# The Electronic Structure and the Photoelectron Spectrum of (Tetramethylallene) Iron Tetracarbonyl

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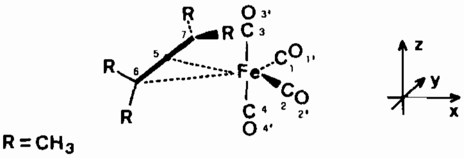
*The vertical ionization potentials of (tetramethylallene) iron tetracarbonyl (1) are investigated by means of many-body perturbation theory in the framework of a semiempirical INDO Hamiltonian. The ionization energies in the outer valence region are reproduced with high accuracy by the Green's function approach. The PE bands are traced back to molecular orbitals that are strongly localized at the 3d center or that result from bonding and antibonding linear combinations between fragment orbitals of Fe(CO)$_4$ and the allene ligand. The ground state properties of 1 are analyzed on the basis of the INDO results and are compared with MO properties of the Fe(CO)$_4$ ethylene complex 2.*

## Introduction

Reorganization effects are of significant importance if photoelectron (PE) spectra of transition metal compounds are compared with results of MO calculations [1]. For the assignment of these PE data the validity of Koopmans' theorem [2] cannot be assumed ($I_{v,j} = -\epsilon_j$). As a result of strong electronic reorganization in the case of ionization processes out of strongly localized MO's, $-\epsilon_j$ differs from the measured vertical ionization potential.

Recently we have demonstrated that PE spectra of larger transition metal compounds can be analyzed by means of the many-body perturbation theory in combination with an improved semiempirical INDO Hamiltonian [3]. The capability of the method has been verified in the case of Ni complexes with organic $\pi$-ligands [4, 5], in open metallocenes [6] as well as in various carbonyl derivatives in the 3d series [7, 8].

In the present contribution the results of Green's function calculations on (tetramethylallene) iron tetracarbonyl (*1*) are analyzed. The PE spectrum of *1* has been published recently [9] and has been assigned on the basis of qualitative arguments without theoretical calculations. In the following we indicate that computational results are essential for the interpretation of the low energy PE spectrum of *1*.



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## Theory

The vertical ionization potentials in the Green's function formalism are given by the zeros of the inverse Dyson equation [10]:

$$G^{-1} = (G^0)^{-1} - \Sigma(\omega) = \omega I - \epsilon - \Sigma(\omega) = 0 \qquad (1)$$

G symbolizes the matrix of the Green's function while $G^0$ is the free counterpart. If canonical Hartree-Fock (HF) orbitals are used as one-electron basis, $(G^0)^{-1}$ is given by $\omega I - \epsilon$; $\epsilon$ represents the diagonal matrix of the canonical HF orbitals, I is the unit matrix of proper size and $\omega$ stands for the energy coordinate that has to be determined. $\Sigma(\omega)$ is the so called self-energy part, which contains corrections to $-\epsilon_j$ due to relaxation and correlation. Conveniently, $\Sigma(\omega)$ is expanded in different orders of perturbation leading to the infinite series (2) [11, 12].

$$\Sigma(\omega) = \Sigma^{(2)}(\omega) + \Sigma^{(3)}(\omega) + \ldots\ldots + \Sigma^{(\infty)}(\omega) \qquad (2)$$

In the case of canonical HF orbitals $\Sigma^{(1)}(\omega)$ vanishes and the second order element is the leading term in the perturbational expansion [13].

In our recent studies on organometallic carbonyl systems [7, 8], we have shown that a sufficient approximation to eqn. (2) is received if $\Sigma^{(2)}(\omega)$ is renormalized by an effective contribution $\Sigma^{\text{ren}}(\omega)$, taking into account the perturbational corrections from orders 3 to $\infty$ [14]. Equation (3) is described in detail in refs. 8 and 14.

$$\Sigma^{\text{eff}}(\omega) = \Sigma^{(2)}(\omega) + \Sigma^{\text{ren}}(\omega) \qquad (3)$$

To determine the $\omega$ parameter in eqn. (1) we have used approximations that have been applied in most semiempirical Green's function calculations [15].

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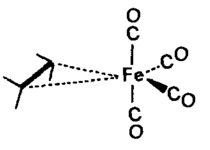
It is assumed that $\Sigma^{\mathrm{eff}}(\omega)$ is diagonal and $\omega$ has been determined by means of a Taylor series expansion near the Koopmans' pole ($\omega_j \rightarrow \epsilon_j$) avoiding the iterative search of the zeros of $G^{-1}$.

The computational framework for this investigation is an INDO extension to the 3d series [3] designed to reproduce PE data of organometallics in the outer valence region. Bond lengths and bond angles of *1* were derived from the structural data of ethylene iron tetracarbonyl (*2*) [16] and of allene [17]. Thus FeC–carbonyl distances of 1.80 and 1.84 Å have been selected, while the Fe–olefin separation amounts to 2.12 Å. In the allene moiety a CC distance of 1.43 Å has been assumed for the complexed $\pi$ unit and 1.31 Å for the other $\pi$-group; these values were extrapolated from *2* and the bond lengths in allene. Standard parameters have been accepted for the methyl groups [18]. In analogy to *2* an equatorial coordination of the allene ligand has been presumed.



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## Ground State Properties of *1*

The electronic structure of the related ethylene complex *2* has been analyzed by various theoretical models with different degrees of sophistication (*e.g.* one-electron calculations of the Extended Hückel type [19], a semiempirical CNDO approach [20], HFS-$X_\alpha$ calculations [21] and an *ab initio* study [22]). MO calculations on *1* with the lower molecular symmetry have not been published.

The electronic structure of *1* in the outer valence region is best described on the basis of the interaction diagram displayed in Fig. 1. The high lying MO's of the allene complex are constructed from the fragment orbitals of the $Fe(CO)_4$ unit (right side) and the $\pi/\pi^*$ set of the organic ligand (left). The MO sequence of the $C_{2v}$ $Fe(CO)_4$ fragment is well known, and has been discussed by R. Hoffmann and coworkers [19, 23]. The orbital energies in Fig. 1 correspond to the INDO model.

In Table I the MO sequence of *1* is summarized. The highest occupied MO of the Fe complex (−9.11 eV) is derived from $3d_{xy}$ of the $Fe(CO)_4$ fragment stabilized due to $(\pi^*)_x$ of the complexed $\pi$ moiety. The Fe contribution of MO 44 amounts to 54%. The following complex MO (−9.34 eV) is the antibonding linear combination between $3d_{x^2-y^2}$ and $(\pi)_x$ of the allene ligand. The ligand $\pi$ character (50%)

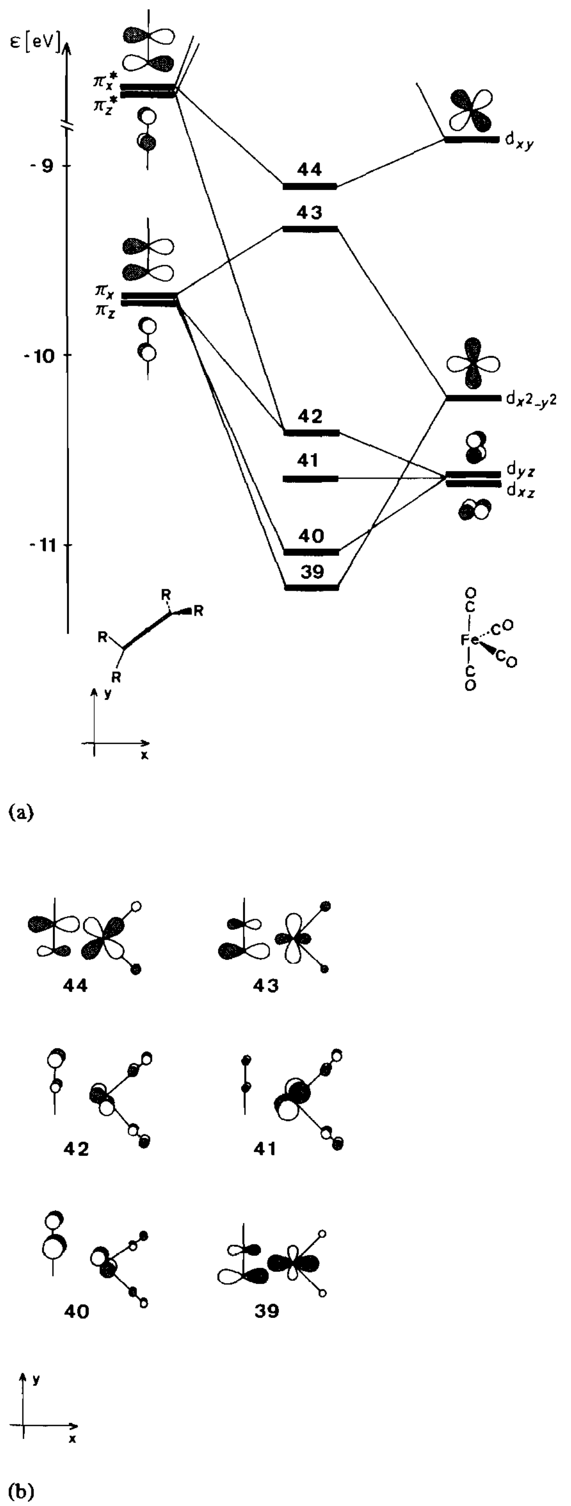

Fig. 1. 1a: Valence orbitals of (tetramethylallene) iron tetracarbonyl (center) as derived from the fragment orbitals of tetramethylallene (left) and the high lying orbitals of the $Fe(CO)_4$ moiety. A schematical representation of the MOs of *1* is given in 1b. 1b: Schematical representation of the high lying MOs of *1*.

TABLE I. Valence Orbitals of (Tetramethylallene) Iron Tetracarbonyl According to an INDO Calculation. The Orbital Energies ($\epsilon_i$) Are Given in eV. The Composition (%) and the Type of the Orbital Wave Function Are also Indicated. The Numbering Scheme for the Orbitals Corresponds to the Configuration of the Valence Electrons. B = Bonding Linear Combination; AB = Antibonding Linear Combination.

| MO | MO-Type | | $\epsilon_i$ | % Fe | % allene | % CO |
|---|---|---|---|---|---|---|
| 44 | $3d_{xy}$, $(\pi^*)_x$ | B | −9.11 | 53.8 | 21.6 | 24.6 |
| 43 | $3d_{x^2-y^2}$, $(\pi)_x$ | AB | −9.34 | 33.8 | 50.1 | 16.1 |
| 42 | $3d_{xz}/3d_{yz}$, $(\pi)_z$ | AB | −10.42 | 56.7 | 36.2 | 7.2 |
| 41 | $3d_{xz}/3d_{yz}$ | | −10.65 | 86.4 | 3.7 | 9.9 |
| 40 | $3d_{xz}(3d_{yz}$, $(\pi)_z$ | B | −11.04 | 31.6 | 56.7 | 11.7 |
| 39 | $3d_{x^2-y^2}$, $(\pi)_x$ | B | −11.22 | 58.0 | 38.2 | 3.8 |

exceeds the Fe 3d amplitude (34%). The associated in-phase combination (MO 39) is predicted at −11.22 eV. In this MO the Fe participation (58%) is predominant while $(\pi)_x$ is reduced to 38%. The energy gap between MO 43 and MO 39 ($\Delta\epsilon = 1.88$ eV) is close to the corresponding splitting pattern in *2* [8, 19, 22].

In contrast to *2*, where only $3d_{x^2-y^2}$ is involved in an occupied bonding and antibonding MO with remarkable contributions from the fragments, the allene ligand in *1* allows the formation of a second metal 3d/ligand πMO pair due to $(\pi)_z$ of the adjacent double bond and $3d_{xz}/3d_{yz}$. The MO's 42 and 40 can be classified as out-of-phase and in-phase linear combinations between $3d_{xz}/3d_{yz}$ of Fe and $(\pi)_z$ of the allene moiety. In the upper component (MO 42 at −10.42 eV) the iron amplitude (57%) exceeds the ligand π character (36%). This ratio is changed in MO 40 at −11.04 eV. The separation between the MO pair 42/40 ($\Delta\epsilon = 0.62$ eV) is only one third of the gap between MO 43 and MO 39, as only one carbon center of $(\pi)_z$ shows a considereable overlap with the 3d set of the iron side. Fig. 1 shows that a net destabilization of $(\pi)_z$ in the out of phase combination is prevented, due to the admixture of the $(\pi^*)_z$ acceptor orbital.

The Fe 3d AOs $3d_{xz}$ and $3d_{yz}$ belong to different irreducible representations in the ethylene complex *2*. The allene ligand in *1* reduces the molecular symmetry and therefore allows a strong mixing between $3d_{xz}/3d_{yz}$. Both AO's are coupled in the MO pair 42/40 in such a way that the 3d amplitude is directed to the complexed carbon $(\pi)_z$ center enhancing the metal ligand interaction (see Fig. 1b).

In the center of gravity of the two MO pairs 43/39 and 42/40, respectively, a complex orbital is predicted ($\epsilon_i = -10.65$ eV) which is predominantly localized at the 3d center (86%). Here $3d_{xz}$ and $3d_{yz}$ are combined to a linear combination where the coupling to the allene ligand is minimized.

The INDO results for *1* can be summarized as follows. Within the occupied fragment orbital set of the $Fe(CO)_4$ moiety, $3d_{xy}$ is stabilized due to a metal to ligand charge transfer. For the AO's $3d_{x^2-y^2}$ and $3d_{xz}/3d_{yz}$ no pronounced net stabilization is found as the interaction with $(\pi)_x$ and $(\pi)_z$ of the allene ligand leads to bonding and antibonding complex orbitals with significant contributions from both fragments; smaller stabilizing components in these MO's are due to the π* acceptor of the cumulative diene. The MO's 43, 42, 40 and 39 therefore cannot be classified as pure ligand or metal 3d orbitals. The metal ligand coupling is weak only in the case of MO 41, where the Fe 3d character is largest.

In Tables II and III we have collected the net charges [24] and the Wiberg bond indices [25] of *1*. The most important charge excess in the allene unit is predicted at the central carbon atom. The net charges and bond indices for the carbonyl groups clearly indicate the differences of metal to ligand charge transfer and ligand to metal coupling within the equatorial and axial CO groups. $3d_{z^2}$ of the iron center is an effective acceptor for 5σ of the axial CO ligands. The bonding interaction to the two equatorial carbonyl groups differs dramatically; the metal to ligand charge transfer is more pronounced in the case of $C_1O_1'$. The corresponding $C_1O_1'$ bond index is reduced to 2.044. A stronger ligand to metal coupling

TABLE II. Net Charges of (Tetramethylallene) Iron Tetracarbonyl According to an INDO Calculation.

| Center | Net Charge |
|---|---|
| Fe | −0.053 |
| $C_1$ | 0.235 |
| $C_2$ | 0.162 |
| $C_3$ | 0.244 |
| $C_4$ | 0.244 |
| $O_1'$ | −0.344 |
| $O_2'$ | −0.201 |
| $O_3'$ | −0.272 |
| $O_4'$ | −0.272 |
| $C_5$ | −0.126 |
| $C_6$ | −0.016 |
| $C_7$ | −0.032 |

TABLE III. Wiberg Bond Indices of *1* According to an INDO Calculation.

| Bond | Bond Index |
|---|---|
| $FeC_1$ | 0.299 |
| $FeC_2$ | 0.325 |
| $FeC_3$ | 0.466 |
| $FeC_4$ | 0.466 |
| $FeC_5$ | 0.372 |
| $FeC_6$ | 0.370 |
| $FeC_7$ | 0.031 |
| $C_1O_1'$ | 2.044 |
| $C_2O_2'$ | 2.286 |
| $C_3O_3'$ | 2.163 |
| $C_4O_4'$ | 2.163 |
| $C_5C_6$ | 1.408 |
| $C_5C_7$ | 1.903 |

is predicted for the second equatorial carbonyl function.

## The Calculated Ionization Potentials

The He(I) PE spectrum of the allene iron tetracarbonyl complex *1* has been measured by Worley and coworkers [9] while the ionization potentials of the free tetramethylallene ligand have been reported by Heilbronner *et al.* [26]. The degenerate πMO of tetramethylallene has a vertical IP of 8.53 eV [26]. In *1* four band maxima have been detected in the outer valence region. Peak ①, ② and ③ belong to a common bandsystem where ② is the maximum and ① and ③ are the low and high energy shoulders. The IP s as determined by Worley *et al.* [9] amount to 7.84, 8.24 and 8.50 eV. A second band is found at 9.28 eV.

According to Worley *et al.* [9] peak ② is assigned to the complexed πMO while ① and ③ are associated to ionization events out of Fe 3d MOs. This assignment in conflict with intensity arguments derived for transition metal compounds [27] on the one hand and differs from measured ionization energies of related iron carbonyl complexes on the other [28]. The INDO results of the foregoing section have furthermore demonstrated that the Fe 3d allene π coupling is so strong that it makes no sense to assign ionization energies on the basis of unperturbed fragment orbitals.

In Table IV and Fig. 2 the results of the Green's function approach are summarized; 14 hole- and 10 particle-functions have been considered in the calculation of the self-energy part. The renormalized ansatz of the self-energy operator allows the straightforward interpretation of the ionization events in the lower energy region. The low energy shoulder at 7.84 eV is the result of an ionization process out of the complex HOMO (MO 44). In second order a reorganization energy of 1.61 eV is predicted; this value is reduced by 0.36 eV due to the renormalization procedure. Calculated (7.86 eV) and measured (7.84 eV) IP differ only by 0.02 eV.

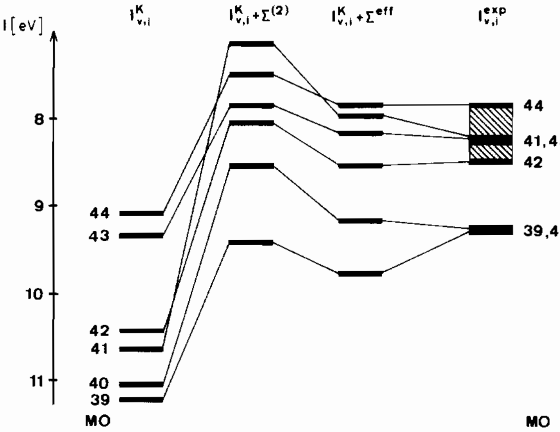

Fig. 2. Comparison between the first ionization events in the PE spectrum of *1* ($I^{exp}_{v,j}$) with calculated ionization energies assuming the validity of Koopmans' theorem ($I^K_{v,j}$) and using the corrections due to the expansion of the self-energy part in the inverse Dyson equation ($\Sigma^{(2)}$ and $\Sigma^{eff}$).

TABLE IV. Comparison between the Experimentally Determined Vertical Ionization Potentials ($I^{exp}_{v,j}$) of (Tetramethylallene) Iron Tetracarbonyl and Calculated ones Assuming the Validity of Koopmans' Theorem ($I^K_{v,j}$) and Using the Inverse Dyson Equation by a Second Order and a Renormalized Approximation for the Self-Energy Part. All Values in eV.

| Band | MO | $I^K_{v,j}$ | $I^K_{v,j} + \Sigma^{(2)}_{jj}(\omega_j)$ | $J^K_{v,j} + \Sigma^{eff}_{jj}(\omega_j)$ | $I^{exp}_{v,j}$ |
|---|---|---|---|---|---|
| 1 | 44 | 9.11 | 7.50 | 7.86 | $8.84_{sh}$[a] |
|  | 41 | 10.65 | 7.15 | 7.97 | $8.24_{max}$[b] |
|  | 43 | 9.34 | 7.85 | 8.19 |  |
|  | 42 | 10.42 | 8.06 | 8.56 | $8.50_{sh}$[a] |
| 2 | 39 | 11.22 | 8.56 | 9.19 | 9.28 |
|  | 40 | 11.04 | 9.43 | 9.76 |  |

[a] sh: shoulder. [b] max: maximum.

The band maximum (8.24 eV) is assigned to ionization events of electrons from the MOs 41 and 43. Theory predicts ionization energies of 7.97 and 8.19 eV, leading to a calculated center of gravity (8.08 eV) which is close to the experimental maximum. The largest reorganization energies are encountered in MO 41 with a Fe 3d amplitude in the orbital wave function exceeding 85%. In second order of perturbation $I^K_{v,j}$ is reduced by 3.50 eV, the contribution due to $\Sigma^{ren}(\omega)$ amounts to $-0.82$ eV. Relaxation and correlation are less important in the case of MO 43 where Koopmans' defects of 1.49 eV and $-0.34$ eV are encountered.

The high energy shoulder in the first band system is assigned to MO 42; the calculated IP differs only 0.06 eV from the experimental value. In second order of perturbation a reduction of the ionization energy of 2.36 eV is calculated. This defect is then renormalized by $-0.50$ eV.

Peak ④ thus must correspond to electron ejections out of the MO's 39 and 40. The calculated center of gravity (9.48 eV) is in sufficient agreement with the measured band maximum. Table IV demonstrates that the electronic reorganization is important in both ionization processes. The calculated defects amount to 2.66/ $-0.63$ eV in the case of MO 39 and to 1.61/ $-0.33$ eV, respectively, for MO 40.

A comparison of Table I and Table IV demonstrates that the first band system has its origin in ionization events from two antibonding metal ligand linear combinations (MO 42 and MO 43), from one MO with predominant Fe 3d character (MO 41) and from one Fe 3d fragment orbital stabilized *via* the $(\pi^*)_x$ acceptor of the cumulative diene (MO 44). The second band system then corresponds to the in-phase partner functions of the antibonding components of the first maxima (MO 39 and MO 40).

## Conclusions

It has been demonstrated that the vertical ionization energies of *1* in the outer valence region can be calculated with high accuracy (even in the framework of a semiempirical MO model) if the many-body perturbation theory beyond the HF picture is employed. It has been verified that the deviations from Koopmans' theorem are large for all ionization events. In any case, reorganization energies are predicted that exceed 1 eV. In analogy to recent studies a close correspondence between calculated Koopman's defects and the localization properties of the orbital wave function is encountered. The largest net deviation (2.68 eV) from $I^K_{v,j}$ is found in the case of the strongly localized Fe $3d_{xz}/3d_{yz}$ combination.

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