Correlation Effects and the Bonding and Cr–C Bond Strength in $Cr(CO)_6$

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A large-scale *ab initio* configuration interaction calculation of $Cr(CO)_6$ shows the importance of correlation effects in describing the charge distribution and in predicting the Cr–C bond strength in this molecule.

The metal–carbon bond in transition metal carbonyls is usually discussed in terms of σ-donation from the highest filled (5σ) molecular orbital (MO) of CO and π-back-bonding into the first virtual MO (2π) of the ligand. Such a description has been confirmed and quantified by *ab initio* MO calculations at the single determinantal (Hartree Fock) level.[1,2] Our initial calculation[1] on $Ni(CO)_4$ and $Cr(CO)_6$ revealed a net negative charge on the CO ligand, as did subsequent larger basis set calculations.[2] However, to date, no calculation of a well characterized transition metal carbonyl which included correlation effects has been reported, although such calculations on the species NiCO have been described.[3]

To assess the importance of electron correlation in the description of the metal-ligand binding in transition metal carbonyls, we here describe a configuration interaction (CI) calculation of $Cr(CO)_6$, together with an analysis of the resulting multi-determinantal wavefunction.

The calculation was carried out in a basis of Gaussian functions. For carbon and oxygen a (9s5p) basis contracted to (3s2p) was used.[4] For chromium a (12s6p4d) basis contracted to (4s2p2d)[5] was supplemented by additional s and p functions of exponent 0.4, together with a diffuse d function of exponent 0.0972.[6] The chromium basis was thus (5s3p3d), resulting in a total of 137 contracted Gaussian functions for the molecular calculation. A calculation of the $^1A_{1g}$ ground state of $Cr(CO)_6$, at the experimental molecular geometry,[7] within the Hartree Fock (HF–SCF) approximation resulted in a calculated molecular energy of -1717.2739 a.u., considerably lower than the value obtained previously.[1] A Mulliken analysis of this wavefunction is shown in Table 1, and compared with that from a calculation of the CO molecule, in the same Gaussian basis, at the experimental bond length. From these atomic populations the considerable $3d(t_{2g}) \rightarrow CO(\pi^*)$ and smaller $CO(\sigma) \rightarrow 3d(e_g)$ electron transfer are evident resulting in a net ligand charge of $-0.022e$ in the complex. From the calculated molecular energies for $Cr(CO)_6$ and CO, and the calculated energy of $Cr(^7S)$, a Cr–C bond strength of 72 kJ mol^{-1} is obtained, to be compared with the experimental value of 107 kJ mol^{-1}.[8]

Table 1. Calculated charge distribution in $Cr(CO)_6$ and CO.[a]

	HF–SCF	CI
Chromium orbital		
4s	0.191	0.194
4p	0.017	0.017
$3d(t_{2g})$	5.058	4.938
$3d(e_g)$	0.660	0.700
Atomic charge	+0.134	+0.212
Carbon orbital		
$2p\pi$	1.125 (0.955)	1.214 (1.078)
$2p\sigma$	1.021 (1.028)	1.016 (1.024)
Atomic charge	+0.238 (+0.354)	+0.160 (+0.242)
Oxygen orbital		
$2p\pi$	3.075 (3.045)	3.012 (2.935)
$2p\sigma$	1.348 (1.492)	1.345 (1.490)
Atomic charge	−0.260 (−0.354)	−0.195 (−0.242)

[a] The values for CO are given in parentheses.

A restricted amount of electron correlation was then included by carrying out a CI calculation using configurations generated by single and double excitations from the HF wavefunction. The active MOs in this CI expansion were those derived from the $Cr[3d(t_{2g}),3d(e_g),4s]$ and $CO(5\sigma,1\pi,6\sigma,2\pi)$ orbitals. The CI expansion thus included 42 active electrons and resulted in *ca.* 49000 configurations. The calculation was carried out using the direct CI method[9] on the CDC 7600 of the University of Manchester Regional Computing Centre. This calculation yielded a correlation energy of 0.4166 a.u., the HF–SCF configuration contributing only 78% to the final CI wavefunction, thus showing the importance of including correlation effects. A Mulliken analysis of this CI wavefunction, obtained *via* the natural orbitals, is shown in Table 1, where it is compared with that from the corresponding CI calculation on free CO. A comparison between the SCF and CI atomic populations and charges shows that significant charge redistribution occurs upon the inclusion of correlation. In particular the 3d(t_{2g}) population is decreased and the 3d(e_g) population is increased, leading to an increase in the chromium formal charge from +0.134e to +0.212e. There is an associated increase in the charge on *each* ligand from −0.022e at the SCF level to −0.035e upon inclusion of correlation, owing to an increase in the π-population of each ligand of 0.03e. Thus the degree of both π-back bonding and σ-donation is increased upon the inclusion of correlation. This is reflected in an increase in the calculated Cr–C bond strength to 140 kJ mol^{-1} when the CI wavefunction is used. Although this value is now somewhat larger than the experimental value (107 kJ mol^{-1}), which may be attributed to superposition errors, the calculation described herein demonstrates the importance of including correlation effects for a quantitative description of the electronic structure of transition metal carbonyls.

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