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Citation: The Journal of Chemical Physics 141, 134705 (2014); doi: 10.1063/1.4896558
View online: http://dx.doi.org/10.1063/1.4896558
View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/141/13?ver=pdfcov
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J. Vac. Sci. Technol. B 23, 1726 (2005); 10.1116/1.1942508
Formation of unique trimer of nitric oxide on Cu(111)

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(Received 16 July 2014; accepted 4 September 2014; published online 7 October 2014)

We report that NO molecules unexpectedly prefer a trimeric configuration on Cu(111). We used scanning tunneling microscopy (STM) at 6 K, and confirmed that the NO molecule is bonded to the face-centered-cubic hollow site in an upright configuration. The individual NO molecule is imaged as a ring protrusion, which is characteristic of the doubly degenerate $2\pi^*$ orbital. A triangular trimer is thermodynamically more favorable than the monomer and dimer, and its bonding structure was characterized by STM manipulation. This unique behavior of NO on Cu(111) is ascribed to the threefold symmetry of the surface, facilitating effective mixing of the $2\pi^*$ orbitals in a triangular configuration. © 2014 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4896558]

I. INTRODUCTION

NO has a high chemical affinity for metals, and NO–metal interactions are important in chemical syntheses,1 biological processes,2 and heterogeneous catalysis.3 Because of the relevance to catalytic reduction of toxic NO, from exhaust gases, the reaction, bonding structure, and valence state of NO on metal surfaces have been studied intensively.4–6 As a result of the presence of an unpaired electron in its $2\pi^*$ orbital, the bonding structure is complex, and depends on the coverage and temperature as well as on the nature of the surfaces. One of the important characteristics of NO is that it forms a dimer, (NO)$_2$, via overlap of an unpaired electron, on metal surfaces as well as in the gas7 and condensed phases.8,9,10 It has been proposed that the catalytic reduction of NO proceeds via the formation of a (NO)$_2$ intermediate on Ag(111),10–13 represented by $2\text{NO} \rightarrow (\text{NO})_2 \rightarrow \text{N}_2\text{O} + \text{O}$. A similar catalytic reduction mechanism via dimer formation has been proposed on Cu,14–16 Au,17–19 and transition metal20–22 surfaces. Moreover, NO dimers on coinage-metal surfaces have attracted attention because of their photochemical reactions such as NO desorption23,24 and reductive $\text{N}_2\text{O}$ and $\text{N}_2$ formation.25 Intramolecular coupling therefore plays an important role in the catalytic reduction of NO on metal surfaces.

On Cu(111), the initial adsorption state of NO at $T \approx 100$ K was reported to be a monomeric species.26–32 The bonding geometry was initially proposed to be a bent structure on the bridge site, based on comparison with the N–O stretching frequency of nitrosyl complexes.26–28 However, the use of the vibrational frequency as a guide to determining the bonding site of NO on a metal surface was questioned,33 and an upright NO molecule on the threefold site was proposed as a candidate for the adsorption structure on Cu(111).29 This was later supported by theoretical calculations.34–37 With increasing coverage, NO sequentially forms the p(3×3) and (\sqrt{7}×\sqrt{7})R19.1° overlayers.29 It was proposed that the unit cells were occupied by one NO molecule at coverages of 0.11 and 0.14 ML (1 ML = 1.76 × 10$^{15}$ molecules/cm$^2$) for the former and latter phases, respectively. On the other hand, Sueyoshi et al.28 determined the coverage for the p(3×3) phase to be 0.44–0.56 ML, using Auger electron spectroscopy (AES). The structure of the overlayer, i.e., how many NO molecules occupy the unit cell, therefore remains controversial. It was shown that $\text{N}_2\text{O}$ formation occurs from these overlayers,29 implying that attractive NO–NO coupling occurs in these phases.

In this work, we investigated the adsorbed state of NO on Cu(111), using scanning tunneling microscopy (STM). Direct imaging of individual NO molecules allows us to determine that the bonding site is the face-centered-cubic (fcc) hollow site. At low temperature (15 K), NO exists mainly as a monomer, as a result of limited diffusion across the surface. An individual NO molecule is imaged as a characteristic ring, which is ascribed to the doubly degenerate $2\pi^*$ orbital. At elevated temperature (80 K), NO diffuses and, unexpectedly, forms a trimer with a triangular configuration. The trimeric configuration is therefore thermodynamically stable. This unusual behavior of NO on a surface is ascribed to the threefold symmetry of the substrate. It was found that the trimer constitutes p(3×3) and (\sqrt{7}×\sqrt{7})R19.1° overlayers at coverages of 0.33 and 0.43 ML, respectively.

II. EXPERIMENTAL

The STM experiments were carried out in an ultrahigh-vacuum chamber at either 6 or 80 K (USM-1200, Unisoku). An electrochemically etched tungsten tip was used as the STM probe. Single-crystalline Cu(111) was cleaned by repeated cycles of Ar$^+$ sputtering and annealing. The surface was exposed to NO gas via a tube doser positioned ~1 cm from the surface, at either 15 or 80 K, through a variable-leak valve. For scanning tunneling spectroscopy (STS), the $dI/dV$ curve was obtained numerically from the I–V curve or obtained using a lock-in amplifier with a modulation voltage of 1 mV$\text{rms}$ at 590 Hz, with the feedback loop open. Each spectrum was displayed after subtraction of $dI/dV$ obtained over the clean surface at the same tip height. The $dI/dV$ images were obtained using a lock-in amplifier with a modulation voltage of 20 mV$\text{rms}$ at 2 kHz, with the feedback loop closed.

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III. RESULTS AND DISCUSSION

Figure 1(a) shows a typical STM image of Cu(111) exposed to NO at 15 K. The image was obtained at 6 K. The main feature at low temperature is a ring-shaped protrusion, which is assigned to an isolated NO molecule. Molecular clusters composed of two (dimer) or three (trimer) NO molecules were also observed, as described in detail below. The bonding site of NO is the fcc hollow site, based on the position relative to Cu adatoms, which are known to be located at the fcc hollow sites42 (see Figs. S1 and S2 in the supplementary material43). The characteristic ring protrusion directly displays the projection of the doubly degenerate $2\pi^*$ orbital, suggesting that NO is adsorbed in an upright configuration. These results are in agreement with theoretical calculations.34–37 Figure 1(b) shows a $dI/dV$ curve recorded over the ring (cross in Fig. 1(a)). The curve shows a peak at the Fermi level, which is ascribed to the $2\pi^*$ state. The complementary $dI/dV$ images are displayed in Fig. 1(c). The $dI/dV$ images show ring protrusion only near the Fermi level. The doubly degenerate $2\pi^*$ orbital is therefore retained, and partially occupied, on Cu(111). The molecule belongs to the $C_{3v}$ point group and the degeneracy of the $2\pi^*$ orbital is retained on the surface. This is in contrast to the case of NO/Cu(110), where the twofold symmetry of the surface degrades the molecular symmetry to $C_{2v}$, thereby lifting the degeneracy.38,39 The width of the $2\pi^*$ resonance is quite small (~0.1 eV), which reflects weak coupling of NO with the Cu(111) surface.40,41 Recently, it was revealed, using STM, that NO retains a localized spin moment on Au(111), giving rise to a Kondo resonance state at 9 K.44 This is ascribed to the weak interaction of NO with a coinage-metal surface, resulting in the survival of an unpaired electron in its $2\pi^*$ orbital.13,45,46 In contrast, the unpaired electron is readily quenched on transition metal surfaces.35,47 The interaction with Cu surfaces is intermediate between these cases, and our result indicates that the open-shell structure is retained on Cu(111) as well as on Cu(110);38 however it still has to be determined whether or not the magnetic moment is retained.

We produced a dimer and a trimer from individual NO molecules by STM manipulation. Figure 2(a) shows STM images of three NO molecules on Cu(111) at 6 K ($V = 30$ mV, $I = 5$ nA). A dimer was produced by manipulating one molecule toward another, as shown by the arrow. (b) STM image of produced dimer, together with remaining monomer. (c)–(e) STM images of dimer in three orientations ($V = 30$ mV, $I = 5$ nA). Lines represent the lattice of surface Cu atoms, and the dots indicate the fcc hollow sites, showing the approximate positions of the molecules. The interaction with the STM tip induced the dimer to rotate among (c)–(e). The image sizes are $38 \times 32$ Å for (a) and (b), and $18 \times 18$ Å for (c)–(e).
The hexagonal-close-packed (hcp) hollow site was produced by application of a voltage pulse of 0.5 V to the trimer in terms of orbital mixing between the molecules on the surface. Figure 4 shows schematic energy diagrams of the frontier orbitals for NO, (NO)2, and (NO)3. A series of orbitals are depicted (not calculated), according to those for gas-phase molecules. Note that the energy levels are broadened on the surface, as observed in the STS curves for NO (Fig. 1(b)) and (NO)2 (Fig. 3(c)). On formation of a dimer, four mixed orbitals are produced with the bonding states occupied, which makes the dimer more stable than the monomer. The oval protrusion observed for the dimer (Fig. 2(b)) reflects the 2b1 orbital located near the Fermi level. On formation of a trimer, four mixed orbitals are produced, in which two levels are doubly degenerate. The STM images of the trimer (Figs. 1(a) and 3(d)) show the shape of 6a1 orbital for the dimer and the 5a1 orbital for the trimer with respect to that of the 2π* orbital for the monomer (Fermi level) are represented by E7a1 and E5a1, respectively (Fig. 4). The energy gain of the 6e orbital located at the Fermi level is negligible, therefore the stabilization energy of the dimer is |E7a1| per molecule, whereas that of the trimer is 2|E5a1|. In the case of |E5a1| > 1.5|E7a1|, the trimer would therefore be energetically more favorable than the dimer. We propose that this is achieved because of the threefold symmetry of the substrate. The substrate mediates mixing between the 2π* orbitals, which is maximized for the trimer in a triangular configuration. Note that we should consider orbital mixing with surface states and charge transfer between the NO molecules and substrate to evaluate the relative stabilities of the trimer and the dimer precisely. A theoretical approach would be helpful in elucidating the origin of this unusual and intriguing behavior of NO on Cu(111).

position between the molecules (cross in Fig. 3(b)) shows a peak at the Fermi level (discussed later). It is remarkable that NO adopts a trimeric configuration on the surface. Figure 3(f) shows a typical image of Cu(111) exposed to NO at 80 K. Depression of the triangular shape is dominant on the surface, which is identical to the case for the trimer produced by manipulation. The trimer is therefore thermodynamically stable on Cu(111). The trimer is dominant even at low coverage (Fig. 3(f)), suggesting that NO molecules diffuse across the surface and are encountered to form a trimer at 80 K. On formation of a dimer, four mixed orbitals are produced, in which two levels are doubly degenerate. The STM images of the trimer (Figs. 1(a) and 3(d)) show the shape of 6e orbital, which is observed at the Fermi level in the corresponding STS curve (Fig. 3(c)). The relative stabilities of the dimer and trimer are based qualitatively on the total energy difference of the valence electrons. The energies of the 7a1 orbital for the dimer and the 5a1 orbital for the trimer with respect to that of the 2π* orbital for the monomer (Fermi level) are represented by E7a1 and E5a1, respectively (Fig. 4). The energy gain of the 6e orbital located at the Fermi level is negligible, therefore the stabilization energy of the dimer is |E7a1| per molecule, whereas that of the trimer is 2|E5a1|. In the case of |E5a1| > 1.5|E7a1|, the trimer would therefore be energetically more favorable than the dimer. We propose that this is achieved because of the threefold symmetry of the substrate. The substrate mediates mixing between the 2π* orbitals, which is maximized for the trimer in a triangular configuration. Note that we should consider orbital mixing with surface states and charge transfer between the NO molecules and substrate to evaluate the relative stabilities of the trimer and the dimer precisely. A theoretical approach would be helpful in elucidating the origin of this unusual and intriguing behavior of NO on Cu(111).
Sueyoshi et al. observed that as the coverage increased, a p(3×3) superstructure emerged, for which the NO coverage was estimated to be 0.44–0.56 ML by AES at 100 K. In contrast, Dumas et al. proposed that the coverage of the p(3×3) structure was 0.11 ML, because they observed a single N–O stretching peak by infrared spectroscopy at 88 K, suggesting that only one species is present in the unit cell. Figure 5(a) shows a typical STM image of NO/Cu(111) at 80 K. The trimer (triangular depression) is locally arranged with p(3×3) periodicity. We therefore find that the unit cell of the p(3×3) structure is occupied by a trimer with a local coverage of 0.33 ML, as shown in Fig. 5(b). Note that the unit cell involves only one equivalent species, and this structural model is consistent with the single peak for the N–O stretching mode. Figure 5(c) shows an image of NO/Cu(111) at higher coverage (0.37 ML). At this coverage, individual trimers were imaged as protrusions rather than depressions. We postulate that this originates from unavoidable modification of the tip apex by a NO molecule (“molecular” tip).

IV. CONCLUSIONS

In summary, we investigated the adsorption and valence states of NO on Cu(111), using STM. Individual NO molecules adsorbed at 15 K show a ring protrusion characteristic of the doubly degenerate 2π* orbital. The 2π* orbital is partially filled, suggesting that the NO monomers remain radicals, and can therefore interact with each other through electronic coupling. At elevated temperatures, the molecules aggregate to form a dimer and then a trimer. The electronic coupling is possibly maximized in a triangular configuration on Cu(111), giving rise to the unexpected trimer formation. We propose a new structural model for the overlayers of NO/Cu(111). The trimer constitutes the p(3×3) and (√7×√7)R19.1° overlayers at coverages of 0.33 and 0.43 ML, respectively.

ACKNOWLEDGMENTS

A.S. acknowledges the support of the Japan Society for the Promotion of Science.
