Structure of CO Adsorbed on Cu(100) and Ni(100)

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The Cu(100)$c(2\times2)$-CO and Ni(100)$c(2\times2)$-CO structures have been examined by dynamical low-energy electron diffraction intensity analysis using the (00), $(\frac{1}{2}\frac{1}{2})$ and (10) beams measured at 80 K (Cu) and 120 K (Ni) substrate temperatures. The analysis is compatible with a vertical terminal-CO arrangement, Cu-C and C-O bond lengths of 1.90 ± 0.10 and 1.15 ± 0.10 Å, respectively, for Cu/CO, and Ni-C and CO bond lengths of 1.80 ± 0.10 and 1.10 ± 0.10 Å, respectively, for Ni/CO.

Vibrational spectroscopy of CO adsorbed in the $c(2\times2)$ structure on Ni(100)[1] and Cu(100)[2] shows that the molecule adsorbs in a terminal configuration i.e., on top of a metal surface atom with the carbon bonded to the nickel as sketched in Fig. 1. This is an empirical determination that relies on a comparison of the metal–adsorbed-carbon and carbon-oxygen vibrational frequencies with the vibrational frequencies of metal carbonyls. Other structural parameters such as the bond lengths and the orientation of the molecular axis have to be determined by other methods. Recently we examined this structure model for the Ni(100)$c(2\times2)$-CO system by a low-energy electron diffraction (LEED) structure analysis.[3] We found best agreement between experiment and theory for a surprisingly short vertical separation between C and O of 0.95 Å. This led us to suggest that the molecular axis was inclined with respect to the surface normal so that the actual CO bond length was close to the value 1.15 Å found in Ni$(CO)_4$. A simultaneous ultraviolet photoemission spectroscopy (UPS) investigation of a densely packed CO layer on Ni(100)[4] suggested, however, that the molecular axis was normal to the surface. The UPS measurement was later repeated for the Ni(100)$c(2\times2)$-CO system with essentially the same conclusion.[5] This contradiction has led us to investigate the structures of the similar Cu(100)$x(2\times2)$-CO system by LEED. We find excellent agreement between experiment and theory for a vertical metal–terminal-CO configuration. Some experimental observations for this system have brought us to reinvestigate the Ni(100)$c(2\times2)$-CO system recording new experimental intensity data at lower temperatures and with improved structure quality.

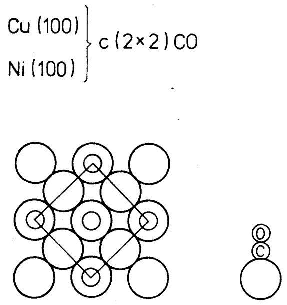

FIG. 1. Model of the vertical terminal-CO arrangement for the $c(2\times2)$-CO structures on Cu(100) and Ni(100).

The Cu(100)$c(2\times2)$-CO experiments have been performed in a combined LEED-EELS (electron energy-loss spectroscopy) system at 80 K substrate temperature while the Ni(100)$c(2\times2)$-CO experiments were made at 120 K in a separate LEED system. The LEED intensities were measured by an automatically tracking photomultiplier. The measurement time for an energy range of 100 eV was 30 sec per beam at a primary-beam current of about 0.2 μA (~1 mm beam diameter). For these conditions a particular beam could be scanned once without any significant change in the recorded intensity distribution because of electron-induced desorption and/or decomposition. This was checked by recording the same beam in three separate energy intervals exposing a fresh $c(2\times2)$-CO structure for each interval. A set of low-index LEED beams was recorded by either forming a new $c(2\times2)$-CO structure for each beam or by translating the specimen to expose an area which had not been previously hit by the electron beam. The intensity spectra have been recorded at normal or near normal [(00) beam] incidence of the primary beam.

It was found to be of particular importance that the substrate surface was fully covered with the $c(2\times2)$-CO structure. The common overlayer-substrate beams will otherwise show an intensity too pronounced in energy ranges where the substrate reflections are intense. This problem was not severe for Cu(100) where at 80 K the $c(2\times2)$-CO structure nucleated in a narrow coverage range (0.45–0.50) close to the optimum (0.50). The adsorbate characteristic $(\frac{1}{2}\frac{1}{2})$ beam reached maximum intensity just before compression of the CO layer began. For Ni(100), however, the $(\frac{1}{2}\frac{1}{2})$ beam could reach maximum intensity although the substrate surface was only covered to about 0.4. This manifested itself in too low a work-function change and pronounced substrate related peaks in the (00)- and (10)-beam LEED spectra, and was the major cause of the flaw in our previous experimental data. This complication depended crucially on the quality of the substrate surface and was essentially eliminated by forming the $c(2\times2)$-CO structure at 300 K on a thoroughly argon-ion–cleaned substrate—exaggerating the CO exposure somewhat so that the $(\frac{1}{2}\frac{1}{2})$-beam intensity decayed about (10–20)% below its maximum value.

The intensity calculations in this work were made as described previously[3] with some minor modifications. We now use 45 beams and eight phase shifts in order to extend calculations to higher energies. The muffin-tin zeros, $V_{\rm MT}$, of the substrates were taken to be -12.8 eV for copper and -12.5 eV for nickel after allowing for the work-function change due to the adsorbed CO. In our calculations, *we do not allow an arbitrary translation in energy of the curves,* once the substrate $V_{\rm MT}$ is fixed from the clean-surface spectra. Calculations with the same $V_{\rm MT}$ in the CO layer as in the bulk gave spectra that were too low in energy when conventional bond lengths were used. The peaks can be shifted to higher energies either by (i) shortening bond lengths or by (ii) applying a lift to $V_{\rm MT}$ in the CO overlayer. For the new data, the second alternative was favored on the basis of relative intensities of peaks, and a lift of 5.5 eV provided the shift desired. It is not unreasonable that the potential between CO molecules, which are rather far apart and well outside the substrate, should be much less than between the copper or nickel atoms.

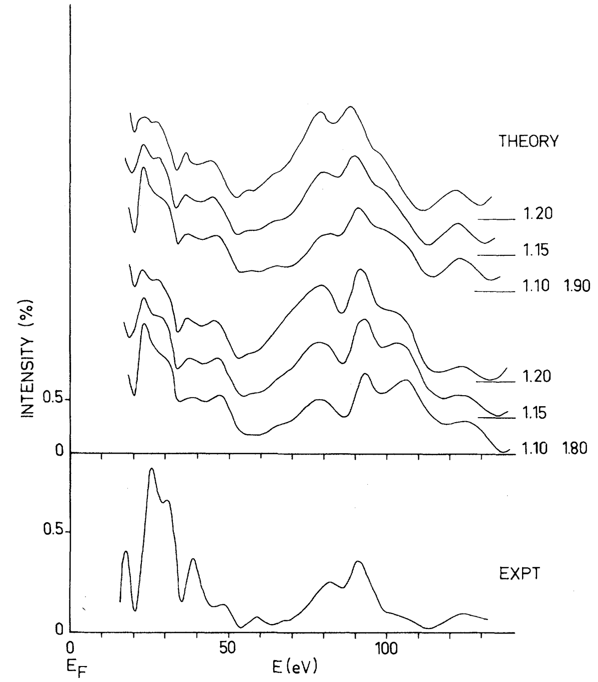

FIG. 2. Top panel shows calculated $(\frac{1}{2}\frac{1}{2})$-beam spectra for the Cu(100)$c(2\times2)$-CO structure if one assumes a vertical terminal-CO arrangement and Cu-C bond lengths of 1.80 and 1.90 Å and C-O bond lengths of 1.10, 1.15, and 1.20 Å. The bottom panel shows the corresponding experimental spectrum.

The vertical terminal-CO configuration for the Cu(100)$c(2\times2)$-CO structure (see Fig. 1) has been examined for a range of Cu-C (1.7–2.0 Å) and C-O (0.9–1.2 Å) bond lengths. Figure 2 (here all energies are referred to $E_{\rm F}$, the Fermi energy) shows a comparison of the experimental $(\frac{1}{2}\frac{1}{2})$ beam, recorded at 80 K and normal incidence, with a set of calculated spectra for a range of bond lengths close to the optimum fit. The spectra, as calculated above for 1.90-Å Cu-C and 1.10–1.15-Å C-O bond lengths, are in very good agreement with the experimental spectrum both with respect to peak positions and relative intensities. Also, the absolute intensity at low electron energies agrees well. The experimental intensity becomes too low at high energies because of thermal vibrations. This effect is particularly strong in the higher-order beams, e.g. the (11) beam, where we can show that thermal vibrations are essential for a full interpretation. Evidence of large vibrational amplitudes is already available from electron-stimulated desorption ion angular distribution (ESDIAD[6]) and angle-resolved x-ray photoemission spectroscopy (XPS) experiments.[7] The influence of thermal vibrations on the higher-order (11) and $(\frac{3}{2}\frac{1}{2})$ beams will be treated in detail in a later publication. Figure 3 shows a comparison of the experimental (00)- (3° angle of incidence, [010] azimuth) $(\frac{1}{2}\frac{1}{2})$-, and (10)-beam spectra with spectra calculated for 1.90-Å

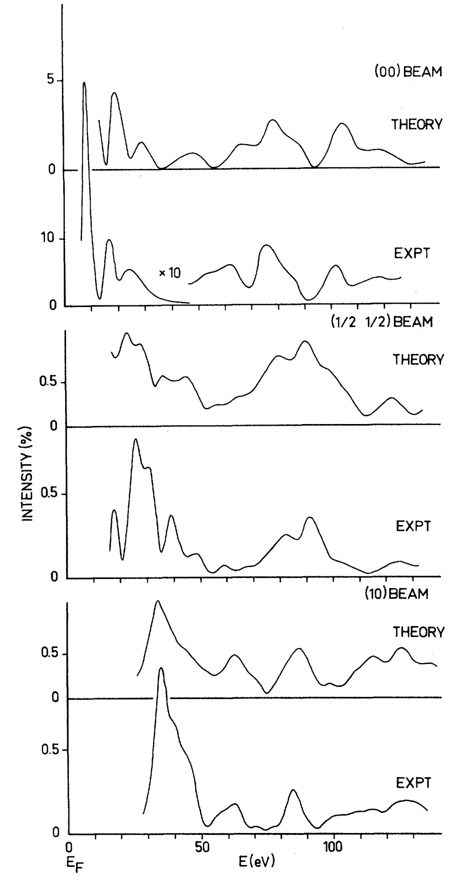

FIG. 3. Comparison of experimental and calculated (00)-, $(\frac{1}{2}\frac{1}{2})$-, and (10)-beam spectra for the Cu(100)$c(2\times2)$-CO structure at optimal agreement. The calculation corresponds to a vertical terminal-CO arrangement with the Cu-C and C-O bond lengths 1.90 Å and 1.15 Å, respectively.

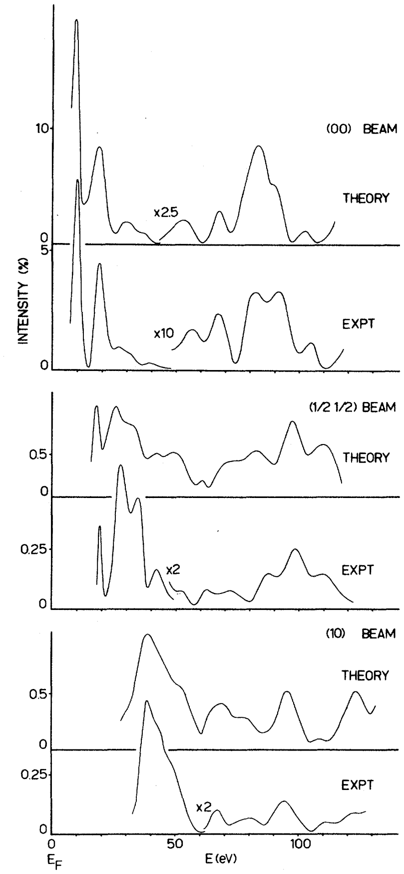

FIG. 4. Comparison of experimental and calculated (00)-, $(\frac{1}{2}\frac{1}{2})$-, and (10)-beam spectra for the Ni(100)$c(2\times2)$-CO structure at optimal agreement. The calculation corresponds to a vertical terminal-CO arrangement with the Ni-C and C-O bond lengths 1.80 Å and 1.10 Å, respectively.

Cu-C and 1.15-Å C-O bond lengths and the same muffin-tin lift as above. The agreement for the (00) and (10) beams is most satisfactory and approximately as good as for the $(\frac{1}{2}\frac{1}{2})$ beam [the only noticeable discrepancy is observed around 50 eV in the (00) beam]. We thus conclude that the Cu(100)$c(2\times2)$-CO structure is compatible with a vertical terminal-CO arrangement and that the Cu-C and C-O bond lengths are 1.90± 0.10 and 1.15± 0.10 Å, respectively.

We have analyzed the Ni(100)$c(2\times2)$-CO system in the same way using our new experimental data.[8] The experimental (00), $(\frac{1}{2}\frac{1}{2})$, and (10) beams (normal incidence) recorded at 120 K substrate temperature are shown in Fig. 4 together with the corresponding spectra calculated for a vertical terminal-CO configuration and Ni-C and C-O bond lengths of 1.80 Å and 1.10 Å, respectively. Both theory and experiment show great similarities between nickel and copper and the analysis has been performed along parallel lines. The agreement between theory and experiment is very good for this choice of structural parameters.

Working on two closely related systems has enabled us to resolve inaccuracies in our earlier work by cross checking from one system to the other. The good agreement between theory and experiment now seen for both systems and the cross correlation with other workers of the nickel data open the way to further analysis of small-molecule adsorption at surface.

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Polymer Problem Studied by a Loop Elimination Resembling the Renormalization-Group Theory

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The expansion of self-avoiding chains is studied through a progressive elimination of loops, resembling the renormalization group. The exponents for the mean square extension and for the number of walks are estimated in dimensionality $d = 4 - \epsilon$, 3, and 2.

Some time ago a new method has been proposed for the study of self-avoiding polymer chains.[1] One eliminates all the loops from ideal chains consisting initially of N^0 links, creating an ensemble of self-avoiding chains of a shorter length $N \leqslant N^0$, while preserving the initial end-to-end distance $\vec{R}$. The elimination of the loops (i.e., interactions) proceeds from shortest to longest, resembling the renormalization-group (RG) theory. The property studied is the scaling law for the chain expansion coefficient α^2:

$$\alpha^2 = \langle R^2 \rangle / N a^2 \sim N^{\kappa}, \tag{1}$$

where a is the link length. An estimate of the eliminations employing a mean-field approximation yielded[1] the Flory-like[2] result $\kappa = (4 - d)/(2 + d) = \epsilon/(6 - \epsilon)$, where $d = 4 - \epsilon$ is the chain's dimensionality. Yet de Gennes's extension[3] of the RG ϵ expansion[4] to polymers led to $\kappa = \epsilon/8 + 15\epsilon^2/256 + \ldots$, which disagrees sharply with an expansion of the Flory-like result for small ϵ. The present Letter shows that carrying through the elimination without recourse to mean-field theory gives successive approximations for κ (ordered according to the complexity of the eliminations, not according to powers of ϵ). Reexpression in powers of ϵ leads to an exact agreement with de Gennes's first term and to a fair agreement with the second; the successive approximations seem to converge rapidly and present an interesting alternative to the regular RG approach.

The elimination method will be reviewed briefly (for details see Ref. 1). Loops of length $j' = 1, 2, \ldots, j$ are eliminated successively in a sequence of steps from a starting ensemble of ideal chains of length N^0. Basically four types of loops have to be considered: (a) the simple type, j rides atop a nonlooped chain; (b) and (c) "figure eight" double loops, with j atop another loop j', where $j' \leqslant j$ or $j' > j$, respectively; and (d) the overlapping type, with j and j' intersecting one another. Clearly throughout the elimination,

$$\langle R^2 \rangle = N^0 a^2. \tag{2}$$

At the jth step we derive a new ensemble, consisting of chains of length N and restricted to order j, i.e., the self-avoiding property extends to all loops of length $j' \leqslant j$. Two difficulties are ignored: (a) the polydispersity of the chain length N, for given N^0 (or vice versa), and (b) the redundancy in the derived ensemble due to arrangements of the $N^0 - N$ links in loops atop each N "backbone"; this redundancy is essentially (but not entirely[1]) independent of the N chain shape and to that extent immaterial.

First we observe (see Ref. 1) that a restricted chain of order j and of length N obeys

$$\alpha_j^2 = \langle R^2 \rangle / N a^2 \sim j^{\kappa}, \quad j \ll N, \tag{3}$$

with the same value of κ as in Eq. (1). We proceed and consider restricted chains of order j and of a fixed length N, supposedly originating from N^0 (which increases with j). In view of Eqs. (2) and (3)

$$\alpha_j^2 = N^0 / N. \tag{4}$$

Let φ_j be the average frequency of loops of length j on the N chains. The average number of links