

SURFACE SCIENCE LETTERS

**GEOMETRY, VIBRATIONAL FREQUENCIES, AND IONIZATION POTENTIALS FOR CO/Ni(100); EXPLANATION OF THE DISAPPEARANCE OF THE  $5\sigma$  PEAK IN PES**

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Using a cluster of 14 Ni atoms to model a Ni(100) surface, we used ab initio methods [generalized valence bond (GVB)] to study CO chemisorbed at the on-top site. Reported are the optimum geometry, vibrational frequencies, and ionization potentials. We propose a new explanation for the two lowest levels of free CO ( $5\sigma$  and  $1\pi$ ) reducing to one level of chemisorbed CO.

Using a cluster of 14 Ni atoms to model an Ni(100) surface, we have used ab initio methods (generalized valence bond) to calculate geometry, vibrational frequencies and ionization potentials for CO chemisorbed at the on-top site.

The Ni<sub>14</sub> cluster consisted of atoms at the corners and faces of a cube, and the CO was bonded to an Ni atom at the center of one face. This on-top site has been established by EELS experiments [1] and infrared spectroscopy [2] to be the dominant site for Ni(100)-c(2 × 2)-CO. Thus, all eight nearest neighbors to the bonding site are included along with a third layer of atoms (needed for the cluster to better mimic the solid). The Ni atoms were described as in previous studies [3,4] and for C and O a double zeta basis was used. The two pi bonds of CO were correlated [5], i.e., GVB(2/4), since the correlation error in the CO sigma pairs is far smaller than that in the pi pairs.

The calculated geometry for CO bonded to Ni<sub>14</sub> is  $R_{\text{NiC}} = 1.94^3 \text{ \AA}$ ,  $R_{\text{CO}} = 1.14^6 \text{ \AA}$ , and  $\theta(\text{NiCO}) = 180^\circ$ . Early LEED studies for CO/Ni(100) were interpreted in terms of a bent NiCO,  $\theta(\text{NiCO}) = 146^\circ$  [6] or in terms of a very short CO bond distance of 0.95 Å [6]. However, UPS studies [7] provided clear evidence that  $\theta(\text{NiCO}) = 180^\circ$  and subsequent LEED studies led to  $\theta(\text{NiCO}) = 180^\circ$  with  $R_{\text{NiC}} = 1.72 \text{ \AA}$  and  $R_{\text{CO}} = 1.15 \text{ \AA}$  [8] or  $R_{\text{NiC}} = 1.80 \text{ \AA}$  and  $R_{\text{CO}} = 1.10 \text{ \AA}$  [9] (uncertainties of 0.1 Å). In comparison, the experimental geometry for Ni(CO)<sub>4</sub> is  $R_{\text{NiC}} =$

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184 Å and  $R_{\text{CO}} = 1.15$  Å [10]. Since the Ni atom has  $d^{10}$  character in  $\text{Ni}(\text{CO})_4$  and  $d^9$  character on the surface we would expect *longer* NiC distances on the surface (for low coverage) and suggest  $R_{\text{NiC}} = 1.9$  Å as the minimum likely geometry. The LEED experiments may lead to systematic errors due to the very nonspherical nature of the orbitals on C and O and from the assumptions concerning the spatial variation in the electron-ion-core potential ( $V_0$ ).

Using reduced masses appropriate for NiCO (triatomic), we obtain the following vibrational frequencies ( $\omega_e$ ):  $\bar{\nu}_{\text{NiC}} = 401$   $\text{cm}^{-1}$ ,  $\bar{\nu}_{\text{CO}} = 2129$   $\text{cm}^{-1}$ ,  $\bar{\nu}_{\text{NiCO}(\text{bend})} = 327$   $\text{cm}^{-1}$ . In comparison, for free CO we calculate  $\bar{\nu}_{\text{CO}} = 2200$   $\text{cm}^{-1}$  (the experimental values are  $\omega_0 = 2143$   $\text{cm}^{-1}$  and  $\omega_e = 2170$   $\text{cm}^{-1}$  [11]). Thus, the calculated CO frequency drops 71  $\text{cm}^{-1}$  upon bonding to  $\text{Ni}_{14}$ . For  $\text{Ni}(\text{CO})_4$  (gas phase) the experimental frequencies ( $\omega_0$ ) are [12]  $\bar{\nu}_{\text{NiC}} = 371$   $\text{cm}^{-1}$ ,  $\bar{\nu}_{\text{CO}} = 2132$   $\text{cm}^{-1}$ . For  $c(2 \times 2)\text{-CO}$  on  $\text{Ni}(100)$ , EELS [13] leads to ( $\omega_0$ )  $\bar{\nu}_{\text{NiC}} = 480$   $\text{cm}^{-1}$  and  $\bar{\nu}_{\text{CO}} = 2068$   $\text{cm}^{-1}$ , in fair agreement with our calculations. Using a  $\text{Ni}_5\text{CO}$  cluster, Richardson and Bradshaw [14] deduced fundamental frequencies ( $\omega_e$ ) of  $\bar{\nu}_{\text{NiC}} = 437$   $\text{cm}^{-1}$ ,  $\bar{\nu}_{\text{CO}} = 2088$   $\text{cm}^{-1}$ , and  $\bar{\nu}_{\text{NiCO}(\text{bend})} = 410$   $\text{cm}^{-1}$ .

Our calculations lead to a bond energy of  $D_e(\text{Ni}_{14}\text{-CO}) = 1.34$  eV or  $D_{298\text{ K}}(\text{Ni}_{14}\text{-CO}) = 1.29$  eV (29.7 kcal mol $^{-1}$ ) and  $\Delta S_{298\text{ K}} = -35.18$  cal mol $^{-1}$  K $^{-1}$  in good agreement with experimental values of 1.30 eV [15,16].

The photoelectron spectrum [17,19] of gas phase CO shows peaks at 14.01 eV ( $5\sigma$ ), 16.91 eV ( $1\pi$ ), and 19.72 eV ( $4\sigma$ ) with a higher energy peak at 38.90 eV ( $3\sigma$ ) (MO assignments in parentheses). However, for CO adsorbed on  $\text{Ni}(100)$ , only two CO-derived peaks are observed, at 8.0 and 11.0 eV below the Fermi level (i.e.,  $\sim 13.2$  and 16.2 eV absolute ionization potential) [7]. The 11 eV peak is assigned to the  $4\sigma$  orbital and the broad peak at 8.0 eV is interpreted in terms of overlapping  $5\sigma$  and  $1\pi$  levels [7,18]. The broad 8.0 eV peak has not been clearly resolved into  $1\pi$  and  $5\sigma$  components; however, angle-resolved photoemission studies have been interpreted in terms of a  $5\sigma$  bonding level located ( $0.5 \pm 0.2$  eV) higher in binding energy than the  $1\pi$  level (that is, the  $1\pi$  and  $5\sigma$  levels are reversed upon chemisorption) [7].

We calculate ionization potentials by carrying out self-consistent GVB calculations for each ion state. For the  $\sigma$  ionizations both CO  $\pi$  bonds were correlated just as for the ground state, for the  $\pi$  ionizations only the remaining  $\pi$  pair was correlated. These are difficulties in solving self-consistently higher states of the same symmetry as a lower state; however, we were able to obtain fully self-consistent wavefunctions in all cases.

The calculated ionization potentials for free CO are 13.05 eV ( $5\sigma$ ), 16.14 eV ( $1\pi$ ), 20.12 eV ( $4\sigma$ ), and 39.87 eV ( $3\sigma$ ), whereas for  $\text{Ni}_{14}\text{CO}$  the values are (using the geometry calculated for neutral  $\text{Ni}_{14}\text{CO}$ ) 15.78 eV ( $5\sigma$ ), 14.95 eV ( $1\pi$ ), 19.51 eV ( $4\sigma$ ), and 37.74 eV ( $3\sigma$ ). Thus we find that the positions of the  $5\sigma$  and  $1\pi$  orbitals reverse (0.83 eV separation), just as deduced from experiment ( $0.5 \pm 0.2$  eV separation).

In fig. 1 are the energies of the ion states as a function of distance. Here we see

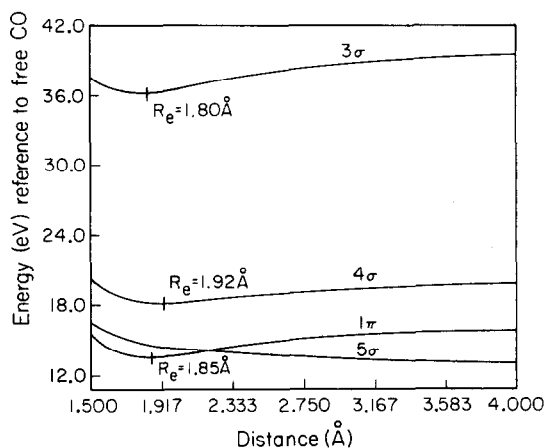


Fig. 1. Potential curves for  $\text{CO}^+$  interacting with  $\text{Ni}_{14}$  (on-top site).

that the  $1\pi$ ,  $4\sigma$ , and  $3\sigma$  ion states are all strongly bound ( $D_e = 2.55$ ,  $1.94$ , and  $3.65$  eV, respectively;  $R_e = 1.85$ ,  $1.92$ , and  $1.80$  Å, respectively); however, *the  $5\sigma$  ion state is very weakly bound* ( $D_e = 0.16$  eV and  $R_e = 5.05$  Å). The reason for this is that the Ni–C bond is due to the  $5\sigma$  orbital that interacts directly with the Ni surface. The  $1\pi$ ,  $4\sigma$ , and  $3\sigma$  ion states all have a doubly-occupied  $5\sigma$  orbital (as does the ground state) and all lead to strong, short bonds (the bond is stronger and shorter than for the ground state due to the net charge on the CO). However, the  $5\sigma$  ion state has only one electron in the bonding  $5\sigma$  orbital and consequently makes a very weak bond. For cases such as the  $1\pi$ ,  $4\sigma$ , and  $3\sigma$  ionizations, the geometry of the ion state is similar to that of the ground state and the Franck–Condon envelope is narrow. However, since the  $5\sigma$  ion state does not bind to the surface, the Franck–Condon envelope is very broad. We suggest that because of this effect the observed peaks in the PES are dominated by the  $1\pi$  and  $4\sigma$  transitions and that the  $5\sigma$  level is a very broad feature not discernible at the current level of resolution. This may explain why all cases in which associatively chemisorbed CO has been observed on single crystals lead to just the two peaks.

An experimental test of our suggestion would be to monitor photon-stimulated desorption of ions produced while carrying out the PES. The  $\text{CO}^+$  yield should be most closely related to the cross section for  $5\sigma$  ionizations, and we predict that this would be very broad.

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