

# Adsorption structures of NO/Pt(111) investigated by scanning tunneling microscopy

M. Matsumoto<sup>a)</sup>

*Institute for Molecular Science, Myodaiji, Okazaki 444-8585, Japan, and Institute of Industrial Science, University of Tokyo, Minato-ku, Tokyo 106-8558, Japan*

N. Tatsumi, K. Fukutani, and T. Okano<sup>b)</sup>

*Institute of Industrial Science, University of Tokyo, Minato-ku, Tokyo 106-8558, Japan*

T. Yamada, K. Miyake, K. Hate, and H. Shigekawa<sup>c)</sup>

*Institute of Applied Physics, Center for TARA, and CREST, Japan Science and Technology Corporation (JST), University of Tsukuba, Tsukuba 305-8573, Japan*

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The adsorption structure of nitric oxide (NO) on Pt(111) was studied at 10 and 70 K by scanning tunneling microscopy (STM). The island growth modes at both temperatures are similar except for the domain size of the  $2 \times 2$  structure. In these low temperature region, two phases can coexist at medium coverages. These phases are assigned to the two NO species occurring at different stretching-vibrational frequencies observed in the previous vibrational spectroscopic studies. The relative location of two different species observed by STM and its stretching-vibrational frequencies suggests that the adsorption sites of NO on the Pt(111) surface at low and high coverages correspond to the hollow and the on-top sites, respectively. © 1999 American Vacuum Society. [S0734-2101(99)22404-9]

## I. INTRODUCTION

The adsorption and reaction of nitric oxide (NO) on transition metal surfaces have been the objects of considerable interest due to their importance in the catalytic conversion of automotive exhaust.<sup>1-3</sup> In addition, the unpaired electron in the antibonding  $2\pi^*$  orbital of NO increases the variety of reactions, which has attracted much attention of chemists for many years. Many efforts have been made to determine the adsorption structures of NO on the platinum surfaces,<sup>4-11</sup> but there still remains a controversy.

It is known that NO adsorbs molecularly on the Pt(111) surface. In the temperature range between 80 and 160 K, a  $1490 \text{ cm}^{-1}$  peak at low coverages and a  $1710 \text{ cm}^{-1}$  peak at high coverages are detected by electron energy-loss spectroscopy (EELS)<sup>4,5</sup> and infrared absorption spectroscopy (IRAS).<sup>6-8</sup> These peaks were first assigned to the N-O stretching vibrations of monomer and dimer species, respectively.<sup>4</sup> Later, Gland and Sexton adopted a "site model" based on a comparison of the stretching-vibrational frequency of the adsorbed NO with that of NO in nitrosyl complexes.<sup>5</sup> They suggested that NO occupies a bridge site at low coverages and transits to an on-top site as the coverage increases. This site model has been supported by many groups.<sup>6,8,9</sup> On the contrary, from a dynamical low-energy electron diffraction (LEED) analysis, Materer *et al.*, concluded that the three-fold face-centered-cubic (fcc) hollow site is the most probable adsorption site for the  $2 \times 2$  ordered structure of NO on Pt(111) at the saturation coverage of  $\theta_{\text{NO}} = 0.25 \text{ ML}$ .<sup>10</sup> Their report reopened a controversy over the adsorption structure of NO on Pt(111). Ge and King cal-

culated the adsorption energies of NO on Pt(111) using density-functional theory (DFT) with the generalized gradient approximation (GGA).<sup>11</sup> They also found that the fcc hollow site is most stable, supporting the LEED result.

Recently, Loffreda *et al.* evaluated the stretching-vibrational frequencies of NO on Pd(111) and Rh(111) by DFT calculations.<sup>12</sup> They found that the vibrational frequency of NO on the most stable fcc hollow site is in better agreement with the experimental value than that on the bridge site which has been regarded as the most probable adsorption site of NO so far. Their results posed a general question on the adsorption site determination from the comparison of the vibrational frequency to that of nitrosyl complexes. Thus, the structure determination of NO is not yet solved not only on the Pt(111) but also on other transition metal surfaces.

Scanning tunneling microscopy (STM) is one of the most powerful techniques for the determination of surface structures. However, the number of reported STM studies of adsorbed gas molecules on metal surfaces is still limited. For NO on Pt, only one report for NO/Pt(001) by Song *et al.* has been published before.<sup>13</sup> To our knowledge, NO/Pt(111) has not yet been investigated by means of STM.

In this article, we report the STM observation of the NO Molecules on Pt(111) at 10 and 70 K. Measurement at low temperatures enables us not only to observe the mobile gas molecule fixed in the measurement time scale but also to observe several different metastable species at the same time. This is necessary for the identification of the different species which has the same periodicity, because a simultaneous atomic resolution of the substrate and the adsorbate is not frequently possible in STM. On the basis of the coverage dependence of the STM images and the data reported in pre-

<sup>a)</sup>Electronic mail: masuakiiis.u-tokyo.ac.jp

<sup>b)</sup>Electronic mail: okano@iis.u-tokyo.ac.jp

<sup>c)</sup>Electronic mail: hidemi@ims.tsukuba.ac.jp

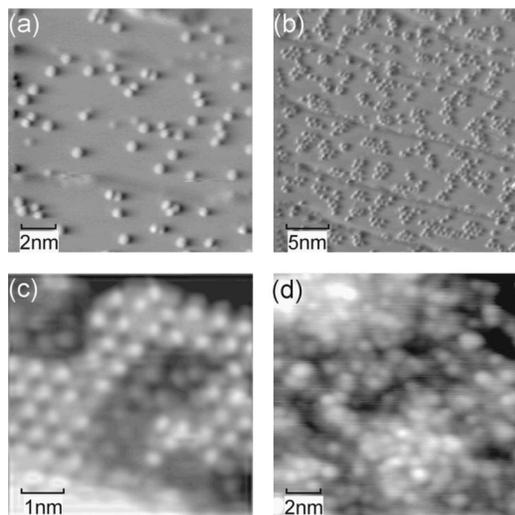


FIG. 1. STM images of NO/Pt(111) at 10 K: (a)  $\theta_{\text{NO}} \approx 0.03$  ML, (b)  $\theta_{\text{NO}} \approx 0.06$  ML, (c) medium, and (d) high coverages. (a),(b),(d):  $V_{\text{tip}} = 0.5$  V,  $I_t = 0.5$  nA, (c):  $V_{\text{tip}} = 0.1$  V,  $I_t = 5$  nA. (a),(b): current image, (c),(d): topographic image.

vious LEED and vibrational studies, the adsorption structure of NO molecules on the Pt(111) surface is discussed.

## II. EXPERIMENT

The STM measurements were carried out in an ultrahigh-vacuum chamber equipped with a low-temperature STM unit (Unisoku, USM-601) and LEED.<sup>14</sup> The base pressure was lower than  $1 \times 10^{-8}$  Pa. The Pt(111) sample was cleaned by repeated cycles of Ar<sup>+</sup> ion sputtering and annealing at 1400 K. To reduce carbon contaminations, repeated cycles of annealing under  $2 \times 10^{-5}$  Pa of oxygen at 1100 K and flashing to 1400 K were performed. The sample was heated with a Ta heater and the temperature was measured with an optical pyrometer throughout the cleaning process. The sample cleanliness was checked by LEED and STM. The STM unit is attached to the bottom of a liquid helium reservoir directly, allowing measurements at 9 K with liquid helium. Using liquid nitrogen as a cryogen, the lowest measurement temperature of about 70 K was achieved by evacuating the cryostat to reduce the vibration caused by bubbling of liquid nitrogen. Measurements in the temperature ranges of 20–70 K and 90–250 K were difficult because of the large thermal drift. The sample temperature was measured with a Au–Fe 0.07%/chromel thermocouple attached to the STM unit. NO gas was introduced into the vacuum chamber through a variable leak valve and a 1/8 in. capillary tube directed to the sample surface. The NO coverage was estimated from the STM image. The scale was calibrated by measuring STM images of the Si(111)- $7 \times 7$  structure at several temperatures.

## III. RESULTS AND DISCUSSION

STM images of NO/Pt(111) after exposing the sample to NO at 10 K are shown in Fig. 1. The tip bias ( $V_{\text{tip}}$ ) and the tunnel current ( $I_t$ ) of our STM measurements were 0.1–0.5 V and 0.5–1 nA, respectively. The occupied states are ob-

served. The parameters for all images are given in the figure captions. Under these conditions, NO molecules are observed as bright spots. Any dips, which were assigned to oxygen or nitrogen atoms in the STM images of NO/Ru(0001),<sup>15</sup> could not be observed in our STM images of NO/Pt(111) at 10 and 70 K. This shows that the NO does not dissociate on Pt(111) in this temperature region. When the tunnel resistance was reduced ( $V_{\text{tip}} = 0.1$  V,  $I_t = 10$  nA), individual platinum atoms could be resolved. However, in this case, the images of NO particles were distorted by the interaction of the tip and the molecules, and we could not determine the adsorption site from the STM images directly. As revealed by repeated scans of the same surface area, the NO molecules were not displaced or desorbed by the interaction with the tip under the conditions presented in this report.

At very low coverages [Fig. 1(a), 0.03 ML], most of the NO molecules adsorb on the surface randomly. Some of them already form dimers or trimers. The distance between the molecules in these dimers and trimers is about 0.55 nm, which is about twice the nearest neighbor Pt–Pt distance of the Pt(111) surface. Therefore, these dimers are different from the gas phase dimers, in which the distance between the molecules is 0.224 nm. At medium coverages, these dimers and trimers grow into  $2 \times 2$  islands [Fig. 1(b), 0.06 ML]. These islands are small and they consist of small domains whose phases do not match with each other. The number of the molecules in one domain is less than ten. This is considered to be caused by the very low mobility of NO at 10 K. As the coverage increases, a second phase of adsorbed molecules appears on the surface. In Fig. 1(c), the bright spots construct  $2 \times 2$  structures in the region from the left-bottom to the right-top side of the image. In addition, less bright spots can be seen in the space between the  $2 \times 2$  islands of the bright spots and also construct  $2 \times 2$  structures. These two kinds of bright spots show the presence of two different molecular species, as will be discussed later. At very high coverages, NO condenses on the surface in multilayers [Fig. 1(d)]. In this case only a rough surface can be seen by STM without any regular structures on the surface. The estimation of the coverage and the number of layers from the multilayer image is difficult because the second layer molecules cannot be observed by STM.

STM images after exposing the sample to NO at 70 K are shown in Fig. 2. At very low coverages [Fig. 2(a), 0.04 ML], many isolated molecules and some  $2 \times 2$  islands exist on the surface. As the coverage increases [Fig. 2(b), 0.14 ML],  $2 \times 2$  islands grow in size and number. The islands consist of more than 20 molecules, which means they are larger than at 10 K. This reflects the higher mobility of NO at 70 K. Several bright spots indicated by arrows exist in Fig. 2(b) and, at higher coverages, also construct  $2 \times 2$  structures as indicated in Fig. 2(b). At very high coverages, NO also condenses on the surface [Fig. 2(d)]. These images indicate that the adsorption structure of NO at 70 K is qualitatively similar to that at 10 K. The main difference between them is the do-

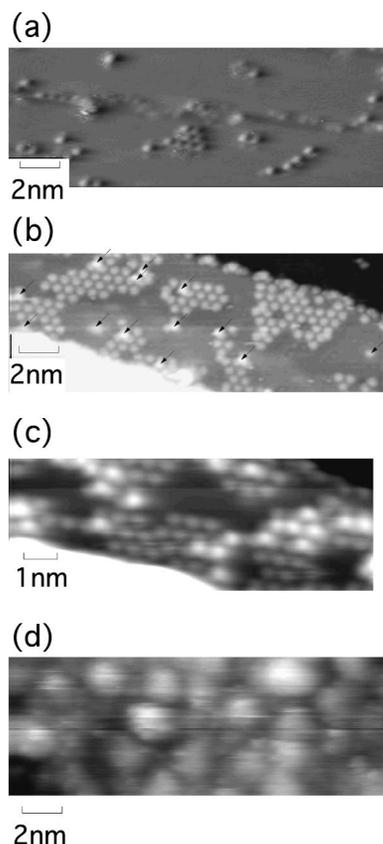


FIG. 2. STM images of NO/Pt(111) at 70 K: (a)  $\theta_{\text{NO}} \approx 0.03$  ML, (b)  $\theta_{\text{NO}} \approx 0.14$  ML, (c) medium, and (d) high coverages. (a),(b),(d):  $V_{\text{tip}} = 0.5$  V,  $I_t = 0.5$  nA, (c):  $V_{\text{tip}} = 0.1$  V,  $I_t = 1$  nA. (a): current image, (b),(c),(d): topographic image.

main size which is closely related to the mobility of the NO molecules.

We focus on the two different molecular species observed in Fig. 1(c). A large scale image where both species coexist is shown in Fig. 3(a). The characteristic features can be summarized as follows. (i) Two kinds of molecular species are present on the surface. (ii) Both species construct  $2 \times 2$  structures. (iii) The heights of the bright and the less bright species are 0.087 and 0.04 nm, respectively, as indicated in the profile plot of Fig. 3(b). (iv) The bright (“higher”) species is located on the threefold hollow site of the less bright (“lower”) one.

According to the previous vibrational studies at a sample temperature of about 100 K, the stretching-vibrational frequencies of N–O on Pt(111) at low and high coverages are  $\approx 1490$  and  $\approx 1710$   $\text{cm}^{-1}$ ,<sup>4–6</sup> respectively. The  $2 \times 2$  LEED pattern was observed only at high coverages, previously.<sup>4,6</sup> The LEED pattern was observed at a coverage where only the vibrational frequency of  $1490$   $\text{cm}^{-1}$  is measured by IRAS at 90 K and it was confirmed that the  $2 \times 2$  LEED pattern also appears under this condition.<sup>16</sup> Furthermore, it was shown that the LEED intensity versus energy ( $I$ – $V$ ) curves change at higher coverages. This suggests the presence of two different  $2 \times 2$  phases of NO/Pt(111).

The measurement temperature of our STM is lower than

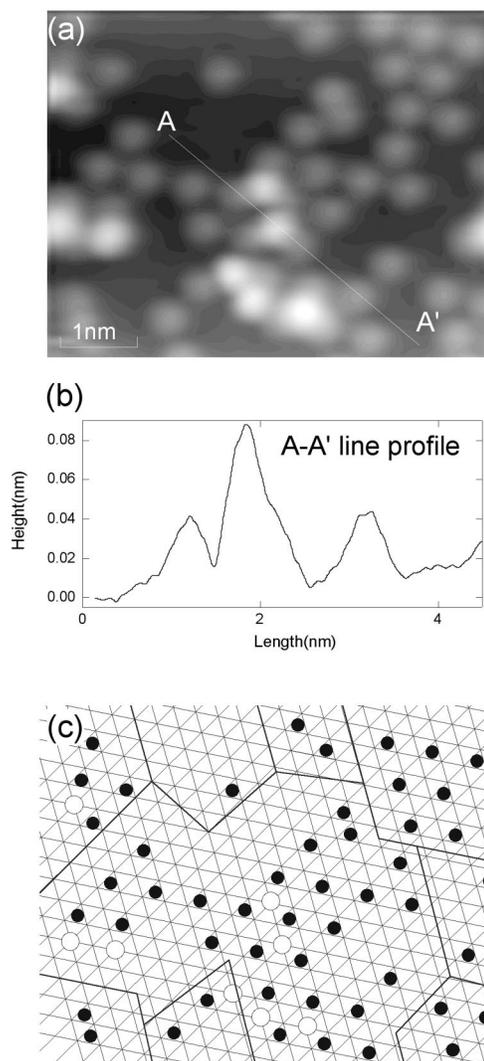


FIG. 3. (a) STM topographic image of NO adsorbed on Pt(111) at 10 K.  $\theta_{\text{NO}} \approx 0.15$  ML.  $V_{\text{tip}} = 0.1$  V,  $I_t = 1$  nA. (b) Profile plot along A–A' line in Fig. 2(a). The heights of higher and lower species are 0.087 and 0.04 nm, respectively. (c) A model for NO/Pt(111) at low temperature. The closed and open circles correspond to the lower and the higher species, respectively. The thick line indicates the domain boundary of NO adsorbates. The thin line indicating the platinum lattice is drawn on the assumption that the lower species adsorbs on the threefold hollow site of Pt(111).

that in those studies. However, in IR spectra measured at 25 K, no additional peaks appear before condensation occurs.<sup>17</sup> We also confirmed that the two kinds of species exist after annealing the sample to 100 K. Therefore, the structure of NO/Pt(111) at the temperatures of our measurements is likely to be similar to the one at about 100 K. In our coverage dependent STM measurements, the lower species first appears, while the higher species appears at higher coverages. Therefore, we suppose that the lower and higher species in the STM can be assigned to the two species observed in the vibrational studies at the frequencies of  $1490$  and  $1710$   $\text{cm}^{-1}$ , respectively. Due to the higher mobility at higher temperatures, molecules will adsorb to yield a dense layer of lower species before the higher species grows, but in the

low-temperature region, both species can coexist even at low coverages.

From the height analysis, we found that the higher species is twice as high as the lower one. But both the heights of these species as well as the difference in heights between them are considerably shorter than the N–O distance (0.117 nm) in gas phase. The heights in the STM images do not indicate the real corrugation. The heights rather reflect the electronic structure of the surface near the Fermi level. Similar two types of STM images have been measured for the carbon monoxide (CO) molecules on Pt(111) previously.<sup>18</sup> The heights were determined to be 0.044 and 0.007 nm in this case. These images were calculated by electron scattering quantum chemical technique and assigned to the two distinct binding sites (the on-top and the bridge sites, respectively).<sup>19</sup> The STM image of CO on the hollow site was also calculated and it was suggested that the height of the species on this site is lower than that on the bridge site. No calculations of adsorbed NO molecules have been performed yet, but the difference of the apparent height can also be related to the difference of the adsorption site because of the similarity of the molecular orbital and bonding mechanism between NO and CO. From the relative locations of the two species in the STM, two combinations of the site occupation can be expected. One possibility is the occupation of hollow [hexagonal-close-packed (hcp) or fcc] and the on-top sites, and the other is the occupation of the fcc and the hcp hollow sites. The occupation of the bridge and the on-top sites which has been adopted previously is not preferable because a molecule on the on-top site does not sit on the center of the three molecules on the bridge site. The large difference in the stretching-vibrational frequencies of N–O is inconsistent with the occupation of both hollow sites. Therefore, we suggest that the lower and the higher species adsorb on the hollow and the on-top sites of the Pt(111) surface, respectively. We cannot determine which hollow site, fcc or hcp, is preferable from our STM results only. The dynamical LEED analysis concluded that the fcc hollow is the most probable adsorption site of NO,<sup>10</sup> and it was suggested to be the structure at low coverages.<sup>16</sup> The DFT calculation showed that the fcc hollow is the most stable adsorption site.<sup>11</sup> This also suggests that the fcc hollow is the first occupied site at low coverages. From this discussion, we suppose that the lower and higher species adsorb on the fcc hollow and the on-top sites, respectively. The model for the STM image of Fig. 3(a) is shown in Fig. 3(c).

#### IV. CONCLUSIONS

STM images of NO/Pt(111) were measured at 10 and 70 K. The adsorption structure at 70 K is similar to that at 10 K except for the  $2 \times 2$  domain size. At low coverages, the NO molecules adsorb on the surface randomly. As the coverage is increased, they construct two different phases of  $2 \times 2$  structures. And at high coverages, they condense in multilayers. The higher and the lower  $2 \times 2$  species observed at medium coverages are assigned to the stretching-vibrational frequencies of 1490 and 1710  $\text{cm}^{-1}$  measured in the previous vibrational studies, respectively. From the relative locations of these two different species in the STM images, the adsorption sites of the lower and the higher species are supposed to be the fcc hollow and the on-top sites, respectively.

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