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High-Spin Chemical Bonding of MCS and MCO (M = Sc, Ti, V, Cr, Cu)

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Abstract: The chemical bonding in the ground states of MCS (M = Sc, Ti, V, Cr, Cu) is compared to that of MCO. The CI calculations were done to determine the bond strength, the electron sharing, and the bond distances of these molecules. The result shows that the M–CS bonding is much stronger than that of M–CO. The electron sharing between M and CS is also larger than that between M and CO. All the MCS molecules are stable for dissociation into the ground states of M + CS, as in MCO. In Cr–CS and Cu–CS, there exists indeed a chemical bond, although weak. In contrast, there is no chemical bond in Cr–CO and Cu–CO, save very weak van der Waals interaction. The bond strength between M and CS (M and CO) decreases consistently going from ScCS to CuCS (from ScCO to VCO). The greater stability of MCS when compared to MCO may be explained by the much lower activation energy of $CS \rightarrow CS^-$ when compared to $CO \rightarrow CO^-$, 20 vs 140 kJ mol^{-1}.

I. Introduction

The first-row transition metal monocarbonyl molecules, MCO, were intensively studied during the last 15 years (see ref 1). These molecules were experimentally observed in matrix-isolation or in the gas phase. The attractive and repulsive molecular electronic states of MCO were respectively correlatd to the d^ns^1 and the d^ms^2 atomic states. The ground states of ScCO, TiCO, VCO, and CrCO (and CuCO) were known to have high total electron spin values and their spatial symmetries were determined. The electron distributions in these symmetries allow a maximum exchange, thus contributing to their stability. The M–CO bond energies of these molecules were determined with reasonable precision. The lowest electronic states of other molecules, MnCO, FeCO, CoCO, and NiCO, containing one or more closed d subshells were also determined but with less precision. This was due to a difficulty in accurately describing the lowest electronic states of these metal atoms by including the correlation energy related to the closed subshells. A common characteristic of all the MCO molecules with the exception of CuCO is the existence of many electronic states of different symmetries whose potential energies are close. This originates from the only moderate breaking of the metal atom spherial symmetry in creating a chemical bonding between M and CO. The nature of chemical bonding in these apparently simple molecules, in particular concerning the 3σ (according to the valence-only counting) donation and $2\pi^*$ back-donation,[2] was much debated in various levels of quantum chemical calculations.

The aim of this work is to compare the ground states of the MCO molecules with those of the isoelectronic MCS molecules. The MCS molecules are calculated with the molecular orbital single-and-double configuration interaction (MO-SDCI) method. The corresponding MCO molecules are also calculated with the same method, employing equivalent basis sets for the purpose of fair comparison. The strength and the nature of chemical bonding in the MCS and MCO molecules with M = Sc, Ti, V, Cr, Cu will be discussed in this paper. The MCS molecules were only briefly studied in the past.[3] This work does not aim to determine highly precise potential energies (PEs). It would be satisfactory for this work to explain the general tendencies of energy-related characteristics and wave functions.

II. Methods

The all-electron restricted Hartree-Fock (RHF) calculations were completed using the ASTERIX program package.[4] The SDCI calculations were completed using the CI program by Brooks and Schaefer[5] with the graphical unitary group approaches by Paldus[6] and Shavitt.[7] The canonical MOs resulting from the RHF calculation were employed for SDCI calculation. All valence occupied and virtual orbitals were used in the CI calculations. To the SDCI calculated potential energies (PEs) were added the correction energies determined according to the simple formula given by Langhoff and Davidson,[8] which proved to improve the size consistency. For example, the SDCI calculation gave the molecular energy of CuCS with infinite Cu–CS distance 60 kJ mol^{-1} higher than the sum of the SDCI energies of Cu and CS, whereas the L&D correction reduced this relative energy discrepancy to 29 kJ mol^{-1}. The corresponding values for other molecules are (38 → -2) for ScCS, (13 → 3) for TiCS, (34 → 20) for VCS, and (27 → 15) for CrCS. The L&D correction slightly increased the M–CO and M–CS bond energies: 2 kJ mol^{-1} for ScCO, <1 kJ mol^{-1} for TiCO, 2 kJ mol^{-1} for VCO, 3 kJ mol^{-1} for CrCO, <1 kJ mol^{-1} for CuCO, 6 kJ mol^{-1} for ScCS, 8 kJ mol^{-1} for TiCS, 3 kJ mol^{-1} for VCS, 4 kJ mol^{-1} for CrCS, and 11 kJ mol^{-1} for CuCS.

For the metal atoms, 14s11p Gaussian type orbitals (GTOs) contracted to 8s6p atomic basis functions (ABFs) by Wachters[9] and 6d GTOs → 3d ABFs by Rappé et al. were used.[10] This basis set is sufficiently flexible to describe the $3d^n4s^2$, $3d^n4s^1$, $3d^{n+1}4s^1$, and $3d^{n+1}$ atomic states. For carbon and oxygen atoms, a Huzinaga's basis[11] of 10s6p GTOs → 4s2p was augmented with one diffuse s-kind GTO and one diffuse p-kind GTO to optimally describe the anion atoms. The exponents of these diffuse GTOs are 0.04440 (s) and 0.03009 (p) for the carbon atom and 0.07519 (s) and 0.05149 (p) for the oxygen atom. The final basis for carbon and oxygen is 5s3p ABFs. For the sulfur atom, a S^- basis by McLean and Chandler[12] of 12s9p GTOs → 6s5p ABFs was used. The C–S internuclear distance of free CS calculated with CI was 159 pm, the experimental value being 154 pm.[13] The C–O internuclear distance of free CO calculated with CI was 118 pm, which is also slightly longer than the experimental value, 113 pm.[13] The CI calculated dipole moment of CO is very weak, 0.03 D, as supported by the experimental value, 0.1098 ± 0.0011 D. Our calculated value for CS is 1.70 D, which is quite close to the experimental value, 1.97 ± 0.02 D. The electron affinity of the free CS molecule calculated in the SDCI and L&D correction was -20 kJ mol^{-1}, and that of CO was -140 kJ mol^{-1}.

The spin-spatial symmetry of the ground states of the MCS and MCO molecules was determined by trying different molecular configurations based upon the previous studies on ScCO,[14-17] TiCO,[16,18] VCO,[16,19,20]

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Table I. Ground State Dissociation Energies (D_e, kJ mol^{-1}) into the Lowest M + CS or M + CO Dissociations and Bond Distances (R_e, pm) of MCS and MCO[a]

M	states	R_e(M-CO)	R_e(C-O)	D_e(M-CO)[b]	R_e(M-CS)	R_e(C-S)	D_e(M-CS)[b]
Sc	$^4\Sigma^-$	211	121	6 (145)	206	164	116 (255)
Ti	$^5\Delta$	205	120	12 (92)	201	164	111 (191)
V	$^6\Sigma^+$	204	121	41 (68)	200	160	100 (127)
Cr	$^7\Sigma^+$	≃235	119	2 (2)	212	158	53 (53)
Cu	$^2\Sigma^+$	≃219	119	4 (4)	202	158	34 (34)

[a] Due to the grid sizes, the precision is about ±2 kJ mol^{-1} and ±2 pm (except the bond lengths of CrCO and CuCO). [b] In parentheses are the dissociation energies into the $3d^n4s^1$ + $^1\Sigma^+$ asymptote.

Table II. 3σ Donations (D) from CO or CS to M and $2\pi^*$ Back-Donations (BD) from M to CO or CS Near the Equilibrium Geometry[a]

M	D(MCO)	BD(MCO)	D(MCS)	BD(MCS)
Sc	0.25	0.60	0.50	0.95
Ti	0.20	0.40	0.40	0.70
V	0.15	0.25	0.30	0.45
Cr	0.10	0.05	0.25	0.20
Cu	0.10	0.05	0.20	0.05

[a] Rounded to the nearest multiples of 0.05 electron (a.u.).

CrCO,[21] and CuCO.[22-28] The lowest four electronic states of ScCS were previously calculated by the author.[29] The collinear approach of M–CS with the carbon atom facing the metal atom was studied. The C_{2v} point-group symmetry was used for the RHF and CI calculations with the M–C–S (M–C–O) direction taken as the symmetry axis. The weights of different configuration state functions (CSFs) and the natural molecular orbitals (NMOs) are used for analysis of the CI wave functions.[30] Only the valence electrons have been counted for the ordering of the MOs.

III. Results

The dissociation energies into the lowest states of M + CS or M + CO ($3d^n4s^2$ + $^1\Sigma^+$ for Sc, Ti, V; $3d^n4s^1$ + $^1\Sigma^+$ for Cr, Cu) and the equilibrium internuclear distances of the ground states of the MCS and MCO molecules are reported in Table I. All the ground states of MCS and MCO molecules are bound, and they are stable for dissociation into the lowest M + CS or M + CO dissociations. All these ground states have the metal atoms in the $3d^n4s^1$ atomic configuration. The ground states of MCS and MCO with M = Cr, Cu are made from the lowest dissociation asymptotes of M + CS or M + CO, while the ground states of MCS and MCO with M = Sc, Ti, V adiabatically correlate with the first excited dissociation asymptotes. The bond energies of MCS or MCO, with respect to the dissociation into the $3d^n4s^1$ + $^1\Sigma^+$ states of M + CS or M + CO, are monotonously decreasing in going from Sc to Cu. The M–CS equilibrium distance shortens in going from Sc to V and from Cr to Cu. The M–CO equilibrium distances may be divided into two groups: the relatively shorter group (M = Sc, Ti, V) and the longer group (M = Cr, Cu). The equilibrium distance between C and S tends to shorten in going from Sc to Cu, whereas the equilibrium distance between C and O varies little in going from Sc to Cu. The Sc, Ti, and V atoms make two half π bonds with CS and CO. The Cr and Cu atoms make only very weak bonding of van der Waals character with CO. In contrast, these two atoms chemically bond with CS, although this bonding is not strong.

The ground state SDCI wave functions of the M–CS and M–CO molecules are analyzed in terms of the "3σ-donation" (the metal population of the 3σ MO) and "$2\pi^*$-back-donation" (the CS or CO part of the 2π MO) in Table II. These quantities, which may represent the electron exchanges between M and CS (M and CO), are not observables but only convenient definitions to explain the chemical bonding between M and CS or CO. For clarity, these quantities are rounded to the nearest multiples of 0.05 electron (a.u.) in Table II. The result shows that the degrees of both donation and back-donation decrease in going from Sc to Cu.

ScCS and ScCO. Both ScCS and ScCO molecules have the same predominant ground-state CSF of $4\sigma^1 2\pi_x^1 2\pi_y^1$ ($^4\Sigma^-$). The weight of this CSF in the SDCI wave function is 87% for ScCS and 88% for ScCO near the equilibrium geometry. The nonbonding 4σ electron is an sp hybrid avoiding the CS or CO electrons. This 4σ NMO is $0.69s\text{–}0.24p_\sigma$ (ScCS) and $0.78s\text{–}0.19p_\sigma$ (ScCO) near the equilibrium geometry. Van Zee and Weltner[17] observed the ScCO molecules in solid argon matrices and gave a simple estimation for the metal 4s character of 58% from the ESR spectra. Frey and Davidson[15] gave the dissociation energy into the Sc(^{2}D) + CO($^1\Sigma^+$) of 21 kJ mol^{-1} using a quasidegenerate variational perturbation method, whose value is 15 kJ mol^{-1} larger than our value. Barnes and Bauschlicher[16] extrapolated the dissociation energy into the $3d^24s^1(^4F)$ + $^1\Sigma^+$ state (which is 139 kJ mol^{-1} above the dissociation into the ground states) using a modified coupled-pair functions method, obtaining 164 kJ mol^{-1} which is 19 kJ mol^{-1} larger than our value. The Sc–CO equilibrium distance calculated by F&D, 212 pm, and that by B&B (MCPF), 211 pm, fall in the same range as the present value, 210 ± 2 pm. The C–O equilibrium distance calculated by F&D, 118 pm, and that by B&B, 121 pm, are also in agreement with the present value, 121 ± 2 pm. Other details of the ground state and the excited states were reported previously.[29]

TiCS and TiCO. The weight of the principal $^5\Delta$ CSF, $4\sigma^1 2\pi_x^1 2\pi_y^1 1\delta_{xy}^1$, in the SDCI wave function is 86% in TiCS and 88% in TiCO near the equilibrium geometry. The nonbonding single electron (4σ) is an sp hybrid directed away from the CS or CO, with the NMOs of $0.78s\text{–}0.19p_\sigma$ (TiCS) and $0.88s\text{–}0.14p_\sigma$ (TiCO) near the equilibrium geometry. The Ti–CO bond energy with respect to the $3d^34s^1(^5F)$ + $^1\Sigma^+$ state (80 kJ mol^{-1} above the dissociation into the ground states) as extrapolated by B&B[16] is 135 kJ mol^{-1}, which is 43 kJ mol^{-1} larger than the present value, 92 ± 2 kJ mol^{-1}. The Ti-CO equilibrium distance calculated by B&B, 206 pm is in agreement with the present value 205 ± 2 pm. The C-O equilibrium distance calculated by B&B (MCPF), 120 pm is also in agreement with the present value 120 ± 2 pm.

VCS and VCO. These molecules have a $^6\Sigma^+$ ground state with the principal CSF of $4\sigma^1 2\pi_x^1 2\pi_y^1 1\delta_{x^2-y^2}^1 1\delta_{xy}^1$ with weights of 85% in VCS and 89% in VCO near the equilibrium geometry. The nonbonding 4σ electron is an sp hybrid polarized away from the

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CS or CO, with the NMOs of 0.82s–0.15p_σ (VCS) and 0.90s–0.10p_σ (VCO) near the equilibrium geometry. ESR spectroscopy by Van Zee et al.[20] showed two forms (linear and nonlinear) of VCO molecule in argon matrices with estimated metal 4s characters of 33% and 21%. Our V–CO bond energy with respect to the $3d^4 4s^1(^6D) + {}^1\Sigma^+$ state (27 kJ mol^{-1} above the dissociation into the ground states), 68 ± 3 kJ mol^{-1}, is much smaller than the extrapolation value by B&B,[16] 111 kJ mol^{-1}. Our calculated V–CO bond distance, 203 ± 2 pm, is in agreement with that of B&B (MCPF), 203 pm. Our calculated C–O equilibrium distance, 121 ± 2 pm, is also in agreement with that of B&B (MCPF), 119 pm. The lowest $^6\Delta$ state with the principal CSF of $4\sigma^1 5\sigma^1 2\pi_x^1 2\pi_y^1 1\delta_{xy}^1$ is only slightly higher than the $^6\Sigma^-$ ground state, with the well-to-well transition energy of 35 kJ mol^{-1} for VCO and 24 kJ mol^{-1} for VCS.

CrCS and CrCO. Whereas the CrCO has only a very shallow equilibrium well and practically no electron sharing occurs between Cr and CO, the CrCS is bound by a chemical bond, although weak, involving a small electron sharing. The principal $^7\Sigma^+$ CSF, $4\sigma^1 5\sigma^1 2\pi_x^1 2\pi_y^1 1\delta_{xy}^1 1\delta_{x^2-y^2}^1$, weighs 89% of CrCS and 90% of CrCO in the SDCI wave function near the equilibrium geometry. The 4s electron of Cr is slightly hybridized in the backward direction from CS (CO) as 0.83s–0.17p_σ in CrCS and 0.87s–0.13p_σ in CrCO near the equilibrium geometries.

CuCS and CuCO. The $^2\Sigma^+$ states of CuCS and CuCO have the predominant CSF of $4\sigma^2 2\pi_x^1 2\pi_y^2 1\delta_{x^2-y^2}^2 1\delta_{xy}^2 5\sigma^1$ which weighs 89% in CuCS and CuCO near the equilibrium geometries. The Cu 4s electron is slightly hybridized in the backward direction from CS (CO) as 0.90s–0.10p_σ (CuCS) and 0.92s–0.98p_σ (CuCO) near the equilibrium geometries. Merchan et al.[28] did variation-perturbation calculations using transformed MOs for CuCO. They found a van der Waals bonding with the bond energy of the order of 1 kJ mol^{-1} and with a large uncertainty about the Cu–CO bond length. A recent ESR study of CuCO in argon matrices by Kasai and Jones[25] reported the 4s character of 67% and the 4p_σ character of 8%. The extremely shallow well shape of the ground states of CrCO and CuCO did not permit the determination of sufficiently precise M–CO equilibrium internuclear distances.

IV. Discussion

It is interesting that the amount of electron sharing (donation/back-donation) between M and CS (and between M and CO), which decreases in the order of ScCS > TiCS > VCS > CrCS or ScCO > TiCO > VCO > CrCO, is in parallel with the increasing $s^1d^n \rightarrow s^1d^{n-1}$ ionization potential: 5.12 eV (Sc), 6.00 eV (Ti), 6.82 eV (V), 8.28 eV (Cr). The strength of the M–CS and M–CO bonds is roughly proportional to the amounts of donation and back-donation (compare Tables I and II). Indeed, the decreasing M–CS bond strength in going from M = Sc to Cu is in parallel with the decreasing electron sharing. The stronger bonding between M and CS than between M and CO, given the same metal atom, is also parallel with the larger electron exchange between M and CS in comparison with that of M and CO. Thus the MCS and MCO molecules satisfy a widely accepted rule of thumb that the degree of electron sharing between atoms determines the bond strength. It is also noteworthy that the C–S equilibrium distance decreases steadily in going from ScCS to CuCS, as the M–CS bond strength decreases. This is in agreement with a common argument in adsorption study that the equilibrium C–O (here C–S) is inversely proportional to the metal to CO (here CS) bond strength. Nevertheless, no such tendancy can be observed for MCO. The shorter bond distances of ScCO, TiCO, and VCO, when compared with those of CrCO and CuCO, reflect the existence of chemical bonding in the former group and the absence of it in the latter group.

The increasing disagreement of the bond energy in going from ScCO to VCO between the SDCI method and the extrapolation from modified coupled-pair functions method shows the difficulty in precisely evaluating the electron correlation effect when the number of d electrons increases. The higher order electron correlation effect than the SDCI tends to lower the MCO (and probably MCS) molecules in comparison with the dissociated states. On the other hand, the pair functions method and its derivatives tend to exaggerate the bond energies. The real bond energies of M–CO and M–CS are expected to be somewhat larger than our values. The tentative values are 155 kJ mol^{-1} for ScCO, 110 kJ mol^{-1} for TiCO, and 90 kJ mol^{-1} for VCO. The bond energies of M–CS for M = Sc to Cu should also be overestimated. The accurate calculation of the extremely small bond energies for the CrCO and CuCO is a very delicate task in the state of the art, and the present work does not claim a great attention for their values in Table I.

The notion of the atomic orbital population is artificial and it is only a convenient means of explaining the molecular wave functions, as well as the atomic orbital character estimated in the ESR spectra. One should not expect to have a quantitative agreement between these two different definitions.

The larger 3σ electron donation of MCS in comparison with that of MCO may be explained by the higher energy level of the 3σ MO of CS (–0.474 eV) in comparison with CO (–0.561 eV). The stronger electron concentration toward the metal atom (1.93 e^- of carbon used as 1.30s–0.63p_σ) of the nonbonding 3σ electron pair of CS than that of CO (1.80 e^- of carbon used as 1.22s–0.58p_σ) may also facilitate the donation. The polarization (or hybridization) of the 4s metal electron is stronger in MCS than in the corresponding MCO. This may be partly explained by the charge-dipole interaction. The vanishingly small dipole moment of CO should cause a weaker hybridization of the metal 4s electron in comparison with the CS case whose dipole moment is not negligible (see section II). This difference of 4s hybridization also must be related to the larger 3σ donation in MCS compared to that of MCO. The resulting nonbonding MO (4σ in M = Sc, Ti, V, Cr; 5σ in M = Cu) has a significantly lower orbital energy in MCS than in the corresponding MCO, except for M = Cu. This should contribute to the greater stability of MCS in comparison with that of MCO. The larger metal electron (back)-donation to CS than to CO may be explained by the difference of the electron affinity of the accepting group. As explained previously (section II), whereas the PE of CO^- is calculated to be 140 kJ mol^{-1} higher than that of CO, the PE of CS^- is calculated to be only 20 kJ mol^{-1} higher than that of CS.

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