believe that it corresponds to a (local) minimum. We made also some test calculations on planar $M_4Si_4$ structures, without obtaining a stabilization relative to **4**. Solid compounds display exactly this findings: while MC compounds occur only as acetylides $M_2C_2$, MSi phases contain only heterocubanes $M_4Si_4$ (M = Na, K, Rb, Cs).[10–12,14] There is, however, no experimental proof up to now for the $Li_4Si_4$ cluster in the solid state. This may be due to the lacking of favorable 3D structure with the small Li atoms. Very recent results reveal that ternary compounds $M_3LiSi_4$ do exist, where the Li atoms cover faces of $Si_4$ tetrahedrons.[29]

The relative stability of **1** and **2** over **3** and of **4** over **5** shows that bridged structures are favored. These have longer Si–Si and M–Si bond lengths.

Figure 2 shows pseudopotential electronic charge density difference maps obtained by subtracting the electronic charge densities of $Si_2$ and the two Li atoms (positioned as in $Li_2Si_2$) from that of $Li_2Si_2$ (structure **1**). Clearly, charge density is accumulated along the lines connecting Li with Si. In structures **1**, **2**, and **4** the densities make us believe that multicenter bonding is a prominent feature of the more stable arrangements $M_xSi_x$.

In order to enforce this statement we calculated the shared electron numbers,[30] which give indications about the bond strength. The values for three-center-bonding $Si_2M$ in structures **1**, **2**, and **4** are 0.2–0.3 (for comparison: $M_2Si \sim 0$; B–H–B in diborane = 0.7). In structure **3** the value is negligible. The four-center shared electron number for $Si_3M$ is around 0.1. Another significant multicenter character is to be seen for the $Si_4$ tetrahedron (0.3 for the three-center part, 0.2 for the four-center part).

A qualitative explanation for the relative stability of the different configurations needs, however, some more investigations. An orbital picture might be of some help. This can be obtained by using the internally consistent SCF orbital energies, which sum up to give the total energy of the molecule under consideration[31] (see Tables IV–VII). For the $M_2Si_2$ molecules the stabilization of $\pi$ orbitals (and destabilization of the $\sigma$ orbitals) when going from **3** to **2** and from **3** to **1** is evident from symmetry considerations with a minimal basis set. The most pronounced effects can be observed on the highest $\sigma$ and lowest $\pi$ orbital. The destabilization of the $\sigma$ is exceeded by the stabilization of the $\pi$ orbital. Curiously, the change in the orbital energy of the highest occupied molecular orbital (HOMO) reproduces quite well the energy differences between the conformers (e.g., 0.031 mhartree between structures **2** and **3** of $Li_2Si_2$). This holds also for the $M_4Si_4$ structures. As the HOMO makes no contribution to the M–Si bonding (with a minimal basis set) in conformations **2** and **3** (or **4** and **5**), it seems necessary to include some indirect effects to explain the relative stability of the bridged structures, such as the avoiding of spatial crowding with longer bonds.[19]

## Conclusions

In accordance with experimental data our calculations confirm that a bent $\mu_2$-$M_2Si_2$ arrangement and a $\mu_3$-$M_4Si_4$ heterocubane structure are the most stable species of the arrangements investigated here. Bridging positions for the M atoms are favored in any case. The bent $\mu_2$-$M_2Si_2$ cluster can be regarded as a prestructure of the $\mu_3$-$M_4Si_4$ unit which itself is a distorted part of a NaCl-like arrangement.

$M_2Si_2$ can dimerize with a considerable gain in energy to $M_4Si_4$. This is consistent with mass spectrometric and solid-state investigations that favor the latter.

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**Registry No.** $Li_2Si_2$, 111470-14-5; $Na_2Si_2$, 111470-15-6; $Li_4Si_4$, 111470-16-7; $Na_4Si_4$, 39293-86-2.

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# Characterization of the Temporary Anion States of Metal Carbonyl Complexes: An MS–X$\alpha$ and ETS Study of $Cr(CO)_6$ and $Fe(CO)_5$

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**Abstract:** The electron affinities in the 0–5 eV energy range have been determined for chromium hexacarbonyl and iron pentacarbonyl by means of multiple scattering X$\alpha$ calculations. The total electron scattering cross sections have been estimated with the continuum MS–X$\alpha$ method. The computational results are compared with the electron transmission spectra and used for the assignment of the experimental features. The ET spectrum of $Fe(CO)_5$ is presented and assigned for the first time and that of $Cr(CO)_6$ is reassigned. For both complexes, all the anion states associated with electron capture into the orbitals deriving from the ligand $2\pi^*$ MOs and into the metal empty d orbitals are assigned to resonances occurring in the 0.4–2.6 eV energy region of the ET spectra. A charge density analysis reveals that a net electronic charge transfer occurs from the ligands to the metal, owing to the acceptor capability of the metal 4s and 4p orbitals. This is consistent with the experimentally observed average stabilization of the anion states localized at the CO ligands with respect to the $\Pi$ anion state of free CO.

The determination of ionization energies (IEs), electron affinities (EAs), and spatial distributions of frontier molecular orbitals (MOs) is important for a better understanding of the bonding and of the catalytic properties of transition-metal complexes. Ultraviolet photoelectron spectroscopy together with theoretical calculations have provided a wealth of information on the occupied MOs, whereas the corresponding information on the unoccupied levels is often quite scarce.

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We have recently determined energy and localization properties of the low-lying anion states of bis π-ligand[1,2] and mixed π-ligand–carbonyl[3] complexes by means of electron transmission spectroscopy (ETS) and MS–Xα calculations using the transition-state procedure. Here, we extend our investigation to the metal carbonyl complexes $Cr(CO)_6$ and $Fe(CO)_5$, including total elastic electron scattering cross section calculations.

The assignment of the ET spectrum of $Cr(CO)_6$ has been the subject of controversy. Previous MS–Xα calculations[4] correlated the spectral features below 1 eV to electron capture into the $10t_{1u}$, $6e_g$ (of mainly Cr 3d character), and $4t_{2g}$ orbitals and the three most intense resonances to electron capture into the very diffuse $3t_{2u}$, $7e_g$, and $5t_{2g}$ orbitals, in order of increasing energy. Further, as reported in a subsequent paper by the same authors,[5] electron capture into the $9t_{1u}$, $2t_{2u}$, $3t_{2g}$, and $2t_{1g}$ orbitals (that is, all the empty orbitals deriving from the CO $2\pi^*$ orbitals[6]) was predicted to give rise to stable anion states.

Quite different results were obtained by ab initio RHF SCF calculations,[7] according to which the three most intense resonances are associated with $T_{1u}$, $T_{2g}$, and $T_{2u}$ anion states, in order of increasing energy, no anion states being present below 1 eV. The authors also argued that the $E_g$ and $T_{1g}$ states are not observed in the ET spectrum. The absence of temporary anion formation in the 0–1 eV energy range, however, is in contrast with electron dissociative attachment experiments.[5,8]

## Experimental Details and Computations

Our electron-transmission apparatus is in the format devised by Sanche and Schulz[9] and has been previously described.[10] The present spectra have been obtained by using the apparatus in such a mode as to detect the nearly total electron scattering cross section.[11] The energy scales were calibrated with reference to the $(1s^12s^2)^2S$ anion state of He. The estimated accuracy is ±0.05 eV.

Multiple scattering Xα (MS–Xα) calculations[12,13] were carried out on the title metal carbonyl complexes at their experimental geometries.[14] The values of the local exchange parameters (α) were taken from the tabulation of Schwarz,[15] and a valence-weighted average was employed for the inter- and outer-sphere regions. The radii ratios for the atomic spheres were determined by using the nonempirical procedure of Norman.[16] The radii were chosen as 7.4045, 2.1700, 1.6071, and 1.6332 $a_0$ for the outer, Cr, C, and O spheres, respectively, in $Cr(CO)_6$ and 7.2479, 2.0898, 1.5913, 1.5864, 1.6203, and 1.6198 $a_0$ for the outer, Fe, $C_{eq}$, $C_{ax}$, $O_{eq}$, and $O_{ax}$ spheres, respectively, in $Fe(CO)_5$. These radii satisfy the virial ratio $(-2T/V = 1)$ in the neutral complexes. The double counting correction proposed by Herman[17] was used in the normalization process of the molecular orbitals. Partial waves up to $l = 1$ and 4 for the C and O and for the metal and outer spheres were used, respectively. Core orbitals were not frozen during the SCF procedure, and the potential converged to better than $5 \times 10^{-3}$ at any point. The parameters employed for bis(benzene)chromium have been reported in ref 2.

Ionization energies and attachment energies are computed with use of the transition-state procedure.[18] A positively charged sphere, having a radius twice as large as that of the outer sphere, was used to estimate the attachment energies.[1,4]

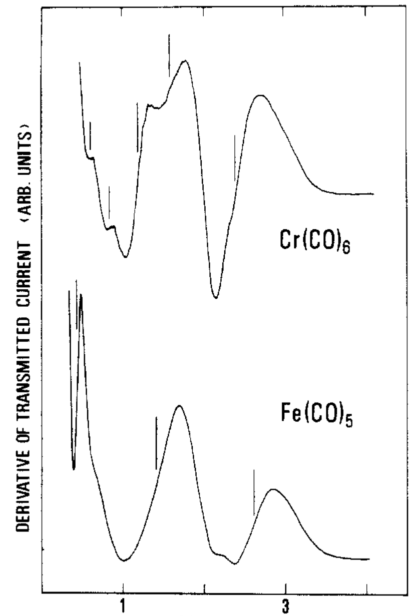

**Figure 1.** Derivative of the electron current transmitted through chromium hexacarbonyl and iron pentacarbonyl vapors as a function of electron energy.

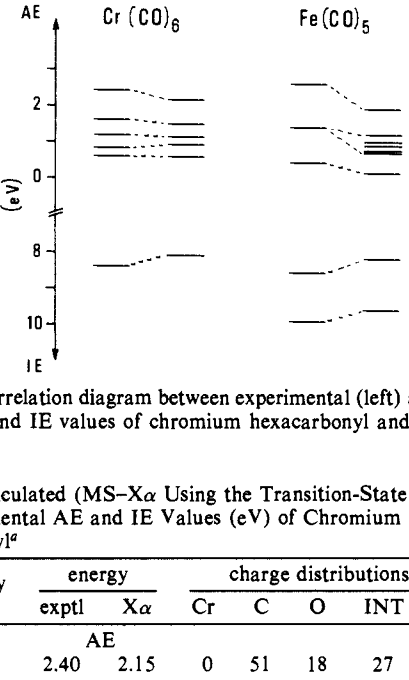

**Figure 2.** Correlation diagram between experimental (left) and MS–Xα (right) AE and IE values of chromium hexacarbonyl and iron pentacarbonyl.

**Table I.** Calculated (MS–Xα Using the Transition-State Procedure) and Experimental AE and IE Values (eV) of Chromium Hexacarbonyl[a]

| symmetry $O_h$ | energy | | charge distributions (%) | | | | |
|---|---|---|---|---|---|---|---|
| | exptl | Xα | Cr | C | O | INT | OUT |
| | AE | | | | | | |
| $T_{1g}$ | 2.40 | 2.15 | 0 | 51 | 18 | 27 | 4 |
| $E_g$ | 1.61 | 1.5 | 31 | 7 | 2 | 4 | 56 |
| $T_{2g}$ | 1.19 | 1.15 | 18 | 15 | 3 | 17 | 47 |
| $T_{2u}$ | 0.86 | 0.95 | 1 | 40 | 22 | 38 | 0 |
| $T_{1u}$ | 0.61 | 0.6 | 1 | 24 | 7 | 29 | 39 |
| | IE | | | | | | |
| $T_{2g}$ | 8.40 | 8.1 | 63 | 4 | 13 | 20 | 0 |

[a] The calculated Transition-state charge distributions are also included. IE value taken from ref 26.

The cross sections were calculated by using the continuum multiple scattering Xα method (CMS–Xα).[19] The potentials for the continuum calculations were generated from transition-state calculations, according

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to the method proposed by Davenport et al.[20] However, cross sections[21,22] computed with the program of Davenport are greater by a factor of 2 than those calculated by our program, probably owing to a double sum over the spin coordinates. The cross sections were computed at 0.01-eV intervals.

The charge distributions in the neutral molecules were evaluated by partitioning the inter- and outer-sphere charges among the atoms according to the procedure of Case and Karplus,[23] thus avoiding the approximation of attributing all the charge in these regions to the ligands.[24]

The calculations were performed on the VAX 11/780 computer of the theoretical chemistry group in Bologna.

## Results and Discussion

**$Cr(CO)_6$.** The $Cr(CO)_6$ ET spectrum is reported in Figure 1. The spectrum agrees with that previously reported in the literature by Giordan et al.[4]

The experimental and MS–X$\alpha$ calculated attachment energies (AEs, that is, the negative of the vertical EAs), together with the calculated localization properties of the corresponding anion transition states, are given in Table I. Also the IE from the filled metal d orbitals has been calculated, in order to test the reliability of the theoretical method.

The theoretical data are in close agreement with experiment (see also Figure 2). In particular, the four $^2T$ anion states, originating from the CO $2\pi^*$ orbitals, and the $^2E_g$ anion state, associated with the empty Cr 3d orbitals, are all calculated to lie above zero energy and have their counterpart in the spectrum. These theoretical findings are also supported by the evaluation of Giordan et al.,[25] based on PES and UV spectral data, that electron capture into the lowest empty orbital ($9t_{1u}$) should give rise to an unstable anion state.

In the 0–5-eV energy range no anion states associated with electron capture into $\sigma^*$ orbitals are calculated.

The most stable anion state ($^2T_{1u}$) and the second one ($^2T_{2u}$), both calculated to lie below 1 eV, are ascribed to the weak spectral features occurring at 0.61 and 0.86 eV. The first intense resonance (1.19 eV) is related to the $^2T_{2g}$ anion state, with mainly CO $2\pi^*$ character but with large contributions from the filled metal d orbitals of the same symmetry (see Table I). The next resonance (1.61 eV) is associated with electron capture into the empty $6e_g$ (mainly Cr 3d) orbital. Finally, the last resonance (2.40 eV) is assigned to the $^2T_{1g}$ anion state.

The calculated energy ordering of the anion states localized on the ligands can be explained on the basis of a simple MO picture. In $Cr(CO)_6$, for overlap reasons, the carbonyl $2\pi^*$ orbitals can experience strong mutual interactions (giving rise to the $t_{2g}$ and $t_{1g}$ orbitals) in planes defined by the ligands, and weak interactions (giving rise to the $t_{1u}$ and $t_{2u}$ orbitals) perpendicular to these planes. In the absence of interactions with the metal orbitals, the in-phase combinations ($t_{2g}$, $t_{1u}$) should be stabilized and the out-of-phase combinations ($t_{1g}$, $t_{2u}$) destabilized with respect to the $2\pi^*$ MO of free CO. Their energies should thus follow the ordering $t_{2g} < t_{1u} < t_{2u} < t_{1g}$. However, the computed AEs reveal that the $^2T_{2g}$ state is slightly less stable than the $^2T_{1u}$ and $^2T_{2u}$ states. This result can be traced back to the fact that only the $t_{2g}$ orbital can interact by symmetry with the occupied metal d orbitals. The large participation of the Cr 3d filled orbital in the $^2T_{2g}$ anion state (see Table I) is consistent with a large destabilization of the latter.

The present MS–X$\alpha$ calculations give systematically higher AE values than those obtained by Giordan et al.[4] using the same computational method. The large intensity of the 1.2- and 2.4-eV resonances does not seem consistent with the small or null localization in the atomic spheres of the anion states (see Table IV of ref 4) to which the resonances were assigned. In our opinion, the previous MS–X$\alpha$ results are affected by severe approximations, such as the following: (i) most of the attachment energies were not evaluated with the transition-state method but were estimated assuming the same electronic relaxation for the various MOs; and (ii) no correction to the X$\alpha$ wave functions was performed to take into account the large overlap between atomic spheres in the CO frame. As pointed out by Herman,[17] this correction is necessary for atoms linked by a triple bond.

Our present assignment of the spectrum of $Cr(CO)_6$ also differs from that derived on the basis of ab initio RHF SCF calculations.[7] Concerning the energy sequence of the anion states, at the ab initio level the $^2T_{2u}$ state is calculated higher in energy than the $^2T_{2g}$ and $^2E_g$ states. However, the most significant discrepancy concerns the magnitude of the attachment energy values, much higher than those found with the X$\alpha$ method. Vanquickenborne and Verhulst[7] were thus led to doubt the existence of resonances below 1 eV and to suppose that the resonance due to electron capture into the $t_{1g}$ orbital (calculated at 4.84 eV) is not visible in the ET spectrum because of its high energy. This interpretation, however, disagrees with experimental evidence: anion fragment formation in $Cr(CO)_6$ within 1 eV of threshold has been confirmed by electron dissociative attachment spectroscopy,[5,8] and resonances in the 4–6-eV energy range are usually observed in ETS. Besides, the nonvisibility of the $^2E_g$ state predicted in ref 7 is also in contrast with the present results.

The lack of radial flexibility of LCAO wave functions is probably responsible for computing excessively high attachment energies, since the atomic basis set optimized for bound states cannot adequately describe the uppermost singly occupied MOs, which are spatially very diffuse. It is worth noting, however, that the first IE value (8.4 eV[26]) is also better reproduced by the present calculations (8.1 eV) than by ab initio calculations (9.8 eV[7]).

The present assignment leads to the interesting observation that the mean value (0.75 eV) of the experimental AEs into the $t_{1u}$ and $t_{2u}$ orbitals, not mixed with the metal orbitals, is much lower than that of the CO $2\pi^*$ orbital (about 2.0 eV[27]). The charge density distribution calculated in neutral $Cr(CO)_6$ indicates that a sizable charge transfer (0.84 e) takes place from the ligands to the metal, the electronic configuration of Cr being [Ar] $d^{5.58}$ $s^{0.39}$ $p^{0.72}$ $f^{0.13}$ $g^{0.03}$. The greater nuclear attraction experienced by the trapped electron thus accounts for the lowering of the AE values with respect to the free CO ligand. Because of the antibonding character of the CO $2\pi^*$ orbital, this stabilization could be partly due to the C–O bond length increase upon complexation (about 0.01 Å[14,28]). Inspection of the individual contributions in the angular momentum basis functions reveals that, with respect to a Cr $d^6$ configuration, there is indeed a charge transfer (0.42 e) from the d orbitals of chromium to the ligands, but there is an even greater one from the ligands to the empty metal orbitals.

The present results thus demonstrate the importance of Cr 4s and 4p orbitals in bonding.

**$Fe(CO)_5$.** The ET spectrum of iron pentacarbonyl is given in Figure 1; the AEs, the two IEs from the filled d orbitals, and the ion state localization properties are presented in Table II.

The ET spectrum shows three distinct features: a sharp resonance centered at 0.43 eV and two broader ones at 1.39 and 2.58 eV.

According to the MS–X$\alpha$ calculations, no anion state is stable and $\Sigma$ anion states are not present in the 0–5-eV energy range. The calculations suggest that the first and the last resonances are due to electron capture into e″ orbitals, resulting from the strong interaction between the out-of-plane $2\pi^*$ orbitals of the equatorial ligands and those of the axial ligands. This interaction is similar to that occurring in the $t_{2g}$ and $t_{1g}$ orbitals of $Cr(CO)_6$. The resonance observed at 1.39 eV in the ET spectrum is very broad,

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**Table II.** Calculated (MS–Xα Using the Transition-State Procedure) and Experimental AE and IE Values (eV) of Iron Pentacarbonyl[a]

| symmetry $D_{3h}$ | energy exptl | energy Xα | Fe | $C_{eq}$ | $O_{eq}$ | $C_{ax}$ | $O_{ax}$ | INT | OUT |
|---|---|---|---|---|---|---|---|---|---|
| | AE | | | | | | | | |
| E″ | 2.58 | 1.9 | 1 | 16 | 7 | 18 | 6 | 29 | 23 |
| $A_2'$ | | 1.2 | 1 | 41 | 21 | 0 | 0 | 37 | 0 |
| $A_2''$ | | 1.0 | 1 | 29 | 10 | 1 | 0 | 25 | 34 |
| E′ | 1.39 | 0.9 | 1 | 4 | 2 | 30 | 16 | 39 | 8 |
| E′ | | 0.75 | 7 | 16 | 9 | 0 | 0 | 35 | 33 |
| $A_1'$ | | 0.7 | 57 | 8 | 1 | 10 | 2 | 16 | 6 |
| E″ | 0.43 | 0.15 | 12 | 8 | 9 | 8 | 9 | 44 | 10 |
| | IE | | | | | | | | |
| E′ | 8.6 | 8.2 | 58 | 7 | 8 | 1 | 2 | 24 | 0 |
| E″ | 9.9 | 9.6 | 75 | 1 | 4 | 1 | 6 | 13 | 0 |

(charge distributions (%): Fe, $C_{eq}$, $O_{eq}$, $C_{ax}$, $O_{ax}$, INT, OUT)

[a] The calculated transition-state charge distributions are also included. IE values taken from ref 29.

considering its low energy, and should derive from the five anion states calculated between 0.7 and 1.2 eV (see Table II and Figure 2).

The lowest ($^2A_1'$) of these states corresponds to electron capture into the iron $d_z$ orbital. The computed AE (0.7 eV) is lower than that found for the $e_g$(d) orbital of chromium hexacarbonyl, in line with the increase in the effective nuclear charge that occurs on going from the $d^6$ to the $d^8$ system. The other anion states calculated in the 0.7–1.2-eV energy range are essentially localized at the ligands, and do not involve appreciable interactions between axial and equatorial CO groups, as shown in Table II. As a consequence, the splitting between these anion states is small.

As expected, the out-of-phase combination of the $2\pi^*$ orbitals lying in the equatorial plane (associated with the $^2A_2'$ state) is destabilized and the in-phase combination (associated with the first $^2E'$ state) is stabilized with respect to the $^2A_2''$ state. However, the interaction between the $2\pi^*$ orbitals lying in the equatorial plane is smaller than that in $Cr(CO)_6$, due to a decrease of the overlap on going from a square to a trigonal arrangement of the equatorial atoms.

In $Fe(CO)_5$ a strong net charge transfer (0.83 e) is calculated from the ligands to the metal atom, the electronic configuration of Fe being [Ar] $d^{7.31}$ $s^{0.43}$ $p^{0.95}$ $f^{0.11}$ $g^{0.03}$. As observed for chromium hexacarbonyl, in the case of iron pentacarbonyl the sizable average stabilization of the anion states localized at the ligands, with respect of free CO, is also consistent with the charge distribution calculated here and with the C–O bond length increase upon complexation.[14]

### Calculated Total Scattering Cross Sections

Although MS–Xα calculations, where all the states are shifted to lower energy and treated as bound states, have been shown to closely reproduce the experimental AE values for transition-metal complexes,[1-3] the direct calculation of the scattering cross section is in principle a more correct theoretical approach toward the ET experiment. However, an accurate description of the electron–molecule interaction presents difficulties.[30] Dehmer and Dill[19] have demonstrated that the continuum multiple scattering Xα method gives good results when applied to diatomic molecules. However, this computational method was less successful in reproducing the ET spectrum of a larger molecular system like $Cr(CO)_6$.[5] The calculated total scattering cross section, in fact, displayed only two peaks in the 0–3-eV energy range, using various transition-state potentials (taken from ref 4) for describing the short-range electron–molecule interactions.

We have performed the calculation of the total scattering cross section for $Cr(CO)_6$ and $Fe(CO)_5$, using transition-state potentials (generated by the MS–Xα calculations reported in the previous section) corresponding to $t_{2g}$ and e″ orbital occupation, respectively. This choice was suggested by the delocalization of these orbitals over the whole complex. The results are presented in Figure 3. For $Cr(CO)_6$, we verified that the choice of a different transition-state potential (e.g., $t_{1u}$) does not significantly change the results. The scattering cross section calculated for $Cr(CO)_6$ displays four peaks at energies close to the corresponding values observed in the ET spectrum, except for the $t_{2g}$ peak which is rather low in energy. In agreement with the ET spectrum, the sharpest peaks occur in the $t_{2g}$ and $t_{1g}$ channels. The greatest discrepancy with experiment consists of the absence of a peak in the $t_{2u}$ channel. The substantial improvement with respect to the previously reported cross section[5] could be due to the use of an MS–Xα molecular potential adequate for reproducing the experimental AE values.

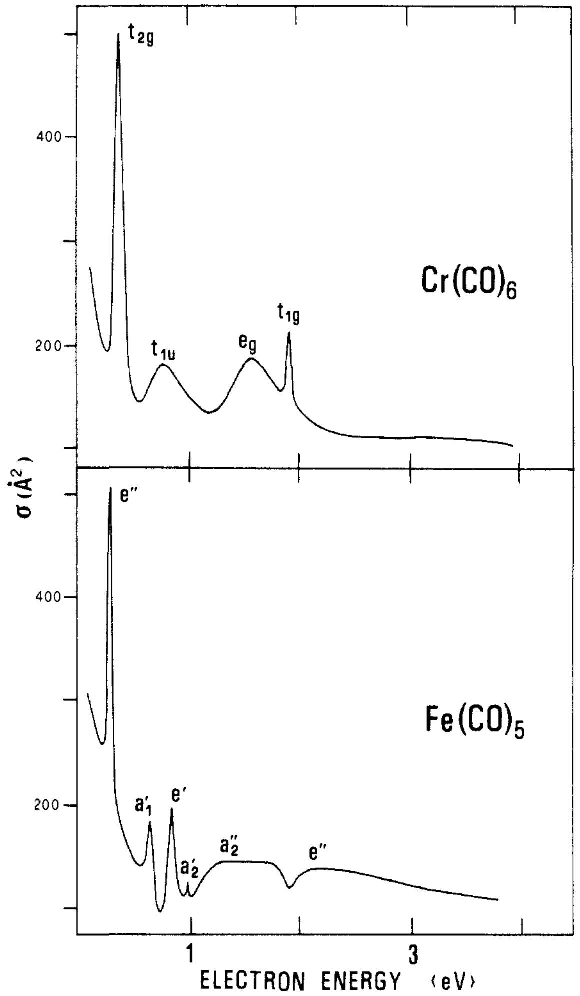

**Figure 3.** Calculated total electron scattering cross sections for chromium hexacarbonyl and iron pentacarbonyl.

In line with the assignment of the ET spectrum of $Fe(CO)_5$ given above, the calculated scattering cross section displays a sharp peak in the e″ channel at 0.3 eV and a broader one of the same symmetry at about 2.2 eV. In the energy region where the second (unresolved) resonance is experimentally observed, the calculated electron scattering cross section shows resonances in the $a_1'$, e′, $a_2'$, and $a_2''$ channels. Inspection of the partial cross sections shows

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that the flat peak occurring between 1 and 2 eV is due to the superposition of the slowly decreasing $a_2''$ signal with a broad signal in the e″ channel (not indicated in Figure 3). Accordingly, a diffuse anion state of E″ symmetry of mixed-valence Rydberg character (not given in Table II) is calculated at about 1.2 eV with the transition-state procedure. The rather sharp decrease resulting below 2 eV in the calculated total cross section could indeed correspond to the weak feature experimentally observed in the ET spectrum at nearly the same energy.

The higher resolution of the computed cross sections with respect to the ET spectra is a consequence of considering fixed nuclei in the scattering process. This approximation results in the loss of the Franck–Condon profile, the peak widths being determined only by the shape of the potential (i.e., the anion lifetime). Dehmer and Dill[19] have shown that integration of the cross section over the vibration normal coordinate in $N_2$ sizably increases the computed peak width. This procedure, however, is not easy to apply to large molecular systems.

Further improvements for a better description of the scattering process would require higher angular momentum basis functions in the atomic and in the outer-sphere regions, and a more accurate formulation of long-range electron–molecule interactions.[31]

## Charge Distributions

The present MS–X$\alpha$ calculations, in line with the ET spectra, predict a sizable negative charge (0.8 e) on the metal atom of $Cr(CO)_6$ and $Fe(CO)_5$. This result is in contrast with HF–Slater calculations on $Fe(CO)_5$,[29] according to which the iron atom has a large (1.88 e) positive charge, and also in apparent contrast with the reduction of the $C_{1s}$ and $O_{1s}$ IEs, with respect to free CO, observed in the XPS spectra of gaseous iron pentacarbonyl.[32] However, calculations of Freund et al.[33] ascribed these IE shifts to large changes in the relaxation effects upon ionization in free and complexed CO, rather than to the charge distributions in the neutral states. The same conclusion was suggested by the failure of Koopmans' theorem calculations in reproducing the observed IE shifts.[32]

In a previous ETS and MS–X$\alpha$ study of (benzene)chromium tricarbonyl, (cyclopentadienyl)manganese tricarbonyl, (butadiene)iron tricarbonyl, and (cyclopentadienyl)cobalt tricarbonyl[3] we found charge distributions analogous to those obtained here for the carbonyl complexes, that is, a largely negative metal center.

It is interesting to note that a number of LCAO calculations on transition-metal complexes lead to the opposite conclusion. For this reason, we were prompted to extend the MS–X$\alpha$ charge distribution analysis also to bis(benzene)chromium, for which LCAO calculations predict a large positive charge at the chromium atom (2.66 e,[34] 0.98 e[35]).

Once again, the MS–X$\alpha$ charge distribution gives opposite results, a sizable charge transfer (1.01 e) occurring from the benzene rings to the metal. This result is indeed consistent with the variation of chemical properties of the benzene ring upon complexation. In particular, bis(benzene)chromium shows an abnormally high acidity,[36,37] bis(fluorobenzene)chromium undergoes nucleophilic substitution reactions under very mild conditions,[38] and NMR studies indicate that a (benzene)chromium group has a similar electron-withdrawing effect on an aromatic ring as do four fluorine atoms.[39]

The reasons for the systematic discrepancy between the LCAO and MX–X$\alpha$ methods in calculating charge distributions in transition-metal complexes deserve further accurate analysis. We tentatively suggest here two possible factors: (i) the LCAO basis set for heavy atoms is usually worse than that for the light ligand atoms (this causes an increase of calculated electron density on the latter[40]); and (ii) the Mulliken population analysis contains the approximation that the overlap population is equally shared between two atomic orbitals.

The strongly reduced positive charge (0.98 e) on the Cr atom calculated in ref 35 (where numerical basis sets were used) with respect to that (2.66 e) calculated in ref 34 is consistent with the above point i).

## Conclusions

The present MS–X$\alpha$ calculations, including the correction for the overlap between atomic spheres, reproduce the ET spectra and the first IE values of $Cr(CO)_6$ and $Fe(CO)_5$. This theoretical approach has again demonstrated its suitability for calculating the energies and localization properties of anion states of transition-metal complexes. The calculated electron scattering cross sections, however, are only in qualitative agreement with experiment.

According to the present study, the empty metal 4p and 4s orbitals are involved to a great extent in the ligand–metal bonding. The experimentally observed stabilization of the anion states localized at the ligands, with respect to the $\Pi$ anion state of free CO, is consistent with the sizable charge transfer (about 0.8 e) from the ligands to the metal calculated at the MS–X$\alpha$ level. Similarly, a large positive charge is calculated at the benzene ligands in bis(benzene)chromium, in agreement with reactivity and NMR data.

The present charge distribution results are in line with those obtained in a previous ET and MS–X$\alpha$ study on $\pi$-ligand transition-metal carbonyls.[3] Charge distribution data obtained with LCAO methods predict a large positive charge at the metal center and are systematically in contrast with our MS–X$\alpha$ results.

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**Registry No.** $Cr(CO)_6$, 13007-92-6; $Fe(CO)_5$, 13463-40-6.

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