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Theoretical study of the CO interaction with 3*d*-metal surfaces

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Ab initio molecular-orbital calculations of the M-CO systems (M=Sc to Cu) combined with Pauling's resonating-valence-bond theory indicate that CO adsorption only on Sc, Ti, V, Cr, Mn, and Fe surfaces will be dissociative, and nondissociative on Co, Ni, and Cu surfaces, in agreement with the experimental evidence. The nature of the chemical bond, charge transfer, Fermi level, and other parameters of the CO interaction with 3*d*-metal surfaces is analyzed. The CO dissociation is described as a charge-transfer process with bonds resonating among the metal, C, and O atoms. CO dissociation in activated catalytic processes on modified 3*d* surfaces is discussed.

I. INTRODUCTION

The interaction of CO with 3*d*-transition-metal surfaces[1–35] continues to be of great experimental and theoretical interest. From a theoretical point of view,[1–19] the π back donation can be correctly ascribed as the primary interaction in the CO absorption process. Experimental evidence has established that absorption of CO on first-row transition-metal surfaces Sc to Fe leads to dissociation of CO, whereas for Co to Cu the CO remains adsorbed on the surface.[20]

In this paper the metal-CO charge-transfer process is discussed in terms of Pauling's resonating-valence-bond theory[36,37] and *ab initio* molecular-orbital calculations. Experimental data for absorption (dissociative or molecular) on transition-metal surfaces have been rationalized in terms of the magnitude of charge transfer from metal to CO. It is found from our *ab initio* unrestricted Hartree-Fock (UHF) Mulliken populations that each metal from Sc to Fe is positively charged in the M-CO system. For Co, Ni, and Cu, however, no net charge-transfer to CO is found. In resonating-valence-bond theory, the existence of unsynchronized resonance of covalent bonds between the surface and CO determines the extent of dissociative adsorption. Therefore, metal→CO charge transfer, which leads to C-O dissociation, indicates an activated process due to unsynchronized resonating covalent bonds between the metal atom and the molecule. The CO dissociation on irradiated Mott insulator surfaces and other modified 3*d* surfaces is also analyzed in terms of the resonating-valence-bond mechanism of interaction.

II. COMPUTATIONAL PROCEDURES

The HONDO program of Dupuis-Watts-Villar-Hurst (1987) was employed to perform the unrestricted Hartree-Fock self-consistent field (UHF-SCF) molecular-orbital (MO) calculations. For the transition-metal atoms Wachter's (62111111/51111/32) basis set was used.[38] For carbon and oxygen the Whitman and Hornback (511/21) basis set[39] was used. The metallic surface is represented by only one atom. These monocarbonyl complexes have been studied by several groups[3,5,7,9,11,13,14,17] and can be considered as zero-order approximation models for describing chemisorption processes on metallic surfaces. Calculated properties of M_NCO clusters as a function of N has shown that small clusters can satisfactorily model CO adsorption. MO calculations of Rosén, Grundevik, and Morović[14] showed that NiCO reproduces the main features of the electronic structure obtained with larger Ni clusters. Although large cluster calculations provide a better representation of the chemisorption interaction, Bagus and Muller[5] found that even the simplest CuCO cluster shows the effect of Cu to CO π back donation.[2] This has also been confirmed by Bauschlicher *et al.* (see Ref. 3 and references therein). Different adsorption sites can, in principle, be represented by assuming different 3*d*-metal surface electronic configurations.

In the present study the M-CO distance was taken from the experimental values available for the corresponding carbonyl complexes:[12] $R(\mathrm{ScCO})=2.05$ Å, $R(\mathrm{TiCO})=2.03$ Å, $R(\mathrm{VCO})=2.01$ Å, $R(\mathrm{CrCO})=1.92$ Å, $R(\mathrm{MnCO})=1.86$ Å, $R(\mathrm{FeCO})=1.84$ Å, $R(\mathrm{CoCO})=1.82$

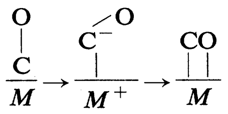
Å, $R(\text{NiCO})=1.80$ Å, $R(\text{CuCO})=2.00$ Å. These are the same values used by Sung and Hoffman in Ref. 1. The C-O distance was fixed at the isolated molecule value of 1.15 Å in all the calculations. This seems to be a reasonable assumption since the variation of energy levels with varying C-O distance is small.[14] It is found experimentally that bond lengthening in the adsorbed molecule is minimal.[20] It must be observed that our main goal is not to obtain theoretical values of spectroscopic accuracy, but to describe the general trends of CO adsorption on 3*d*-transition-metal surfaces. It is hoped that this procedure may ultimately enable predictions about catalytic behavior.

III. THE INTERACTION MODEL

In this paper adsorption behavior is analyzed in terms of Pauling's resonating-valence-bond theory[36] and *ab initio* molecular orbital calculations. This theory is applicable here since the *M*-CO interaction is dominated by charge transfer. In the resonating-valence-bond picture, unsynchronized resonance of covalent bonds describes charge transport in metals by transferring a bond from one atom to the next, accompanied by the creation of M^+, M^0, and M^- states,

$$M-MM \rightarrow M^+M-M^- . \qquad (1)$$

Unsynchronized resonance, however, requires that the atom receiving a bond (M or M^+) have an orbital available for its reception (occupied in M^-). It is the existence of such an orbital, the lowest unoccupied $2\pi^*$ MO, that permits the interaction of CO as a Lewis π acid with the metal surface. Then, for the surfaces with $M \rightarrow$CO charge transfer, the unsynchronized resonating-valence-bond mechanism of CO dissociation can be written schematically as



$$\frac{\begin{array}{c}\text{O}\\ |\\ \text{C}\end{array}}{M} \rightarrow \frac{\begin{array}{c}\diagup\text{O}\\ \text{C}^-\\ |\end{array}}{M^+} \rightarrow \frac{\begin{array}{c}\text{CO}\\ |\;|\end{array}}{M} . \qquad (2)$$

The first electron-transfer step leads to bond formation between the surface (which acquires a positive charge represented by M^+) and the carbon atom of CO. In the second step, the C—O bond is transferred to the metal surface. The dissociation occurs when the electron returns to the surface, restoring electrical neutrality as must occur in a catalytic process. The electron traverses a closed loop while dissociating the CO molecule.

An early step in the sequence of reactions of CO promoted by metal catalysts appears to be the coordination of CO to a metal atom.[13] This is described in the first step of the mechanism. The metal attacks the carbon atom since the unoccupied 2π MO is mainly localized on

TABLE I. Gross atomic populations, metal→CO charge transfer, and back donation (BD) for different states of the *M*-CO ($M=$Sc to Cu) systems.

System	State	Metal	Carbon	Oxygen	BD
ScCO	$^2\Pi$	0.10	0.39	−0.49	0.28
	$^4\Sigma^-$	0.30	0.17	−0.47	0.48
	$^4\Delta$	0.43	0.04	−0.47	0.57
	$^4\Phi$	0.25	0.18	−0.43	0.36
	$^2\Sigma^+$	−0.08	0.42	−0.34	0.00
TiCO	$^3\Delta$	0.71	−0.10	−0.61	0.76
	$^5\Delta$	0.35	0.21	−0.56	0.47
	$^3\Sigma^-$	0.19	0.25	−0.44	0.37
VCO	$^6\Sigma^+$	0.20	0.32	−0.52	0.30
	$^4\Pi$	−0.08	0.53	−0.45	0.05
	$^6\Delta$	0.25	0.28	−0.53	0.31
CrCO	$^5\Sigma^-$	0.71	−0.11	−0.60	0.98
	$^5\Sigma^+$	−0.02	0.47	−0.45	0.12
	$^7\Sigma$	0.20	0.31	−0.51	0.26
MnCO	$^6\Pi$	0.82	−0.23	−0.59	0.96
	$^6\Sigma^+$	−0.06	0.49	−0.43	0.04
	$^6\Delta$	0.17	0.32	−0.50	0.24
FeCO	$^5\Sigma^-$	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
	$^5\Delta$	−0.08	0.51	−0.43	0.04
CoCO	$^4\Phi$	−0.06	0.50	−0.44	0.06
	$^4\Delta$	0.70	−0.32	−0.39	0.96
NiCO	$^3\Delta(3d^84s^2)$	−0.06	0.51	−0.45	0.06
	$^1\Sigma^+$	0.72	−0.14	−0.58	0.94
	$^3\Delta(3d^94s^1)$	0.13	0.39	−0.52	0.23
	$^3\Pi$	0.69	−0.31	−0.38	0.96
CuCO	$^2\Sigma^+$	−0.00(2)	0.49	−0.49	0.08
	$^2\Pi$	−0.05	0.51	−0.46	0.01

it. The extent of $3d \rightarrow 2\pi^*$ back donation is directly correlated to the strength of the M-CO bond.[1–19] The CO $5\sigma \rightarrow$metal-$3d$ donation contributes to reduce the excess negative charge on CO; however, it was found that there is very little CO 5σ to metal-$3d_\sigma$ donation if the $3d_\sigma$ shell is also filled.[2,40] By occupying the antibonding $2\pi^*$ MO the C—O bond is weakened. The charge-transfer process leads to a buildup of negative charge mainly on carbon, although a significant portion delocalizes onto oxygen as well.

Table I presents *ab initio* UHF-SCF charge-transfer data for the linear M-CO systems ($M =$Sc to Cu). For $M =$Sc to Fe in the ground state, we find net charge transfer from the metal to CO; for $M =$Co, Ni, and Cu, no net charge transfer to CO is observed. This implies that unsynchronized bond resonance occurs only on Sc, Ti, V, Cr, Mn, and Fe surfaces, that is, for systems where dissociative adsorption character is experimentally observed. For dissociative adsorption the net charge on carbon remains negative compared with that of a free molecule, in agreement with the resonating-valence-bond interaction mechanism.

Table II gives the gross atomic populations and bond indices for bent Fe-CO at different angles. Charge transfer between Fe and CO increases as the CO goes from the "end-on" arrangement to the "lying-down" configuration with simultaneous weakening of the C—O bond. Two mechanisms are mainly responsible for this C—O bond weakening. First, as Fe—CO bends, the Fe—C bond changes character from sp to sp^2 hybridization and loses the triple-bond structure of CO. Second, as the Fe$\rightarrow$CO charge transfer increases, the population of the CO antibonding orbitals increases, weakening the C—O bond. This increase in charge transfer arises from the new overlap of the $3d_\delta$ orbitals (in the linear structure) of Fe with the CO sp^2 and π orbitals in the bent structure. Since our initial Fe electronic configuration was $\pi^2\delta^3\sigma^1 4s^1$, charge transfer from the metal δ orbitals should make a significant contribution to C—O bond weakening. It has been shown experimentally that in the predissociative state (α_3 state[28] or a state[22]) of CO on Fe(100) that CO is tilted by approximately 45° with respect to the Fe surface.[21] This state also has a very low stretching frequency (1210 cm^{-1}), indicating a substantially weakened C—O bond.[22–24] Similar observations have been reported for CO on Cr(110) (Ref. 41) and Mo(100) (Ref. 42) surfaces. A more detailed discussion of the activation process of CO on Fe(100) will be published elsewhere.[19] The observed preference for charge transfer in the bent structure is consistent with our proposed model, since a bent and charged adsorbed molecule is predicted as the intermediate state in the second step.

IV. CHARGE TRANSFER AND ELECTRONIC STRUCTURE

Table I also presents a comparison of the magnitude of charge transfer for different metal electronic configurations. As expected, for a given metal, the occupation of the $3d_\pi$ molecular orbitals leads to higher back donation. Occupation of the $3d_\sigma$ and $3d_\delta$ MO's at the expense of the $3d_\pi$ results in a decrease of the metal$\rightarrow$CO charge transfer. The σ donation from CO $5\sigma \rightarrow$metal $3d_\sigma$ is found only in cases where the $3d_\sigma$ level is empty or half occupied, but metal $3d \rightarrow$CO π back donation is usually larger and is reflected in a positively charged metal atom. On the other hand, the metal $4s$–CO 5σ interaction is expected to be repulsive due to the Pauli exclusion principle.[3,7] Table I shows that the charge transfer for the $3d^{n+1}4s^1$ metal configuration is higher than that corresponding to the $3d^n4s^2$ configuration. However, the $4s^1$ configuration also has an additional $3d$ electron which further increases the charge transfer. The small bonding contribution from the metal $4p$ orbitals calculated here has been noted previously.[3,5,7,16] It is evident from Table I that the electronic configuration of the metal is a primary factor in determining the extent of charge transfer and therefore the occurrence of dissociation.

The CO levels undergo important changes throughout the series. For dissociative adsorption the CO 4σ, 1π, and 5σ levels are shifted to higher energies, in particular, for the cases where the $2\pi^*$ MO is occupied (i.e., TiCO, CrCO, MnCO, and FeCO). The Fermi level (identified as the highest occupied MO) undergoes small variations across the series and different electronic configurations of the same metal have similar Fermi levels. The Fermi levels and the 1π-4σ orbital energy differences are shown in

TABLE II. Gross atomic populations, bond indices (BI), and Fermi level for the bent FeCO molecule.

Angle	Metal	Carbon	Oxygen	BI(Fe—C)	BI(C—O)	Fermi level (eV)
90°	−0.08	0.51	−0.43	0.16	2.17	−4.3
85°	0.01	0.46	−0.47	0.17	2.15	−4.7
75°	0.10	0.39	−0.48	0.30	2.10	−5.0
60°	0.30	0.19	−0.49	0.49	2.02	−5.6
55°	0.36	0.15	−0.51	0.52	1.99	−5.7
45°	0.41	0.10	−0.51	0.53	1.98	−5.9
35°	0.40	0.10	−0.50	0.53	1.98	−5.9
25°	0.40	0.11	−0.51	0.52	1.97	−5.9
15°	0.42	0.11	−0.53	0.51	1.93	−5.9
0°	0.56	0.03	−0.59	0.46	1.81	−6.1

Table III. There are only small differences in the average value ($\pi_x + \pi_y$ spin up and down) of this quantity in the series. The calculated 1π-4σ energy separations for chemisorbed CO (Table III) are larger than in the gas phase [estimated to be 2.75 eV (Ref. 20)], in agreement with Broden *et al.*[20] Photoemission spectra[20] yield an energy separation of 3.5 and 3.1 eV for FeCO and NiCO, respectively, in reasonable agreement with the present UHF results.

Accurate identification of the ground state of *M*-CO systems is difficult and requires highly correlated wave functions.[16] To assist this assessment, we compare present results with previous theoretical predictions of the ground-state configuration and present an analysis of the charge transfer for different electronic configurations.

ScCO. Using the interaction mechanism discussed in Sec. III, the four lowest states of ScCO are found to be dissociative. Table I shows that the Sc charge is positive for the $^2\Pi$, $^4\Sigma^-$, $^4\Delta$, and the $^4\Phi$ states, indicating net $M \rightarrow$CO charge transfer. The $^2\Pi$ state is found to be the ground state with a Sc charge of 0.10+ (all charges in a.u.). The $^2\Sigma^+$ excited state (2.5 eV above the ground state) has no $M \rightarrow$CO charge transfer. The $^4\Sigma^-$ state (1.4 eV above the ground state) exhibits the largest back donation among the configurations studied, approximately twice that of the $^2\Pi$ state. Jeung[11] found that the $^2\Pi$ state is the least repulsive of the doublet states (Σ, Π, and Δ) but also found the $^4\Sigma^-$ to be the ground-state configuration, in agreement with recent high-level *ab initio* calculations.[4]

TiCO. For TiCO the $^3\Delta$ state is found to be only 0.1 eV below the $^3\Pi$ state. More extended calculations put the $^5\Delta$ below the $^3\Delta$.[4,9] Both the quintet and triplet states have net $M \rightarrow$CO charge transfer and are predicted to dissociate CO. Also the $^3\Sigma^-$ state (1.9 eV above the ground state) can dissociate the CO molecule.

VCO. The high spin $^6\Sigma^+$ state is found to be the ground state, in agreement with higher levels of theory.[4] Both ground and $^6\Delta$ states are predicted to have $M \rightarrow$CO charge transfer leading to CO dissociation. In addition, the $^4\Sigma^+$ state is dissociative, but not the $^4\Pi$ which exhibits no net charge transfer.

CrCO. The calculated ground state $^5\Sigma^-$ has large $M \rightarrow$CO charge transfer. The first-excited $^5\Sigma^+$ state (0.3 eV above the ground state) has no net $M \rightarrow$CO charge transfer. However, the $^7\Sigma^+$ state has relatively large charge transfer and lies only 0.5 eV above the ground state.

MnCO. The ground state in MnCO is found to be $^4\Pi$ with high back donation (0.96) and charge transfer. The calculated first-excited $^6\Sigma^+$ state (0.6 eV above the ground state) has no net charge transfer.

FeCO. The ground-state configuration corresponds to the $^5\Sigma^-$ state, in agreement with Bauschlicher *et al.*[3] who find this state to be bound and the $^3\Delta$ and $^3\Sigma^+$ states to be repulsive at the complete active space self-consistent field level. On the other hand, Berthier, Daoudi, and Suard[9] identify the ground state to be the low-spin $^3\Sigma^-$ state. The four low-lying states of FeCO are dissociative.

CoCO. The ground state $^4\Phi$, exhibits negative charge on Co rather than CO, and is not predicted to induce CO dissociation. The first low-lying state ($^4\Delta$) 7.0 eV above the ground state displays high back donation.

NiCO. The $^3\Delta$ state arising from the Ni $3d^8 4s^2$ configuration is found to be the ground state. Other theoretical studies have either identified $^3\Delta$ (Refs. 3, 4, 7, and 9) or $^1\Sigma^+$ (Refs. 10, 16, and 17) as the ground state. In the present calculations the $^3\Delta$ ground state has no $M \rightarrow$CO charge transfer, and does not lead to CO dissociation in the Pauling model. On the other hand, all the computed excited states, $^1\Sigma^+$, $^3\Delta$ ($4s^1 3d^9$), and $^3\Pi$ are predicted to dissociate CO. The first three low-lying states are found to be very close in energy. This may explain the observation of CO dissociation on the Ni(111) surface at high pressures.[30] Configuration interaction (CI) calculations by Walch and Goddard[7] support the $^3\Delta$ ground-state configuration, but also point out that both the Ni $4s^1 3d^9$ and $4s^2 3d^8$ atomic configurations are important at the distances considered here.

CuCO. The two low-lying doublets for CuCO, $^2\Sigma^+$ (ground state), and $^2\Pi$, shown in Table I, are in agreement with results of Berthier, Daoudi, and Suard.[9] Neither of these states are predicted to lead to CO dissociation. Comparison of the energy-level diagrams for these two states shows that in the former configuration the Cu $3d$ levels are dispersed to higher energies and present higher back donation. In addition, the ground-state $3d$ bandwidth is larger than in the first excited state.

V. CONCLUSIONS

Insight on the behavior of CO on the $3d$-transition-metal surfaces has been gained by analyzing *ab initio* UHF-SCF charge transfer and electronic structures of the *M*-CO (*M* = Sc to Cu) systems. The observed CO dissociation on surfaces of metals prior to Fe in the Periodic Table can be rationalized in terms of resonating-valence-bond theory. The resonating-valence-bond mechanism of catalytic CO dissociation on metal surface involves two steps: $M \rightarrow$CO charge transfer, and CO dissociation with electron transfer back to the metal. The electron transfer covers a complete cycle in which the CO bond is broken

TABLE III. Fermi level and 1π-4σ energy difference for the linear systems in the ground-state configuration (in eV).

	ScCO	TiCO	VCO	CrCO	MnCO	FeCO	CoCO	NiCO	CuCO
Fermi level (−)	5.2	5.7	4.9	4.5	6.0	6.4	5.6	5.6	4.6
$\Delta\varepsilon(1\pi - 4\sigma)$	4.0	3.9	3.9	4.0	4.0	4.2	4.4	4.0	4.0

and electroneutrality of the catalytic surface is maintained. The tilted precursor state of dissociation involves strong $M \rightarrow$CO charge transfer.

In general, the higher the $3d$ occupation the greater the $M \rightarrow$CO charge transfer in the first step of the resonating-valence-bond mechanism. However, high $3d$ occupation, as in Co, Ni, and Cu, hinders the second step of the mechanism in which the electron returns to the surface. The second step is facilitated by the availability of surfaces having unoccupied orbitals, even for those surfaces containing highly electronegative elements or vacant orbitals. Matrix isolation electron spin resonance (ESR) studies, for example, confirm the interaction between the lone-pair electrons of CO and vacant orbitals of the Cu atom.[34] A Mott insulator, for instance, fulfills the conditions for both of the charge-transfer steps in the mechanism. However, to obtain CO dissociation, it is necessary to have unsynchronized resonating covalent bonds on the surface. Because an insulator does not present resonating valence bonds, it is necessary to excite the surface in order to reach the conduction state and achieve CO dissociation. Both x-ray and uv photoelectron spectroscopy studies have found that sulfur, oxygen, and carbon adlayers all reduced the binding of CO (as well as H) and inhibited CO dissociation.[22,29,32] In addition, infrared spectra studies have shown that on a surface carbide no CO adsorption is observed.[26] Auger-electron-spectroscopy results lead to the conclusion that less CO is adsorbed when the surface contains more oxygen.[31] This is consistent with the finding that the conductivity of the poisoned surface is decreased compared to the clean surface. Hence, it is necessary to excite the surface in order to generate the required unsynchronized resonance of the covalent bonds for CO dissociation. The interaction between vibrational modes of the adsorbed CO molecule and excitations in the metal have been studied by infrared spectroscopy.[25,27] Further, surface chemistry induced by the action of energetic photon or electron beams is an area of strong current interest.[43] By varying the surface potential of the metal, the adsorptive process can be better controlled.[44] Such activated dissociation processes could be investigated in photoassisted experiments to ascertain, for example, whether irradiation of the modified catalytic $3d$ surface leads to more efficient dissociation.

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