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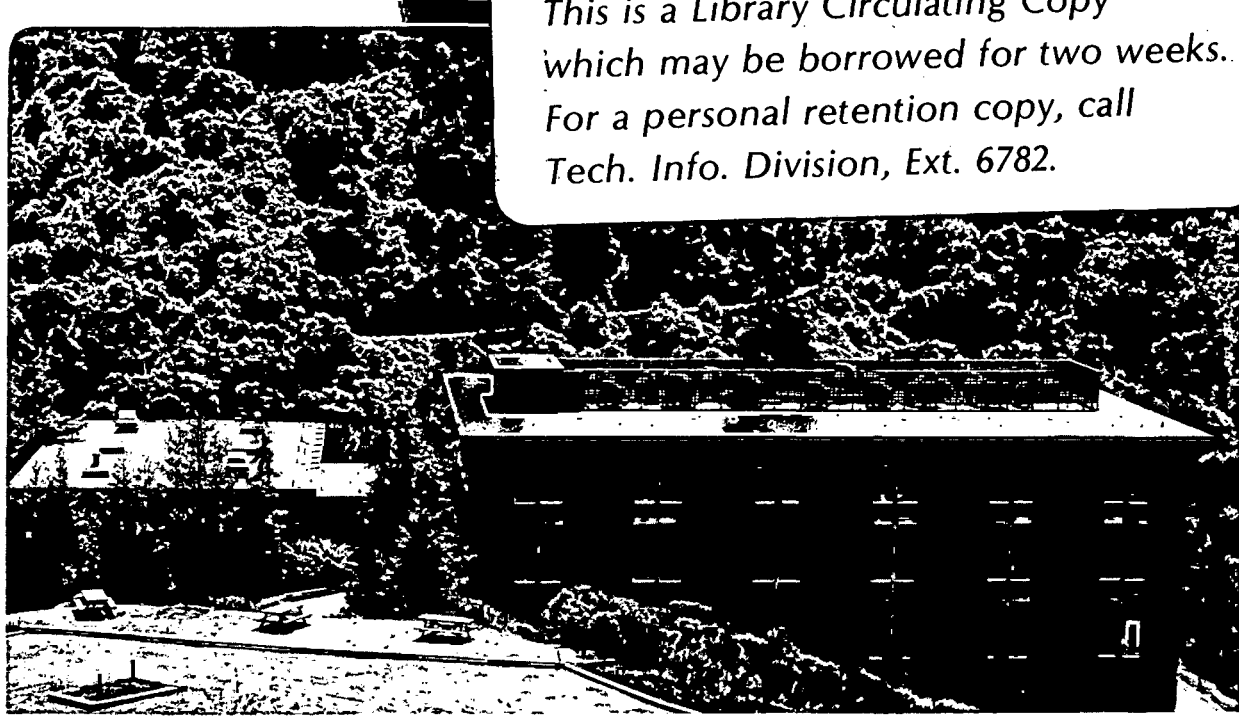

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LEED INTENSITY ANALYSIS OF A SURFACE STRUCTURE WITH THREE CO MOLECULES IN THE UNIT CELL, Rh(111) (2x2)-3CO: COMPACT ADSORPTION IN SIMULTANEOUS BRIDGE AND NON-SYMMETRIC NEAR-TOP SITES

M.A. Van Hove, R.J. Koestner and G.A. Somorjai

Materials and Molecular Research Division
Lawrence Berkeley Laboratory

and

Department of Chemistry
University of California
Berkeley, California 94720

ABSTRACT

The first Low-Energy Electron Diffraction intensity analysis of the structure of molecules adsorbed at several different surface sites yields, for the compact Rh(111) (2x2)-3CO structure, symmetric bridge sites and non-symmetric near-top sites, which are separated by only ~ 2.85Å. CO molecules in near-top sites are shifted sideways by ~ 0.5Å from ideal top sites, but are tilted by only about 5° from the surface normal. These results support an antiphase domain model of high-coverage CO structures on metal surfaces in general.

High-coverage molecular CO overlayers on single-crystal metal surfaces can yield valuable insights into the relative importance of adsorbate-adsorbate and substrate-adsorbate interactions. This is a subject of active debate.[1-3] At high coverage the tendency for CO to occupy high-symmetry sites (top, bridge or hollow sites) is counteracted by steric effects that prevent molecules from approaching each other too closely. Strong repulsive interaction would force molecules into low-symmetry sites determined by a close-packed hexagonal CO lattice, with a more complex bonding character than at high-symmetry sites, and may induce tilting of the CO axis away from the surface normal. Among the many known high-coverage CO overlayer structures,[2] there is one that is particularly favorable for LEED intensity analysis, which is required to determine bond lengths and bond angles: Rh(111) (2x2)-3CO has a small unit cell containing only three molecules, which allows both a clearcut High-Resolution Electron Energy Loss Spectroscopy (HREELS) investigation and appropriate Low-Energy Electron Diffraction (LEED) calculations. In addition, the traditional assignment of CO vibrational frequencies to different adsorption sites can hereby be tested for the first time at high coverages for asymmetric sites.

HREELS measurements and LEED patterns have been reported previously for the CO/Rh(111) system.[4,5] They indicate top-site adsorption up to 1/3 monolayer coverage and, from 1/3 to 3/4 monolayer, additional occupation of bridge sites. The 1/3 and 3/4 monolayer coverages give rise to a $(\sqrt{3}x\sqrt{3})R30°$ and a (2x2) LEED pattern, respectively, the first of which was analyzed with LEED calculations to confirm the top-site occupation and to obtain bond lengths and bond angles.[6]

Our LEED experiments were carried out in a conventional UHV system with 4-grid LEED/Auger optics, using the photographic method to obtain spot intensities.[7] The 3/4 monolayer coverage can only be obtained in the presence of a

CO background pressure of 10^{-6}-10^{-5} torr near room temperature. The LEED data were taken at ~ 240K and consist of 5, 8 and 8 independent beams at normal incidence ($\theta = 0°$), at $(\theta,\phi) = (10°,0°)$ and at $(\theta,\phi) = (20°,0°)$, respectively. Only the normal-incidence data were used in the structural analysis in order to benefit from the higher available symmetry. Further experimental details will be reported elsewhere.(8)

The theoretical LEED calculations are based on the Combined Space Method[8] used previously in structural determinations. The 3-molecule-per-unit-cell overlayer constitutes a single layer within which the spherical-wave representation is used, while metal atoms are grouped in individual layers; the plane-wave representation is applied in the spaces between the layers so defined, in the form of Renormalized Forward Scattering.(9) The most time-consuming part of the computation is the multiple-scattering treatment within the 6-atom-per-unit-cell overlayer. We have, therefore, applied three levels of approximation in this part using a recently developed approach(10) for the first time in a structural determination. The first approximation is computationally efficient, as it neglects all multiple scattering within the overlayer (kinematic approximation). The second level of approximation, which is more accurate but also more time-consuming, adds all multiple scattering within each CO molecule; this is accomplished by a modification of the Reverse Scattering Perturbation (RSP) scheme.(10) The third and most time-consuming level of approximation allows the conventional RSP scheme to converge, achieving the usual degree of accuracy of dynamical LEED calculations.

Non-structural parameters for the Rh(111)(2x2)-3CO calculations were chosen identical to those used in our previous study(6) of Rh(111)($\sqrt{3}$x$\sqrt{3}$)R30°-CO. For determining the structural parameters, the three levels of approximation allow a rough but time-efficient first scan for reasonable structures, followed by

more refined searches at higher computational accuracies. Five R-factors are used to compare experiment and theory.[6]

On the basis of the HREELS results and a coverage determination by Auger Electron Spectroscopy and Thermal Desorption Spectroscopy,[11] a molecular arrangement of CO on Rh(111) of the kind shown in Figure 1 is very likely. The CO molecules can be distributed in a roughly hexagonal lattice, such that both 2-fold and 1-fold coordinated sites are occupied. Any deviations from a planar hexagonal arrangement will be caused by the metal-adsorbate interactions. We varied five independent structural parameters, defined in Figure 1, that would describe such deviations: metal- to bridge-site carbon layer spacing, bridge- to top-site carbon layer spacing, C-O bond lengths (taken identical in both sites), bridge- to top-site carbon distance parallel to the surface and tilt angle of the top-site molecules.

This basic structural model proved already quite successful even with the least accurate theoretical approximation, so that there was no need to consider radically different models. A rough optimization of the structure, using the least accurate approximation, produced atomic positions that were also quite satisfactory in terms of bond lengths and bond angles. The next better approximation confirmed these results and noticeably improved the quality of the agreement between theory and experiment. Finally, the most accurate calculations improved the agreement somewhat more and allowed further refinement of the atomic positions. The best Zanazzi-Jona and Pendry R-factor values were found to be 0.25 and 0.47, respectively.

The optimized structure is shown in Figure 1, where the resulting refined interatomic distances and other relevant parameters are indicated, except for the tilt angle Θ_{CO}, which is found to be $-5 \pm 15°$. The significant findings are as follows. The near-top molecules are shifted away from the hexagonal

lattice positions, towards the ideal top positions, by about 0.25Å, indicating a preference for on-top bonding; they are prevented from reaching the on-top positions by the proximity (at 2.85 ± 0.2Å) of the bridge-bonded molecules. The near-top molecules, despite their distance of 0.53Å from the ideal on-top site do not apparently adopt a linear Rh-C-O configuration, but the CO axes stay more parallel to the surface normal. They do have a larger Rh-C layer spacing than the bridge-bonded molecules (1.87 vs. 1.52Å), i.e. the CO overlayer is buckled.

Thus, the HREELS vibrational frequency assignment yielding top and bridge CO sites[4] is confirmed, but it is a significant finding that the assignment holds even for near-top sites removed as much as ~ 0.5Å from the ideal top site, where a Rh-C-O bond angle of about 15° can occur. Such a asymmetrical bonding could produce a detectable Rh-C-O bonding mode in HREELS, which was, however, not unambiguously detected: it could have overlapped with one of the two M-CO stretch modes or it may have been too weak in intensity. Furthermore, the 2:1 occupation of near-top and bridge sites is to be compared with the approximate 1.5:1 ratio of CO stretch peak heights in the HREELS spectrum, indicating a rough proportionality of site occupation and peak heights.

Concerning bond lengths, the C-O distance of 1.15 ± 0.1Å is not surprising, while the Rh-C distances of 1.94 ± 0.1Å and 2.03 ± 0.07Å for near-top and bridge sites, respectively, exhibit values and trends compatible with those known in metal carbonyl clusters for different binding sites: for top (bridge) sites, Rh-C distances of 1.81-1.93Å (2.01-2.11Å) and C-O distances of 1.09-1.17Å(1.14-1.17Å) are found in clusters.[12]

The optimum intermolecular distances resulting from our analysis (ignoring the small corrections due to the CO layer buckling) are shown in Figure 1: we find rather small distances of 2.85 and 2.88Å, which may be compared with inter-

molecular distances in molecules containing carbonyls and in CO and CO_2 crystals. In syn-1,6:8,13-biscarbonyl[14]annulene[13] two CO's are bridge-bonded across a 14-carbon ring with CO axes diverging by 21°, with a distance between CO centers of 2.96Å. In the three molecules $[(CO)_4\ M\text{-}P(CH_2)_2]_2$, with M = V, Cr and Mn,[14] there are pairs of nearly parallel carbonyls linearly bonded to the two metal atoms: the distances between CO centers are 3.29, 3.12 and 3.50Å for V, Cr and Mn, respectively. In the cubic α-CO crystal,[15] any C or O atom has near neighbors in other molecules at distances of 3.46 (C-O), 3.57 (C-C and O-O) and 3.69 Å(C-O). In the cubic CO_2 crystal,[15] which has linear OCO molecules, one finds interatomic distances between near molecules of 3.17 (C-O), 3.23 (O-O) and 3.98Å (C-C).

An Angle-Resolved Ultraviolet Photoemission Spectroscopy[16] study of the high-coverage Pt(100) c(4x2)-3CO structure concludes that some of the CO molecules in that structure may be tilted by 10-15° from the surface normal. This result is consistent with a recently proposed model for this surface,[2] based on high-symmetry sites.

All the abovementioned comparisons support our structural results. These are important for the general understanding of the high-coverage CO structures that occur on single-crystal metal surfaces. The antiphase domain model[12] which takes into account both the LEED observations and the vibrational data, unlike the competing incommensurate quasi-hexagonal model, is consistent with the results reported here. Its only drawback has been the need for relatively small CO-CO distances of the order of 2.7-3.0Å, which our present study shows are acceptable.

In summary, a detailed LEED intensity analysis of Rh(111)(2x2)-3CO, using a three-level approximation scheme for efficiency in the structural search, has produced results that cast light on the relative strength of CO-CO and metal-CO

interactions and, in particular, on how close two CO adsorbed molecules can approach each other. Strong distortions away from a hexagonal CO overlayer are found that reveal the predominance of the attractive metal-CO interactions. Two-site occupation is observed, confirming a previous HREELS analysis; one of the sites consists of asymmetrical near-top bonding with a CO axis possibly tilted about 5° from the surface normal, despite a 16° tilt of the Rh-C axis from the surface normal. The Rh-C and C-O bond lengths are in good agreement with known values in metal carbonyl clusters. CO-CO distances as small as 2.85 ± 0.2Å are found which are consistent with comparable values in carbonyl clusters and CO and CO_2 crystals. These results support the antiphase domain model for high-coverage CO adsorption structures on single-crystal surfaces.

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FIGURE CAPTION

Fig. 1: The Rh(111)(2x2)-3CO surface structure, showing its projections onto the surface plane (at bottom) and onto a structural mirror plane (at top); a (2x2) unit cell is outlined. Large circles represent Rh atoms, the dotted ones being outside the plane of the figure. Small dotted circles indicate C and O positions satisfying a hexagonal CO overlayer of coverage 3/4 (one unit cell of which is outlined), while small full circles indicate the optimum positions found in this study (but leaving all CO axes perpendicular to the surface). The independent structural parameters are labelled and some of the optimum interatomic and interlayer distances are indicated.

Rh(111) (2×2) - 3 CO

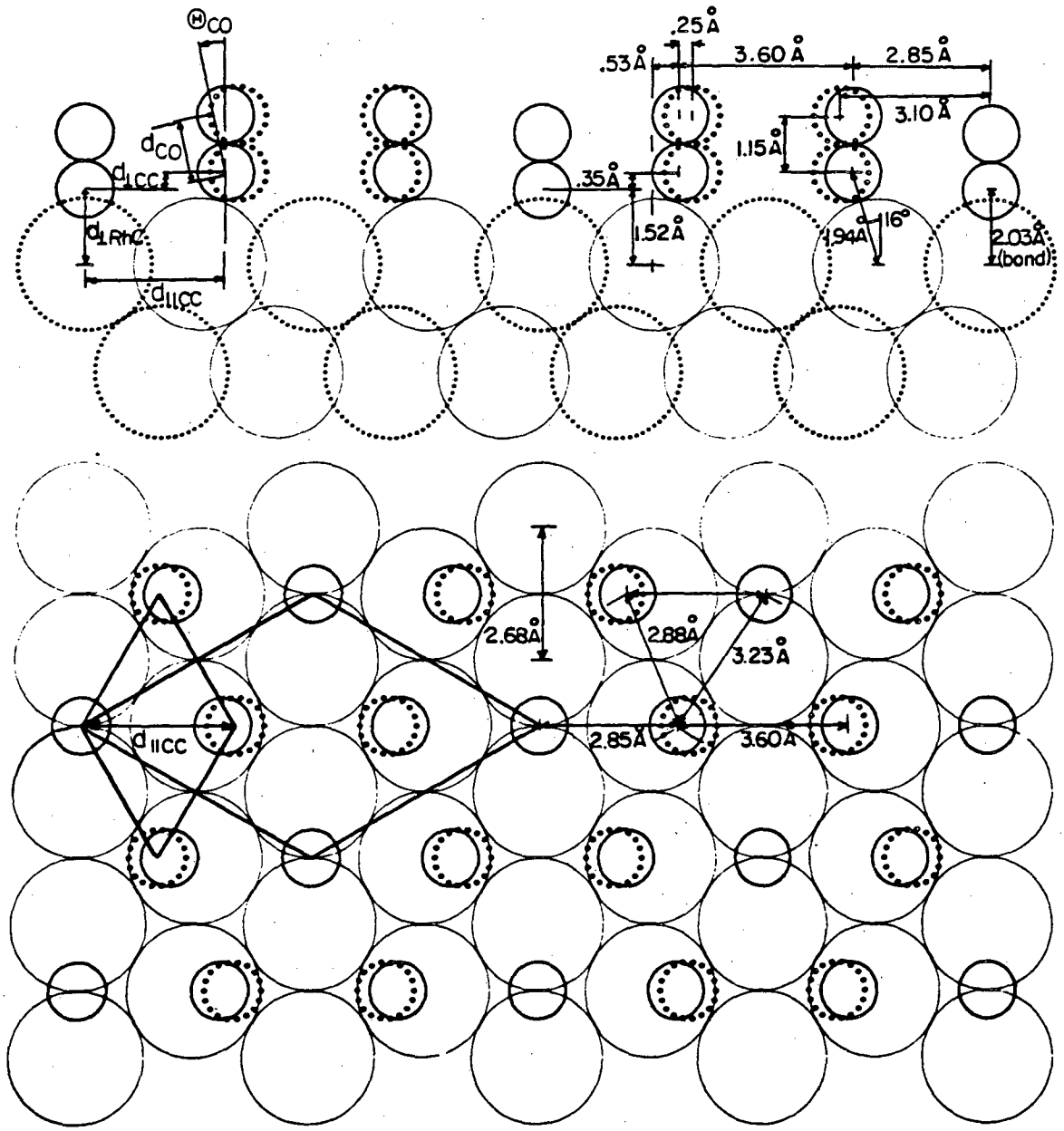

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Fig. 1

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