cleaning procedure and provided a LEED pattern for clean Au(111) with the expected \((\sqrt{3} \times 22)\) rect. reconstruction [21,22]. Each integral order spot was surrounded closely by a hexagonal cluster of six additional spots. The reconstruction amounts to a 4\% contraction in the surface layer.

A microcapillary array gas doser was used to expose the surface with a direct flux of high-purity \( \text{NO}_2 \) [1]. Because \( \text{NO}_2 \) readily decomposes to NO in the UHV chamber, comparing \( \text{NO}_2 \) uptake from random flux exposures to directed flux exposures to directly obtained the actual exposure provided by microcapillary array was not possible. However, it will be shown in the results section that \( \text{NO}_2 \) is adsorbed at 175 K and below with a constant sticking coefficient of unity. Using this value, exposures of \( \text{NO}_2 \) that were used to achieve the various \( \text{NO}_2 \) coverages in this paper we estimated. Exposures are reported in Langmuirs (1 L = 3.0 \times 10^{14} \text{ molecules/cm}^2 \) for \( \text{NO}_2 \) at 298 K).

TPD experiments were performed in line-of-sight of the QMS, approximately 4 cm away from the ionizer. The heating rate was 8.5 K/s. Signals at 12, 14, 18, 28, 30, 32, 44, and 46 amu were monitored. No signals above background effects due to NO and \( \text{NO}_2 \) were detected from any masses except those at 14, 30, and 46 amu. Line-of-sight desorption into the ion gauge was also performed to show that all of the desorption states were accounted for.

The HREELS spectra were recorded typically with a resolution of 80 cm\(^{-1}\), a beam energy of 5 eV, and a beam current of 0.1 nA. The elastic peak typically had \( 2 \times 10^4 \) counts/s from the clean Au(111) surface. All of the spectra, including those of the warm-up experiments, were taken with the crystal at 100 K.

3. Results

3.1. Temperature programmed desorption

The results of a series of TPD experiments on Au(111), performed as a function of \( \text{NO}_2 \) exposure at 100 K, are shown in fig. 1. TPD was carried out to 800 K. The desorption of \( \text{NO}_2 \) was detected by monitoring mass 46. The top panel shows that \( \text{NO}_2 \) exposures at 100 K result in the desorption of \( \text{NO}_2 \)
I. The figure shows desorption spectra from Au(111) for NO$_2$ exposures at 100 K. Except for a desorption state at 170 K, NO follows NO$_2$ with the expected cracking ratio.

From a state that has a peak temperature of 230 K at low NO$_2$ coverages. The peak temperature decreases slightly to 220 K at higher NO$_2$ coverages. This indicates that NO$_2$ desorption occurs with first-order kinetics, and that the activation energy for NO$_2$ desorption decreases slightly with increasing surface coverage. Using Redhead analysis [23] and assuming a pre-exponential factor of $10^{13}$ s$^{-1}$, the activation energy for desorption is approximately 14 kcal/mol. In the next section, HREELS will be used to show that this state is populated by an NO$_2$ chemisorbed species that is bonded to the surface in a single specific geometry. Fig. 1 also shows that the chemisorbed state is saturated by exposures greater than 2.2 L and the desorption of NO$_2$ from a second state takes place at a lower temperature. Additional exposures, greater than those shown in fig. 1, confirm that desorption from this states takes place with zero-order kinetics. This has been seen before when NO$_2$ desorbs from N$_2$O$_4$ multilayers adsorbed on other metal surfaces [1-3,5,11]. For N$_2$O$_4$ on Pt(111) [1], the NO$_2$ desorption rate cuts off sharply on the high temperature side of the multilayer peak, as would be expected for a zero-order desorption state. However, the desorption of NO$_2$ from the N$_2$O$_4$ multilayer on Au(111) has a
trailing edge on the high temperature side at about 160 K that extends into the first-order desorption state. This indicates that the N₂O₄ multilayer interacts with chemisorbed NO₂ to some degree during heating.

The NO signal detected during TPD is shown in the lower panel in fig. 1. This signal is mainly the result of the dissociation of a fraction of NO₂ in the ionizer of the mass spectrometer. The subtle mismatch in the lineshapes of the NO₂ and NO desorption spectra is the result of the slower pumping speed of the UHV system for NO. This is with the exception of the desorption of NO at 170 K which does not track the desorption of NO₂. However, the desorption of O₂ that would be expected if NO₂ decomposed to yield NO and oxygen atoms is not detected. Also, oxygen was not detected with AES on the surface after the desorption of NO₂. In addition, NO was found to not adsorb on clean Au(111). Experiments that are presented in the HREELS section further establish that the desorption of NO at 170 K is not the result of NO₂ decomposition. Instead, it is shown that the desorption of NO at 170 K is due to the decomposition of N₂O₃ on the surface that was formed by the reaction between adsorbed NO₂ and gas-phase NO present in the background. Therefore, all NO₂ is reversibly adsorbed on Au(111) regardless of the exposure.

Two NO₂ uptake curves are shown in fig. 2. These were constructed from the integrated areas of desorption spectra. The NO₂ coverages were estimated using AES and TPD. A 0.2 μA beam current was used for AES and the crystal
was moved rapidly to minimize the electron beam damage. Even though electron stimulated desorption was very rapid, the AES O/Au peak-to-peak ratio, when compared to an established AES coverage calibration for oxygen atoms on Pt(111) [24], could be used to determine that the NO₂ chemisorbed saturation coverage is at least 0.4 ML. The NO₂ saturation coverage on Pt(111) has been established [1]. A comparison of the integrated NO₂ desorption spectra from Au(111) and from Pt(111) for the same QMS multiplier gain and distance from the ionizer was used to provide an additional estimate of 0.4 ML for the NO₂ chemisorbed saturation coverage on Au(111).

The straight line in fig. 2 for the total amount of NO₂ refers to NO₂ adsorbed at 100 K and therefore includes NO₂ uptake into both the chemisorbed and the physisorbed states. These data in addition to other data taken at higher NO₂ exposures show that the NO₂ sticking coefficient at 100 K is independent of NO₂ coverage. This has been observed before on clean and oxygen atom precovered Pt(111) [1,2] as well as on Ru(001) [3]. The NO₂ sticking coefficient for the Pt(111) studies was determined to be unity for both the chemisorbed and the physisorbed layers below 170 K. NO₂ uptake onto multilayers of N₂O₄ should proceed with uptake kinetics that are independent of the single crystal substrate. Therefore, the constant slope of the curve in fig. 2 for the total amount of NO₂ adsorbed indicates that the sticking coefficient for NO₂ is also unity for both the chemisorbed and physisorbed states on Au(111) at 100 K.

The desorption of NO₂ from the chemisorbed state is the same whether adsorption is carried out at 100 or at 175 K. Adsorption was carried out at 175 K to generate the chemisorbed NO₂ uptake curve in fig. 2. This exposure temperature removed the possibility of any features of the zero-order desorption state being included in the integration. The initial slope of the curve matches the slope for the total NO₂ uptake at 100 K and shows that initial NO₂ uptake at 175 K also has a sticking coefficient of unity.

Oxygen atoms can be adsorbed on Au(111) by exposing the crystal to ozone at 300 K [19]. From these experiments, it has been determined that the onset of O₂ desorption occurs at about 450 K. In this study, Au(111) was given 50 L exposures of NO₂ at temperatures up to 450 K to determine if NO₂ could be used to generate oxygen atoms on the surface. After such exposures, no oxygen was detected by AES on the surface, nor was the desorption of O₂ detected by TPD. Thus, NO₂ dissociation proceeds only with a relatively large activation energy. If a preexponential factor of 10¹³ s⁻¹ for a first-order dissociation reaction is assumed, a lower limit on the barrier to NO₂ dissociation on Au(111) can be estimated to be 25 kcal/mol.

3.2. High resolution electron energy loss spectroscopy

Au(111) was given a 2.0 L NO₂ exposure at 100 K and then allowed to sit in the background of residual gases for approximately 10 minutes. The resulting
vibrational spectrum is shown at the bottom of fig. 3. Considering that the desorption experiments indicate that NO₂ is only reversibly adsorbed on the surface and that gas-phase NO₂ only has three vibrational modes, the spectrum is surprisingly complicated. Five distinct energy losses can be seen in the spectrum in addition to two or more losses in the region of 450 to 650 cm⁻¹. The most surprising feature in the spectrum is the energy loss at 1890 cm⁻¹, since this is essentially the stretching frequency of NO in the gas-phase [25]. However, NO does not adsorb on clean Au(111) and NO₂ does not decompose on this surface. Therefore, chemisorbed NO₂ must facilitate the uptake of NO from the background. The specific manner in which this occurs will be shown later in this section.

The HREELS spectrum at the top of fig. 3 shows that a greatly simplified vibrational spectrum is obtained when the clean crystal is exposed to 2.0 L of NO₂ at 175 K and then immediately scanned using HREELS. The population of the 170 K NO desorption state is avoided at this exposure temperature and the energy loss at 1890 cm⁻¹ is dramatically attenuated. The intensities of the losses at 250 and 1270 cm⁻¹ and in the region of 450 to 650 cm⁻¹ are also diminished while the energy losses at 800 and 1180 cm⁻¹ remain. Both of these peaks are attenuated in off-specular scans and other vibrational modes due to impact scattering are not detected. This indicates that the observed losses are due to dipole scattering [26,27]. NO₂ adsorbed with C₂ᵥ symmetry
Table 1
Comparison of the vibrational frequencies (cm$^{-1}$) of the Au(111) O,O'-nitrito surface chelate with those of gas-phase NO$_2$, the nitrite ion, and chelating NO$_2$ found in a Ni coordination compound

<table>
<thead>
<tr>
<th>Mode</th>
<th>NO$_2$ gas-phase</th>
<th>NO$_2$ NaNO$_2$</th>
<th>NO$_2$ Ni($\alpha$-picoline)$_2$(NO$_2$)$_2$</th>
<th>NO$_2$ Au(111) O,O'-nitrito surface chelate</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\delta$ (NO$_2$)</td>
<td>750</td>
<td>830</td>
<td>862</td>
<td>800</td>
</tr>
<tr>
<td>$v_s$ (ONO)</td>
<td>1318</td>
<td>1335</td>
<td>1199</td>
<td>1180</td>
</tr>
<tr>
<td>$v_a$ (ONO)</td>
<td>1618</td>
<td>1250</td>
<td>1272</td>
<td>1180 a)</td>
</tr>
</tbody>
</table>

a) Implied from off-specular HREELS data.

would only allow the surface–molecule stretch, the ONO bend, and the ONO symmetry stretch to be observed in accordance with the surface dipole selection rule. The surface–molecule stretching vibration may have a frequency of less than 200 cm$^{-1}$, since it was not detected. The ONO bend and the ONO symmetric stretch are assigned respectively to the energy losses at 800 and 1180 cm$^{-1}$. Since a new energy loss was not observed in the off-specular scan, the frequency of the ONO asymmetric stretch must be near that of the ONO symmetric stretch and is tentatively assigned a frequency of 1180 cm$^{-1}$. The vibrational frequencies of NO$_2$ chemisorbed on Au(111), gas-phase NO$_2$, the nitrite ion and chelating NO$_2$ found in Ni($\alpha$-picoline)$_2$(NO$_2$)$_2$ are listed in table 1 for comparison. In the discussion section, a comparison of the vibrational frequencies will be used to identify that NO$_2$ chemisorbed on Au(111) in an orientation that is shown schematically in fig. 3.

Fig. 4 shows the results of HREELS experiments that establish that the formation of a new compound, N$_2$O$_3$, is responsible for the NO uptake by the surface saturated with chelating NO$_2$ and the additional vibrational frequencies at 250, 1270, and 1890 cm$^{-1}$ and in the 450 to 600 cm$^{-1}$ region that were observed at 100 K. First, the surface is saturated with the NO$_2$ surface chelate at 175 K (lower spectrum). This surface is then exposed to 10 L of NO at 100 K (middle spectrum). All four loss peaks thought to be associated with the uptake of NO in fig. 3 are clearly enhanced by this procedure. Larger exposures of NO produce no further increase in the energy loss intensities. The uptake of NO alone on the NO$_2$ modified surface cannot account for this number of new vibrational frequencies. Even if NO could be adsorbed in a bent configuration, this could only contribute three new vibrational frequencies. Therefore, NO must interact with chemisorbed NO$_2$ in a manner that allows four new vibrational modes to be observed. The resulting set of energy losses is assigned as the characteristic vibrational spectrum of N$_2$O$_3$ adsorbed in an upright configuration with a symmetry of C$_s$ or lower. The frequency assignments are listed in table 2 with 250, 450–600, 800, 1180, 1270, and 1890 cm$^{-1}$ corresponding respectively to the N–N stretch, the N$_2$O$_3$ torsional
modes, the ONO bend, the ONO symmetric stretch, the ONO asymmetric stretch, and the stretch of the NO-like component. The details of the identification of $N_2O_3$ adsorbed on Au(111) are treated in the discussion section. The

Table 2
Comparison of the vibrational frequencies (cm$^{-1}$) of the Au(111)–$N_2O_3$ surface complex with those of gas-phase NO and $N_2O_3$ in CH$_2$Cl$_2$

<table>
<thead>
<tr>
<th>Mode</th>
<th>NO gas-phase [25]</th>
<th>$N_2O_3$ in CH$_2$Cl$_2$ [34]</th>
<th>$N_2O_3$ Au(111)–$N_2O_3$ surface complex [this work]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\nu$ (O$_2$N–NO)</td>
<td>253</td>
<td>250</td>
<td></td>
</tr>
<tr>
<td>$\rho$ (O$_2$NNO)</td>
<td>614</td>
<td>450–650</td>
<td></td>
</tr>
<tr>
<td>$\delta$ (NO$_2_3$)</td>
<td>772</td>
<td>800</td>
<td></td>
</tr>
<tr>
<td>$\nu_s$ (NO$_2$)</td>
<td>1291</td>
<td>1180</td>
<td></td>
</tr>
<tr>
<td>$\nu_a$ (NO$_2$)</td>
<td>1600</td>
<td>1270</td>
<td></td>
</tr>
<tr>
<td>$\nu$ (NO)</td>
<td>1876</td>
<td>1849</td>
<td>1890</td>
</tr>
</tbody>
</table>
formation of N₂O₃ can be reversed by warming the surface to 175 K, as shown in the upper spectrum of fig. 4. The NO₂ surface chelate remains unperturbed while evidence of adsorbed N₂O₃ is all but completely removed.

The desorption spectrum of NO from the saturated N₂O₃ condition is partially obscured by the desorption of NO from the supports of the sample holder. Nevertheless, a peak at 170 K for the desorption of NO from the decomposition of N₂O₃ under this condition can still be seen.

In fig. 5, the HREELS spectra show that N₂O₃ multilayers form on top of the chemisorbed NO₂ surface chelate with increasing NO₂ exposure at 100 K. A 2.2 L exposure of NO₂ at 175 K saturates the surface with chelating NO₂. A 2.7 L NO₂ exposure at 100 K also saturates the surface with chelating NO₂. At this temperature and exposure, however, the vibrational frequencies unique to adsorbed N₂O₃ are also apparent. Some of the vibrations indicative of physisorbed N₂O₃ are also present at 440, 770, and 1755 cm⁻¹ [1–3,5]. The NO₂ symmetric stretch in N₂O₄ at 1280 cm⁻¹ also contributes to the N₂O₃ mode shown in fig. 4 at 1270 cm⁻¹. The vibrational features of N₂O₄ continue
Fig. 6. HREELS spectra as a function of annealing temperature beginning with an N₂O₄ multilayer generated from 43 L NO₂.

to increase with increasing NO₂ exposures, while those of chelating NO₂ and N₂O₃ decrease. At 43 L, the intense losses of N₂O₄ (the spectrum is only amplified relative to the elastic peak by a factor of 10) completely dominate the spectrum. The combination bands of N₂O₄ at 1535 cm⁻¹ (2ν(NO₂)) and 2055 cm⁻¹ (δ(NO₂) + ν₅(NO₂)) are clearly evident at this coverage. The vibrational frequencies of adsorbed N₂O₄ have been discussed [3] and are essentially identical to N₂O₄ physisorbed on other surfaces [1–5].

The HREELS spectra obtained in N₂O₄ multilayer warm-up experiments are shown in fig. 6. Warming to 170 K removes all features of N₂O₄. Only energy losses due to N₂O₃ and NO₂ are present at this temperature. The intensities of the losses in the spectrum are uncharacteristically weak and poorly defined. This suggests that the N₂O₄ multilayer perturbs the N₂O₃/NO₂ chemisorbed layer in some manner and is consistent with the TPD experiments in which NO₂ desorption from the N₂O₄ multilayer extends into the chemisorbed NO₂ desorption state. Finally, in the top spectrum of fig. 6, HREELS confirms that all of the nitrogen oxides have desorbed by 300 K.
3.3. Low energy electron diffraction

The clean Au(111) surface is reconstructed, giving a \((\sqrt{3} \times 22)\) rect. pattern [21,22] as described in the experimental section. An NO\(_2\) coverage as low as 0.15 ML lifts the reconstruction and sharp \((1 \times 1)\) spots are observed. For coverages of \(\theta_{\text{NO}} > 0.25\) ML, a diffuse \((\sqrt{3} \times \sqrt{3})R30^\circ\) LEED pattern is obtained. While a \((\sqrt{3} \times \sqrt{3})R30^\circ\) structure corresponds to a coverage of 1/3 ML for a primitive basis, the diffuse spots of the LEED pattern for NO\(_2\) on Au(111) may be the result of compression and/or disorder in the chemisorbed layer. This would be consistent with the saturation NO\(_2\) coverage of 0.4 ML estimated in the TPD section. N\(_2\)O\(_4\) physisorbed layers attenuate the intensity of this LEED pattern, and when approximately 5 layers of N\(_2\)O\(_4\) are condensed on the surface, no LEED spots are visible.

3.4. NO and N\(_2\)O adsorption

Both NO and N\(_2\)O did not adsorb on clean Au(111) at 95 K as determined by TPD and AES. The adsorption of NO was also not observed on a polycrystalline gold film at 77 K [6]. However, the adsorption of N\(_2\)O on a gold film at 77 K has been observed previously with UPS [6].

No uptake of N\(_2\)O occurred upon exposure of a chemisorbed layer of chelating NO\(_2\) at 95 K to N\(_2\)O. This is in contrast to the formation of N\(_2\)O\(_3\) by exposure of chelating NO\(_2\) to NO described previously. This result is consistent with chelating NO\(_2\) undergoing radical–radical reactions: gas-phase NO is a radical, gas-phase N\(_2\)O is not.

4. Discussion

4.1. Adsorption geometry of NO\(_2\) on Au(111)

The C\(_{2v}\) symmetry of the NO\(_2\) surface complex simplifies the consideration of the possible NO\(_2\) adsorption geometries [28] to chelating and nitro-bonded NO\(_2\). Schematic representations of both of these adsorption geometries are shown in fig. 7. For either isomer, the ONO bend and the ONO symmetric stretch are totally symmetric within the point group of the adsorption complex and are therefore observable in an HREELS specular scattering geometry in accordance with the surface dipole selection rule [26,27].

There are analogous examples for both of these NO\(_2\) linkage isomers coordinated in the form of the nitrite ion (NO\(_2^-\)) in transition metal compounds [28]. The frequency of the ONO bend is typically insensitive to the bonding geometry of NO\(_2\) and occurs between 817 and 863 cm\(^{-1}\). This agrees closely with the 800 cm\(^{-1}\) frequency assigned in this paper for the ONO
Fig. 7. Schematic models of the two possible NO₂ surface species chemisorbed with C₂ᵥ symmetry: (a) chelating and (b) nitro-bonded.

bending mode of NO₂ on Au(111). The frequency of the ONO symmetric stretch, on the other hand, is sensitive to the bonding geometry of NO₂ coordinated in transition metal complexes. The frequency of this vibrational mode is in the range of 1171 to 1225 cm⁻¹ for the chelating isomer [28–30]. The vibrational frequencies of a specific example of chelating NO₂ in Ni(α-picoline)_2(NO₂)_2 are provided in table 1. The vibrations of the ONO symmetric stretch in the nitro isomers have frequencies higher than that of the chelate and are in the range of 1306 to 1392 cm⁻¹. Therefore, the ONO symmetric stretching frequency of 1180 cm⁻¹ for NO₂ on Au(111) suggests that NO₂ is adsorbed in a chelating configuration on this surface. In accordance with inorganic nomenclature [28,31], this specific adsorption geometry yields a Au(111) O,O'-nitrito surface chelate. This assignment is greatly strengthened by the following additional spectroscopic and chemical evidence.

The nitro adsorption isomer has been identified on Pt(111) precovered with oxygen atoms [2] and on Ru(001) coadsorbed with oxygen atoms and NO [3,5]. It has an ONO symmetric stretching frequency of 1270 and 1300 cm⁻¹ respectively on these surfaces. This is in good agreement with the range of the ONO symmetric stretching frequency established for nitro coordination in transition metal complexes and is 90 cm⁻¹ higher than the ONO symmetric stretching frequency for the NO₂ species chemisorbed on Au(111).

The difference in the relative intensities of the ONO bend and the ONO symmetric stretch in the vibrational spectra of NO₂ adsorbed in a nitro geometry [2,3,5] and NO₂ chemisorbed on Au(111) also makes it clear that NO₂ is adsorbed in a distinctly different bonding geometry on Au(111). The nitro adsorption isomer has relative intensities of 4:3 for the ONO bending vibration:ONO symmetric stretching vibration when it is adsorbed on oxygen atom precovered Pt(111) [2] as well as when it is coadsorbed with NO and oxygen atoms on Ru(001) [3,5]. The relative intensities of the same vibrational modes of NO₂ chemisorbed on Au(111) are conspicuously different from this. Instead, the spectrum at the top of fig. 3 shows that the relative intensities are approximately 1:2 for the ONO bend:ONO symmetric stretch.

The unique ability of NO₂ chemisorbed on Au(111) to react with NO to form N₂O₃ reversibly provides strong chemical evidence that NO₂ is adsorbed
in a chelating geometry. NO₂ adsorbed as the nitro isomer is not in the proper orientation to react with NO to form N₂O₃ in an upright configuration [2,3,5].

4.2. Bonding in the Au(111) O,O'-nitrito surface chelate

The understanding that has been developed about the bonding of NO₂⁻ in a large number of coordination compounds may be extended to suggest a possible description of the bonding of the NO₂ chelating isomer on Au(111). In coordination compounds, chelating NO₂ has essentially the same structure as the free nitrite ion [28]. The ONO bond angle ranges from 109 to 115° and is much smaller than the 134° angle of the ONO bond in gas-phase NO₂. Another common characteristic of the chelate in transition metal complexes is for the angle subtended by the oxygen atoms coordinated to the metal center to be unexpectedly small. It ranges from a maximum of 60° to as low as 47°. This fact has suggested that the chelate may coordinate effectively as a singular entity rather than as formal bidentate species [28]. This could be true on metal surfaces. Also, as the ONO and the OMO bond angles suggest in transition metal complexes, NO₂ is often bonded in an asymmetrical chelating geometry [28]. However, if this were the case for NO₂ adsorbed on Au(111), the surface complex would have C₃ symmetry. The different NO bond lengths would split the degeneracy of the ONO asymmetric and symmetric stretching frequencies. If this were the case, both of these modes would be directly observable with HREELS, thus, the Au(111) O,O'-nitrito surface chelate not only has C₃v symmetry, its conformation is well-defined. The fact that the (√3 × 22) rect. LEED pattern of reconstructed clean Au(111) is lifted by NO₂ chemisorption implies that the NO₂ binding site is also well-defined. Although the chemisorption bond strength is only about 14 kcal/mol, the interaction between the NO₂ chelate and the surface is strong enough to affect the surface morphology.

Although the bonding of NO₂ in coordination compounds can be used to broaden the view of NO₂ adsorption on Au(111), it must be emphasized that the schematic representations of the Au(111) O,O'-nitrito surface species that are used throughout this paper are intended to provide an illustration that is consistent with the experimental observations: NO₂ is bonded to the surface through the oxygen atoms with C₂ᵥ symmetry overall. These schematics are not intended to imply an assignment of the bond orders, the bond angles, or the occupancy of a specific site. Specifically, we cannot determine if the two oxygen atoms are bonded to the same metal atom or to two or a more different metal atoms.

The factors that determine which NO₂ linkage isomer is preferred in a specific coordination compound have been considered [28]. These factors include kinetic, steric, and electronic effects. However, the relative importance
of these factors and how they determine a specific manner of coordination is not well-understood. The existence of a large number of weakly interacting, short-lived NO₂ adsorption intermediates that has been postulated to explain the high sticking coefficient for NO₂ on other surfaces [1,2] is reasonable on Au(111) as well. This implies that a kinetic limitation on a possible adsorption geometry may not be applicable on metal surfaces. From a steric viewpoint, the Au(111) and the Pt(111) surfaces are essentially the same. Steric influences, therefore, do not explain why NO₂ adsorbs exclusively as a chelate on Au(111) while it adsorbs exclusively through the nitrogen atom and the oxygen atom to form a bridge-bonded species on Pt(111). Therefore, electronic effects must be the cause of the selective adsorption geometry of NO₂ on these metal surfaces. Considering that the two isomers are only weakly adsorbed on both Pt and Au surfaces, the electronic factors that determine the adsorption preference may be subtle. The non-bonding electrons on the nitrogen atom and the oxygen atoms in NO₂, as well as the flexibility of NO₂ to adjust intramolecular bond-orders, are responsible for the ability of NO₂ to coordinate in over seven types of geometries in transition metal complexes [28]. Certainly these same properties of NO₂ allow it to respond selectively to the electronic differences of the Au(111) and Pt(111) surfaces. UPS spectra of chelating NO₂, bridge-bonded NO₂, and nitro-bonded NO₂ are significantly different and attest to the extensive rehybridization that NO₂ can undergo when chemisorbed. This will be the subject for a forthcoming paper [10].

A simple resonance structure analysis of the surface complex shows that the NO₂ surface chelate may benefit from significant resonance stabilization. It also indicates that the NO bond order in NO₂ is always less than two but never less than one. The fact that NO₂ does not dissociate on the surface confirms that a high NO bond order is maintained. Resonance structures of the Au(111) O,O'-nitrito surface chelate also show that the nitrogen atom always has at least a non-bonded pair of electrons with the possibility of having an unpaired electron on it as well. Although the surface chelate may not bear a formal negative charge, the presence of significant electron density on the nitrogen atom is consistent with changes in the work function of the surface. An increase of 1.6 eV in the work function takes place upon adsorption of a saturation coverage of chelating NO₂ on Au(111) [10]. This is twice the value observed for a similar coverage of bridge-bonded NO₂ on Pt(111) [10] in which an NO bond is nearly perpendicular to the surface. As to whether NO₂ chemisorbed on Au(111) has an unpaired electron on the nitrogen atom, electron spin resonance experiments that probe paramagnetic properties, recently demonstrated in ultrahigh vacuum on other adsorption systems [32] could be used to study this. Regardless of the radical character of the NO₂ surface chelate, its reactivity towards gas-phase NO to produce adsorbed N₂O₃ shows that it is capable of undergoing radical–radical types of reactions.
4.3. The Au(111)–$\text{N}_2\text{O}_3$ surface complex

$\text{N}_2\text{O}_3$ is dissociated extensively in the gas-phase to $\text{NO}$ and $\text{NO}_2$. At 195 K and 0.1 Torr, only about 0.5% remains undissociated. Nevertheless, this is sufficient for microwave studies in which the bond angles, bond lengths, and dipole moment of $\text{N}_2\text{O}_3$ have been determined [33]. In order to confidently obtain the vibrational frequencies of $\text{N}_2\text{O}_3$, it is necessary to minimize its decomposition by freezing it at 123 K or dissolving it in $\text{CS}_2$ (218 K) or in $\text{CH}_2\text{Cl}_2$ (243 K) [34]. The vibrational frequencies of $\text{N}_2\text{O}_3$ obtained from a Raman study using the latter conditions are listed in table 2. Infrared studies performed under the other conditions listed previously, as well as in the gas-phase, were unable to access frequencies low enough to directly observe the nitrogen-nitrogen stretch at 253 cm$^{-1}$. However, the close agreement among the vibrational spectra of $\text{N}_2\text{O}_3$ in the frequency range that is common to each of the studies [34] clearly shows that $\text{N}_2\text{O}_3$ in $\text{CH}_2\text{Cl}_2$ is not substantially different from $\text{N}_2\text{O}_3$ in the gas-phase.

The agreement between the vibrational frequencies of $\text{N}_2\text{O}_3$ in $\text{CH}_2\text{Cl}_2$ and $\text{N}_2\text{O}_3$ adsorbed on Au(111) that are listed in table 2 is extremely good, except for the frequencies of the ONO symmetric and asymmetric stretching modes. However, an examination of the relationship between the vibrational frequencies of both gas-phase NO$_2$ and gas-phase NO to $\text{N}_2\text{O}_3$ in $\text{CH}_2\text{Cl}_2$ shows that the discrepancy in the ONO stretching modes is to be expected. The top portion of the correlation diagram in fig. 8 emphasizes that the vibrational frequencies of $\text{N}_2\text{O}_3$ in $\text{CH}_2\text{Cl}_2$ are essentially the summation of the vibrational frequencies of gas-phase NO$_2$ and gas-phase NO plus the frequencies of the N–N stretch and the torsional modes of $\text{N}_2\text{O}_3$. The weak coupling of the NO$_2$ and NO vibrational modes may be attributed to the very weak nitrogen–nitrogen bond of 9.7 kcal/mol [35]. In the results section it was shown that the desorption rate of NO from the unimolecular decomposition of $\text{N}_2\text{O}_3$ on the surface reached a maximum at 170 K. From this temperature and the assumption of a frequency factor of $10^{13}$ s$^{-1}$, the nitrogen–nitrogen bond energy of adsorbed $\text{N}_2\text{O}_3$ can be estimated to be 10 kcal/mol. It then follows that the simple summation of the vibrational frequencies of the adsorbed NO$_2$ and gas-phase NO components should also be the basis of the vibrational spectrum of adsorbed $\text{N}_2\text{O}_3$. The bottom portion of the correlation diagram in fig. 8 illustrates this point. The formation of $\text{N}_2\text{O}_3$ on the surface removes the degeneracy of the ONO asymmetric and symmetric stretching frequencies in the adsorbed NO$_2$ components, as is expected [28], and the frequency of the ONO asymmetric stretch increases to 1270 cm$^{-1}$. The symmetry of the $\text{N}_2\text{O}_3$ surface complex is lowered from that of the surface chelate to $C_s$ if the planar conformation that is stable in the gas-phase [33] holds true on the surface. If rotation about the nitrogen–nitrogen bond is significant, the symmetry may be as low as $C_1$. Since the ONO asymmetric mode is totally symmetric in either
Fig. 8. Correlation diagrams that compare the vibrational frequencies of $\text{N}_2\text{O}_3$ in CH$_2$Cl$_2$ and $\text{N}_2\text{O}_3$ adsorbed on Au(111). Values are taken from tables 1 and 2.

Point group, it is observable in either case in an HREELS specular scattering geometry. The vibrational frequencies of the torsional modes in adsorbed $\text{N}_2\text{O}_3$ are clustered in the range of 450 to 650 cm$^{-1}$ and the frequency of the nitrogen–nitrogen stretch is virtually identical to the nitrogen–nitrogen stretch of $\text{N}_2\text{O}_3$ in CH$_2$Cl$_2$. The NO component in adsorbed $\text{N}_2\text{O}_3$ has a vibrational frequency that is 14 cm$^{-1}$ higher than gas-phase NO. This is not expected from the vibrational frequency of the NO component in $\text{N}_2\text{O}_3$ dissolved in CH$_2$Cl$_2$ that is given in table 2. However, such an increase in the vibrational frequency of NO has been observed in transition metal complexes when it is coordinated in the form of $\text{NO}^+$ [29,36].

Delocalization of the electron that occupies the $\pi^*$ orbital in gas-phase NO to form the N–N bond in adsorbed $\text{N}_2\text{O}_3$ would increase the bond order and cause the stretching frequency to increase above the 1876 cm$^{-1}$ frequency of the neutral species. This suggests that the NO component in the $\text{N}_2\text{O}_3$ surface complex may have some partial positive character. The lowering of the work function by $-0.8$ eV when the NO$_2$ surface chelate is transformed to $\text{N}_2\text{O}_3$ [10] is consistent with this suggestion. This is another example that $\text{N}_2\text{O}_3$ adsorbed on Au(111) is very similar to gas-phase $\text{N}_2\text{O}_3$. The work function
measurements suggest the direction of the dipole moment in N₂O₃ is the same for both cases, with the positive end near the NO component and the negative end near the NO₂ component [33]. In gas-phase N₂O₃, the dipole moment has a magnitude of 2.122 debye and has a direction that runs nearly parallel to the axis of the nitrogen–nitrogen bond. The nitrogen–nitrogen bond is over 50% longer than the nitrogen–nitrogen bond in N₂ and has a value of 1.864 Å [33]. These properties of N₂O₃, combined with its adsorption in an upright configuration, should contribute to a large dynamic dipole moment with a significant component perpendicular to the surface. This explains the intense energy loss at 250 cm⁻¹, shown in fig. 4, that corresponds to the nitrogen–nitrogen stretching mode for adsorbed N₂O₃.

There are other isomeric forms of N₂O₃ that may be considered to explain the uptake of NO by NO₂ chemisorbed on Au(111). An N₂O₃ species has been isolated in a nitrogen matrix at 20 K that is symmetric with four nitrogen–oxygen bonds (O=N–O–N=O) [37]. However, the formation of this N₂O₃ isomer on the surface can easily be ruled out in view of the previous discussion. From its physical properties, it would not be expected to have the vibrational frequencies with the relative intensities shown in fig. 4 for the Au(111)–N₂O₃ surface complex. Also, the ONO–NO bond is quite weak and is estimated to be less than 5 kcal/mol [37]. Although the existence of a stable O=N–O–N=O species on the surface is unlikely, transient species such as this N₂O₃ isomer and other less well-defined weakly interacting NO₂·NO adducts may be important to the kinetics of formation of the Au(111)–N₂O₃ surface complex.

5. Summary

NO₂ is reversibly adsorbed on Au(111) to form a Au(111) O,O'-nitrito surface chelate with C₂ᵥ symmetry. NO₂ interacts strongly enough with the surface, having a chemisorption bond strength of 14 kcal/mol, to lift the reconstruction associated with clean Au(111). A chemisorbed saturation coverage of about 0.4 ML of NO₂ can be achieved at 100 K. The NO₂ surface chelate is capable of unique reactivity, and when exposed to NO at 100 K, N₂O₃ can be formed on the surface in an upright configuration. The Au(111)–N₂O₃ surface complex has similar characteristics to N₂O₃ in the gas-phase. The formation of N₂O₃ on the surface can be reversed by warming to 175 K to leave chelating NO₂ unperturbed on the surface.

Acknowledgements

Financial support for this work from the National Science Foundation through a grant given to Sievers Research Inc. as a part of the SBIR program
contact no. IFI8521288, the National Acid Precipitation Assessment Program, and the Donors of The Petroleum Research Fund, administered by the American Chemical Society, through grant no. 19695-AC5 is gratefully acknowledged. We would like to thank David M. Zehner for advice concerning the preparation of the Au(111) crystal.

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