

# A Novel Low-Temperature Adsorption State of Nitric Oxide on a Rh(111)–p(2 × 2)–CCH<sub>3</sub> Surface Studied by Reflection–Absorption Infrared Spectroscopy and Auger Electron Spectroscopy

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Adsorption of nitric oxide (NO) at a low surface temperature (120 K) onto a well-ordered ethylidyne (CCH<sub>3</sub>) adlayer chemisorbed on Rh(111) was studied by reflection–absorption infrared spectroscopy (RAIRS) and Auger electron spectroscopy (AES). The study revealed that adsorption of NO takes place as a second adlayer on top of the CCH<sub>3</sub> adlayer with the NO intermolecular axis lying parallel to the surface. This is manifest by the strong perturbation of the ethylidyne methyl group by the NO molecule resulting in the observation of the asymmetric C–H stretch mode, which is normally forbidden in RAIRS by the metal surface selection rule. Remarkably, under those conditions, no RAIRS features of the NO molecule could be observed even when exposing the surface at a dynamic NO pressure of  $1 \times 10^{-6}$  Torr. In addition, this mechanism appears to be independent from adsorption of NO at room temperature in which the molecule adsorbs onto the metal surface in defected regions of the ethylidyne overlayer and, therefore, supporting the description of the NO adsorption as a second surface layer at low surface temperature. Auger electron spectroscopy was used to confirm the presence of NO species adsorbed as a second adlayer on top of a CCH<sub>3</sub> adlayer.

## Introduction

Rhodium surfaces are recognized as an effective metal catalyst for the reduction of nitrogen oxides (NO<sub>x</sub>) to molecular nitrogen (N<sub>2</sub>),<sup>1,2</sup> for the oxidation of NO and CO,<sup>3–5</sup> and, if hydrocarbons are coadsorbed at the surface, for the production of water.<sup>6,7</sup> Generally, the reason for the reactivity between NO and transition metal surfaces is the presence of an unpaired electron in the NO 2π\* orbital leading to a facile dissociation on several transition metals.<sup>8</sup> Therefore, studies of reactions of CO and NO or NO and ethene (C<sub>2</sub>H<sub>4</sub>) on Rh(111) are of great importance and hence well documented.<sup>9–14</sup> The majority of these studies have used UHV techniques. Temperature-programmed reaction spectroscopy (TPRS) has been used to determine the evolution of the surface products as a function of the coverage of one species with respect to the other and the surface temperature. Vibrational spectroscopy, in particular high-resolution electron energy-loss spectroscopy (HREELS), was applied to the investigation of the coadsorption of NO with molecular oxygen (O<sub>2</sub>) and CO<sup>15</sup> and the coadsorption of NO with ethylidyne.<sup>16</sup> Others, for example, make use of molecular beam techniques for determining activation energies for the reaction products<sup>17</sup> or for studying the kinetics of the isothermal reduction of NO by measuring the partial pressure of the reactants and the products as a function of time.<sup>18</sup>

The adsorption of each of these gases on Rh(111) is also well reported. NO adsorbs molecularly on Rh(111) only at low surface temperature (100–200 K). From vibrational spectroscopy, LEED, and X-ray photoelectron diffraction studies, it was found that NO adsorbs on both fcc and hcp 3-fold hollow sites at low coverage and populates the atop site as the coverage is increased, leading to a (2 × 2) structure at a saturation coverage

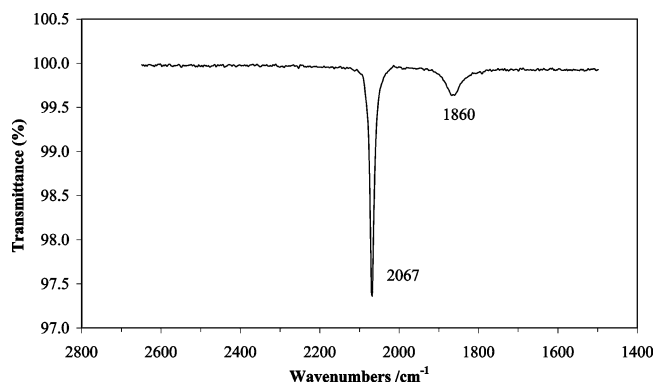
of 0.7 ML.<sup>19,20</sup> C<sub>2</sub>H<sub>4</sub> chemisorbs on Rh(111) at low surface temperature with the C–C axis parallel to the surface in a π-bond configuration, and on heating of the sample above 250 K, it dehydrogenates to form an ordered ethylidyne (CCH<sub>3</sub>) adlayer with the molecule bound in a 3-fold hollow hcp site, with the C–C axis perpendicular to the surface. With increase of the surface temperature above 350 K, it decomposes to produce C<sub>2</sub>H and CCH species.<sup>21</sup> LEED studies of the ethylidyne species report a p(2 × 2) structure with a saturation coverage of a quarter monolayer.<sup>22</sup>

In this article, we report a new aspect of the interaction at low surface temperature of NO postadsorbed on a saturated ethylidyne adlayer on Rh(111), using reflection–absorption infrared spectroscopy (RAIRS) and Auger electron spectroscopy (AES). We present evidence for a strong perturbation of the methyl group (CH<sub>3</sub>) due to adsorption of NO. In particular, it was found that NO adsorption induces a deformation in the symmetry of the methyl group making the asymmetric C–H stretch an infrared active mode in RAIRS. The adsorption of NO is believed to occur as a second adlayer in which it is proposed that the molecule exerts a dipolar interaction against the methyl group. At room temperature, the adsorption of NO is limited at defected regions of the ethylidyne adlayer (as well as for the low surface adsorption), where it can bond directly with metal surface. We also present evidence for the low surface temperature adsorption of NO with its intermolecular axis parallel to the surface. Finally, Auger electron spectroscopy was used to actually confirm that the NO species adsorbed as a second adlayer at low surface temperature.

## Experimental Section

All the experiments were carried out in a stainless steel ultrahigh vacuum (UHV) chamber, which has been described in some detail previously.<sup>23,24</sup> Essentially, the UHV chamber is

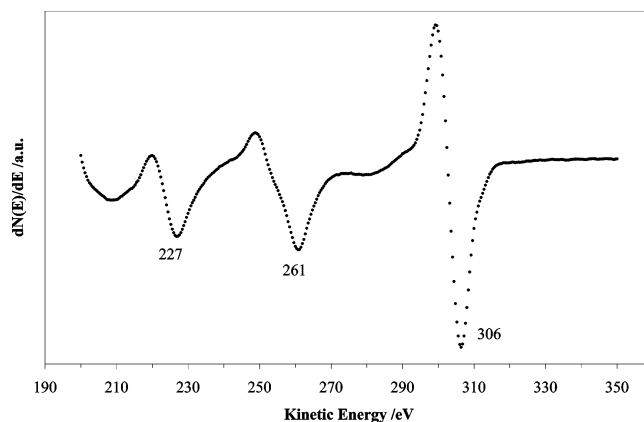
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**Figure 1.** RAIR spectrum following adsorption of 5 L of CO on clean Rh(111) surface.

pumped by a 9-in. liquid-nitrogen-cooled diffusion pump (Edwards E09) to a base pressure of better than  $1 \times 10^{-10}$  Torr after baking. The UHV chamber is coupled with a triply differentially pumped supersonic molecular beam system and contains two levels. The upper level includes an argon ion sputter gun (VG Microtech AG21), an electron gun (VG Scientific LEG 22), and a hemispherical electron energy analyzer (VG Microtech Clam 100) for Auger electron spectroscopy (AES). The lower level comprises a fixed quadrupole mass spectrometer (VG Quadrupole Micromass Q7) in line-of-sight with the molecular beam entrance, a rotatable quadrupole mass spectrometer (VG Quadrupole Micromass PC300D) used for monitoring residual partial pressures and for temperature-programmed desorption (TPD) measurements, two differentially pumped KBr windows for RAIRS experiments, and a micro-channel plate assembly (Photek VPM218) for ion detection used in quantum-state-resolved scattering measurements. RAIR spectra were recorded using a Fourier transform infrared spectrometer (Bio-Rad FTS-60A) with infrared radiation incident on the sample at grazing angle of approximately  $87^\circ$  with respect to the surface normal. The reflected light was collected and focused on a liquid-nitrogen-cooled mercury cadmium telluride (MCT) detector.

The surface sample consists of an 8 mm diameter rhodium single-crystal disk cut to within  $0.5^\circ$  of the (111) plane. It can be heated resistively to 1300 K and cooled to 100 K through contact with a liquid nitrogen reservoir. The surface temperature is monitored by a K-type chromel–alumel thermocouple spot-welded onto the edge of the crystal. Initial cleaning of the surface consisted of several cycles of argon ion sputtering and annealing at 1000 K for 2 min. Routine cleaning cycles consists of oxidation in an oxygen partial pressure of  $1 \times 10^{-7}$  Torr for 10 min at a surface temperature of 700 K and subsequently annealing at 1100 K for 3 min. The cleanliness of the surface was doubled checked by means of AES and RAIRS measurements of adsorbed CO. The latter is an effective probe of surface cleanliness, since the RAIRS features of CO are known to be crucially sensitive to surface contamination. The surface was considered clean when exposing the Rh(111) crystal to 10 L of CO ( $1 \text{ L} = 1 \times 10^{-6}$  Torr s) resulted in a CO RAIR spectrum having two bands at characteristic frequencies: one major peak between 2065 and 2068  $\text{cm}^{-1}$  corresponding to the C–O stretch of CO adsorbed in an atop site and a second less pronounced and broader peak around 1860  $\text{cm}^{-1}$  corresponding to the C–O stretch of CO adsorbed on multiply coordinated site of the rhodium surface. Figure 1 shows the CO RAIR spectrum indicating a clean Rh surface, and Figure 2, the Auger electron



**Figure 2.** Auger spectrum of clean Rh(111) surface.

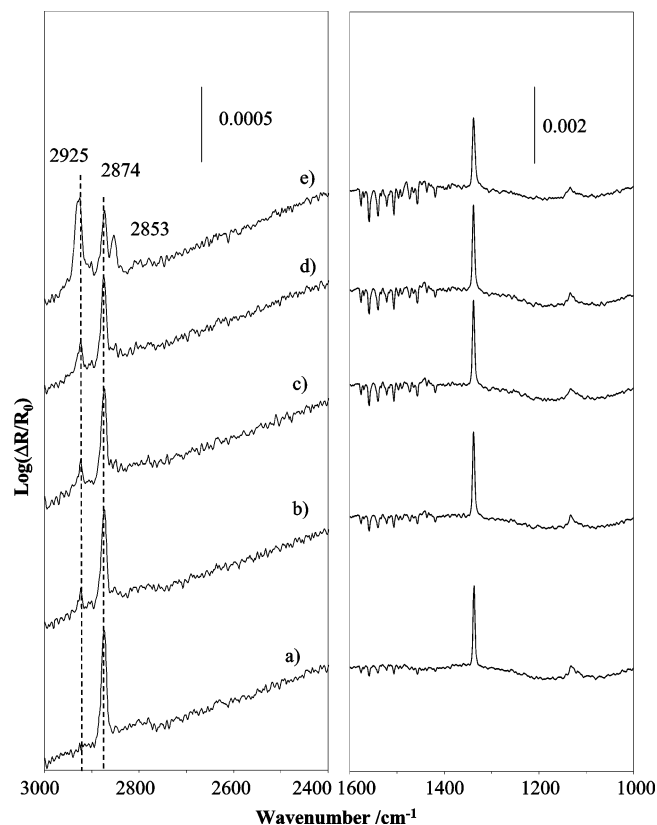
The ethylidyne adlayer was formed by exposing the clean Rh surface to 5 L of C<sub>2</sub>H<sub>4</sub> at room temperature, which is sufficient for the species to dehydrogenate and rearrange to form a saturated adlayer of chemisorbed ethylidyne (CCH<sub>3</sub>). The ethylidyne RAIRS spectrum shows resonances at 1124, 1337, and 2872  $\text{cm}^{-1}$  which can be assigned to the  $\nu_s(\text{C}-\text{C})$ ,  $\delta_s(\text{CH}_3)$ , and  $\nu_s(\text{C}-\text{H})$  vibrations, respectively.<sup>16</sup> Measurements by others indicate that this layer exhibits a p(2 × 2) structure corresponding to a saturation coverage of 0.25 ML.<sup>22</sup> Once the surface was cooled at 120 K, the NO was postadsorbed by back-filling the UHV chamber at appropriate pressures.

## Results and Discussion

The RAIR spectra contain no baseline correction or other kind of data manipulation and therefore are presented as they were acquired. In all the measurements, the ethylidyne adlayer was formed at room temperature at an exposure that saturates the metal surface. Since the background spectrum is previously recorded at 120 K, the baseline of the sample spectrum (i.e. with the adsorbate) is inevitably affected by the fact that the sample hardly returns to the same exact position after the ethene adsorption at room temperature and the subsequent recooling to the recording temperature of 120 K. This inevitably affects the intensity of the infrared radiation.

Figure 3 shows a sequence of RAIR spectra following the adsorption of NO at 120 K on Rh(111)-CCH<sub>3</sub>. All spectra are recorded at 1024 scans with 4  $\text{cm}^{-1}$  resolution. The spectrum in Figure 3a is the ethylidyne overlayer and essentially shows the three characteristic observable modes as previously discussed (i.e. the  $\nu_s(\text{C}-\text{C})$  at 1132  $\text{cm}^{-1}$ , the  $\delta_s(\text{CH}_3)$  at 1336  $\text{cm}^{-1}$ , and the  $\nu_s(\text{CH}_3)$  at 2873  $\text{cm}^{-1}$ ). The spectrum in Figure 3b was recorded following a 1.5 L dosing of NO on Rh(111)-CCH<sub>3</sub> at 120 K. Two noticeable features are present in this spectrum. First, a strong new band is evident at 2925  $\text{cm}^{-1}$ . Second, there is no clear evidence of any characteristic vibrations due to NO. The rest of the ethylidyne modes are left practically unchanged although the intensity of the  $\nu_s(\text{CH}_3)$  mode at 2873  $\text{cm}^{-1}$  has slightly reduced. Further exposure of this surface to 3.5 L (5 L in total), to 9 L (14 L in total), and to dynamic pressure of  $10^{-6}$  Torr resulted in the spectra c–e of Figure 3, respectively. Remarkably, it can be seen that the band at 2925  $\text{cm}^{-1}$  has increased, the  $\nu_s(\text{CH}_3)$  mode at 2874  $\text{cm}^{-1}$  has lost additional intensity, and a new band has developed at 2853  $\text{cm}^{-1}$  when NO is dosed at dynamic pressure. The rest of the spectra remained unchanged showing no absorption band, which can be associated with the NO molecule.

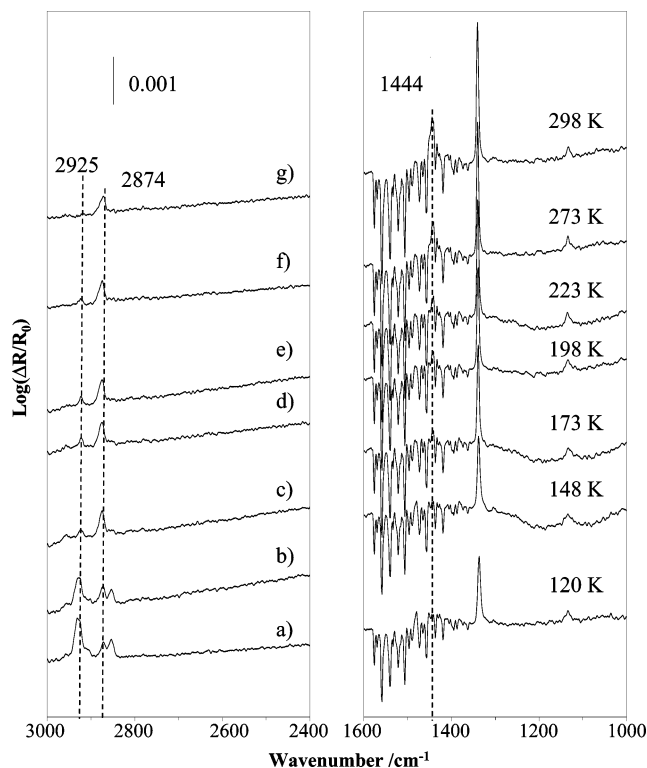
Following the above exposure to NO at 120 K, the gas phase was evacuated and RAIR spectra were recorded as a function



**Figure 3.** RAIR spectra recorded at 120 K of (a) CCH<sub>3</sub> adlayer, (b) 1.5 L of NO, (c) 5 L of NO, (d) 14 L of NO, and (e)  $1 \times 10^{-6}$  Torr of NO dynamic pressure on Rh(111)–CCH<sub>3</sub> at 120 K, respectively.

of the temperature at which the surface was sequentially heated. Each sample spectrum was recorded after the surface had been recooled to 120 K. This sequence is shown in Figure 4. The first spectrum of the sequence, labeled a, was recorded approximately 90 min after the spectrum shown in Figure 3e and represents the surface as it was before the temperature-dependent RAIRS experiments were performed. This time was necessary to allow the NO background pressure in the main chamber to recover below  $1 \times 10^{-9}$  Torr. An increase in the intensity of the peaks at 2925 cm<sup>-1</sup> and at 2853 cm<sup>-1</sup> is clearly visible with respect the spectrum at NO dynamic pressure shown in Figure 3e. In addition, the latter peak is now even bigger than the peak at 2874 cm<sup>-1</sup>. The rest of the spectrum is essentially the same. This indicates hysteresis in the degree of perturbation of the ethynylidyne spectrum which may result from structural changes in the ethynylidyne and NO layers which are slow at 120 K. Starting from the spectrum in Figure 4a, the surface was heated in steps of approximately 25 K as indicated in the margin of each spectrum. Two important observations can be made from this sequence. First, the band at 2925 cm<sup>-1</sup> is considerably suppressed as the surface is heated at 173 K, although it does remain observable even at high annealing temperatures. This could be due to readsorption of the NO from the background pressure. Second, the feature around 1444 cm<sup>-1</sup> becomes increasingly intense as the temperature is raised from 225 K to room temperature. These two considerations together with the fact that the two extra bands at 2925 and 2853 cm<sup>-1</sup> grow as the NO exposure is increased allow some initial interpretations on possible processes occurring at the interface.

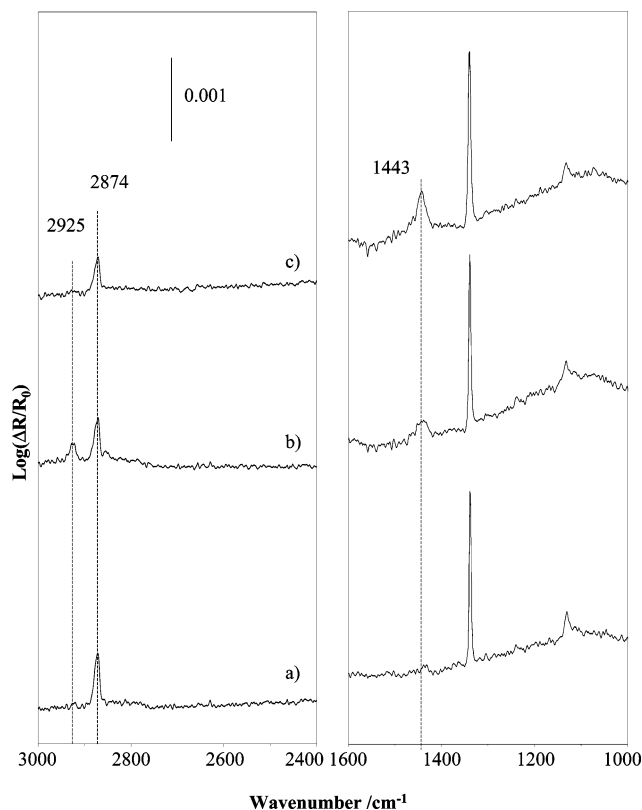
In the first instance, the band at 2925 cm<sup>-1</sup> is undoubtedly recognized as the antisymmetric CH<sub>3</sub> stretch of the ethynylidyne species,<sup>25</sup> which is normally forbidden in RAIR spectroscopy by the surface metal selection rule. Therefore, the appearance



**Figure 4.** RAIR spectra recorded at 120 K of Rh(111)–CCH<sub>3</sub> + NO as a function of the annealing temperature which is indicated at the margin. The spectrum in (a) was recorded 90 min after the spectrum in Figure 3e to allow evacuation of the gas phase.

of this band indicates that the NO molecule is on the adlayer and considerably perturbing the symmetry of the CCH<sub>3</sub> adlayer. On the other hand, if the NO is on the adlayer, and the RAIR spectra do not show characteristic resonances even at a dynamic NO pressure of  $10^{-6}$  Torr, then it is reasonable to speculate that the NO molecule is sitting on the adlayer with its intermolecular axis parallel to surface and, therefore, invisible to RAIRS. If this were the case, then the growth of the peak at 1444 cm<sup>-1</sup>, as the surface is heated to room temperature, might be explained by a migration of the NO molecule from the second adlayer to the first adlayer as CCH<sub>3</sub> becomes more mobile at higher annealing temperatures. However, it is also possible that the growth of the peak at 1445 cm<sup>-1</sup> is simply due to the fact that the NO in the background pressure readsorbed on the surface as the CCH<sub>3</sub> was heated.

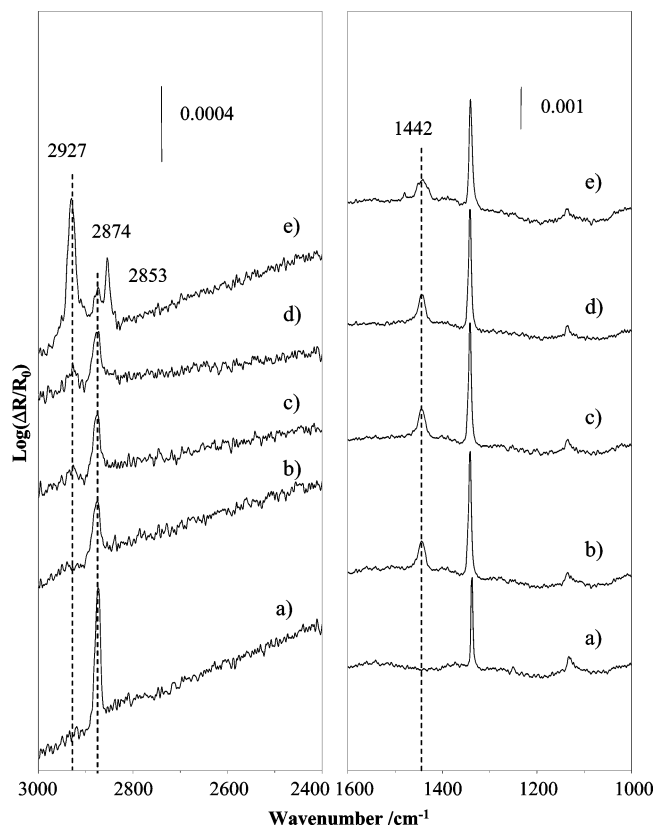
To answer this question, a simple experiment was conducted, consisting of adsorbing a few Langmuirs of NO onto the Rh(111)–CCH<sub>3</sub> surface at 120 K, followed by annealing at 360 K. In this way, possible adsorption from the NO in the gas phase can be considered negligible, if not absent. Figure 5 shows the RAIR spectra from this experiment, all recorded at 120 K, with 1024 scans at 4 cm<sup>-1</sup> resolution. The spectrum Figure 5a is the CCH<sub>3</sub> adlayer, with resonances at 2874, 1338, and 1130 cm<sup>-1</sup>. The spectrum Figure 5b is recorded following the exposure to 10 L of NO at 120 K and clearly shows the peaks at 2925 cm<sup>-1</sup> and at 2853 cm<sup>-1</sup>. In addition, a decreased intensity of the  $\nu_s$ -(CH<sub>3</sub>) mode at 2874 cm<sup>-1</sup> is observed. Also the small band around 1440 cm<sup>-1</sup> associated with the NO adsorbed onto the metal in defected regions is visible. This weak resonance is also present when the NO is adsorbed at room temperature, and therefore, it is not believed responsible for the appearance of the two extra bands. The spectrum Figure 5c was recorded following annealing at 330 K for 1 min. Remarkably, the two extra bands are suppressed and the peak around 1443 cm<sup>-1</sup> is



**Figure 5.** RAIR spectra recorded at 120 K of (a) CCH<sub>3</sub> adlayer, (b) 10 L of NO on Rh(111)-CCH<sub>3</sub> at 120 K, and (c) after heating the surface at 330 K for 1 min.

now sharper and significantly more intense than the peak in the previous spectrum. When the top spectrum was recorded, the total pressure in the main chamber was considerably lower than in the previous experiment. Together with the fact that the experiment itself took considerably less time, this significantly reduces the possibility of NO readsorbing onto the surface during the time interval necessary to cool to 120 K (typically 10 min) to record the sample spectrum. Therefore, to explain the growth of the 1443 cm<sup>-1</sup> band as the surface is heated (and without the NO gas persisting in the main chamber), it appears reasonable to suppose that the NO molecule is sitting on top of the CCH<sub>3</sub> adlayer at low surface temperature. As the temperature is raised, some of the molecules desorb and some of them could experience the greater mobility of the CCH<sub>3</sub> adlayer, which can then make the adsorption to the metal more favorable since the intensity of the peak at 1443 cm<sup>-1</sup> band is found to increase by about three times.

Finally, to reinforce the idea that the appearance of the two extra bands is due to the NO adsorbing as a second adlayer and not associated with coadsorption of NO in the first layer, the Rh(111)-CCH<sub>3</sub> surface, prior to experiment, was preexposed with 5 L of NO at room temperature and subsequently cooled to 120 K. Figure 6 shows the sequence of RAIR spectra recorded at 120 K for increasing NO exposure. Spectrum 6a is the CCH<sub>3</sub> adlayer on Rh. Spectrum 6b is the Rh(111)-CCH<sub>3</sub> + 5 L NO surface dosed a room temperature. We have now prepared a surface where NO has chemisorbed in any gaps or defects left in the ethylidyne adlayer producing a substantial peak at 1442 cm<sup>-1</sup>. Subsequently, this surface was exposed to NO at 120 K. It can be seen in Figure 6c that, at 5 L NO exposure, a very small feature appears around 2927 cm<sup>-1</sup>. With addition of a further 5 L of NO, the small band becomes more pronounced (Figure 6d). Finally, at dynamic NO pressure of 10<sup>-7</sup> Torr, the major band in the C-H region is the resonance at 2927 cm<sup>-1</sup>,

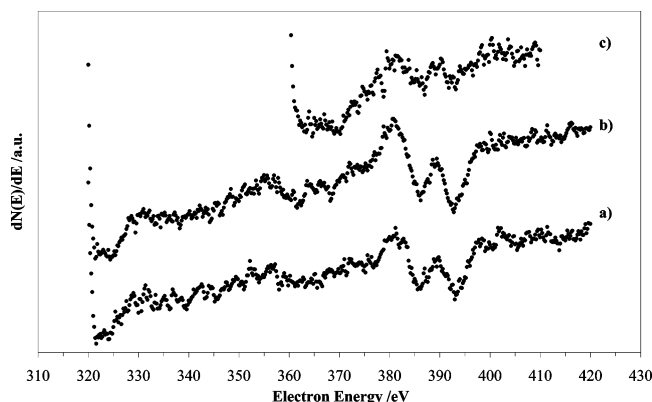


**Figure 6.** RAIR spectra of (a) Rh(111)-CCH<sub>3</sub> and (b) 5 L of NO adsorbed on Rh(111)-CCH<sub>3</sub> at 300 K. Spectra in (c)–(e) are following NO adsorption at 120 K on Rh(111)-CCH<sub>3</sub> + NO, the surface prepared in (b), at exposures of 5 L, 10 L, and 1 × 10<sup>-7</sup> Torr dynamic pressure, respectively. All spectra are recorded at 120 K.

the second most intense is the peak at 2853 cm<sup>-1</sup>, and the  $\nu_s(\text{CH}_3)$  band is drastically reduced (Figure 6e). In addition, the NO region remains essentially unchanged as the NO exposure is increased, except that in a dynamic pressure of NO the peak is slightly broadened. This result provides further evidence that the appearance of the two extra bands in the methyl stretching region is not linked to the development of the band at 1442 cm<sup>-1</sup>. The perturbation of the methyl spectrum is, we suggest, due to NO adsorbed in a second layer.

Auger electron spectroscopy was then used to confirm that NO does indeed adsorb in the ethylidyne adlayer at 120 K. The advantages of using AES are that it can unambiguously detect nitrogen and also that the shape of the N (KVV) Auger peak should be characteristic of molecular NO. On the other hand, the main drawback is that Auger spectroscopy is known to be an invasive technique, which can possibly alter or modify the surface under investigation. To minimize possible effects due to the electron beam, this was defocused to a size of approximately 3 mm and the beam current was limited to a value of about 0.5  $\mu\text{A}$ . Preliminary Auger spectra following adsorption of NO at 120 K on clean Rh(111) were used to verify whether those conditions were met. Figure 7a shows Auger spectra of nitrogen signal following exposure of 10 L, and Figure 7b shows spectra following additional 10 L (20 L in total) of NO on clean Rh(111). The two spectra were sequentially recorded at a scan rate of 2 eV s<sup>-1</sup>, giving an acquisition time of 50 s. The nitrogen Auger spectrum shows two main peaks at 386 and 393 eV in good agreement with previously reported spectra.<sup>26</sup> The peaks in the spectrum b corresponding to 20 L of total NO exposure are consistently more pronounced than that of 10 L (spectrum a). This fact reasonably indicates that during the first scan on





**Figure 7.** Nitrogen (KVV) Auger spectra recorded at 120 K following (a) 10 L exposure of NO on Rh(111), (b) 20 L exposure of NO on Rh(111), and (c)  $10^{-6}$  Torr of NO dynamic pressure on Rh(111)–CCH<sub>3</sub>. All NO doses were made at a surface temperature of 120 K.

the 10 L of NO surface, possible effects due to the electron beam on the NO adlayer were minimal. Since the position of the nitrogen peaks is found to be limited to the energy range of 370–400 eV, this allows the scanning region for the Auger spectrum of NO adsorption on Rh(111)–CCH<sub>3</sub> surface to be restricted. Therefore, in this way the time for which the surface is exposed to the electron beam is reduced by half. Figure 7c shows the Auger spectra of NO on Rh(111)–CCH<sub>3</sub> acquired at 120 K at NO dynamic pressure of  $1 \times 10^{-6}$  Torr, where the scanning region is limited to 50 eV. The similarity between the line shape and position of the three spectra is notable. From this one can conclude that the NO molecule is on the adlayer and that it can be detected by AES under the chosen experimental conditions. It should be noted that the fact that the surface was exposed to NO at a dynamic pressure does not invalidate the conclusion that the NO has been found to adsorb as a second adlayer on top of the CCH<sub>3</sub> adlayer, since Auger spectroscopy can only be sensitive to species in the gas phase at pressures far in excess of  $1 \times 10^{-6}$  Torr. Further important information obtained from this measurement is an estimate of the coverage of the NO adsorbed on top of the Rh(111)–CCH<sub>3</sub> adlayer. The ratio between the intensities of the nitrogen Auger transitions of the NO molecule adsorbed on clean rhodium and on the CCH<sub>3</sub> adlayer can approximate the ratio between the respective values of coverage. Therefore, given a saturation coverage in the range of 0.65–0.7 ML for NO on clean Rh(111),<sup>19</sup> the maximum coverage of NO adsorbed as a second adlayer is estimated to be of the order of 0.3 ML. It should be noted that this estimate is considered as a lower limit of the amount of the adsorbed NO on Rh(111)–CCH<sub>3</sub>, since in principle NO desorption due to the electron beam cannot be excluded.

To conclude this investigation, it is worth mentioning that RAIRS studies were also conducted using CO on Rh(111)–CCH<sub>3</sub> system at 120 K. Surprisingly, exposing the surface to CO at low surface temperature over a wide range of exposures including at dynamic pressure of  $1 \times 10^{-7}$  Torr does not produce any appreciable effect (results not shown). This might lead us to conclude that the unpaired electron of NO in the antibonding  $2\pi^*$  orbital is in some way responsible for the behavior observed in the NO postadsorption measurements.

## Conclusions

RAIRS studies of the static interaction between NO and Rh(111)–CCH<sub>3</sub> system at 120 K have revealed a significant influence on the symmetry of the methyl group. In particular, the adsorption of NO induces the appearance of two extra bands

in the C–H spectral region at 2925 and 2853  $\text{cm}^{-1}$ , which grow as the amount of NO exposure is increased. The first resonance is characteristic of the antisymmetric C–H stretch, which is a forbidden mode in RAIR spectroscopy, and therefore its presence indicates that a nonzero component of the dipole moment normal to the surface is induced by the presence of the NO molecule. The second resonance reasonably might reflect the distortion of the symmetry of the  $\nu_s(\text{CH}_3)$  mode which results in a resonance close to 2872  $\text{cm}^{-1}$ . At the same time, the  $\nu_s(\text{CH}_3)$  band at 2872  $\text{cm}^{-1}$  becomes consistently depleted, but it is never suppressed. This observation can be explained by supposing that the interaction of NO and the CCH<sub>3</sub> adlayer is localized and therefore limited to some methyl groups rather than to the whole CCH<sub>3</sub> adlayer. On the other hand, the NO spectral region seems to remain unperturbed as this effect is observed with the increasing NO exposure and even at dynamic NO pressures. This suggests that the NO molecule adsorbs in a second adlayer with its intermolecular axis parallel to the surface.

In addition, the perturbation on CCH<sub>3</sub> adlayer induced by the NO exposure at low temperature is also clearly observable if the Rh(111)–CCH<sub>3</sub> surface is preexposed with NO at room temperature. This fact indicates that adsorption of NO at 300 K does not alter the CCH<sub>3</sub> adlayer in a manner likely to influence the adsorption of NO at 120 K, since this adsorption takes place on the defected regions of the CCH<sub>3</sub> adlayer as previously discussed. Once those particular regions are initially saturated with NO, further exposure to NO up to a dynamic NO pressure at 120 K produces no change in that particular spectral region. Auger electron spectroscopy allowed the identification of the NO species adsorbed as a second adlayer, under chosen experimental conditions. From the results, an estimated coverage of 0.3 ML was found by comparing with peak intensities of NO adsorbed on clean Rh(111) at 120 K.

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