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Threefold-coordinated hollow adsorption site for Ni(111)-$c(4\times2)$-CO: A surface-extended x-ray-absorption fine-structure study

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Surface-extended x-ray-absorption fine-structure studies on the Ni(111)-$c(4\times2)$-CO system show that CO adsorbs in threefold-coordinated hollow sites. This result is in conflict with the adsorption-site determination via molecular vibrational frequencies, which for this system led to an assignment of a bridge site.

During the 1970s and 1980s a large number of surface structures were solved by analysis of low-energy electron-diffraction (LEED) intensities. As a result information about adsorbate-substrate bond lengths and adsorption sites became available.[1] Relatively few results were obtained for molecular adsorbates, however, for which the LEED analyses are especially demanding. The advent of synchrotron-radiation-based structural methods such as surface-extended x-ray-absorption fine structure (SEXAFS) and energy-scan photoelectron diffraction (PED) in the 1980s did not significantly change the situation regarding these adsorbates. Other surface-sensitive techniques which probe surface structure less directly have therefore been used to gather structural information on adsorbed molecular layers. Thus vibrational spectroscopy, in the form of both infrared reflection-absorption spectroscopy (IRAS) and high-resolution electron-energy-loss spectroscopy (HREELS), has proved particularly successful in assigning adsorption sites for adsorbed diatomic molecules. By comparison with measured vibrational frequencies in inorganic clusters of known structure, the accepted picture seems to be that adsorption on a specific site on a given crystal face should give rise to a typical vibrational frequency falling in a defined and rather narrow range and, furthermore, that the ranges for adsorption on different sites on the same surface should not seriously overlap.[2] However, only a few adsorption-site assignments based on vibrational spectroscopy have been tested to date by LEED,[3–9] SEXAFS,[10] or PED.[11,12] Whereas the results of the latter methods are in agreement with the results of vibrational spectroscopy for all the CO adsorption structures studied, recent SEXAFS (Ref. 10) and PED (Ref. 12) studies of Ni(111)-$c(4\times2)$-NO have shown that the assignment of adsorption site based on vibrational frequencies for this system is in error. Here we present the results of a SEXAFS study of Ni(111)-$c(4\times2)$-CO which are also in disagreement with the interpretation of vibrational studies,[13–15] and thus cast doubt on the general reliability of structural assignments based on vibrational frequencies alone.

LEED studies of CO adsorption on Ni(111) show the following sequence of patterns: $(\sqrt{3}\times\sqrt{3})R\,30°$,[16] $c(4\times2)$,[17] and $(\sqrt{7}/2\times\sqrt{7}/2)R\,19,1°$,[17] corresponding to CO coverages of 0.33 monolayer (ML), 0.5 ML, and 0.57 ML, respectively. The measured frequency of the CO stretching vibration shifts continuously from about 1815 cm^{-1} at very low coverages[13,18] to about 1910 cm^{-1} at 0.5 ML.[13–15] At saturation coverage (0.57 ML) an additional frequency of about 2050 cm^{-1} appears.[14,15] The frequencies of 1815, 1910, and 2050 cm^{-1} have been assigned to threefold-coordinated hollow sites,[15,18] bridge sites,[13–15] and atop sites,[14,15] respectively. The only direct structural analysis performed to date for the CO/Ni(111) system suggested a bridge site for the $(\sqrt{3}\times\sqrt{3})R\,30°$ structure.[11]

The SEXAFS study of Ni(111)-$c(4\times2)$-CO clearly favors a threefold hollow CO adsorption site, in conflict with the assignment of a bridge site by vibrational spectroscopy. By taking into account the information from the normal-incidence LEED pattern we arrive at a structural model with both fcc and hcp sites occupied. This involves a rather small, closest CO-CO separation of 2.88 Å, which may have implications for the orientation of the CO molecular axis.

The experiments were conducted at the electron storage ring BESSY in Berlin with the grazing-incidence plane-grating monochromator SX-700 I.[19] The SEXAFS data were taken above the carbon and oxygen K edges in both the partial and the total electron yield mode at normal ($\theta=90°$, E vector parallel to the surface) and near-grazing ($\theta=20°$) x-ray incidence. They were analyzed by the conventional Fourier-transform method[20] and by a curve-fitting procedure.[21] In both cases linearized O-Ni phase shifts[22] were used. Partial (one data set) and total (two data sets) yield measurements gave identical results. The Ni(111) crystal was cleaned by successive cycles of argon-ion bombardment, annealing at 650 K and heating to 800 K. It was characterized by Auger electron spectroscopy and LEED. Carbon monoxide exposures and SEXAFS experiments were performed at 150 K. Sharp and high-contrast $c(4\times2)$ LEED patterns characteristic of a well-ordered structure were obtained after CO exposures of about 1 L for all data sets.

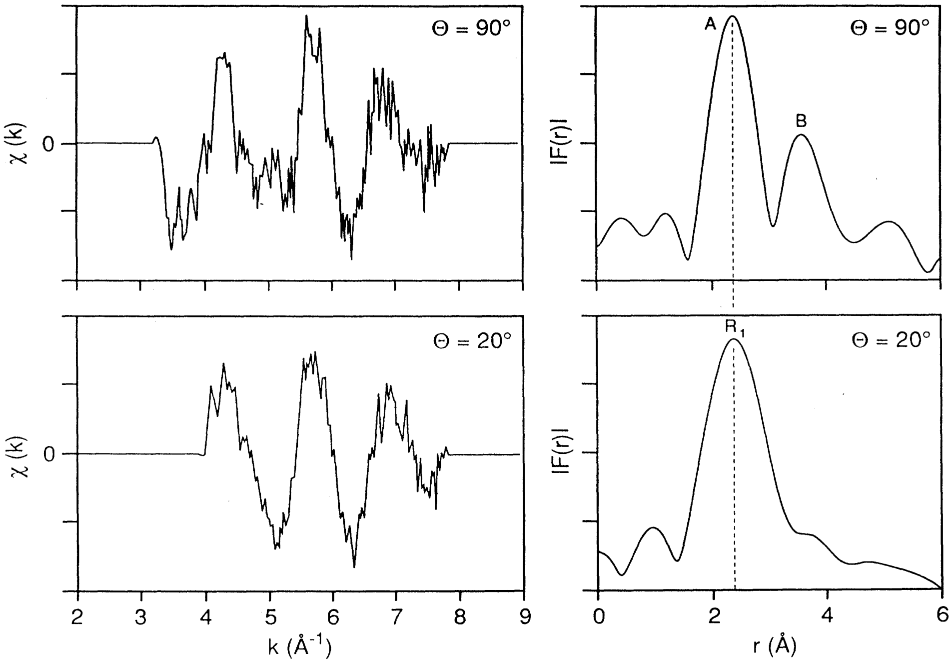

FIG. 1. Background-subtracted oxygen *K*-edge SEXAFS spectra (left) for Ni(111)-$c(4\times2)$-CO taken at $\theta=90°$ (top) and $\theta=20°$ (bottom) and their Fourier transforms (right).

In Fig. 1 background-subtracted oxygen *K*-edge SEXAFS spectra for Ni(111)-$c(4\times2)$-CO (left) taken at $\theta=90°$ (above) and $\theta=20°$ (below) are shown together with their Fourier transforms (right). The latter are dominated by a peak which after phase shift correction yields an O-Ni distance of about 2.65 Å for both polarizations (cf. Table I). A second peak can be seen in the transform of the data for 90°, the analysis of which yields a distance of roughly 3.7 Å. Due to the polarization dependence of the SEXAFS amplitude,

$$A_i(k)\propto N_i^*=3\sum_{i=1}^{j}\cos^2\alpha_{ij},\quad \alpha_{ij}=\sphericalangle(\mathbf{E},\mathbf{r}_{ij}) \tag{1}$$

(where N_i^* is the effective coordination number of the *i*th shell and α_{ij} is the angle between the **E** vector at the absorbing atom site and the vector $\mathbf{r}_{ij}$ from the absorbing atom to the *j*th atom in the *i*th shell), the measured distance for $\theta=20°$ must correspond to the nearest-neighbor (nn) O-Ni distance (R_1). The assignment of the peaks in the Fourier transform for $\theta=90°$ depends, however, on the type of the CO adsorption site. Assuming a threefold-coordinated hollow site, peaks *A* and *B* would correspond to the nn and next-nn (nnn) O-Ni distance, respectively, whereas for a bridge site due to limited resolution the nn and nnn distances would overlap and create peak *A*, so that peak *B* then would correspond to the third-nearest-neighbor O-Ni distance.

To distinguish between bridge and hollow adsorption sites we simulated our spectra assuming a C-O axis orientation parallel to the surface normal.[11,13,23–25] From the simulations for the 90° data the heights above the surface of the C and O atoms were determined (cf. Table I), which in the case of a hollow site compare well with the expected intramolecular CO bond length of about 1.15 Å,[1,3,4] but lead to a completely erroneous value for the latter assuming a bridge site (cf. Table I). This is clear evidence for CO adsorption in hollow sites. It should be mentioned in this respect that the measured nn C-Ni bond length of 1.78±0.10 is close to the nn C-Ni bond length for Ni(100)-$c(2\times2)$-CO.[1,3,4] The assignment of the hollow adsorption sites is strongly supported by comparing the simulations for hollow and bridge sites with each other. The best fit for the 90° data assuming a hollow site is shown in Fig. 2 (top). Also shown in Fig. 2 (bottom) is the simulation for 20° obtained with exactly the same parameters as for 90°. The experimental data are nicely reproduced. A definitely much worse fit to the

TABLE I. Measured C-Ni and O-Ni distances, *R*, corresponding heights above the surface of the C and O atoms, *z*, and $\Delta z=z_0-z_c$ values (which should measure the C-O bond lengths) for CO adsorption in hollow and bridge sites.

			z (Å)		Δz (Å)	
	θ (deg)	R (Å)	Hollow	Bridge	Hollow	Bridge
C edge	90	1.78±0.10	1.05±0.17	1.27±0.14	1.19±0.23	0.71±0.21
O edge	90	2.66±0.05	2.24±0.06	1.98±0.07		
	20	2.64±0.07				

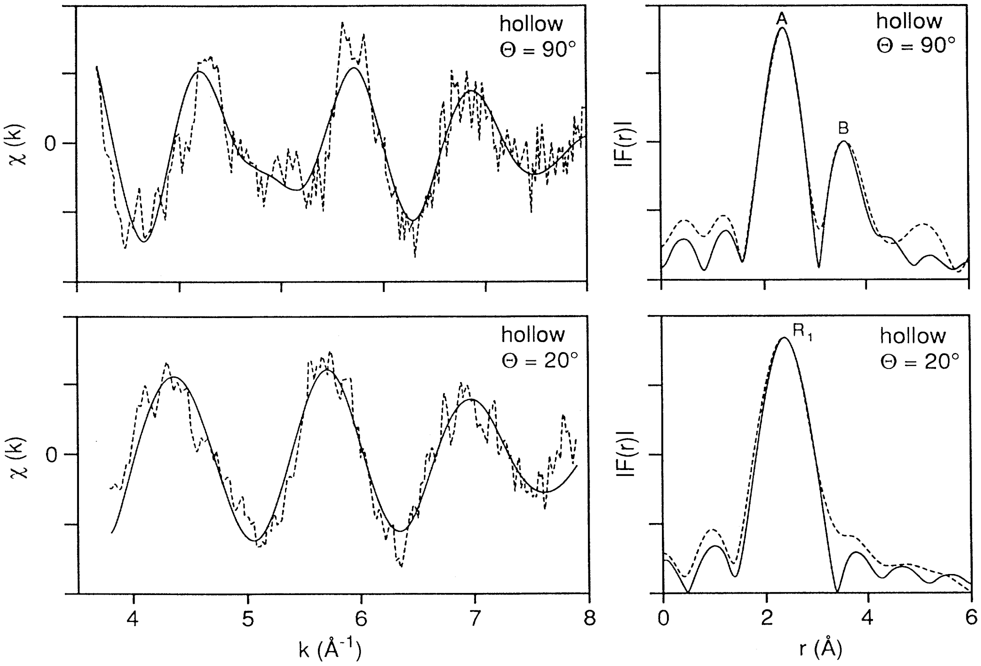

FIG. 2. SEXAFS simulations (left, solid lines) for $\theta=90°$ (top) and $\theta=20°$ (bottom) assuming a threefold-coordinated hollow site compared with experiment (dashed lines) and their Fourier transforms (right). The simulation for 20° was performed with exactly the same parameters as for 90° (best fit).

experimental data for $\theta=90°$ is obtained by assuming a bridge site. This is depicted in Fig. 3 (top). The reliability factor for this simulation is 25% higher than that for the hollow site simulation in Fig. 2. Neither the SEXAFS oscillations nor the width of the dominating Fourier peak are reproduced. The corresponding relative contributions of the nn (1), nnn (2), and third (3) nearest-neighbor O-Ni distances to the overall simulation are shown in the right panel of Fig. 3 (top). Moreover, as according to Eq. (1) the nnn contribution nearly vanishes for $\theta=20°$ (cf Fig. 3, bottom, right panel), peak A for a bridge site would be shifted by more than 0.2 Å relative

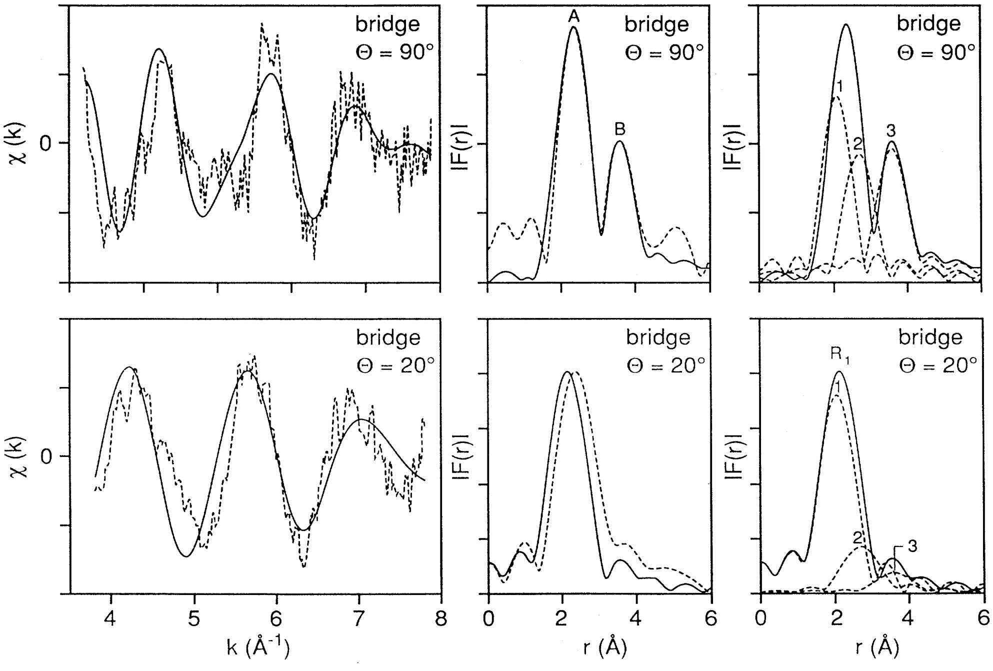

FIG. 3. Left, middle: SEXAFS simulations (solid lines) for $\theta=90°$ (top) and $\theta=20°$ (bottom) assuming a bridge site compared with experiment (dashed lines) and their Fourier transforms. The simulation for 20° was performed with exactly the same parameters as for 90°. Right: Single-shell contributions R_1,R_2, and R_3 (dashed lines) to the overall simulations (solid lines).

to peak R_1, which is not observed (cf. Table I). This is also demonstrated in Fig. 3 (bottom) by a simulation for 20° which was performed again with exactly the same parameters as for 90°.

For a threefold-coordinated hollow site, there are two possible arrangements of CO molecules in a $c(4\times2)$ structure with a coverage of 0.5 ML. These are depicted in Figs. 4(a) and 4(b) together with the well-known model involving bridge sites [Fig. 4(c)]. In model (b) CO molecules are either in fcc hollow or hcp hollow sites at a separation of 2.49 Å, whereas in model (a) fcc and hcp sites are mixed and the closest intermolecular distance measures 2.88 Å. In both models the CO-CO separation is substantially shorter than the corresponding value of 3.29 Å for the bridge model (c). A distinction between models (a) and (b) is not possible from our SEXAFS data. More information is obtained, however, by a careful inspection of the observed LEED patterns. In Fig. 4 (bottom) are shown the calculated normal-incidence LEED patterns corresponding to the full surface space-group symmetry of models (a)–(c), taking into account the occurrence of three rotationally degenerate domains of the $c(4\times2)$ structures. Due to the presence of the glide-plane symmetry in models (b) and (c), but not (a), alternate spots along the glide-line directions through the 0,0 beam are missing for each domain in the LEED patterns for (b) and (c), as, for example, the $\frac{1}{2}\frac{1}{2}$, $\frac{1}{2}0$, $0\frac{\bar{1}}{2}$, $\frac{\bar{1}}{2}\frac{\bar{1}}{2}$, $\frac{\bar{1}}{2}0$, and $0\frac{1}{2}$ beams. The observed normal-incidence LEED patterns at a number of energies contain these beams, and are therefore consistent with model (a) but not (b) or (c). Further support for the model comes from the observation that the beams indicated by open circles in (a), which are excluded in a kinematic calculation for the adsorbed layer, and which can be regarded as resulting solely from multiple scattering, are generally observed to be relatively weak.

Our conclusion that the Ni(111)-$c(4\times2)$-CO structure involves occupation of threefold hollow sites by CO molecules is in disagreement with previous interpretations of vibrational data for this system made by a number of workers. It is important, therefore, to consider if this disagreement could be in any way related to differences in surface preparation. According to Ref. 14, adsorption of 0.5-ML CO at 140 K (as compared to the 150 K used in the present work) results in a well-ordered $c(4\times2)$ structure in which all CO molecules are located in twofold bridge sites. However, at coverages above and below 0.5 ML a mixed adsorption into on-top and bridge sites is reported. The question therefore arises as to whether or not our results could be influenced by such a mixed adsorption. There are three arguments which seem to rule out a significant influence of mixed adsorption on our results. First, as already mentioned, the quality of the LEED patterns for the $c(4\times2)$ structure was exceptionally good. Second, SEXAFS measurements made for repeated preparations of the structure were extremely reproducible, despite undoubted errors in the reproducibility of the coverage. Third, from the polarization dependence of the SEXAFS amplitude it follows that occupation of on-top sites would give a zero contribution to the dominating nn SEXAFS peak in the 90° spectrum and thus the measured bond length would still be the correct

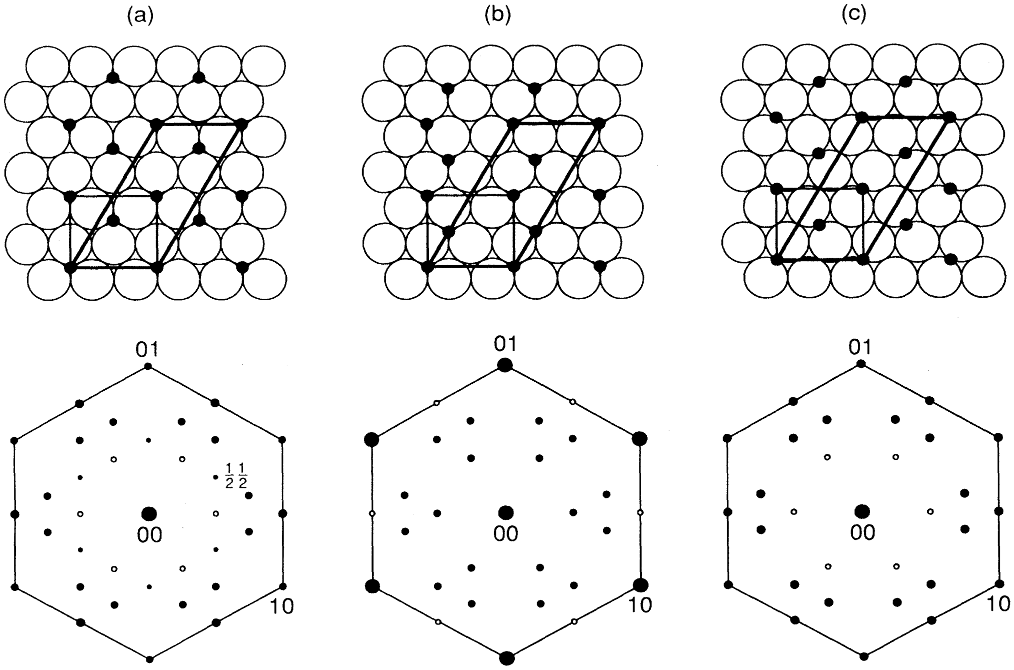

FIG. 4. Top: Models for Ni(111)-$c(4\times2)$-CO corresponding to a coverage of 0.5 ML. CO molecules (small filled circles) are in (a) inequivalent (fcc and hcp) hollow sites; (b) either fcc or hcp hollow sites; (c) inequivalent bridge sites. Bottom: Corresponding calculated normal incidence LEED patterns. Beams which are excluded in single scattering and result only from multiple scattering are marked by open circles.

nn bond length for the dominant adsorption site. Here it can be emphasized that the absolute value of this bond length is the strongest argument for occupation of a hollow site rather than a bridge site.

The present conclusions apply only to the $c(4\times2)$ structure. It is nevertheless interesting to consider their possible relevance for the $(\sqrt{3}\times\sqrt{3})R30°$ and $(\sqrt{7}/2\times\sqrt{7}/2)R19°$ structures observed at 0.33 and 0.57 ML, respectively. For the former structure a photoelectron diffraction study[11] led to the conclusion that twofold bridge sites were occupied. Since vibrational spectra show the existence of additional on-top sites in a wide coverage range below 0.5 ML,[14] the possibility of a change in bonding site with coverage cannot be excluded. The same holds for the $(\sqrt{7}/2\times\sqrt{7}/2)R19°$ structure. This structure cannot be formed with a combination of on-top and hollow sites on an unreconstructed substrate.

Finally, we have to consider the closest CO-CO separation of 2.88 Å in the proposed structure. Such a distance could involve a strong repulsion[26] which according to experience[27] would lead to a significant dispersion of the frustrated translational mode in HREELS although such an effect would be less important for molecules adsorbed in hollow sites as opposed to on-top sites. In any event, no dispersion has been observed, however, for the Ni(111)-$c(4\times2)$-CO system.[28] This could be explained by a slight tilting of the CO molecules away from the surface normal which reduces the repulsion. Although a number of different experimental techniques have been applied in determining the perpendicular orientation of the CO molecules,[11,13,23–25] none of them is more accurate than ±10°. This also holds for the present SEXAFS study. And a tilting of 10° (or even less) would completely relieve the repulsion.

In summary, our SEXAFS study on Ni(111)-$c(4\times2)$-CO has shown that the CO molecules occupy threefold-coordinated hollow sites in conflict with the adsorption site assignment via vibrational frequencies. This result and similar ones for Ni(111)-$c(4\times2)$-NO suggest that structural assignments based on vibrational spectroscopy are not unambiguous.

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