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The He(I) Photoelectron Spectrum of $Fe(CO)_4CS$

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The He(I) photoelectron (PE) spectrum of $Fe(CO)_4CS$ (1) has been recorded and compared with that of $Fe(CO)_5$ (2). It is demonstrated that the positions of the bands originating from 3d orbitals are shifted only slightly if one CO moiety in 2 is replaced by CS. The sequence of the first two ionization potentials originating from the CS group (7σ on top of 2π) is changed in 1 in comparison to the free ligand. The measured vertical ionization potentials are compared with Green's function results obtained with a semi-empirical INDO-Hamiltonian.

Introduction

Recently we have investigated the electronic structure of various iron tetracarbonyl carbene complexes by means of He(I) photoelectron (PE) spectroscopy and molecular orbital calculations [1–3]. We have tried to correlate the electronic structure of these species with that of the unperturbed $Fe(CO)_5$. But in all cases studied the molecular symmetry of the $Fe(CO)_4$ moiety was perturbed significantly. Therefore it was of interest to study the PE spectrum of $Fe(CO)_4CS$ (*1*), a species belonging to the point

TABLE I. Valence Orbitals of $Fe(CO)_4CS$ According to an INDO Calculation. The Composition (%), the Type as well as the Irreducible Representation (Γ_j) of the MO Wave Function are Indicated.

MO	Γ_j	MO-Type	ϵ_j (eV)	% Fe	% CS	% CO_{ax}	% CO_{eq}
1a (C_{3v})							
28/29	14e	$3d_{x^2-y^2}/3d_{xy}$	−10.35	61.7	12.9	2.0	23.4
26/27	13e	$3d_{xz}/3d_{yz}$	−11.19	78.0	11.3	5.3	5.4
24/25	12e	CS(2π), $3d_{xz}/3d_{yz}$, $3d_{x^2-y^2}/3d_{xy}$	−13.12	18.2	70.6	1.5	9.7
23	$23a_1$	CS(7σ), $3d_{z^2}$, CO_{eq} (1π)	−13.77	5.2	47.9	10.1	36.8
1b (C_{2v})							
29	$25a_1$	$3d_{z^2}/3d_{x^2-y^2}$	−10.24	61.9	15.2	7.7	15.2
28	$12b_2$	$3d_{yz}$	−10.29	62.7	15.1	5.6	16.6
27	$12b_1$	$3d_{xz}$	−11.16	72.5	20.4	6.2	0.9
26	$3a_2$	$3d_{xy}$	−11.42	84.9	0.0	8.9	6.2
25	$11b_1$	CS(2π), $3d_{xz}$	−12.66	10.3	62.0	20.2	7.5
24	$11b_2$	Cs(2π), $3d_{yz}$	−13.47	6.2	90.5	1.3	2.0
23	$24a_1$	CS(7σ), $3d_{z^2}/3d_{x^2-y^2}$ CO_{ax} (1π)	−14.46	30.0	37.4	28.0	4.6

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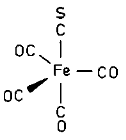
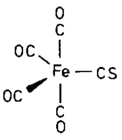
TABLE II. Atomic Populations and Net Charges of $Fe(CO)_4CS$ According to the INDO-Hamiltonian.

AO	Fe	AO	C(CS)	S	$C_{ax}(CO)$	O_{ax}	$C_{eq}(CO)$	O_{eq}
1a (C_{3v})								
4s	0.0979	σ	2.6144	3.0115	2.5293	3.1589	2.5873	3.1861
$4p_x/p_y$	0.0708	π	1.2126	3.1730	1.2580	3.0408	1.2386	2.9888
$4p_z$	0.0432							
$3d_{x^2-y^2}/3d_{xy}$	3.6792							
$3d_{xz}/3d_{yz}$	3.4808							
$3d_{z^2}$	0.6272							
Net charge	0.0010		0.1729	−0.1846	0.2128	−0.1996	0.1740	−0.1749
1b (C_{2v})								
4s	0.0980	σ	2.6855	3.0969	2.5188	3.1566	2.5287	3.1139
$4p_x$	0.0424	π	1.1898	3.0564	1.2606	3.0458	1.3070	3.0585
$4p_y$	0.0356							
$4p_z$	0.0361							
$3d_{x^2-y^2}$	0.9438							
$3d_{xy}$	1.7761							
$3d_{xz}$	1.7483							
$3d_{yz}$	1.8115							
$3d_{z^2}$	1.500							
Net charge	0.0082		0.1247	−0.1533	0.2207	−0.2024	0.1643	−0.1724

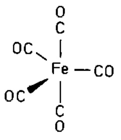
group C_{3v} if the CS ligand occupies the axial position (*1a*) or to point group C_{2v} (*1b*) in the case of the equatorial CS substitution.



1a



1b



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Results and Discussion

Ground State Properties

To obtain the sequence of the molecular orbitals of $Fe(CO)_4CS$ we have carried out molecular orbital calculations of the INDO type [4]. The resulting splitting schemes, similar to that discussed for other MX_4Y species [5, 6], are collected in Table I.

The geometrical parameters used for the $Fe(CO)_4$ moiety were those reported for $Fe(CO)_5$ (*2*) [7]. For the CS ligand the parameters for the free molecule were taken [8]. From Table I it is seen that the three highest occupied MO's of *1a* belong to the irreducible representation E. The HOMO (14e) is found analogous to the HOMO in *2*, predominantly of $3d_{x^2-y^2}/3d_{xy}$ type with antibonding contributions from the carbonyl σ functions of the equatorial CO groups [9]. The 13e combination can be described as a linear combination between $3d_{xz}$ and $3d_{yz}$ and contributions from the π^* orbitals of the CO and CS ligands. It is interesting to note that in $Fe(CO)_5$ the two highest occupied MO's belong to different irreducible representations (E′ and E″) and therefore do not mix. In the *1a* case of $Fe(CO)_4CS$ however, the reduced symmetry allows a mixing between both 3d sets. As a result of this mixing a rotation of the two degenerate complex molecular orbitals results as shown in Fig. 1.

The next two molecular orbitals (12e and $23a_1$) are strongly localized at the CS ligand (see Table I) and thus are different from $Fe(CO)_5$.

The orbitals of the C_{2v} system *1b* are similar to the splitting pattern of the C_{3v} complex with the axial CS ligand. The most important difference lies in the better stabilization of the CS σ orbital due to the stronger coupling with Fe $3d_{z^2}$. According to the INDO model *1a* and *1b* differ by less than 5 kcal/mol in their total energies; this shows that both positions (ax and eq) can be easily exchanged by the CS ligand (*1a* is predicted to be the more stable isomer).

TABLE III. Wiberg Bond Indices of Fe(CO)$_4$CS According to the INDO Calculations.

Bond	C_{3v} *1a* Bond Index	C_{2v} *1b* Bond Index
FeC(CS)	0.6422	0.4725
$FeC_{ax}(CO)$	0.4870	0.4977
$FeC_{eq}(CO)$	0.3606	0.3588
CS	2.0717	2.1877
CO_{ax}	2.2411	2.2330
CO_{eq}	2.3123	2.3160

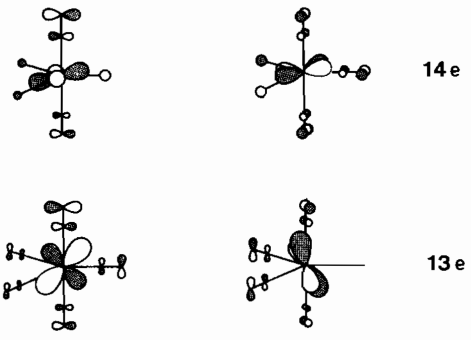

Fig. 1. Schematic representation of the 14e and 13e linear combinations of Fe(CO)$_4$CS in the C_{3v} complex *1a*.

In Tables II and III we have collected the results of a population analysis [10] and the Wiberg bond indices [11] for Fe(CO)$_4$CS. It is seen that we can describe the compound as a d^8 complex in which metal to ligand and ligand to metal charge transfer nearly compensate each other. The Wiberg bond indices in Table III indicate that the CS ligand is bonded strongest in *1a* while the interaction between the equatorial CO groups and the metal is weakest. In the C_{2v} complex with the equatorial CS function C(CS) and C_{ax} show comparable indices.

PE Spectrum of Fe(CO)$_4$CS

The PE spectrum of Fe(CO)$_4$CS is shown in Fig. 2. In the outer valence region below 13.5 eV four maxima are found. The shape of bands ① to ③ is typical for bands arising from ionizations of (nearly) degenerate orbitals of transition metal compounds [12, 13]. The assignment is straightforward by comparison with the PE spectrum of Fe(CO)$_5$ [14, 15]. The latter shows two bands at 8.6 and 9.9 eV very close to bands ① and ② of Fe(CO)$_4$CS. Both bands of *2* are assigned to the highest occupied molecular orbitals ($10e'$ $3e''$). Band ① and ② of *1* therefore should correspond to 14e and 13e in the case of the complex with the threefold axis and to $25a_1/12b_2$ as well as to $12b_1/3a_2$ in the C_{2v} system.

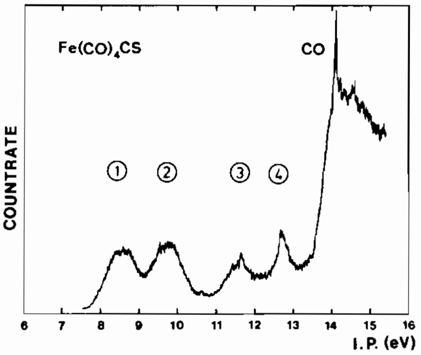

Fig. 2. Gas phase He(I) photoelectron spectrum of Fe(CO)$_4$-CS.

From the foregoing paragraph and the PE spectrum of Fe(CO)$_5$ it seems justified to assign bands ③ and ④ to ligand orbitals, mainly localized at the CS ligand.

In the free CS molecule the first two ionization potentials at 11.4 and 13.0 eV were assigned to ionization events from the orbitals 7σ and 2π [16]. This assignment differs from an assignment based on Koopmans' approximation ($I_{v,j} = -\epsilon_j$) [17], but it can be shown that the inclusion of reorganization effects by means of many body procedures [18, 19] causes the assignment given above. The breakdown of Koopmans' approximation is due to the high symmetry of CS [20] and has also been observed in the diatomic molecules F_2 [21] and N_2 [22]. In the case of the iron tetracarbonyl complex the symmetry constraint is absent; therefore the sequence π on top of σ should be possible. Band shape and band intensities clearly favour the latter assignment.

The arguments listed so far point to a validity of Koopmans' approximation in the case of Fe(CO)$_4$CS. This result is met not very often in connection with transition metal compounds. Usually one observes large reorganization effects for those ionization processes resulting from molecular orbitals strongly localized at the metal [23]. We have encountered such examples in the case of Fe(CO)$_4$CR$_2$ complexes [3], in Fe(CO)$_5$ and the complex between ethylene and Fe(CO)$_4$ [24].

A very efficient way of calculating reorganization effects is Green's function formalism where relaxation and correlation effects in the ground state and in the cationic states are considered. This method has been applied by us in the case of various transition metal compounds [24] and has been used also in the case of *1*. A detailed description of the formalism and the approximations used is given elsewhere [24].

TABLE IV. Comparison between the Experimentally Determined Vertical Ionization Potentials, $I^{e}_{v,j}$, of $Fe(CO)_4CS$ and the Calculated Ones Assuming the Validity of Koopmans' Theorem, $I^{K}_{v,j}$, and Using the Inverse Dyson Equation ($I^{K}_{v,j} + \Sigma^{(2)}_{jj}(\omega_j)$ and $I^{K}_{v,j} + \Sigma^{eff}_{jj}(\omega_j)$). All values in eV.

Band	Γ_j	$I^{K}_{v,j}$	$I^{K}_{v,j} + \Sigma^{(2)}_{jj}(\omega_j)$	$I^{K}_{v,j} + \Sigma^{eff}_{jj}(\omega_j)$	$I^{e}_{v,j}$
1a (C_{3v})					
1	14e	10.35	7.49	9.24	8.5
2	13e	11.19	7.78	9.67	9.7
3	12e	13.12	11.50	12.30	11.6
4	$23a_1$	13.77	13.29	13.47	12.7
1b (C_{2v})					
1	$25a_1$	10.24	7.41	9.09	8.5
	$12b_2$	10.29	7.34	9.14	
2	$12b_1$	11.16	8.10	9.71	9.7
	$3a_2$	11.42	7.70	9.84	
3	$11b_1$	12.66	11.69	12.10	11.6
	$11b_2$	13.47	12.42	12.87	
4	$24a_1$	14.46	13.07	13.82	12.7

The zeros of the inverse Dyson equation [25] which correspond to the ionization energies have been obtained with an approximation for the self-energy part $\Sigma(\omega)$ that takes into account the second order contribution $\Sigma^{(2)}_{jj}(\omega_j)$ to the perturbation expansion and higher order contributions $\Sigma^{eff}_{jj}(\omega_j)$ by means of a renormalization procedure [24]. In the calculation of $\Sigma(\omega)$ 12 hole-states and 11 unoccupied particle-functions have been considered. The calculated ionization potentials are given in Table IV and are displayed in graphical form in Fig. 3.

$$G^{-1} = (\omega I - \epsilon) - \Sigma(\omega)$$

It is seen that the measured ionization potentials are satisfactorily reproduced by the theoretical procedure. Reorganization effects are most pronounced in *1a* for the 13e MO ($3d_{xz}/3d_{yz}$) where the Fe 3d participation is largest. In *1b* $3a_2$ ($3d_{xy}$) and $12b_1$ ($3d_{xz}$) form the MO set with the largest Koopmans' defects predicted in the INDO framework. In the case of the MO's with large CS contributions the ground state MO sequence is not changed when reorganization effects are included. In contrast to the free CS molecule, a decrease of the ionization potential for the π-type (MO 24/25) levels is calculated as various particle-states of π-symmetry are available in the transition metal compound that are able to interact with the MO's 24 and 25 (2π in CS). The calculated ionization potentials indicate that the sequence of the molecular orbitals in the electronic ground state parallels the sequence of the ionization potentials although significant reorganization contributions lead to remarkable deviations from $I^{K}_{v,j}$, the ionization potentials derived under the validity of Koopmans' theorem.

Conclusions

The comparison of the PE spectra of $Fe(CO)_5$ and $Fe(CO)_4CS$ has shown that the nature of the metal 3d orbitals is only slightly perturbed if one CO ligand is changed by a CS substituent. The first IP of the CS derivative is lowered by 0.1 eV due to the hetero ligand (8.5 eV *versus* 8.6 eV). The same reduction is also found in the case of the second ionization event (9.7 and 9.8 eV). On the other hand it has been demonstrated that the sequence of the first two ionization potentials of the carbon–sulfur moiety is changed due to the complexation with the $Fe(CO)_4$ fragment. In the free ligand 7σ (11.4 eV) is found on top of 2π (13.0 eV) while in $Fe(CO)_4CS$ the IP related to 2π (MO's 24/25) is 11.6 eV and MO 23 which is related to 7σ has an ionization energy of 12.7 eV.

The investigation of IR vibrations of $Fe(CO)_4CS$ has shown that the iron pentacarbonyl complex is an admixture of the two isomers *1a* and *1b* [26]. This observation is in line with the INDO results derived for the electronic ground state where only a small energy gap between the C_{2v} and C_{3v} com-

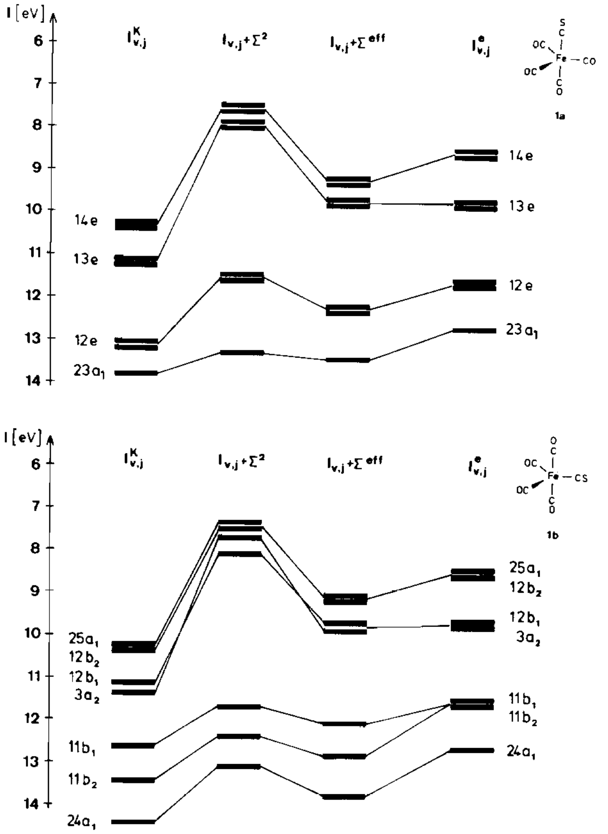

Fig. 3. Comparison between the first bands in the PE spectrum of Fe(CO)$_4$CS ($I^e_{v,j}$) (*1a* and *1b*) with the calculated ionization potentials assuming the validity of Koopmans' Theorem, $I^K_{v,j}$ and using the inverse Dyson equation for a second order ($\Sigma^{(2)}$) and a renormalized (Σ^{eff}) approximation to the self-energy part.

plex has been predicted. The Green's function results for the sequence of the ionization events in *1a* and *1b* have indicated that the two coordination patterns lead to almost identical ionization potentials. This theoretical result is once again in line with the experimental findings. In the PE spectrum of Fe(CO)$_4$CS there is no reference to an admixture with significantly different IP's. The separation of the π and σ ionization events from the carbonyl bands is similar to the PE spectrum of Cr(CO)$_5$CS [27].

Experimental

The iron tetracarbonyl complex was prepared according to the procedure described in ref. 26. The He(I) PE spectrum has been measured on a PS 18 spectrometer (Perkin Elmer Ltd., Beaconsfield, England). It was recorded at room temperature and calibrated with argon. A resolution of about 20 meV of the Ar line was obtained.

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