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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
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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, biological processes, and heterogeneous catalysis. 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. 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 gas and condensed phases. It has been proposed that the catalytic reduction of NO proceeds via the formation of a $(NO)_2$ intermediate on Ag(111), represented by $2NO \rightarrow (NO)_2 \rightarrow N_2O + O$. A similar catalytic reduction mechanism via dimer formation has been proposed on Cu, Au, and transition metal surfaces. More-
sizes are 50 Å × 50 Å for (a) and 13 Å × 13 Å for (c).

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 2π* orbital, suggesting that NO is adsorbed in an upright configuration. These results are in agreement with theoretical calculations.14–37 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 2π* 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 2π* orbital is therefore retained, and partially occupied, on Cu(111). The molecule belongs to the C3v point group and the degeneracy of the 2π* 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 C2v, thereby lifting the degeneracy.38,39 The width of the 2π* 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 2π* 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. STM was used to manipulate the molecule on the left laterally toward another to produce a dimer, as represented by the arrow in Fig. 2(a). The produced dimer is imaged as an oval protrusion, accompanied by a depression (Fig. 2(b)). In the dimer, the 2π* orbitals are mixed, giving rise to the characteristic STM image. Figure 2(c) shows the dimer superimposed with a lattice of surface Cu atoms. The bonding sites of the molecules in the dimer can be inferred from their positions before the manipulation, as shown by the dots in Fig. 2(c). The dots (fcc hollow sites) indicate the approximate positions of NO molecules in the dimer. The molecules might be tilted and displaced from the ideal threefold position to optimize the interaction.13 STM induces the dimer to rotate among the three orientations around a Cu atom, as shown in Figs. 2(c)–2(e). The rotation is induced even at V = 30 mV, which hampers STS measurements over the dimer.

Another NO molecule was manipulated toward the dimer to produce a trimer (Fig. 3(a)). The product is imaged as a triangular depression (Fig. 3(b)). The Cu lattice was superimposed on the image of the trimer (Fig. 3(d)), showing the registry of the trimer to the surface (Fig. S2 of the supplementary material45). The approximate positions of the molecules are shown by dots, which are the fcc hollow sites around a Cu atom. The dI/dV curve (Fig. 3(c)) recorded over the
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 at 80 K. On application of a voltage pulse of 0.5 V to the trimer in Fig. 3(d), another trimer with the molecules located around the dimer orbitals for free NO, (NO)$_2$, and (NO)$_3$. These are not calculated but depicted for qualitative argument of the orbital mixing. A red arrow represents occupation by an electron. The molecular orbitals viewed along the axis from the oxygen side are shown. $E_{7a_1}$ and $E_{5a_1}$ represent the energies of the $7a_1$ orbital for (NO)$_2$, and the $5a_1$ orbital for (NO)$_3$, respectively, with respect to that of the $2\pi^*$ orbital for NO. The $2\pi^*$ and $6\sigma$ levels for the monomer and trimer, respectively, are observed by STS at the Fermi level (Figs. 1b and 3c). The STM image of the dimer (Fig. 2b) indicates that its $2b_1$ level is broadened and contributes to the density of states at the Fermi level.

FIG. 4. Schematic energy diagrams of frontier orbitals for free 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. 1b) and (NO)$_3$ (Fig. 3c). 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. 2b) reflects the $2b_1$ 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. 1a and 3d) show the shape of $6\sigma$ orbital, which is observed at the Fermi level in the corresponding STS curve (Fig. 3c). The relative stabilities of the dimer and trimer are based qualitatively on the total energy difference of the valence electrons. The energies of the $7a_1$ orbital for the dimer and the $5a_1$ orbital for the trimer with respect to that of the $2\pi^*$ orbital for the monomer (Fermi level) are represented by $E_{7a_1}$ and $E_{5a_1}$, respectively (Fig. 4). The energy gain of the $6\sigma$ orbital located at the Fermi level is negligible, therefore the stabilization energy of the dimer is $|E_{7a_1}|/\text{per molecule}$, whereas that of the trimer is $1/2|E_{5a_1}|$. In the case of $|E_{5a_1}| > 1.5|E_{7a_1}|$, 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 $2\pi^*$ 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.\textsuperscript{28} observed that as the coverage increased, a p(3\times3) 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.\textsuperscript{29} proposed that the coverage of the p(3\times3) 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\times3) periodicity. We therefore find that the unit cell of the p(3\times3) 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.\textsuperscript{29} 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);\textsuperscript{56} Fig. S3 of the supplementary material.\textsuperscript{15} In Fig. 5(c), the domains of p(3\times3) and (\sqrt{7}\times\sqrt{7})R19.1° structures coexist, and are labeled A and B, respectively. The unit cells are represented by rhombus frames. The labels B and B′ represent different orientational domains. The area of the (\sqrt{7}\times\sqrt{7})R19.1° domain (B and B′) is around twice as large as that of the p(3\times3) domain (A), while the former phase was not observed at lower coverage (Fig. 5(a)). This is consistent with the previous observation that the p(3\times3) phase was replaced by the (\sqrt{7}\times\sqrt{7})R19.1° phase as the coverage increased.\textsuperscript{29} It is likely that the (\sqrt{7}\times\sqrt{7})R19.1° phase also consists of a trimer, with a local coverage of 0.43 ML. The “trimer-unit” model proposed in this work is therefore in full agreement with the results of previous experiments.

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 2\pi∗ orbital. The 2\pi∗ 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\times3) and (\sqrt{7}\times\sqrt{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.
43] See supplementary material at http://dx.doi.org/10.1063/1.4896558 for the binding site of NO on Cu(111) and STM images with bare metal and “molecular” tips.