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On the Fe–CO molecule*

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Using a perturbational configuration interaction approach, it is found that the Fe–CO molecule has a low-spin ground state (i.e. $^3\Sigma^-$), at variance with similar compounds formed by the first transition elements of this series (e.g. Sc and Ti). Binding energies, interatomic distances and vibration frequencies have been calculated for the $^3\Sigma^-$ state as well as for the $^5\Sigma^-$ high-spin state.

Key words: Transition metals — Bonding of carbon monoxide — Configuration interaction

In the last 10 years, a rather large number of quantum-mechanical calculations have been devoted to the problem of the interaction of a metallic atom, for instance an alkali or a transition element M, with a neutral molecule (e.g. carbon monoxide, CO). These works may be considered as a preliminary step towards the theoretical study of chemisorption processes - and, optimistically, of heterogeneous catalysis - using an appropriate cluster for modelling the reaction sites of a surface. Direct comparison with experimental data has proved to be possible in some cases, because techniques for observing exotic simple molecules with metals (trapping of unstable species in inert-gas matrices, molecular beams ...) have been developed, often based on the impetus of the theoretical results. The present study belongs to this part of quantum chemistry, a research field where the contributions of Professor J. Koutecký and his associates from the Free University of Berlin have been especially numerous and important (see [1–6]).

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* Dedicated to Professor J. Koutecký on the occasion of his 65th birthday

The (Fe + CO) system

When we started to study the interaction between iron and carbon monoxide, in connection with the Fischer-Tropsch reaction, most theoretical information available on (M + CO) systems concerned the atoms of the nickel family (Ni-CO[7–9], Pd-CO[2], Pt-CO[10]), and also Cu-CO[11, 12]. Rather similar configurations are involved in both cases, namely $3d^8 3s^2 \rightarrow 3d^9 4s^1$ for Ni and $3d^{10} 4s^1$ for Cu; hence for these M-CO molecules, which have ${}^{1,3}\Sigma^+$ and ${}^2\Sigma^+$ low-lying states, it was possible to perform standard configuration interaction (CI) calculations. The treatment of lighter transition metals, like Fe, cannot be undertaken so easily, because the presence of many holes into the d shell of M generally produces an intricate spectrum of quasi-degenerate states.

Whereas we were essentially interested in the determination of potential energy curves and vibration frequencies for the (Fe + CO) system and in the nature of the bound lowest state of the Fe–CO molecule, direct calculations of the interaction energy between the metal atom and the CO fragment at fixed inter-atomic distances have been recently presented for Fe–CO as well as for Cu–CO and Ni–CO in various low-lying states [13]. This work, somewhat different from ours in its object, uses complete active space self-consistent field (CASSCF) wave functions in the frame of the constrained space orbital variation technique [14] in order to assess the importance of metal back donation and CO donation contributions to the interaction energies; it does not give definite information about the spin and symmetry of the ground state of Fe–CO, because the zero of energy chosen for the Fe fragment is not the same for each state.

To deal with Fe–CO at the ab initio level, we have used two different approaches: (1) a configuration interaction treatment by perturbation-selected iterations (CIPSI) method [15], whose first conclusions have been given in 1985 in a short account [16], and (2) an additional standard CI treatment with the ASTERIX program [17], whose purpose was to check some points of the preceding study.

Perturbation-variation calculations

In this part of our study, we have included the 18 valence electrons of the (Fe + CO) system, and used the Toulouse pseudo-potentials, fitted to *ab initio* energy spectra of free atoms, to take the effects of the Fe, C and O inner shells into account. For Fe, we possessed a relativistic pseudo-potential reproducing the states $d^6s^2({}^5D)$, $d^7s^1({}^5F)$ and $d^6s^1({}^7D)$ [18].

The occupied and virtual MOs to be considered in the subsequent CI treatment were constructed from Gaussian expansions of double-zeta quality for s and p orbitals and of triple-zeta quality for d orbitals. Contraction schemes of the form $4 \rightarrow 3, 1$ for C and O, and of the form $3 \rightarrow 2, 1$, for the s and p orbitals of Fe and $6 \rightarrow 3, 2, 1$ for its d orbitals were applied to the primitive basis obtained from calculations performed on the free atoms at the SCF level with the pseudo-potentials in question. The MO sets finally retained are those coming from RHF closed-shell calculations, for which it was easy to re-hybridize the Fe atom in a

$(3d^7 4s^1)$ state by lowest-energy diexcitations, and from appropriate RHF open-shell calculations (see Table 1).

Configuration interaction is introduced in the CIPSI method by a perturbation treatment including double excitations with respect to a multi-reference state constructed in an iterative manner. The size of the variational subspace S_0 of CIPSI depends on the starting MO set, and it is possible to improve the convergence of the CIPSI iterative algorithm - as tested by the difference between the second-order corrections given by the so-called Møller-Plesset (MP) and Epstein-Nesbet (EN) partitions [15] - by using the natural orbitals of the S_0 subspace instead of the canonical MOs [19]. Correspondingly, the eigenvalues involved in the MP partition can be taken from an effective Fock operator built according to the Longuet-Higgins-Pople-Nesbet recipe [20], where the contribution of each orbital is multiplied by its occupation number. This is justification for considering natural orbitals as an alternative, for the CIPSI method, to the MC-SCF MOs which are currently used in CI calculations. The resulting MP second-order corrections obtained for test molecules were found to be at least equivalent to those of a standard MP4 treatment from a single reference state.

According to the CIPSI method, the (Fe+CO) system has two low-energy $^{3,5}\Sigma^-$ states that are bound with respect to their asymptotes: $\mathrm{Fe}(d^7 4s^1)(^3\mathrm{F})+\mathrm{CO}(^1\Sigma^+)$ and $\mathrm{Fe}(d^7 4s^1)(^5\mathrm{F})+\mathrm{CO}(^1\Sigma^+)$ respectively. The Δ- and Φ-states are much higher, in opposition to a photoelectron assignment in favour of a $^3\Delta(\pi^4\delta^3\sigma)$ ground state with a binding energy of 1.0 eV [21]. Except in one calculation (MP results in the middle of Table 1, using energies computed from a Fock Hamiltonian with occupation numbers equal to 2) the low-spin $^3\Sigma^-$ state is found below the high-spin $^5\Sigma^-$ state. The corresponding EN binding energies are about 1.3 eV and 0.6 eV, respectively.

Starting with the CIPSI-EN potential energy curves in the vicinity of the equilibrium (middle of Table 1), we have determined the force and interaction constants of the Fe-C and C-O bonds, in order to evaluate the stretching vibration frequencies in both states of the FeCO molecule. We find that for the $^3\Sigma^-$ state, $k_R=3.70$, $k_r=14.17$, $k_{Rr}=-0.36$ md Å^{-1}, and hence the two frequencies are

Table 1. CIPSI energies ($E_{\text{valence}}=-42+E_{\text{CIPSI}}$) and interatomic distances for the equilibrium linear form of FeCO (in atomic units)

		Closed-shell MOs		Open-shell MOs		Natural MOs of	
		$\ldots 2\pi^4 4\sigma^2 5\sigma^2 1\delta^0$		$\ldots 2\pi^4 4\sigma 5\sigma 1\delta^2$		Quintet	Triplet
		$^5\Sigma^-$	$^3\Sigma^-$	$^5\Sigma^-$	$^3\Sigma^-$	$^5\Sigma^-$	$^3\Sigma^-$
$R_{\text{Fe-C}}$		3.32	3.19	3.59	3.42	(3.48)	
$r_{\text{C-O}}$		2.34	2.30	2.27	2.25	(2.17)	
E_{CIPSI}	EN	−0.608	−0.626	−0.778	−0.794	−0.771	−0.785
	MP	−0.634	−0.656	−0.667	−0.650	−0.722	−0.730

546 cm^{-1} and 1986 cm^{-1} respectively, and for the $^5\Sigma^-$ state, $k_R = 2.31$, $k_r = 13.77$, $k_{Rr} = +0.40$ md Å^{-1}, which corresponds to frequencies of 552 cm^{-1} and 1867 cm^{-1}. Experimentally, the vibration spectrum of FeCO trapped in inert-gas matrices has a carbonyl peak at 1898 cm^{-1} corresponding to an approximate force constant of 14.3 mdy Å^{-1} [22], whereas chemisorbed CO on iron has strong absorptions at 1950 cm^{-1} and 580 cm^{-1} corresponding to force constants of 13.9 mdy Å^{-1} and 4.1 mdy Å^{-1} [23].

It can be added that the tendency for the M-CO molecules to have a low-spin ground state is not valid for the first transition elements of the iron family, as shown by calculations on the Sc-CO [5] and Ti-CO [19] systems.

Additional CI calculations

A boring point of the present CIPSI study is the possible role of the inner shells - especially those of the iron *M* shell - embedded in pseudo-potentials, and the finite value (0.02) of the selection threshold for the variational subspace. We have tried to perform additional standard CI calculations with ASTERIX for selected interatomic distances ($R_{Fe-C} = 3.59$ a.u., $R_{C-O} = 2.17$ a.u. using the Huzinaga $(9, 5 \rightarrow 3, 2)$ set for the carbon and oxygen orbitals and the Veillard $(14, 9, 6 \rightarrow 6, 4, 3)$ set for those of iron [24]. Due to computational reasons, the triplet and quintet single reference states were constructed from RHF closed-shell MOs, giving guess energies equal to −1376.904 a.u. for the former and −1376.174 a.u. for the latter. This large energy difference in favour of the triplet state is reduced by the CI treatment; taking an outer active space of 8 electrons distributed among 9 or 11 MOs (i.e. the π_x and π_y orbitals of the CO group, the d_{xy} and $d_{x^2-y^2}$ orbitals of Fe, next σ orbitals including important contributions from the 4*s*, 4*p*, and $3d_{z^2}$ orbitals of Fe, and finally π^* and δ^* orbitals), we obtain the following triplet and quintet energies: −1378.040 a.u. and −1377.317 a.u. respectively in the case of 9 active MOs, and −1378.137 a.u. and −1377.471 a.u. in the case of 11 active MOs. Although the corresponding energy differences could not be reduced further because of the limitations of our CI possibilities, they support our $^3\Sigma$ assignment for the bound ground state of FeCO, in line with the theoretical results available for the isoelectronic system FeN_2 [25].

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