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Determination of the Ni{001}$c(2\times2)$-CO Structure by Low-Energy Electron Diffraction

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We have resolved the inconsistency between low-energy electron diffraction (LEED) and ultraviolet photoemission spectroscopy (UPS) analyses concerning the orientation of molecular CO when chemisorbed in a $c(2\times2)$ structure on the Ni(001) surface. Dynamical analysis of new LEED data indicates that CO stands perpendicular to the Ni surface with the C atom on top of a Ni atom; preliminary results for the Ni-C and C-O separations are 1.72 and 1.15 Å, respectively.

The atomic and electronic structure of CO chemisorbed on surfaces of transition metals, of nickel in particular, has been the object of numerous investigations in recent years by means of ultraviolet photoemission spectroscopy (UPS),[1-4] low-energy electron diffraction (LEED),[5-7] electron energy-loss spectroscopy (EELS),[8] and theoretical calculations.[9-11] Early LEED work[5] suggested that in the Ni{001}$c(2\times2)$-CO structure the CO molecules occupy the fourfold-symmetric hollows of the substrate surface, and most subsequent model calculations adopted such hollows as the adsorption sites.[9] It was in Andersson's EELS study[8] of the same Ni{001}$c(2\times2)$-CO structure that evidence was first presented for CO molecules linearly bonded to Ni atoms, i.e., to the top-atom sites of the substrate net. This model was later confirmed by Li and Tong's calculations of angle-resolved UPS spectra[4] compared with experiment.

A controversy has developed during the last year about the orientation of the CO molecule with respect to the substrate surface. On the one hand, the UPS results of Plummer and coworkers[3] indicated that the molecule stands with its axis perpendicular to the surface with the carbon end down, possible deviations from this orientation being of the order of 10°–15°. On the other hand, a quantitative analysis of the Ni{001}$c(2\times2)$-CO structure with dynamical LEED methods by Andersson and Pendry[7] (AP) was interpreted in favor of a skewed molecule, also with the carbon end down on a top-atom site but inclined at an angle of 34° with respect to the surface normal[7]. This tilted-molecule model was proposed in an effort to explain the apparent agreement between some experimental LEED spectra and those calculated for an unphysically short C-O interlayer distance (0.95 Å). A calculation by Nørskov, Hjelmberg, and Lundqvist[11] attempted to settle the controversy by showing that contraction of a molecular bond is possible upon chemisorption and hence tilting of the CO molecule is not necessary. It is fair to say, however, that the agreement between theory and experiment as obtained by AP for the tilted-molecule model[7] is below current standards in LEED crystallography for a reliable structure determination. For this reason, we decided to repeat both the LEED experiment and the LEED intensity analysis. We report below preliminary results of this investigation.

It was known at the outset that the formation of ordered CO structures on Ni{001} is very sensitive to surface perfection and cleanliness, that well-ordered structures develop only for good surface conditions and preferentially at low temperatures, and that the chemisorbed CO molecules are easily dissociated and desorbed by the primary electron beam used in LEED experiments.[5-8] For these reasons, particular attention was paid to preparation of the CO structure and to minimization of the incident electron current during collection of LEED intensity data. The Ni{001} surface was first cleaned by a series of krypton-ion bombardments (1 keV, 20 μA/cm^2) followed by vacuum anneals at 500°C, then cooled rapidly to liquid-nitrogen temperature (from 500°C in approximately 5 minutes, rapid cooling is needed in order to minimize contamination of the Ni surface prior to chemisorption of CO), and finally exposed while cold to CO gas at 1×10^{-8} Torr to approximately 2 L (1 L = 1μ Torr sec). An exposure of 2.2–2.3 L was determined to be optimal for formation of the $c(2\times2)$ structure.

It was established that an incident electron current of 0.1 μA (beam diameter approximately 1 mm) caused 10% decrease in intensity of the $(\frac{1}{2}\frac{1}{2})$ beam at 100 eV in 50 sec. Since the recording of a typical LEED spectrum required between 2 and 3 min (the intensity data were collected sequentially with the spot-photometer–fluorescent-screen combination), the overall effect of the electron beam was considered too damaging at 0.1 μA. The current was therefore decreased to become as low as 0.05 μA at energies higher than about 100 eV, but the characteristics of the electron gun were such that the current was larger than 0.1 μA below 100 eV and as high as 0.2 μA around 50 eV. To minimize the damage, the sample (about 1 cm long) was translated uniformly at about 1 mm/min in a direction normal to the incident electron beam while the diffracted intensity was being recorded. This procedure ensured that a decrease in intensity no larger than 10% occurred for any beam during each scan, and allowed the recording of at least two spectra for each CO exposure. Many cycles of recleaning and reexposure were needed to collect the data set used in the present study (three spectra at normal incidence and seven at $\theta = 10°$ and $\varphi = 0°$). That significant errors in the angle of incidence were not introduced by the crystal-translation procedure was tested with the clean Ni{001} surface. It was thereby established that the procedure introduced variations of the angle of incidence no larger than 0.3° away from the set angle. The LEED spots could barely be seen with the naked dark-adapted eye and were mostly invisible through the eyepiece of the spot photometer. The spot photometer was therefore made to scan continuously a small area of the screen around the presumed location of the beam under study, and the envelope of the maxima of recorded intensities was taken as the corresponding LEED spectrum.

The orientation of the sample for normal incidence of the incident beam was determined by the equivalence of degenerate beams[12] on the clean Ni{001} surface prior to the final cleaning, cooling, and CO exposure. Helmholtz coils were used to reduce the residual magnetic field in the region around the sample to approximately 0.02 G. At least three spectra were independently recorded for each beam measured, and one of the three was accepted as valid only if all three were in satisfactory agreement with one another. The temperature of the sample during the measurements was maintained at about 100°K.

Comparison between our data and those presented by AP[7] reveals considerable differences in some energy regions and some qualitative agreement in others. Wherever qualitative agreement is found, the AP data appear to be lacking detail and to be weaker in overall intensity.

The intensity calculations were done with the computer program named CHANGE,[13] which allows the treatment of multiple scattering in a surface layer including O, C, and top Ni subplanes in the angular momentum representation and the deeper Ni layers in the beam representation. Five phase shifts and 58 beams were used, the inner potential and the imaginary part of the potential were kept equal in the bulk and in the

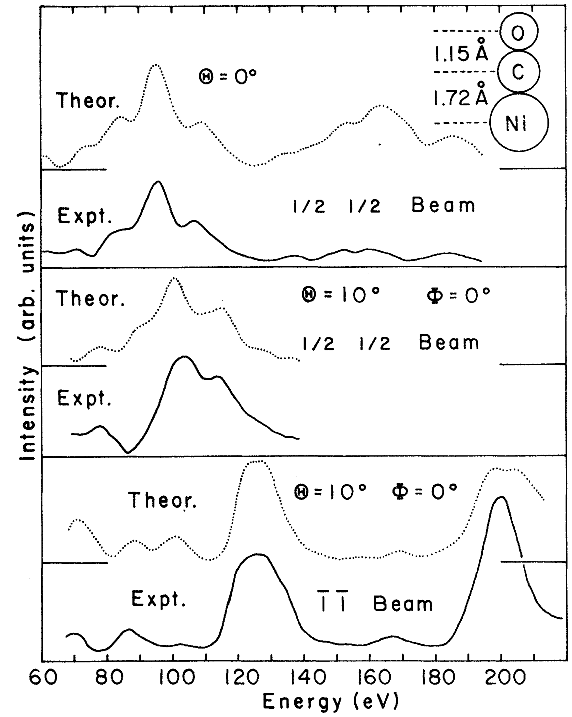

FIG. 1. Comparison between experimental and theoretical LEED spectra from Ni{001}$c(2\times2)$-CO. The structural model is shown schematically on top.

surface layer, the mean square amplitudes of atomic vibrations were also kept the same from bulk to surface and corresponded to a temperature of 100°K.

All structural models tested had the CO molecule perpendicular to the surface, carbon end down, and varied in the choice of adsorption site, Ni-C distance and C-O length. For the adsorption sites we tested the fourfold-symmetrical hollows, the bridge sites, and the top-atom positions. The former two fell immediately out of contention, as the overall agreement with the normal-incidence data was very poor or nonexistent. The top-atom position produced acceptable agreement with all available experimental data both at normal and nonnormal incidence for a C-O distance of 1.15 Å and a Ni-C distance of 1.72 Å (the corresponding distances in the $\mathrm{Ni(CO_4)}$ molecule are 1.145 Å and 1.82 Å, respectively). Some of the LEED intensity spectra obtained with these parameters are compared to their experimental counterparts in Fig. 1. Since the remaining spectra (not shown) also correspond well to the experiment, we conclude that the model is essentially correct. Slight modifications of the structural parameters are likely to be made in the course of the refinement process, presently in progress, which will include the different vibration amplitudes of C, O, and Ni, and the possible anisotropy of the CO vibrations. In addition, at the present time, it appears that the agreement with experiment for some of the integral-order beams might be improved by allowing for a contribution from the clean Ni{001} surface. It is possible that during the measurements the surface may not have been uniformly covered with ordered CO, either because the exposures were somewhat less than optimal or because electron-stimulated desorption and partial dissociation of CO occurred. This possibility will also be investigated in the course of the refinement of the structural model.

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