

Hollow-site molecular adsorption for NO on Pt(111) and Ni(111): Invalidating vibrational site assignment rules

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Dynamical low-energy electron diffraction analyses of ordered structures of NO molecules chemisorbed on Pt(111) and on Ni(111) conclusively yield threefold-coordinated hollow-site adsorption, and reasonable bond lengths. This invalidates long-standing site assignments based on vibrational measurements, calling that approach into question. The results of this study also contrast with the lower-coordinated bridge and top sites found for CO molecules on the same metal surfaces. The NO molecules are oriented close to the surface normal, O end up.

In this paper, we address the controversial adsorption site for two ordered nitric oxide (NO) overlayers on Pt(111) and Ni(111) surfaces using low-energy electron diffraction (LEED). We have determined hollow-site adsorption for the Pt(111)- $p(2\times 2)$ -NO and the Ni(111)- $c(4\times 2)$ -2NO structures. This adsorption site is unexpected based on current interpretations of vibrational spectroscopy data^{1,2} and on contrasting top- and bridge-site bonding of CO on Pt and Ni.³ No additional structural information has been available for Pt(111), however, our hollow-site finding on Ni(111) confirms a recent site determination from surface-extended x-ray-absorption fine structure⁴ (SEXAFS) and from a parallel LEED analysis.⁵

The expectation of a top- or bridge-bonded NO on Pt(111) and Ni(111) arises from the similarities of NO and CO. In inorganic chemistry, the similarity of molecular orbitals leads to bonding in NO-metal complexes which is comparable to that in many CO-metal complexes.⁷ On surfaces, NO and CO occupy the same adsorption site when coadsorbed with ethylidyne on Rh(111).⁸ In addition, CO and NO form almost identical 0.75-monolayer (ML) coverage (2×2) structures on Rh(111).⁹ However, one striking example of the difference between NO and CO adsorption is the significant lack of richness in LEED patterns resulting from NO adsorption as a function of coverage.

A variety of experimental techniques has been used to determine the adsorption geometry and behavior of NO on Pt(111) and on Ni(111).^{1,2,10} Vibrational spectroscopy, both high-resolution electron-energy loss spectroscopy and infrared spectroscopy,² has identified top and bridge sites as possible NO adsorption sites based on the stretching frequency of NO. However, direct interpretation of the NO geometry based on this is problematic due to the strong correlation between stretching frequency and the effective charge on the NO group.¹¹ The sensitivity of LEED to the positions of atomic cores has allowed us to unequivocally determine the bonding site of NO on Pt(111) and on Ni(111).

Our experiments were carried out in two different stainless-steel ultrahigh vacuum chambers equipped for gas analysis, thermal desorption spectroscopy, Auger

electron spectroscopy (AES), and ion sputtering. Each sample was cleaned by repeated cycles of ion bombardment and annealing in oxygen until no impurities could be detected by AES, and the LEED pattern of the clean surface was sharp and free of diffuse background intensities.

LEED data were collected for the Pt crystal using a digital LEED detector.¹² The $p(2\times 2)$ structure was prepared by adsorbing 1 langmuir ($1\text{ L} = 10^{-6}$ Torr sec) of NO at 90 K followed by annealing to 250 K, giving a sharp (2×2) LEED pattern. The crystal was cooled to 90 K and the intensity versus energy (I - V) curves were measured from 90 to 250 eV at normal incidence. A total of three integer and three fractional order symmetry-averaged beams were used in the structural search for the total energy range of 800 eV.

For the Ni crystal, LEED data were collected by Vari-an 4-grid LEED optics with an off-axis electron gun, and a Dage-MTI SIT-68 high-sensitivity video camera interfaced to a PC was used to record the LEED patterns. The $c(4\times 2)$ structure was prepared by adsorbing 6 L of NO at 190 K followed by annealing to 300 K, yielding a sharp $c(4\times 2)$ LEED pattern. The crystal was cooled to 190 K and I - V curves were measured from 30 to 350 eV at normal incidence. A total of two integer and eleven fractional order symmetry-averaged beams were used in the structural search for a total energy range of 2400 eV.

In both cases, normal incidence was verified by comparing symmetry equivalent beams. Additional experiments were performed to check reproducibility. For quantitative analysis of the experimental I - V curves we used an automated search method based on the tensor LEED approximation¹³ and directed by Pendry's R factor (R_p factor).¹⁴ Error bars were estimated using Pendry's method.¹⁴ Further details of the analysis will be published elsewhere.¹⁵

The clean surfaces were structurally analyzed first, to check both experimental setups and computations.¹⁵ Analysis of the Pt(111)- $p(2\times 2)$ -NO and the Ni(111)- $c(4\times 2)$ -2NO overlayers began by optimizing the NO bond length, the height of the molecules above the surface, the buckling of the topmost metal layer, and the relaxation of the topmost metal-metal interlayer spacing for

various adsorption sites. After the best model was identified, we refined the buckling of the second metal layer, the relaxation of the second metal-metal interlayer spacing, and the lateral displacements consistent with the symmetry of the overlayer.

Four different high-symmetry adsorption sites were tried for the $p(2 \times 2)$ overlayer on Pt(111) assuming 0.25-ML coverage. As a check for decomposition, O or N atoms adsorbed in the fcc hollow site were also tried assuming 0.25-ML coverage. In addition, we tested a $p(2 \times 1)$ fcc hollow-site model with 0.5-ML coverage, which would yield a (2×2) diffraction pattern after averaging over the three possible domains. The $p(2 \times 2)$ NO fcc hollow-site model gave by far the best fit between theory and experiment. Allowing relaxation of two metal layers and lateral displacements consistent with a mirror plane and the threefold rotational symmetry ($p3m1$) resulted in the final structure (Fig. 1) with selected $I-V$ curves shown in Fig. 2 and an R_p factor of 0.28. This value is comparable with R_p -factor values obtained with recent extensive LEED analyses for structures of similar complexity which are supported by additional experimental techniques and are not controversial. For instance, $R_p=0.28$ was obtained for the Pt(111)- $p(2 \times 2)$ ethylidyne structure¹⁶ and $R_p=0.32$ for the Rh(111)- $p(2 \times 2)$ ethylidyne structure.^{13(c)}

In the final Pt(111)- $p(2 \times 2)$ -NO structure, the NO has a bond length of 1.18 ± 0.04 Å and a height of 1.28 ± 0.04 Å above the center-of-mass position of the first metal layer. The first and second interlayer spacings, measured from the center-of-mass positions of the respective layers, were determined to be 2.30 ± 0.03 and 2.32 ± 0.04 Å, respectively, compared to the bulk value of 2.26 Å. The first and second layer buckling was 0.07 ± 0.06 and -0.02 ± 0.07 Å, respectively. Here buckling is defined as the height difference between the three symmetry equivalent atoms and the inequivalent atom in the unit cell of a layer. Lateral displacements were within error bars. As a last refinement, the NO was allowed to tilt; a tilt of approximately 10° was observed with a reduction of the R_p factor by 0.04. This is in agreement with the apparent tilt of CO on Ru(0001),^{17(a)} of CO on Rh(111),^{17(b)} of ethylidyne on Rh(111),^{17(c)} and of ethylidyne on Pt(111),¹⁶ all of which we prefer to interpret as an anisotropic wagging vibration rather than a static tilt.

Turning to the NO on Ni(111), a recent SEXAFS analysis⁴ supports hollow-site adsorption on Ni(111), but

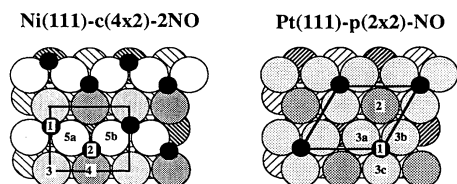


FIG. 1. Top view of the Pt(111)- $p(2 \times 2)$ -NO and Ni(111)- $c(4 \times 2)$ -2NO surfaces. A unit cell is outlined for clarity. The numbering of the NO molecules and of the top metal layer atoms refers to inequivalent atoms in the unit cell.

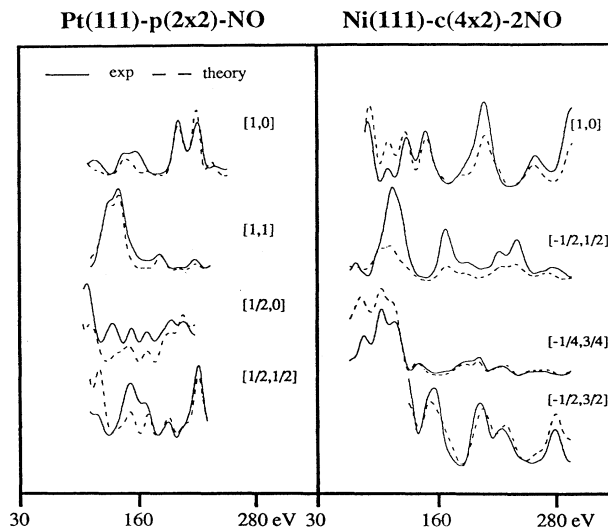


FIG. 2. Selected $I-V$ curves for the Pt(111)- $p(2 \times 2)$ -NO and Ni(111)- $c(4 \times 2)$ -2NO structures, which illustrate overall agreement between theory and experiment for all beams.

was not able to distinguish between fcc and hcp hollow sites. A photoelectron diffraction study⁵ also supports the hollow site, however normal N 1s photoemission was not sensitive to the difference between the hollow and bridge sites and off-normal emission could not distinguish the fcc from the hcp hollow sites. Assuming hollow-site adsorption and 0.5-ML coverage, three simple models are possible due to the three inequivalent hcp and three inequivalent fcc hollow sites for the two NO molecules in the $c(4 \times 2)$ unit cell. Both molecules could be adsorbed in fcc hollow sites (fcc+fcc model) or hcp hollow sites (hcp+hcp model). The third possibility is one molecule adsorbed in a fcc hollow site and the other in a hcp hollow site (fcc+hcp model). In addition to these models, a 0.5-ML coverage bridge+bridge site model and a 0.25-ML coverage fcc site model were examined. The fcc+fcc, the hcp+hcp, and the bridge+bridge models have a glide plane symmetry which was not observed in the LEED pattern. Due to the excellent agreement between theory and experiment for the fcc+hcp hollow-site model, no additional models were investigated. Refinements were made to the fcc+hcp model by allowing relaxation of two metal layers and lateral displacements consistent with a mirror plane symmetry (pm). They resulted in a final structure (Fig. 1) with selected $I-V$ curves shown in Fig. 2 and an R_p factor of 0.13. This value is similar to R_p factors of 0.11 [Ref. 18(a)] and 0.16 [Ref. 18(b)] obtained with recent extensive LEED analyses for atomic adsorption of oxygen on Ni(111), indicating a remarkable agreement for a molecular system.

In the final structure on Ni(111), the NO molecules have a bond length of 1.17 ± 0.04 Å and a height of 1.24 ± 0.04 Å above the center-of-mass position of the first metal layer. Both molecules are shifted approximately 0.10 ± 0.05 Å from the center of the hollow site and tilted approximately $4^\circ \pm 4^\circ$ in the direction of the top site, thereby increasing the distance between neighboring

molecules. The first and second interlayer spacings were determined to be 2.08 ± 0.03 and 2.00 ± 0.03 Å, respectively, compared to the bulk value of 2.03 Å. A total buckling of 0.16 ± 0.04 Å was found for the first layer. The two equivalent atoms in the first layer are displaced upward, while the two inequivalent atoms are displaced downward by the same amount. In the second layer no significant buckling was found. The lateral displacements of the metal atoms were within error bars.

The NO bond length and height above the surface is almost identical for Pt(111) and Ni(111). When compared to ethylidyne¹⁶ or atomic O (Ref. 19) on Pt which are also bonded in the fcc hollow sites, one finds that qualitatively the same relaxations are induced in the substrate, but they are weaker for NO. The longer adsorbate-metal bond for NO implies a weaker adsorbate-metal bond resulting in smaller NO-induced relaxations. The induced relaxations of the Ni substrate are larger than those of Pt; this may be due either to the NO coverage on Ni being twice that on Pt or possibly a stronger NO-metal bond on Ni than on Pt.

These results contradict earlier assignments of adsorption sites from vibrational data.^{1,2} Since LEED provides adsorption sites with much greater reliability, the vibrational assignments must be doubted. Correct interpretation of the vibrational spectroscopy in both cases will require detailed knowledge of the NO-metal bond and additional understanding of the influence of charge transfer

on the NO stretching frequency.

Why does Ni(111) form a well-ordered, higher coverage $c(4 \times 2)$ structure and not a lower coverage $p(2 \times 2)$ structure? Possibly, if the difference in adsorption energies of the fcc and hcp hollow sites were small compared to the thermal energies, entropy could disorder a $p(2 \times 2)$ structure by randomly filling both sites. Temperature programmed desorption^{10(b)} and the identical NO-metal heights for the two adsorption sites in the $c(4 \times 2)$ structure support similar fcc and hcp hollow-site adsorption energies. The formation of a $p(2 \times 2)$ structure on Pt(111) might suggest a larger energy difference between the fcc and hcp hollow sites on Pt(111) than on Ni(111). NO in excess of 0.25 ML on Pt(111) does not produce a $c(4 \times 2)$, but adsorbs in a disordered fashion.²⁰ Why does Pt(111) not form a $c(4 \times 2)$ structure? The lack of fundamental understanding of these structural differences illustrates the need to further analyze the NO-metal bond and the intermolecular interactions in these systems.

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