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Theoretical study of the CO interaction with the Fe(100) surface

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Ab initio unrestricted-Hartree-Fock, effective-core-potential, and multiple-scattering $X\alpha$ molecular-cluster calculations have been performed in order to study the interaction of CO with an Fe(100) surface. The calculated Fe→CO charge transfer in the systems FeCO and Fe_5CO are correlated to the observed CO stretching frequencies on Fe(100). The increasing values of the Fe→CO charge transfer obtained as the molecule inclines in relation to the surface are consistent with the assignment of the low stretching frequency (1210 cm^{-1}) to the precursor state of CO dissociation on the iron surface.

INTRODUCTION

X-ray photoelectron-spectroscopy (XPS) and temperature-programmed-desorption (TPD) studies of CO adsorbed on an Fe (100) surface show that CO adsorbs molecularly in three states, CO(α_1), CO(α_2), and CO(α_3), and that the CO dissociation is correlated with the most tightly bound molecular state, CO(α_3).[1,2] The unusually low observed CO stretching frequencies at 1210–1260 cm^{-1} (Ref. 3) [or 1180–1245 cm^{-1} (Ref. 4)] have been associated with the α_3 molecular-state precursor to dissociation on the Fe(100) surface. The near-edge x-ray-absorption fine-structure (NEXAFS) spectra indicate that this state corresponds to the molecule tilted by 45°±10° with respect to the surface.[3] X-ray-photoelectron diffraction gives a similar structural picture with the molecule being tilted at an angle of 35°±2°.[5] High-resolution electron-energy-loss spectroscopy (HREELS) also shows that the "lying down" binding configuration is consistent with CO-bond weakening.[4] Photoelectron-spectra[6] and fluorescence-yield near-edge spectroscopy[7] (FYNES) studies indicate that the CO molecular orbitals in the α_3 state are extensively rehybridized with respect to the conventional end-on bound CO state. In previous theoretical studies the chemisorbed CO stretching frequencies have been correlated with the forward- and the back-donation charge transfer,[8–13] the primary interaction being Fe($3d$)→CO(2π) back donation.[8] The present molecular-orbital cluster-model calculations show that the Fe→CO charge transfer increases as the molecule is inclined to the surface. In our calculations the substantial weakening of the CO bond, through both the high population of the 2π antibonding orbital and the rehybridization of the CO bonding orbitals, confirms that the tilted molecule is sufficiently weakened to be consistent with stretching frequencies near 1210 cm^{-1} (the α_3 state). Furthermore, the small values of the back donation for the linear FeCO molecule enable us to identify the α_1 and α_2 states [the observed frequencies at 2020–2070 cm^{-1} (Ref. 1) or at 1900–2055 cm^{-1} (Ref. 4)] as the states with the CO molecule adsorbed perpendicular to the surface.

RESULTS AND DISCUSSION

In our previous work we performed *ab initio* self-consistent-field–unrestricted-Hartree-Fock (SCF-UHF) calculations of the M-CO systems (M=Sc to Cu).[10] It must be noted that the amount of charge transfer and other calculated parameters of the CO interaction with the iron surface depend on several factors, including the iron electronic configuration. Table I gives from Ref. 10 the *ab initio* SCF-UHF gross atomic populations and the back donation for the six lowest molecular states of linear FeCO. The calculated ground-state configuration corresponds to the $^5\Sigma^-$ state, in agreement with the complete active space self-consistent-field (CASSCF) calculations of Bauschlicher *et al.*[11,12] The SCF-UHF gross-atomic-population bond indices and Fermi level (defined as the highest occupied molecular orbital) of FeCO relative to the $^5\Delta$ state indicate that although there is no net Fe→CO charge transfer for the CO molecular axis perpendicular to the surface in this state, as the CO molecule is tilted there is increasing Fe→CO charge transfer, a corresponding decrease of C—O bond indices, and the Fermi level moves to more-negative values. Note that

TABLE I. UHF gross atomic populations and back donation for the six lowest states of linear FeCO.

State	Fe charge	C charge	O charge	Back donation
$^5\Sigma^-$	0.74	−0.39	−0.35	0.95
$^5\Sigma^+$	0.82	−0.22	−0.60	0.96
$^5\Phi$	0.81	−0.22	−0.59	0.95
$^3\Sigma^-$	0.72	−0.14	−0.58	0.95
$^5\Pi$	0.01	0.48	−0.47	0.04
$^5\Delta$	−0.08	0.51	−0.45	0.04

the four lowest-lying electronic states of FeCO have large back donation and can be involved in the CO dissociation process. Even though the surface is represented by only one Fe atom, the monocarbonyl complex is useful for modeling the chemisorption of CO on transition-metal surfaces.[10,13,14] Larger-cluster calculations provide a better representation of the chemisorption interaction; however, even the simplest metal monocarbonyl cluster shows the effect of the CO π back donation.[14] The present multiple-scattering (MS) $X\alpha$ calculations give approximately the same back donation for the FeCO and Fe_5CO systems. The increasing Fe→CO charge transfer, and the corresponding decreasing of the C—O bond indices, as the molecule is bent from the end-on configuration, is due to interactions between the Fe $3d_\delta$ (formerly nonbonding) and the Fe $3d_\pi$ orbitals with the rehybridized CO orbitals. The more-negative values of the Fermi level facilitate the Fe→CO charge transfer and, for the bent (45°) predissociative state, the Fermi level is found to be the lowest of all the configurations considered here (Table II).

In order to improve our description of the interaction between CO and the iron surface, the Fe_5CO cluster model is considered. The surface is now represented by four Fe atoms in the form of a square of side 2.87 Å. Below the Fe_4 plane, the fifth Fe atom is equidistant from the four Fe atoms in C_{4v} symmetry with a bond length of 2.48 Å. This is a representation of the fourfold adsorption site of the Fe(100) surface. The Fe distances correspond to those found in the bulk structure of bcc iron. Calculations have been carried out for five CO configurations: the end-on configuration with CO at 90° with respect to the surface, and at 0° and 45° with respect to the surface with the CO placed both diagonally and parallel to Fe_4. The SCF effective-core-potential[15] (ECP) results are summarized in Table II. The highest Fe→CO charge transfer and lowest Fermi levels are found for CO tilted with respect to the surface. In the cases where the molecular symmetry is lowered from C_{4v} to C_s, the system has only one symmetry element, the x-z plane, which makes possible mixing of the s, p_x, and p_z orbitals from the C and O atoms to form a' symmetry orbitals while the p_y orbital retains a'' symmetry. This lowering of molecular symmetry smears the distinction between σ and π charge transfer; it is now possible to have both charge transfer into and out of the CO sp^2 hybrid orbitals. The same holds true for the CO p_y orbital; however, the results seem to indicate that metal back donation is considerably larger than CO→metal donation.

The results of MS $X\alpha$ calculations of FeCO and Fe_5CO are shown in Table III. The muffin-tin-sphere radii are 2.35, 1.57, 1.35, and 6.21 a.u. for iron, C, O, and the outer sphere, respectively. The α parameters are taken from Schwarz.[16] The distances between atoms are the same ones used in the previous UHF (Ref. 10) and the present ECP calculations.

In Table III, back donation is obtained by taking the difference of the CO π population (the sum of the p_x and p_y populations) in the Fe_5CO end-on cluster and the π population of free CO (taken to be 4.0e). Table III shows

TABLE II. ECP charges and Fermi level (FL) in the Fe_5CO cluster model.

CO position	Fe(1)	Fe(2)	Fe(3)	Fe(4)	Fe(5)	C	O	FL
End on (hollow)	0.19	0.10	0.19	0.10	−0.59	0.15	−0.14	−5.86
Bent 45° (pointing to the Fe)	0.30	0.02	0.24	0.02	−0.53	0.10	−0.15	−6.11
Bent 45° (between the four Fe)	0.13	0.13	0.08	0.08	−0.50	0.13	−0.21	−5.94
Lying down (pointing to the Fe)	0.19	0.05	0.18	0.03	−0.53	0.26	−0.18	−5.52
Lying down (between the four Fe)	0.20	0.20	0.03	0.03	−0.54	0.29	−0.21	−5.64

TABLE III. MS $X\alpha$ back donation and Fermi level for different clusters.

Cluster	Back donation	Fermi level
FeCO linear	0.51	−3.94
Fe_5CO end on (hollow)	0.52	−4.67
Fe_5CO bent 45°	0.98[a]	−4.68
Fe_5CO end on (deep hollow)	1.33	−5.20

[a] Total charge accepted by CO.

the importance of the distance to the surface for the calculation of charge transfer. The MS $X\alpha$ back-donated charge goes from 0.53e to 1.33e when the surface to CO distance is shortened from 1.84 Å, relative to the plane of the four Fe atoms taken in the Fe_5CO cluster end-on hollow, to 1.84 Å for the distance from the fifth Fe atom, which is the distance used in the Fe_5CO end-on deep-hollow cluster calculation. For the Fe_5CO cluster end on, the calculated ECP back donation is 0.18e. The difference between the MS $X\alpha$ and *ab initio* ECP values is due to the use of different exchange operators. It has been shown that the local-density $X\alpha$ operator systematically predicts larger charge transfer than the nonlocal Hartree-Fock (HF) operator.[17]

The vibrational frequency of the adsorbed molecule can be taken proportional to the inverse of the back donation. The ratio of the calculated Fe_5CO MS $X\alpha$ back donation for the perpendicular and the bent positions (45°) gives 0.5, in reasonable agreement with the value obtained by comparing the corresponding two observed frequencies, $\frac{1260}{2070}\sim 0.6$. Therefore the α_3 state can be correctly identified as the tilted state of CO on the Fe(100) surface and the α_1 and α_2 states may be associated with perpendicular adsorption. The HREELS spectra[1] show that at low CO coverages a single loss peak clearly dominates at 1210 cm^{-1}. This peak corresponds to the chemisorbed state in which the CO molecule is bent in relation to the surface. Increasing the CO coverage produces a loss peak at 2020 cm^{-1} (and it is shifted to 2070 cm^{-1} at higher CO coverages). This second peak corresponds to the CO molecule chemisorbed perpendicularly to the surface. With the appearance of the second peak at 2020 cm^{-1}, the loss peak at 1210 cm^{-1} shifts to 1260 cm^{-1}, indicating a small decrease of back donation upon "perpendicular" chemisorption.

The change of the CO stretch frequency with tilt angle is an important parameter for understanding the role of frustrated rotations in the dephasing of the CO stretch vibration for CO absorbed on metal surfaces.[18] In addition to the Fe(100) surface studied here, tilted states have been observed for CO on other surfaces.[19–24] It would be of interest to determine whether the strong reduction in CO stretch frequency as the CO bond axis is tilted relative to the surface normal found in this work occurs quite generally, i.e., for other metals and binding sites.

In conclusion, the reported vibrational spectra[1–5] of CO on the Fe(100) surface can be interpreted in terms of two geometries of adsorption: perpendicular and tilted. A tilted precursor state for the CO dissociation is consistent with the present Fe→CO charge-transfer analysis for perpendicular and tilted CO.

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