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Molecular states of CO interaction with 3*d*-metal surfaces

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Ab initio molecular-orbital calculations of the carbonyls of 3*d* transition metals are used to indicate the tilted metal-CO complex as the molecular state precursor of CO dissociation on 3*d* surfaces. The present resonating-valence-bond mechanism for CO dissociation suggests that the tilted state may be observed in all dissociative 3*d* surfaces, that is, from Sc to Fe. Calculations of scandium monocarbonyl are used to understand the effects of inclination on electronic configuration and calculations of Cr_2CO cluster are used to study CO dissociation on the Cr(110) surface and to explain the substantial reduction of CO binding modes found for the tilted state.

I. INTRODUCTION

The problem of explaining the carbon-oxygen stretching frequencies of CO on transition-metal surfaces has been of interest for more than three decades.[1-10] In the Blyholder[1] molecular-adsorption model, all carbon monoxide is adsorbed in a linear metal-carbon-oxygen structure with electron donation from the CO 5σ orbital into surface *d* orbitals, and back donation from the surface *d* orbitals into CO $2\pi^*$ orbitals. The metal atoms have various degrees of coordination with other metal atoms on the surface. The lower-frequency bands are due to CO bonded to metal atoms having less than the maximum number of neighbors. Among early workers, Cotton and Kraihanzel[11] indicated the correlation between charge transfer and stretching frequencies, by showing that as carbon monoxide in hexacarbonyls is replaced with ligands which do not π bond, the availability of electrons to go into π orbitals of remaining carbon monoxide ligands is increased, resulting in a decrease of carbon-oxygen stretching frequencies. Blyholder[1] also indicated that if only a σ bond is formed by the lone-pair electrons on the carbon atom, the carbon-oxygen stretching frequency for carbonyls would be expected to be very close to that of free carbon monoxide. However, if the stretching frequency is shifted to somewhat lower values, this is an indication that π bonding does occur with some charge occupying an antibonding orbital which weakens the carbon-oxygen bond. Sung and Hoffmann[2] also found that when $2\pi^*$ orbitals are partially populated the CO bond is weakened. This results in a reduction of the stretching frequencies.

In spite of its success in describing CO interaction with transition metals, Blyholder's model does not consider the existence of tilted states. When the model was developed there was no evidence that suggested the existence of tilted states. Only recently have these states been observed at unusually low CO stretching frequencies in the range of 1100–1350 cm^{-1}.[3-6] The shift of the C-O frequency to lower values for the tilted states is an indication that surface-CO bond does occur with some charge occupying the CO $2\pi^*$ orbital which weakens the carbon-oxygen bond.[7-10] In our previous work[7] we showed quantitatively that the reduction of the stretching frequency of the adsorbed CO molecule in the tilted state using the Fe_5CO cluster model of the Fe(100) surface can be correlated with the inverse of the population of the CO antibonding orbital. This approximation will again be used in this work. In another paper[8] we made straightforward calculations of stretching frequencies, and observed that such computationally expensive calculations are not compensated for by a good agreement with experiment. Those calculations support our present work, however, indicating that the stretching frequencies are reduced in the tilted state whether we use experimental or optimized interatomic distances. On the other hand, charge transfer, via Mulliken population analysis, is readily available with each *ab initio* calculation, yielding chemical insight into the CO bonding which influences the magnitude of the stretching frequency. In this work, we continue to explore the ideas introduced in our previous work;[7-9] i.e., we use charge transfer to interpret such parameters as stretching frequencies of CO adsorbed on Cr(110) surfaces with the perspective that high quality calculations of vibrational frequencies on large cluster are still prohibitive and not necessarily rewarding for most groups.

The tilted state on the Fe(100) surface has been identified experimentally as the molecular state precursor of CO dissociation.[3-5] In our previous work[7] we used *ab initio* unrestricted Hartree-Fock (UHF), effective core potential (ECP), and multiple-scattering $X\alpha$ (MS-$X\alpha$) molecular-orbital calculations to indicate that the CO tilted state on the Fe(100) surface could be assigned to the precursor state of dissociation. For the Cr(110) surface an atom superposition and electron delocalization molecular-orbital study, in which the one-electron molecular-orbital energies are obtained by diagonalizing a Hamiltonian similar in form to the extended Huckel Hamiltonian, indicated that when lying down, backbonding to CO π^* orbitals is enhanced, weakening the CO bonds.[10] We were thus encouraged also to extend our previous work[7-9] to the Cr(110) surface using the *ab initio* Hartree-Fock linear combination of atomic orbitals (LCAO) method. There is also experimental evidence of a binding configuration for CO molecules on the Cr(110) surface. On this surface there is a large reduction of the molecular binding mode from 1975 cm^{-1} for perpendicular adsorption to 1330 cm^{-1} for bent geometry of adsorption.[6] The gas phase value is 2143 cm^{-1}. A question we will address here is whether the changes of the surface$\rightarrow$CO charge transfer for tilted states are large enough to account for such a substantial reduction of binding frequencies. In our previous work[7] we commented that it would be of interest to determine whether the strong reduction in CO stretch frequency as the CO bond is tilted relative to the surface normal in the Fe(100) surface occurs quite generally, i.e., for other metals and binding sites. The existence of nonlinear (bent geometry) diatomic molecules coordinated to transition metals[12] is a first indication in favor of the occurrence of tilted states on other 3*d* metal surfaces. Also, bent geometry was attributed to several carbonyl hemoglobin compounds.[13] Theoretical studies of the interaction of CO with Na, Mg, and Al surfaces support an adsorption geometry with CO normal to the surface;[14] however, these simple metal surfaces are not dissociative. The tilt angle is also an important parameter for understanding the role of frustrated rotations in the dephasing of CO stretch vibration for CO adsorbed on metal surfaces.[15]

In our previous work[7,9] we used monometal-carbonyl clusters and the mechanism of unsynchronized resonance of covalent bonds, which describes charge transfer in typical metallic systems,[16] (and is discussed in Sec. III), to investigate CO dissociation on 3*d*-metal surfaces, and predicted that the tilted state may occur on dissociative 3*d* surfaces; that is, from scandium to iron. These ideas are further explored in this work, investigating the tilted states and using Cr dimers together with the mechanism of unsynchronized resonance of covalent bonds for CO dissociation. We present arguments as to why there is no CO dissociation on insulator surfaces, and predict activated catalyzed processes leading to dissociation. We also discuss the scandium surface as the simplest model for understanding how *d* orbitals behave in tilted states. The Cr(110) surface is investigated in considerable detail, using a Cr_2CO model with experimental distances and other geometries as well. For the Cr(110) surface we are able to correlate the total charge transfer to CO with the large reduction of the CO binding frequencies in the tilted state.

II. COMPUTATIONAL DETAILS

The HONDO program[17] was used to perform *ab initio* UHF-SCF (self-consistent field), molecular orbital (MO) calculations of *M*-CO systems ($M=$ Sc, Ti, V, Cr, Mn, and Cu). The Fe surface was investigated in two previous papers.[7,9] In our first cluster model the surface is represented by only one metal atom.[9] Calculations in our previous work[7] showed that even this simplest surface model can describe the general features that characterize larger M_5CO clusters.[7-9] Calculated properties of M_nCO clusters as a function of *n* have also shown that small clusters can satisfactorily model CO adsorption. MO calculations showed that NiCO reproduces the main features of the electronic structure obtained with larger Ni clusters.[18] Although larger clusters provide a better representation of the chemisorption interaction, it has been shown[18] that even the simplest CuCO cluster indicates the effect of Cu to CO π back donation. Calculations were also made on the Cr_2CO clusters using Cr(1)-Cr(2) distances representative of the Cr(100) surface. Other distances and various adsorption sites were also considered. The Cr_2CO cluster, which can be considered an improvement to the simple monometal cluster model, is still relatively small enough to make calculations more feasible, and can take into account the metal distance between two atoms in the Cr(110) surface. For the transition metals we use Wachter's basis set[19] with Hay's[20] contraction (3*d*) of the augmented (5*d*) basis set, and for carbon and oxygen we use the Poirier, Kari, and Csizmadia basis set.[21] We fixed the C-O distance at 1.15 Å, the observed value for the isolated molecule.[2,8] When CO is adsorbed and tilted on the Cr surface, the increase of surface-to-CO charge transfer should increase the bond length, which, in turn, should affect the amount of charge transfer reported in this manuscript. Rosen, Grundevick, and Morovic[22] have noted, however, that the variation of energy levels with varying C-O distance is small. We have also emphasized in our previous work[8-10] that the charge transfer obtained using experimental distances yields the required effects of the tilted states on molecular adsorption, dissociation, and reduction of stretching frequencies, and these effects are our primary concern in this paper. In addition, in a separate work[8] we made straightforward unrestricted Hartree-Fock calculations of stretching frequencies optimized geometries for the Cr(110) surface, and concluded that the essential ideas of our theoretical model are reflected in the charge distribution obtained with the experimental distances. The charge transfer is increased and the stretching frequencies reduced in the tilted state using both optimized and experimental distances. The *M*-CO distances were thus taken from experimental value[2,9] available for the corresponding carbonyl complexes: $R(\text{Sc-CO})=2.05$ Å, $R(\text{Ti-CO})=2.03$ Å, $R(\text{V-CO})=2.01$ Å, $R(\text{Cr-CO})=1.92$ Å, $R(\text{Mn-CO})=1.86$ Å, and $R(\text{Cu-CO})=2.00$ Å.

III. MOLECULAR STATES OF SURFACE-CATALYZED CO DISSOCIATION

In our previous work we investigated the Fe(100) surface and the FeCO monocarbonyl.[7] We continue here with the Cr(110) surface, for which the tilted state has also been observed.[6] Let us begin with the simple monocarbonyl. The CrCO model shows general features of charge transfer from *d* orbitals to CO as well as a weakening of the CO bond indice (Table I) as the CO molecule is tilted. In Table II we give the bond indice for Cr_2CO, for different tilt angles and adsorption sites, using experimental and other Cr(1)-Cr(2) distances [Fig. 1(b)] of the Cr(110) surface. The net surface→CO charge transfer is typically larger when CO is tilted. The additional charge transfer for the tilted states contributes to the population increase of the CO antibonding orbitals. For all sites and for all fixed Cr-Cr and surface-CO distances, the CO bond indice decreases as CO is inclined toward the surface. We also note that as we increase the Cr(1)-Cr(2) distance we strengthen the CO bond indice in both the perpendicular and parallel configurations. The differences in the CO bond indice are typically smaller between the onefold and twofold sites than the differences between perpendicular and parallel configurations, which suggests that the important effect is inclination as opposed to site adsorption. We infer that the CO vibrational frequencies around 1975 cm^{-1} reflect differences in site adsorption, whereas the frequencies around 1330 cm^{-1} correspond to the inclined states at these same sites. The increase of the Cr(1)-Cr(2) distance results in a reduction of charge transfer, which suggests that preferential inclination occurs in the direction of the closest Cr atom. As expected, a reduction of surface-CO distance results in increased charge transfer, and an increase of the CO bond distance results in a reduction of the CO bond indice.

Let us now address the important issue of correlating the substantial reduction of the CO binding modes (1975 to 1330 cm^{-1}) with a change in the charge transfer in tilted states. The vibrational frequency of the adsorbed molecule can be taken as proportional to the inverse of the back donation to the CO $2\pi^*$ orbital,[7] which we approximate as the total charge transfer to the CO molecule that reduces CO binding as reflected in a smaller bond indice. In Table III we give the total charge transfer and bond indice for different adsorption sites and Cr(1)-Cr(2) distances. We note that, using the shortest Cr(1)-Cr(2) distance of 2.498 Å, the experimental Cr-C distance of 1.92 Å and the CO experimental distance of 1.15 Å, the ratio of charge transfer between the perpendicular and parallel configurations for the twofold site is 0.64, which compares well with the observed experimental frequency ratio of 0.67 for adsorbed CO.[6] We note that if we use the Cr(1)-Cr(2) experimental distances of 2.88 or 4.07 Å for the Cr(110) surface, with onefold or twofold adsorption sites, the agreement is not as good. These results support experiments[6] that suggest that the binding mode at 1330 cm^{-1} is due to twofold symmetric surface hollow sites with the intramolecular axis nearly parallel to the Cr(110) surface, and that the binding mode at 1975 cm^{-1} is indicative of terminally bound molecules adsorbed and aligned approximately perpendicularly to the surface.

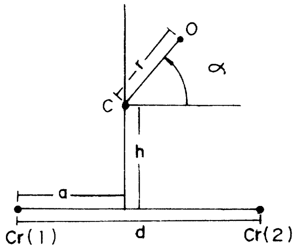

FIG. 1. The Cr_2CO cluster.

TABLE I. Bond indices for MCO systems.

Surface angle[a]	ScCO $S=4$[b]	TiCO $S=5$	VCO $S=6$	CrCO $S=5$	MnCO $S=6$	FeCO $S=5$[c]
	CO bond indice					
90°	2.079	2.109	2.319	2.351	2.080	2.170
60°	2.047	2.089	2.309	2.328	2.040	2.020
30°	1.986	2.031	2.246	2.289	1.960	1.970

[a]See Fig. 1 for definition of surface angle.

[b]S denotes spin multiplicity.

[c]Data taken from Ref. 8.

Let us now turn to the other transition-metal surfaces, including those for which the tilted state has not yet been observed experimentally. Consider first the scandium surface as a simple illustrative case, in which each of the two $3d\pi$ orbitals typically has one electron. The $(3d_\pi)^2(4s\sigma)^1$ electronic configuration of the scandium surface, represented here by the $^4\Sigma^-$ electronic state of the linear ScCO system, is interesting to analyze because with it one can study the behavior of the $3d_{xz}(\pi)$, $3d_{yz}(\pi)$ orbitals in the tilted states. The inclination of the CO molecule, which forms an angle of 30° in relation to the surface, increases the net Sc→ CO charge transfer by almost 50% (from 0.42*e* to 0.59*e*). The major contribution to this increase in charge transfer with CO inclination comes from the 3*d* orbitals. There is also a small ~0.01*e* increase in CO(3*d*)→Sc charge transfer to the $3d_{xy}$ and 4*p* orbitals as CO bends. The ScCO electronic configuration changes from $(3d\pi)^2(4s\sigma)^1$ to $(3d\pi)^1(\text{CO}2\pi^*)1(4s\sigma)^1$, illustrating the important role of Sc $(3d\pi)\rightarrow$CO $(2\pi^*)$ charge transfer. The symmetry of the $3d_{xz}$ and $3d_{yz}$ orbitals is broken with inclination. The Mulliken population of the $3d_{xz}$ orbital increases slightly but the metal →CO charge transfer remains large. On

TABLE II. CO bond indice, Mulliken atomic charges for Cr(1), Cr(2), C, and O for the Cr_2CO cluster.

Site	Angle (deg)	Cr(1)-Cr(2) (Å) distance (*d*)[a]	Surface-C (Å) distance (*h*)[a]	Cr(1) charge[b]	Cr(2) charge[b]	C charge[b]	O charge[b]	C-O Bond indice
onefold	90	2.498	1.00	0.48	0.28	−0.33	−0.43	1.56
onefold	60	2.498	1.00	0.76	0.13	−0.36	−0.53	1.35
onefold	0	2.498	1.00	0.80	0.02	−0.27	−0.55	1.15
onefold	0	2.498	1.40	0.56	0.15	−0.14	−0.57	1.17
onefold	0	2.498	1.55	0.49	0.14	−0.08	−0.55	1.34
onefold	0	2.498	1.92	0.48	0.07	−0.11	−0.44	1.66
onefold	60	2.498	1.92	0.21	0.06	0.02	−0.29	2.03
onefold	90	2.498	1.92	0.33	0.08	−0.16	−0.25	2.07
onefold	90	2.498	2.10	0.00	0.13	0.05	−0.18	2.27
onefold	0	2.498	2.10	0.33	0.09	−0.03	−0.39	1.79
twofold	90	2.498	1.92	0.17	0.29	−0.27	−0.19	2.09
twofold	0	2.498	1.92	0.03	0.68	−0.31	−0.40	1.60
twofold	90	2.880	1.92	0.19	0.19	−0.20	−0.18	2.14
twofold	0	2.880	1.92	0.38	−0.12	0.04	−0.30	1.91
onefold	90	2.880	1.92	−0.05	0.14	0.10	−0.19	2.30
onefold	0	2.880	1.92	0.47	0.02	−0.08	−0.41	1.73
onefold	90	4.070	1.92	−0.10	0.02	0.24	−0.16	2.40
onefold	0	4.070	1.92	0.18	−0.01	0.12	−0.29	1.98
twofold	90	4.070	1.92	0.07	0.07	0.06	−0.18	2.26
twofold	0	4.070	1.92	0.10	−0.07	0.28	−0.31	2.11
onefold	90	4.070	2.10	−0.10	0.02	0.24	−0.16	2.41
onefold	0	4.070	2.10	0.14	0.01	0.09	−0.26	2.07

[a] See Fig. 1.

[b] Mulliken atomic charges.

TABLE III. Total charge transfer and C-O bond indice for parallel and perpendicular geometries, and theoretical and experimental CO frequency ratios for Cr_2CO.

Cr(1)-Cr(2) (Å) distance (*d*)[a]	Site	Angle (deg)	Total charge transfer[b]	BI[c]	Theoretical frequency ratio[d]	Experimental frequency ratio[e]
2.498	twofold	90	0.46	2.09		
2.498	twofold	0	0.71	1.60	0.64[f]	
2.880	onefold	90	0.09	2.30		
2.880	onefold	0	0.49	1.73	0.18	
4.070	onefold	90	−0.08	2.40		
4.070	onefold	0	0.17	1.98		
2.498	onefold	90	0.41	2.07		
2.498	onefold	0	0.55	1.66	0.75	
2.880	twofold	90	0.38	2.14		0.67
2.880	twofold	0	0.26	1.91	1.46	
4.070	twofold	90	0.14	2.26		
4.070	twofold	0	0.03	2.11	4.66	
2.498[g]	onefold	90	0.13	2.17		
2.498[g]	onefold	0	0.42	1.79	0.31	
4.070[g]	onefold	90	−0.08	2.41		
4.070[g]	onefold	0	0.15	1.98		

[a] See Fig. 1. Surface-C distance 1.92 Å.

[b] Mulliken charges.

[c] Bond indice.

[d] Calculated assuming frequencies are inversely proportional to total charge-transfer ratio. See Ref. 8.

[e] See Ref. 7.

[f] Best agreement between experimental and theoretical (charge transfer) frequency ratios.

[g] Cr(1)-C distance is 2.10 Å.

the other hand, charge transfer via the $3d_{yz}$ orbital increases significantly, by $\sim 0.5e$ (the $3d_{yz}$ Mulliken atomic population drops from $0.70e$ to $0.23e$).

In Table I we give the bond indices for different tilt angles for the other dissociative surfaces (TiCO, VCO, CrCO, MnCO, and FeCO). For all the dissociative surfaces through Fe, inclination again leads to a net effect which is the increase of charge transfer and the reduction of C-O bond strength (bond indice) as CO inclines.

Cu is one of the surfaces to the right of Fe in the Periodic Table that is nondissociative with CO. The calculated Mulliken charges for CuCO in the $^2\Pi$ state indicate that in the perpendicular state, there is no back donation to Cu. On the contrary, there are an excess 0.07 electrons on Cu resulting from CO→ Cu charge transfer. If we compare CuCO with FeCO in the $^5\Delta$, which also has a charge surplus in the perpendicular state, we find that when the CO molecule is inclined there is only a small increase in the charge transfer for CuCO (-0.07 to 0.05) as compared to FeCO (-0.08 to 0.40) even though CuCO has more *d* electrons available to participate in back donation to $2\pi^*$ orbitals. The nondissociative surfaces will be investigated in detail in a forthcoming paper.

The process of CO dissociation on 3*d*-metal surfaces can be described in terms of Pauling's resonating valence bond theory[16] and *ab initio* molecular-orbital calculations.[7–9] The theory is applicable since the *M*-CO interaction is dominated by charge transfer.[1,2,7–9] The resonating valence bond theory[13] considers that two electrons with opposed spins and occupying orbitals on adjacent atoms form a covalent bond. These covalent bonds resonate among alternative positions in the metal. During unsynchronized resonance one bond resonates independently from one position to another. The 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, and $M-$ states: $M-MM \rightarrow M^{+}M-M^{-}$ (a bond is formed by the pairing of two electrons such that the bond transfer corresponds to the transfer of one electron from one atom to another). By a succession of shifts of single bonds, a negative charge is seen to move in the systems, typical of metallic behavior.

The unsynchronized resonant states for the surface-catalyzed CO dissociation which we propose[7–9] can be described as follows. In the first step of the mechanism the metal → CO electron transfer leads to bond formation between the surface and the carbon atom of CO. The metal attacks the carbon atom, since the unoccupied π^* molecular orbital, the orbital available for electron reception, is mainly localized on it. The extent of $3d \rightarrow \pi^*$ back donation is directly related to the strength of the *M*-CO bond.[1–3,7] In the second step, the electron returns to the surface, when the C-O bond is transferred to the metal surface, breaking the CO bond and making an O-metal bond. The electron transfer "covers a cycle" (in the sense that the electron leaves and then returns to the surface) in which the CO bond is broken and the electroneutrality of the catalytic surface is maintained. The *M*-C and *M*-O stretching vibrational frequencies are observed in the region of 500 cm^{-1}.[3,4] For the dissociative surfaces from Sc to Fe the first step of the mechanism is satisfied; that is, for all these surfaces there is a net metal → CO charge transfer and a consequent reduction of C-O bond strength.[8] However, the inclination of the molecule in relation to the surface can increase charge transfer and favor dissociation since the CO bond is weakened with increased occupation of the CO antibonding orbital. From the present dissociation mechanism, the tilted state would be an intermediate species in the catalytic process. To transfer the C-O bond to the surface, the CO molecule should incline to a position almost parallel to the surface. We propose that this geometry favors the transfer of electrons in the appropriate direction indicated by the unsynchronized scheme of the resonance of the bonds. If there is only perpendicular adsorption there is an interruption of the process of conduction (dissociation) on the surface. The present qualitative model requires that the surface must have sufficient unsynchronized resonance of the covalent bonds to facilitate electron transfer to the CO molecule. This suggests that an insulator surface cannot dissociate CO. However, if this surface becomes conducting by some process of activation, it could then possibly dissociate CO. During photoconductivity phenomena the irradiation of insulator compounds with light of appropriate wavelength leads to an increase in the number of unsynchronized resonances. It may thus be of interest to observe if the irradiation of insulator surfaces can lead to the dissociation of CO.

IV. CONCLUSION

CO dissociation on 3*d*-metal surfaces is a two-step ($M \rightarrow$CO and CO$\rightarrow M$) charge-transfer process. The tilted state is the precursor of CO dissociation and occurs on dissociative 3*d* surfaces. On the basis of the results discussed in this work, we suggest that activated catalytic processes, arising from irradiation of the surface, may improve CO dissociation. Simple monomer or dimer carbonyl models, in the absence of more sophisticated calculations, can yield useful results for understanding CO adsorption and stretching frequencies on transition-metal surfaces. Total transition-metal → CO charge transfer has proven to be a very useful tool for understanding and explaining the large reduction of CO binding frequencies in tilted states for the Cr(110) surface. This may be also of importance to other workers in view of the present difficulties in making more realistic larger cluster *ab initio* geometry optimization and stretching frequency calculations.

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