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Relaxation in ZnO $(10\bar{1}0)$, (0001), and $(000\bar{1})$ Surfaces and the Adsorption of CO

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Abstract: An atom superposition and electron delocalization molecular orbital study using cluster models shows surface zinc and oxygen ions relax into the (0001), $(000\bar{1})$, and $(10\bar{1}0)$ surfaces. The unsaturated surface zinc ions present surface states consisting of empty 4s, 4p hybridized orbitals with energy levels beneath the empty 4s, 4p band. The filled bands are O 2p nonbonding, Zn 4s + O 2p bonding, and Zn 3d, in order of increasing ionization potential. A study of CO adsorption to an unsaturated zinc ion on the $(10\bar{1}0)$ surface produces an adsorption energy of 12 kcal/mol, a CO bond length decrease of 0.02 Å, and an increase in the CO stretching force constant. The zinc ion unrelaxes to a position above the bulk-like position when CO is coordinated to it. The bonding of CO to zinc consists in closed shell σ donation interactions of the CO 5σ orbital with the filled Zn 3d and Zn 4s + O 2p bands with the antibonding counterpart stabilized by the Zn 4s, 4p surface state orbital. This 5σ donation strengthens the CO bond and transfers charge to the surface. These results support a number of experimental structural, vibrational, and electronic studies in the literature.

Zinc oxide is an effective olefin hydrogenation catalyst. Surface intermediates which play a role in this process have been characterized by Kokes.[1] ZnO also converts CO + H_2 to methanol.[2] The intermediates for this reaction are less well characterized. All that is presently known is that H_2 presumably adsorbs heterolytically[1] and CO coordinates to coordinatively unsaturated Zn^{2+} sites.[1-5] IR[1] and high resolution electron energy loss spectroscopy (HREELS)[4] studies indicate a small strengthening of the CO bond on adsorption. Ultraviolet photoelectron spectroscopy (UPS) shows the bonding of CO to Zn^{2+} is mainly the result of a Zn–C bond resulting from donation from the filled 5σ orbital of CO to the empty Zn 4s + 4p band.[5] An angle resolved UPS (ARUPS) study shows CO adsorbs on Zn^{2+} sites of the $(10\bar{1}0)$ surface at an angle tilted toward the surface about 10° from tetrahedral bond angle.[6] (ZnO has the wurtzite structure as may be seen in Figure 1.)

Some restructuring from the bulk structure has been seen by low energy electron diffraction (LEED) for several clean surfaces; the literature results are summarized in ref 5. On the $(10\bar{1}0)$ surface Zn^{2+} relaxes about 0.5 Å down approximately along the tetrahedral axis and O^{2-} relaxes $\sim$0.1 Å. On the (0001) surface Zn^{2+} relaxes about 0.3 Å down but on the $(000\bar{1})$ surface O^{2-} relaxation has not been determined. There is evidence presented in ref 5 that adsorbed CO unrelaxes the Zn^{2+} on the (0001) surface.

Theoretical work on ZnO seems to be limited to an X_α cluster a molecular orbital calculation by Tossell[7a] and empirically fit tight-binding band calculations.[7b] Tossell assigned the intense 8.5–12-eV UPS emission to Zn 3d electrons, the weak 6–8.5-eV emission to electrons in O 2p + Zn 4s, 4p bonding orbitals, and the intermediate intensity 3–6-eV emission to O 2p nonbonding electrons. These assignments are based on ZnO_4^{6-} cluster orbitals.

In the present study we undertake a rather thorough theoretical examination of the electronic structure of bulk and surface ZnO and the surface relaxations. We then introduce CO and calculate the bonding shifts of the σ orbitals, the vibrational frequency, and structure and the changes in surface Zn^{2+} relaxation. We use the atom superposition and electron delocalization molecular orbital (ASED–MO) theory.[8] In this theory the molecular charge density is partitioned into atomic components and the rest, which is an electron delocalization bonding charge. An exact formalism is used to specify the energy of each bond in terms of two components, a repulsive one and an attractive one. The repulsive one comes from integrating the force on a nucleus due to atom superposition. It is determined without approximation with use of atomic densities from a valence atomic orbital basis set. The attractive component is equal to an integral of the force on the nucleus due to the electron delocalization charge density. This component is, in practice, well approximated by the electron delocalization energy from a one-electron calculation using a modified extended Hückel hamiltonian. Parameters used in the calculations are given in Table I. They are based on literature valence orbital exponents [9,10] (ζ) and valence state ionization potentials[11] (VSIP) with adjustments to approximate self-consistency. For zinc and oxygen these are made by studying diatomic ZnO. The Zn VSIP are increased and the O VSIP decreased by equal amounts in 0.5-eV steps until the calculated charge transfer is close to 0.59 predicted from the electronegativity difference. The oxygen valence s and p exponents are decreased in 0.1-au steps until a reasonable ZnO bond length is obtained from the calculations. The final shifts are 2.5 eV and 0.2 au, producing a charge transfer of 0.87 and a ZnO bond length of 1.69 Å; the ZnO bond length is not, to our knowledge, available from experiment. The calculated value of 1.69 Å is a prediction within several 0.01 Å, we expect, because similar ζ and VSIP shifts for diatomic FeO yield a bond length 0.04 Å longer than experimental.[12] We calculate a ZnO bond length of 1.91 Å in $Zn(OH)_4^{2-}$ for linear ZnOH bonding which compares well with 1.92 Å from a Hartree–Fock calculation.[13] Finally, the accurate values which we calculate for ZnO bond lengths in the surfaces of zinc oxide are further confirmation for our expectations. The CO

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Table I. Atomic Parameters Used in the Calculations: Principal Quantum Numbers, *n*, Ionization Potentials, IP (eV), Slater Orbital Exponents, ζ (au), and Respective Linear Coefficients, *C*, for Double-ζ d Orbitals

	s			p			d					
atom	*n*	IP	ζ	*n*	IP	ζ	*n*	IP	ζ_1	C_1	ζ_2	C_2
Zn^{2+}	4	11.894	2.2	4	6.094	1.9	3	14.1	6.15	0.5980	2.4	0.5670
O^{2-}	2	25.98	2.046	2	11.12	2.027						
C	2	20.0	1.658	2	11.26	1.618						
O	2	28.48	2.246	2	13.62	2.27						

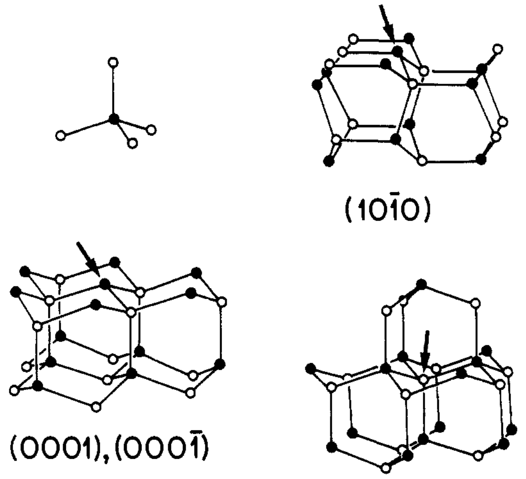

Figure 1. Cluster models of the (0001) (the (000$\bar{1}$) surface cluster is the same as the (0001) cluster with Zn and O interchanged) and (10$\bar{1}$0) surfaces and bulk-coordinated Zn (bulk-coordinated O has Zn and O interchanged). Arrows point out highly coordinated atoms whose properties are discussed in the text.

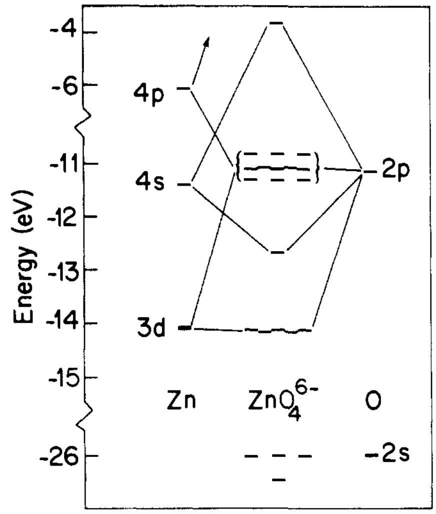

Figure 2. Energy level correlation diagram for the ZnO_4^{6-} cluster.

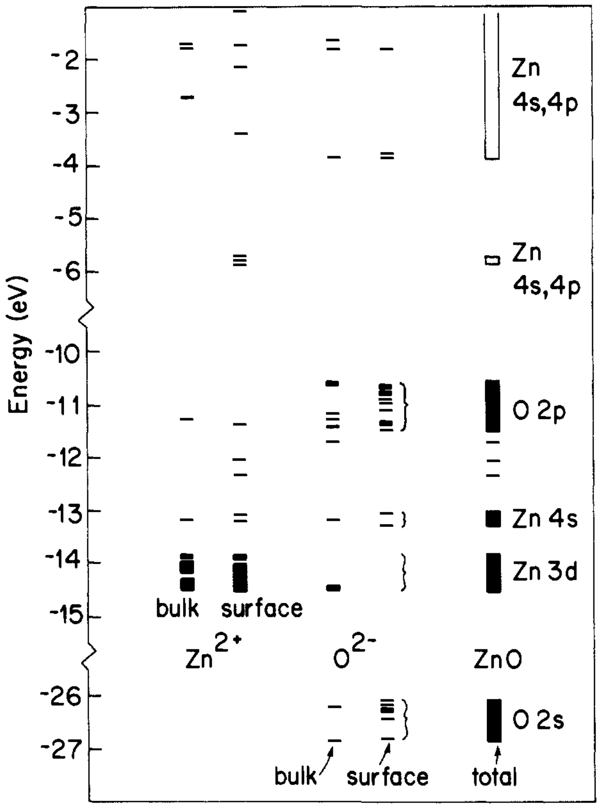

Figure 3. Building up the bulk band structure from orbitals with 0.1 or more electrons on (10$\bar{1}$0) surface and bulk ions according to calculations using the clusters in Figure 1. Arrows in Figure 1 indicate (10$\bar{1}$0) surface Zn^{2+} and O^{2-} positions and bulk-like positions.

parameters are those used previously.[14]

Surface Relaxation, Surface States, and Bulk Electronic Structure

The photoelectron spectra are very similar for the (0001), (000$\bar{1}$), (10$\bar{1}$0), and (11$\bar{2}$0) surfaces of ZnO.[5] We have chosen the (10$\bar{1}$0) surface for our analysis of the surface electronic structures. We used ZnO_4^{6-}, $Zn_{11}O_{11}$, $Zn_{13}O_{14}^{2-}$, $Zn_{14}O_{13}^{2+}$, and $Zn_{13}O_{13}$ cluster models shown in Figure 1. The ZnO_4^{6-} electronic structure we calculate (Figure 2) is qualitatively similar to Tossel's from ref 7a. We see the lowest *t* and *e* set of orbitals, which are mostly Zn 3d in character and slightly bonding to O 2p orbitals, form a narrow group. The next orbital is Zn 4s + O 2p bonding and its antibonding counterpart lies high and empty. The O 2p set is slightly antibonding to the Zn 3d orbitals and at the same time slightly stabilized by the empty Zn 4p orbitals, whose antibonding counterparts lie very high and empty. The larger clusters produce the electronic structure in Figure 3. Several components to the band are shown. The first column shows only those energy levels from a $Zn_{13}O_{14}^{2-}$ cluster for which the orbitals have >0.1 electronic charge on the central bulk-coordinated zinc ion. The second column shows levels determined in a similar way for a surface zinc ion whose coordination neighbors are all themselves fully coordinated in $Zn_{11}O_{11}$. In this determination the central Zn ion (arrow in Figure 1) is relaxed down by 0.05-Å steps into the surface until an energy minimum is reached at 0.4 Å, a predicted value comparing well with the ~0.5 ± 0.1 Å relaxation from a LEED study.[5,15] In our model for relaxation no other atoms positions are varied. The third column of levels is for bulk-coordinated oxygen ions and the fourth for surface oxygen ions, both determined as was done for the zinc ions. According to LEED[15] a 0.05 ± 0.1 Å relaxation is deduced for the surface oxygen ions.[5] We calculate a relaxation of 0.15 Å (to the nearest 0.05 Å) into the surface along the tetrahedral bond direction. This relaxation has no substantial effect on the electronic structure, and the levels for the unrelaxed core are shown in the fourth column of Figure 3. It is noted that with these models the bulk-like Zn^{2+} and O^{2-} ions have the respective charge 0.57 and −0.50 and the corresponding relaxed surface ion charges are 0.68 and −0.74. The sum of all these is the last column of levels, and this comprises

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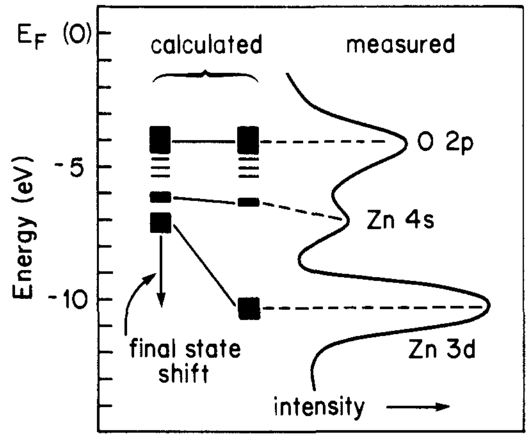

Figure 4. Calculated bands from Figure 3 compared with UPS spectrum of ZnO from ref 5. The first column of calculated energy levels are the initial-state. The second column includes the final-state shifts which accompany ionization as predicted by Tossell in ref 7a. Measured energies are with respect to the Fermi energy, E_F, and the calculated O 2p band is positioned to overlap the UPS 2p peak.

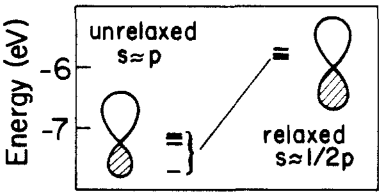

Figure 5. Zn 4s, 4p surface-state shift due to relaxation. Each orbital has 0.1 or more electron on the surface Zn ion, which is indicated by an arrow for the $(10\bar{1}0)$ cluster in Figure 1.

our prediction of the band structure at the surface–bulk interface, which is that sampled by UPS. The agreement of these initial-state energy levels with the UPS spectra of ref 5 is as expected. The first two UPS peaks are separated by 2.5–3 eV and the distance from the middle of the calculated O 2p band to the middle of the Zn 4s band is ~2 eV. A low density of levels between these bands may be responsible for the shoulder seen in ref 5. The middle and third UPS peaks are separated by ~3 eV and the band centers in the calculations are separated by ~1 eV. It is interesting that the final state relaxation shifts from Tossell's X_α calculation produce, when applied to our initial state energy levels, a significantly improved fit to the experimental photoemission spectrum. This is shown in Figure 4. The reason for this apparently lies in the similarity of the treatment of electron correlation in the two one-electron methods. In X_α electron correlation energies are approximated by use of a charge density formulation and the calculations are self-consistent. In our molecular orbital approximation to the electron delocalization energy of the ASED theory we use actual experimental ionization potentials in the hamiltonian and these contain the energy effects of electron correlation. We shift these ionization potentials to obtain proper ionicity in ZnO and in this way approximate self-consistency. Thus UPS measurement shows the Zn 3d band to lie 3.2 eV lower than the initial state levels of both methods, and the Zn 4s band also shifts down 0.2 eV according to ref 7a. As far as the bonding of CO is concerned, the initial state energy levels are the ones to focus on, as discussed below.

The 0.4-Å Zn^{2+} relaxation on the $(10\bar{1}0)$ surface causes a flattening out of the ZnO_3 pyramid. This has an interesting consequence for the 4s–4p hybridized empty dangling bond orbital in the gap between the O 2p band and the conduction band. It is destabilized by the Zn–O bond shortening and it loses 4s character. This is shown in Figure 5. See also ref 7b.

Using the cluster models in Figure 1, we calculate a 0.35-Å relaxation down of the zinc ion on the (0001) surface and a 0.15-Å relaxation down of the oxygen ion on the $(000\bar{1})$ surface. Both are to the nearest 0.05 Å. The experimental situation is unclear in that ref 5 says the zinc relaxation is about 0.3 Å while Lubinsky et al.[16] state 0.2 ± 0.1 Å. According to ref 16 the oxygen relaxations were not determined. Our predicted relaxations for these surfaces are similar to those which we calculate for the $(10\bar{1}0)$ surface, not a surprising result given the same cation and anion coordination for both surfaces.

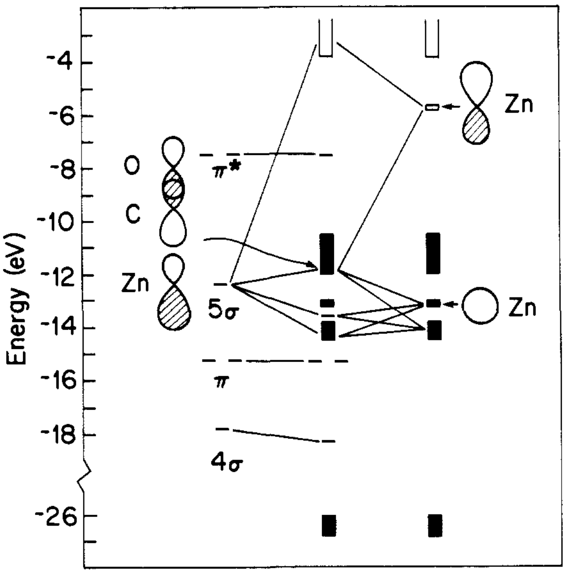

Figure 6. CO 5σ interactions with filled Zn 3d and Zn 4s + O 2p bands showing the stabilization of the antibonding counterpart orbital by a surface-state orbital. CO is bonded to the $(10\bar{1}0)$ Zn^{2+} site shown by the arrow in Figure 1.

CO Adsorption on the $(10\bar{1}0)$ ZnO Surface

CO bonds to the surface zinc ion by donating from its occupied 5σ (σ_p) molecular orbital to the empty Zn 4s + 4p surface state orbital. This is the net result. The bonding is complicated by the two filled Zn valence bands in close resonance with it, as shown in Figure 6. The CO 5σ orbital forms bonding stabilizations with the Zn 3d and 4s orbitals and the antibonding counterpart is occupied. Without the surface state this would be a repulsive closed-shell interaction and CO would only physisorb. However, the empty Zn 4s–4p surface state orbital stabilizes this antibonding counterpart orbital so that a weak bond is possible. The calculated energy levels are in agreement with the photoemission spectra of ref 5, once the final state shift of the Zn 3d band is taken into account. There are three CO 5σ levels. The first lies at the bottom of the O 2p band, as is also seen in the difference spectrum of ref 5. The middle level lies just below the Zn 4s band as seen in the UPS difference spectrum. The third level lies ~1 eV below this and corresponds to the second peak in the difference spectrum which lies at the top of the Zn 3d band, once the final state relaxation of the d band is taken into account. The CO π orbital levels are stabilized only a very small amount by the Zn d orbitals. Once the final state relaxation of the d band is considered these levels will lie near the top of the d band rather than at the bottom as seen in the UPS difference spectra. The 4σ (σ_s*) level is stabilized by 0.5 eV. The distance from the middle 5σ level to the 4σ level is 0.7 eV less than calculated for gas-phase CO. This corresponds to the ~0.5-eV decrease seen in the UPS difference spectra.

The above features are most clearly seen in Figure 7, which compares calculated shifts of CO molecular orbital energy levels on adsorption to UPS measurements. The UPS difference spectrum from ref 5 was obtained by subtracting the spectrum of the clean surface from the spectrum of the exposed surface. We have aligned our calculated 4σ level with the 4σ band from adsorbed CO. It may be seen that the calculated gas-phase 4σ, π, and 5σ spacings agree well with the measured ionization potentials as do their shifts due to adsorption to the ZnO surface.

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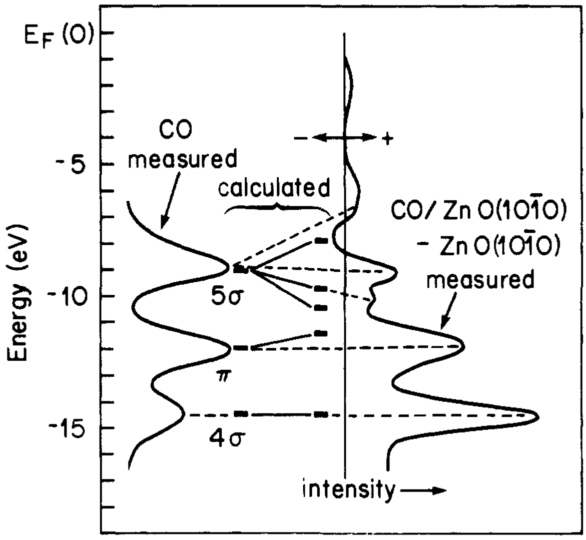

Figure 7. On the right-hand side is the difference spectrum for CO adsorbed on (10$\bar{1}$0) ZnO from ref 5, where it was obtained by subtracting the clean surface spectrum from the CO/surface spectrum. The calculated and experimental 4σ levels are aligned with the CO/surface 4σ peak, and calculated shifts due to adsorption to a Zn site of the (10$\bar{1}$0) surface cluster of Figure 1 are compared to the shifts given in the difference spectrum.

Structure optimization shows the zinc ion to which CO is coordinated unrelaxes. It moves up 0.11 Å (to the nearest 0.01 Å) from the bulk position. This confirms the speculation about unrelaxation in ref 5. The calculated CO adsorption energy of 12.2 kcal/mol agrees with ΔH_0 of 12.0 ± 0.4 kcal/mol found for four different crystal faces.[5] The calculated Zn–C distance is 1.60 Å. We find no tilting of CO (within 5°) away from the tetrahedral orientation, in contrast ot the ARUPS estimate of $\sim$10° toward the surface.[6] However, it has been suggested this tilting may be a characteristic of high coverages,[17] which are not being modeled here.

Calculated properties for gas-phase and adsorbed CO are given in Table II. The gas-phase predictions are good. It is seen that the bond shrinks on the surface due to the stabilization of the 5σ orbital. This orbital is weakly antibonding due to antibonding hybridization of the 3σ (σ_s) orbital. The HREELS vibrational study showed an increase in the CO stretching frequency upon adsorption and this was attributed to the 5σ stabilization.[4] Using the ZnC frequency of 250 cm^{-1}[15] in the ZnCO triatomic approximation with a Zn mass of 65.37, we determine 45 cm^{-1} of the 59 cm^{-1} frequency shift is due to bond weakening. From Table II, the resulting ratio of experimental CO gas phase to adsorbed force constants is 0.96 (no anharmonic corrections are made). The calculated ratio is 0.94.

Table II. Calculated CO Bond Length, R_e (Å), Frequency, ν_0 (cm^{-1}), Stretching Force Constant, k_e (mdyn/Å), Bond Energy, D_0 (kcal/mol), and Atom Charge, q[a]

property	gas-phase CO	adsorbed CO
R_e	1.11 (1.128)	1.09
ν_0	(2143)	(2202)
k_e	19.77 (18.55)	21.01 (19.24)
D_0	220 (256)	
q_C	−0.0669	0.404
q_O	0.0669	0.036

[a] Experimental gas-phase values in parentheses are from the following: Herzberg, G. *Molecular Spectra and Molecular Structure I. Spectra of Diatomic Molecules*; Van Nostrand: New York, 1950. Experimental surface values are from ref 5 and are in parentheses.

With use of a point charge approximation and the data in Table II, our calculated dipole moments for gas-phase and adsorbed CO are 0.185 and 1.02 D, compared to 0.112 and 0.61 D from experiment.[5] Both predicted values are 1.7 times the experimental values, possibly a result of the point charge model, as well as the approximate nature of the calculations.

Conclusions

This study offers strong support for the experimental assignments of photoemission bonds for zinc oxide surfaces when clean and when CO is adsorbed. It also supports the relaxation studies which were made with use of LEED intensity analyses and it verifies the strengthening of the CO bond, in terms of force constant increase, when CO is adsorbed on zinc oxide surfaces. Our results go beyond the prior experimental conclusions in elucidating the orbital interactions responsible for CO adsorption. We find there are three 5σ associated bands as a result of the closed-shell interactions with the filled Zn 3d and Zn 3s + O 2p bands. The highest lying would be antibonding with the surface, resulting in only a physisorption bond to the surface except for the stabilization provided by the Zn 4s, 4p surface state orbital. This surface state, which is important to CO chemisorption, was not previously characterized. It has important consequences to hydrogen adsorption and catalyst conductivity, as will be discussed in a later publication. Our results also support the conjecture in ref 5 that CO adsorption causes surface Zn ions to unrelax, a result of completing the tetrahedral coordination to σ-bonded ligands.

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