Assigning Photoelectron Spectra of Transition Metal Organometallic Complexes on the Basis of Kohn−Sham Orbital Energies

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Kohn−Sham orbital energies may be interpreted as approximate vertical ionization potentials. A new method is proposed to correct the 2−3 eV difference in the measured and predicted vertical ionization potentials produced by standard DFT functionals and basis sets. Negatives of Kohn−Sham orbital energies are shifted so that the orbital energy of the HOMO matches the negative of the first vertical ionization energy obtained as a difference in the energy of the ground-state ion and ground-state neutral molecule at the equilibrium geometry of the latter. This way, photoelectron spectra can be predicted without prior experimental information. Standard DFT functionals (B3LYP, B3PW91, BLYP, B3P86) and basis sets (LanL2DZ, 6-311G**, TZVP) were utilized to probe this method for transition metal carbonyl complexes. At the B3LYP/TZVP level, the first vertical ionization energies were computed with an average difference of 0.00 ± 0.22 eV. A good accordance between the predicted and the experimental ionization energies was achieved, and the orderings of MOs were in line with the most reliable assignments available in the literature.

Introduction

The photoelectron spectra of many transition metal complexes have been known for decades. Initial assignments are usually based on the spectra of a series of compounds or on low-level calculations such as Koopmans' theorem. In several cases, variable photon energy experiments and expensive high-level quantum chemical calculations, which became available for small organometallic complexes only in the last decade, revealed the inadequacy of these assignments. In most organometallic systems recently studied in detail, the assignment of the photoelectron spectra was incorrect.[1,37,48] Therefore, it is of great importance to have a sound tool for the assignment of the photoelectron bands of organometallic complexes. In this study, we intend to introduce a method that is based on Kohn−Sham

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theory and provides a satisfying reproduction of the photoelectron spectra at a computational cost comparable to Koopmans' theorem.

In their recent papers,[2-6] Baerends et al. showed that Kohn–Sham orbitals are better approximations to Dyson orbitals than Hartree–Fock orbitals. Politzer et al. probed this theorem and demonstrated that the negatives of orbital energies provided by standard functionals and basis sets differ from the experimental ionization energies by 1−5 eV.[7] The difference, however, depends only on the functional and basis set, almost identical for all the orbital energies, and the orderings of the orbitals match well with the experimental findings. In an earlier paper, we found that the same is true for cobalt tricarbonyl nitrosyl $(Co(CO)_3NO)$ and its phosphine derivatives.[8] Similar findings have been reported recently by other authors[9,10] for iron and silver complexes, but no detailed study on the effect of the choice of functional and basis set for the transition metal complexes has been published yet.

In the present study, we demonstrate that the first vertical ionization energy can be computed as a difference in the energy of the ground-state ion and neutral molecule with an error of less than 0.25 eV. If the negatives of the Kohn–Sham orbital energies are shifted so that the lowest one matches with the computed first ionization energy, the pattern of the photoelectron spectra can be reproduced. We probe this method on a wide range of transition metal complexes: binary carbonyls, halides, nitrosyls, half-sandwich complexes, hydrides, and alkyl derivatives.

Theoretical Background

Vertical ionization energy is related to the transition in which the ion has the same nuclear geometry as the neutral molecule, rather than its own equilibrium nuclear geometry. Hence, vertical ionization energies are obtained as the energy difference of the ion and the neutral molecule at the equilibrium nuclear geometry of the latter. This method is usually available for the first vertical ionization energy because of the high computational costs of the computation of ion excited states.

According to Koopmans' theorem,[11] the negatives of the Hartree–Fock orbital energies can be taken as vertical ionization energies: $IE_i = -\epsilon_{HF,i}$. This approximation is based on the assumption that the orbital relaxation, which arises upon ionization, can be neglected. Since orbital relaxation stabilizes

the ion, this assumption would lead to an overestimation in the ionization energy. On the other hand, correlation energy, whose absolute value is higher in the neutral molecule than in the ion, is not taken into account in the Hartree–Fock method, by definition. In many cases, the effects of the two assumptions cancel out, and Koopmans' theorem yields ionization energies with a precision better than 1 eV. Therefore, it is a powerful tool in the assignment of the photoelectron spectra of molecules with no transition metals. In the case of the transition metal complexes, however, there is a considerably larger orbital relaxation that may arise upon ionization from the central metal's orbitals, and Koopmans' theorem fails to provide not only a quantitatively but even a qualitatively adequate description of the spectra.

The physical meanings of the Kohn–Sham orbitals and orbital energies are not entirely clear. While, in the case of an exact functional, the energy of the HOMO is known to have a physical meaning as the negative of the lowest vertical ionization energy,[12] $IE_0 = -\epsilon_{KS,0}$, the other KS orbital energies are mainly regarded as auxiliary quantities without physical meaning.[13] In recent years, Baerends et al. argued that KS orbitals are physically meaningful and may be expected to be better approximations of Dyson[14] orbitals than either Hartree–Fock or semiempirical orbitals.[2] In several studies, they showed that the negatives of the Kohn–Sham orbital energies can be interpreted as approximate but rather accurate vertical ionization energies when the Kohn–Sham potentials are constructed from highly accurate ab initio (e.g., CI) densities.[3-6] For simple organic and inorganic molecules (from H_2 through SiO), the negatives of the valence orbital energies match surprisingly well with the experimental values; an average deviation of 0.08 eV was found. Recently, Cioslowski et al.[15] and Cedillo et al.[16] derived a similar Koopmans-like relation between the Kohn–Sham orbital energies and vertical ionization energies. In the study of Politzer et al., the standard functionals (BLYP, B3P86, B3LYP, B3PW91) and basis sets (STO-3G, 3-21G, 6-31G*, 6-31+G**, 6-311+G(3df,3pd)), however, gave disillusioning results, with an average deviation of 1−5 eV, and the same was found in our recent study on the phosphine derivatives of $Co(CO)_3NO$.[8] Despite this, the orbital energies could be used in the assignment of the photoelectron spectra for the following reasons: the ordering of the Kohn–Sham orbitals was in good agreement with the experimental findings and with the results of other high-level quantum chemical calculations (e.g., EOMIP-CCSD); the energy of the HOMO was not a better approximation for the first vertical ionization energy than the other Kohn–Sham orbital energies for the higher vertical ionization energies. Once the negatives of the Kohn–Sham orbital energies were shifted so that the energy of the HOMO and the experimental first vertical ionization energy matched, the average deviations decreased to around 0.2−0.3 eV. This way, the method could be used to assign the photoelectron spectra only with prior experimental information, and it was not possible to predict the vertical ionization energies of a molecule. Generally, this may not be a problem if the experimentally determined photoelectron spectrum is available and there is no doubt about the purity and the identity of the sample. However, this method does not yield a priori photoelectron spectra.

Dynamic electron correlation is taken into account in the modern correlation and hybrid functionals; the ΔDFT first vertical ionization energy, obtained as a difference in the energy of the ground-state ion and ground-state neutral molecule at the equilibrium geometry of the latter, could be expected to match well with the experimental value. This way, the experi-

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Table 1. Vertical Ionization Energies from Hartree−Fock and Density Functional Theorem Calculations

molecule	HF LanL2DZ	HF 6-311G**	B3P86 6-311G**	BLYP 6-311G**	B3PW91 6-311G**	B3LYP LanL2DZ	B3LYP 6-311G**	B3LYP TZVP	exptl
Cr(CO)$_6$	5.89	4.93	9.37	8.62	8.76	9.15	8.55	8.70	8.40[26]
Mn$_2$(CO)$_{10}$	4.91	4.22	8.81	8.02	8.19	8.45	7.97	8.00	8.02[39]
Fe(CO)$_5$	6.37	6.56	8.75	8.00	8.16	8.16	7.98	7.98	8.60[40]
Ni(CO)$_4$	4.44	3.99	9.53	9.08	8.90	9.05	8.73	8.78	8.90[41]
HMn(CO)$_5$	6.27	5.30	9.67	8.96	9.06	9.41	8.86	8.94	8.85[42]
H$_2$Fe(CO)$_4$	7.35	6.93	10.05	9.37	9.44	9.95	9.25	9.30	9.65[42]
HCo(CO)$_4$	4.79	4.28	9.53	8.95	8.92	9.28	8.74	9.04	8.90[42]
(C$_5$H$_5$)$_2$TiCl$_2$	8.01	7.69	8.88	7.84	8.31	8.30	8.82	8.16	8.04[43]
(C$_5$H$_5$)$_2$TiBr$_2$	8.26	8.33	8.69	7.63	8.12	8.10	8.08	8.04	8.29[43]
ClMn(CO)$_5$	6.63	5.74	9.72	8.87	9.11	9.39	8.98	8.97	8.87[39]
BrMn(CO)$_5$	7.90	5.77	9.57	8.68	8.97	9.24	8.84	8.88	8.83[39]
Cr(NO)$_4$	1.97	2.26	9.43	8.42	8.83	9.42	8.78	8.93	8.70[41]
Mn(CO)$_4$NO	6.10	5.17	9.42	8.30	8.81	9.12	8.65	8.76	8.40[44]
Fe(CO)$_2$(NO)$_2$	12.81	4.21	9.34	8.66	8.72	9.21	8.58	8.67	8.56[41]
Co(CO)$_3$NO	5.33	5.84	9.43	9.06	8.73	9.15	8.67	8.82	8.75[8]
(C$_5$H$_5$)$_2$Ti(CO)$_2$	5.03	4.37	6.96	6.18	6.38	6.62	6.29	6.33	6.35[45]
C$_6$H$_6$Cr(CO)$_3$	4.62	4.03	7.96	7.28	7.37	7.71	7.20	7.50	7.42[46]
C$_5$H$_5$Mn(CO)$_3$	5.57	4.66	8.66	7.93	8.06	8.35	7.91	7.95	7.92[47]
C$_5$H$_5$Co(CO)$_2$	4.28	4.05	8.15	7.41	7.56	7.69	7.44	7.49	7.55[48]
CH$_3$Mn(CO)$_5$	6.86	4.98	9.34	8.65	8.73	9.05	8.57	8.65	8.65[49]
C$_2$H$_4$Fe(CO)$_4$	5.54	5.06	9.13	8.17	8.52	8.27	8.30	8.30	8.38[50]
C$_4$H$_6$Fe(CO)$_3$	6.37	6.56	8.75	8.00	8.16	8.16	7.98	7.98	8.23[51]
AD$_{overall}$	−2.22	−3.15	+0.68	−0.10	+0.07	+0.32	−0.05	−0.00	
SD	2.04	1.41	0.20	0.24	0.19	0.31	0.27	0.22	

mental correction can be substituted by a pure quantum chemical correction and the photoelectron spectra can be predicted without prior experimental information. The additional computational cost of the ΔDFT calculation is practically negligible, as it requires only a single-point calculation on the already determined neutral equilibrium geometry.

Computational Details

This study focuses on the transition metal binary carbonyl complexes and their derivatives: hydrides, halides, nitrosyls, half-sandwiches, and alkyl and alkene derivatives. Twenty-two different compounds were investigated with titanium ((η^5-C$_5$H$_5$)$_2$Ti(CO)$_2$, (η^5-C$_5$H$_5$)$_2$TiCl$_2$, (η^5-C$_5$H$_5$)$_2$TiBr$_2$), chromium (Cr(CO)$_6$, Cr(NO)$_4$, (η^6-C$_6$H$_6$)Cr(CO)$_3$), manganese (Mn$_2$(CO)$_{10}$, HMn(CO)$_5$, ClMn-(CO)$_5$, BrMn(CO)$_5$, Mn(CO)$_4$NO, (η^5-C$_5$H$_5$)Mn(CO)$_3$, CH$_3$Mn-(CO)$_5$), iron (Fe(CO)$_5$, H$_2$Fe(CO)$_4$, Fe(CO)$_2$(NO)$_2$, (η^2-C$_2$H$_4$)Fe-(CO)$_4$, (η^4-C$_4$H$_6$)Fe(CO)$_3$), cobalt (HCo(CO)$_4$, Co(CO)$_3$NO, (η^5-C$_5$H$_5$)Co(CO)$_2$), and nickel (Ni(CO)$_4$) atoms as metal centers. Hartree−Fock calculations were utilized with the LanL2DZ[17] and 6-311G**[18] basis sets, and Kohn−Sham orbital energies were obtained with the combination of the 6-311G** basis set and BLYP,[19,20] B3LYP,[21,20] B3P86,[21,22] and B3PW91[21,23] functionals. In the case of the B3LYP functional, the LanL2DZ and TZVP[24] basis sets were also employed. The optimized geometries of the neutral molecules were justified to be minima by the absence of imaginary frequencies. In the special case of benzene chromium tricarbonyl ((η^6-C$_6$H$_6$)Cr(CO)$_3$), the geometry optimization always converged with a negative lowest vibrational frequency, which was assigned to the internal rotation of the benzene ligand. In all other cases, negative frequencies were absent.

To characterize the effectiveness of the different combinations of functionals and basis sets, the predicted ionization energies were compared to the experimental values to see how the photoelectron spectrum could be reproduced. Even more importantly, the ordering of the MOs was compared to the most reliable assignments available in the literature.

In the photoelectron spectra of transition metal complexes, the peaks at higher ionization energies, typically over 14 eV, are not resolved and the experimental ionization energies are ambiguous. That is why we considered only the ionization energies below 14−15 eV. In those rare exceptions, where well-resolved photoelectron spectra are available in the literature, a more detailed

description of the spectrum and the ordering of the molecular orbitals are given in the Results section. In other cases, only statistical values are listed in Table 2. The average absolute differences (AAD) in the predicted and experimental ionization potentials with the standard deviations (SD) of the differences are given for each molecule. The overall average absolute differences (AAD$_{overall}$) and overall average differences (AD$_{overall}$) are also listed in Table 2. Due to the extensive investigations of the selected molecules, detailed assignments of the spectra are available in the literature. The assignments are based on variable photon energy experiments and high-level quantum chemical calculations. The variable photon energy experiments provide direct information on the composition of the corresponding molecular orbitals, and the applied quantum chemical methods include Green's function, configurational interaction (CI), and coupled cluster (EOMIP-CCSD) calculations, which are all superior to Koopmans' theorem.

Wherever possible, we compared our findings to the most recent experimental and theoretical studies available in the literature. Therefore, we did not simply assign the calculated orbital energies in the order in which they occur, but always checked if the symmetry of the orbitals agreed with the states to which the photoelectron peaks were assigned. Even in those cases where a broad band consisted of more than one unresolved photoelectron transitions, the overall structure of the spectra were well reproduced and with the help of the available high-level quantum chemical calculations the orbital energies could be associated unambiguously with the photoelectron bands. When more than one orbital was associated with one ionization energy, the highest orbital energy was used in the statistics. An example of how the orbital energies were assigned to the photoelectron bands can be found in the Results section (Table 3).

All quantum chemical calculations were carried out using the Gaussian 03 Rev. C.02 quantum chemical code.[25]

Results

First Vertical Ionization Energies. The lowest vertical ionization energies were calculated as the difference in the energies of the ground-state ion and neutral molecule at the equilibrium geometry of the latter. The obtained values along with the experimental ones are listed in Table 1. At the Hartree−Fock level, they differ from the experiment by 2−2.5 eV, which

Table 2. Average Differences and the Standard Deviations of Differences for Each Compound: (a) Binary Carbonyls, Hydrides, and Halides; (b) Nitrosyls, Half-Sandwiches, and Alkyl Derivatives

(a)

molecule		HF LanL2DZ	HF 6-311G**	B3P86 6-311G**	BLYP 6-311G**	B3PW91 6-311G**	B3LYP LanL2DZ	B3LYP 6-311G**	B3LYP TZVP
$Cr(CO)_6$	AAD	3.16	2.90	0.48	1.00	0.26	0.32	0.30	0.26
	SD	0.84	1.08	0.28	0.43	0.17	0.25	0.20	0.15
$Mn_2(CO)_{10}$	AAD	2.68	2.31	1.03	0.21	0.42	0.82	0.53	0.37
	SD	0.54	0.63	0.25	0.29	0.24	0.38	0.25	0.25
$Fe(CO)_5$	AAD	1.94	1.58	0.29	1.00	0.41	0.63	0.69	0.71
	SD	1.07	0.94	0.23	0.54	0.46	0.52	0.33	0.33
$Ni(CO)_4$	AAD	2.33	1.98	0.68	0.45	0.31	0.33	0.28	0.24
	SD	0.75	0.96	0.46	0.35	0.27	0.28	0.25	0.19
carbonyls	AAD$_{overall}$	2.53	2.19	0.62	0.67	0.35	0.53	0.45	0.40
	SD	0.80	0.90	0.31	0.40	0.28	0.36	0.26	0.23
$HMn(CO)_5$	AAD	2.03	1.67	0.66	0.27	0.21	0.36	0.17	0.19
	SD	0.98	0.62	0.25	0.17	0.08	0.28	0.19	0.15
$H_2Fe(CO)_4$	AAD	2.38	2.40	0.24	0.38	0.42	0.29	0.62	0.58
	SD	1.64	1.14	0.13	0.19	0.20	0.12	0.23	0.23
$HCo(CO)_4$	AAD	2.67	2.31	0.82	0.14	0.35	0.55	0.36	0.41
	SD	1.06	0.96	0.42	0.12	0.25	0.38	0.14	0.26
hydrides	AAD$_{overall}$	2.36	2.13	0.57	0.26	0.33	0.40	0.38	0.39
	SD	1.23	0.90	0.27	0.16	0.18	0.26	0.19	0.21
$(C_5H_5)_2TiCl_2$	AAD	0.82	0.79	0.27	0.99	0.32	0.43	0.22	0.56
	SD	0.13	0.18	0.08	0.33	0.25	0.29	0.12	0.27
$(C_5H_5)_2TiBr_2$	AAD	0.55	0.59	0.23	1.02	0.37	0.47	0.44	0.56
	SD	0.12	0.15	0.16	0.29	0.18	0.22	0.21	0.29
$ClMn(CO)_5$	AAD	1.40	0.98	0.75	0.95	0.65	0.56	0.73	0.70
	SD	0.89	0.98	1.05	0.49	0.78	0.82	0.62	0.64
$BrMn(CO)_5$	AAD	1.36	0.99	0.76	0.89	0.61	0.61	0.60	0.59
	SD	0.86	0.74	0.95	0.46	0.69	0.74	0.60	0.62
halides	AAD$_{overall}$	1.03	0.84	0.50	0.96	0.49	0.52	0.50	0.60
	SD	0.50	0.51	0.56	0.39	0.48	0.52	0.39	0.46

(b)

molecule		HF LanL2DZ	HF 6-311G**	B3P86 6-311G**	BLYP 6-311G**	B3PW91 6-311G**	B3LYP LanL2DZ	B3LYP 6-311G**	B3LYP TZVP
$Cr(NO)_4$	AAD	3.40	3.12	1.77	0.35	1.16	1.38	1.08	1.24
	SD	2.46	2.60	1.02	0.32	1.02	0.62	0.99	1.04
$Mn(CO)_4NO$	AAD	1.53	1.44	1.15	0.17	0.55	0.85	0.40	0.52
	SD	1.03	0.31	0.14	0.19	0.14	0.24	0.12	0.13
$Fe(CO)_2(NO)_2$	AAD	1.61	1.54	0.74	0.37	0.26	0.62	0.24	0.24
	SD	2.20	2.02	0.36	0.48	0.22	0.46	0.18	0.23
$Co(CO)_3NO$	AAD	2.77	2.41	0.92	0.31	0.16	0.61	0.18	0.29
	SD	1.78	1.13	0.24	0.11	0.16	0.28	0.16	0.23
nitrosyls	AAD$_{overall}$	2.33	2.13	1.15	0.30	0.53	0.87	0.48	0.57
	SD	1.87	1.52	0.44	0.28	0.39	0.40	0.36	0.40
$(C_5H_5)_2Ti(CO)_2$	AAD	1.13	0.97	0.39	1.18	0.69	0.70	0.75	0.72
	SD	0.55	0.32	0.36	0.71	0.48	0.36	0.48	0.48
$C_6H_6Cr(CO)_3$	AAD	1.25	1.06	0.34	0.77	0.46	0.32	0.54	0.29
	SD	0.97	0.97	0.20	0.63	0.42	0.26	0.35	0.33
$C_5H_5Mn(CO)_3$	AAD	2.00	1.82	0.45	0.30	0.28	0.38	0.34	0.33
	SD	0.73	0.43	0.29	0.26	0.11	0.18	0.24	0.21
$C_5H_5Co(CO)_2$	AAD	1.76	1.42	0.79	0.26	0.26	0.25	0.22	0.20
	SD	1.18	0.89	0.27	0.17	0.20	0.22	0.12	0.11
half-sandwich complexes	AAD$_{overall}$	1.54	1.32	0.49	0.63	0.42	0.41	0.46	0.39
	SD	0.86	0.65	0.28	0.44	0.30	0.26	0.30	0.28
$CH_3Mn(CO)_5$	AAD	1.74	1.30	0.41	0.43	0.34	0.43	0.44	0.34
	SD	1.00	0.81	0.26	0.39	0.31	0.17	0.37	0.37
$C_2H_4Fe(CO)_4$	AAD	1.76	1.64	0.58	0.64	0.39	0.42	0.37	0.33
	SD	1.40	1.22	0.41	0.60	0.32	0.36	0.30	0.30
$C_4H_6Fe(CO)_3$	AAD	2.18	1.85	0.35	0.59	0.32	0.30	0.35	0.34
	SD	1.17	1.08	0.29	0.35	0.23	0.15	0.23	0.21
alkyl and alkene derivatives	AAD$_{overall}$	1.89	1.60	0.45	0.55	0.35	0.38	0.39	0.34
	SD	1.19	1.04	0.32	0.45	0.29	0.23	0.30	0.29
overall	AAD$_{overall}$	1.93	1.69	0.64	0.58	0.42	0.53	0.44	0.46
	SD	1.06	0.91	0.37	0.36	0.33	0.34	0.30	0.32
	AD$_{overall}$			0.58	−0.43	−0.02	0.20	−0.11	−0.09
	SD			0.41	0.47	0.41	0.51	0.39	0.40

is due to the complete neglect of electron correlation and is a well-known phenomenon in photoelectron spectroscopy. The DFT functionals reproduce the first vertical ionization energies with an error of only 0.2−0.6 eV because the electron correlation is taken into account in the functionals. The average differences and the standard errors for each functional are also listed in Table 1. The B3LYP functional with the TZVP basis set proved to be the most efficient tool. It predicted the first vertical ionization energies with a difference of 0.00 ± 0.22 eV. Both the precision and the accuracy decrease if a valence double-ζ basis set is used without polarization functions: at the B3LYP/LanL2DZ level an average difference of +0.32 ± 0.30 eV was

Table 3. Assignment of the Photoelectron Spectrum of $(\eta^5\text{-}C_5H_5)Mn(CO)_3$

exptl		Green's function[d]		HF 6-311G**[e]		B3PW91 6-311G**	
IE[b]	MO character[a]	IE	MO character	IE	MO character	IE	MO character
7.92	a′, a″, a′	8.51	a′, a″, a′	8.26	a′, a″	8.06	a″, a′, a′
8.22	(Mn(CO)₃ e + a₁)	8.86	Mn(d)	8.38	(Cp π)	8.06	(Mn(d))
		8.87				8.50	
10.03	a′, a″	10.21	a′, a″	10.13 10.17	a′, a″	9.61	a′, a″
	(Cp π, e₁″)	10.28	Cp(π), Mn(d)	10.70	a′ (Mn(d))	9.70	(Cp π)
12.68	a′, a′, a″			14.05	a′, a″, a′	12.42	a′, a″, a′
	(Cp π, 1a₂″, σ 3 e₂′)			14.07	(Cp(π))	12.66	(Cp(π))
				14.14		12.66	

[a] See ref 37. [b] Pongor, C. To be published. [c] Lichentberger, D. L.; Fenske, R. F. *J. Am. Chem. Soc.* **1976**, *98*, 50. [d] See ref 38.
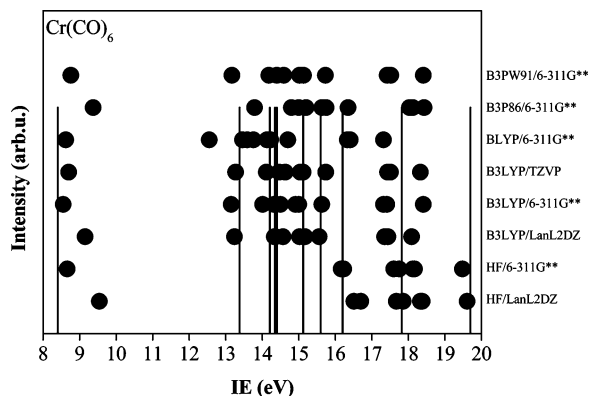
Figure 1. Experimental (vertical lines) and predicted vertical ionization energies (dots) of $Cr(CO)_6$. Note that a correction was applied to the negatives of Kohn−Sham orbital energies but not to Koopmans' theorem. See text for details.

Figure 2. Experimental (vertical lines) and predicted vertical ionization energies (dots) of $HMn(CO)_5$. Note that a correction was applied to the negatives of Kohn−Sham orbital energies but not to Koopmans' theorem. See text for details.

obtained. The parametrization of the functional also affects the results. Although the replacement of the correlation functional of Lee, Yang, and Parr with Perdew and Wang's correlation functional causes only a slight change in the deviations (-0.05 ± 0.27 eV and $+0.07 \pm 0.19$ eV at the B3LYP/6-311G** and B3PW91/6-311G** levels, respectively), Perdew's P86 functional provides significantly lower accuracy ($+0.68 \pm 0.20$ eV at the B3P86/6-311G** level).

Binary Carbonyls ($Cr(CO)_6$, $Mn_2(CO)_{10}$, $Fe(CO)_5$, $Ni(CO)_4$). Sufficiently resolved He I and He II spectra of $Cr(CO)_6$ are available in the literature.[26] The structures of the measured and predicted photoelectron spectra are shown in Figure 1. The DFT functionals give very good results up to 16 eV, but the higher ionization energies are slightly overestimated. At the B3LYP/6-311G**, B3LYP/TZVP, and B3PW91/6-311G** levels almost exact matches with the experimental spectrum were obtained. For comparison, the results of Koopmans' theorem are also shown. According to the original He I/He II study along with the findings of the variable photon energy experiment of Yu et al.,[27] the first peak of the spectrum must be assigned to a molecular orbital with strong d character, while the d character of the subsequent orbitals is much less significant. With all the utilized functionals, the composition and the ordering of the Kohn−Sham orbitals agreee with these findings. According to the Mulliken population analysis, the Cr(d) atomic orbitals have siginificant contribution to the HOMO (t_{2g}). The next orbital (t_{1u}) has almost no d character compared to the subsequent e_g orbital. The orbitals with higher ionization energies can be described as molecular orbitals localized on the ligands.

For the other carbonyls, only the derived statistics are presented in Tables 1 and 2. The B3P86 and BLYP ionization energies provide the worst agreement with the experimental values, while the B3LYP/TZVP values are at the other end of
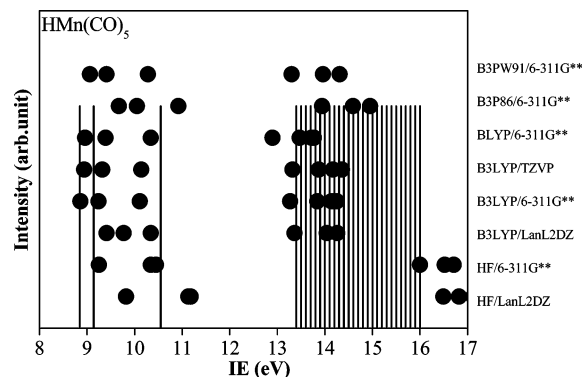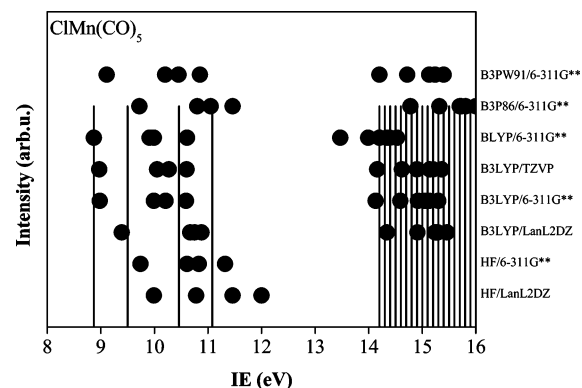

Figure 3. Experimental (vertical lines) and predicted vertical ionization energies (dots) of $ClMn(CO)_5$. Note that a correction was applied to the negatives of Kohn−Sham orbital energies but not to Koopmans' theorem. See text for details.

the spectrum. The case of $Fe(CO)_5$ is an exception, in which a surprising reverse trend can be observed: at the B3P86/6-311G** level, the ionization energies are predicted with an error of 0.29 ± 0.23 eV, while the average absolute difference is 0.71 ± 0.33 eV with the B3LYP functional and TZVP basis set. However, this level of theory is adequate for the assignment of the photoelectron spectra of $Fe(CO)_5$, as the ordering of the MOs is correct here as well. Overall, the B3LYP/TZVP level reproduced the photoelectron spectra of binary transition metal carbonyls with an average difference of 0.40 ± 0.23 eV. The orderings of MOs are in accordance with the latest experimental and theoretical studies[26,28−32,34] for all carbonyls in this study.

Hydrides ($HMn(CO)_5$, $H_2Fe(CO)_4$, $HCo(CO)_4$). Predicted and measured[42] vertical ionization energies of $HMn(CO)_5$ are shown in Figure 2. Three peaks between 8 and 11 eV and the onset of a broad, unresolved band at approximately 13.5 eV
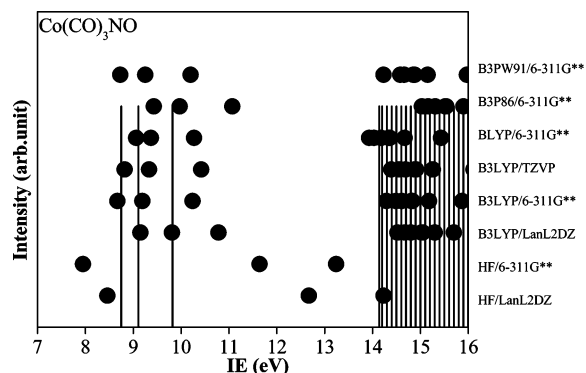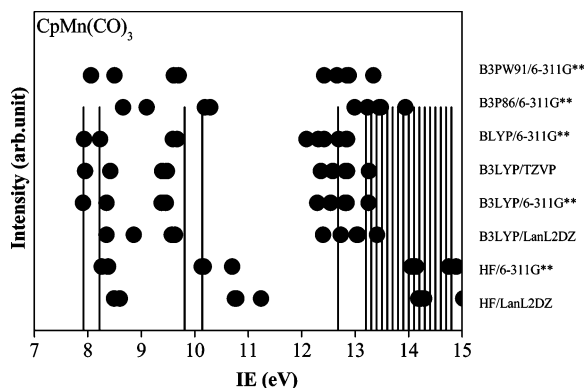
Figure 4. Experimental (vertical lines) and predicted vertical ionization energies (dots) of Co(CO)$_3$NO. Note that a correction was applied to the negatives of Kohn−Sham orbital energies but not to Koopmans' theorem. See text for details.

Figure 5. Experimental (vertical lines) and predicted vertical ionization energies (dots) of CpMn(CO)$_3$. Note that a correction was applied to the negatives of Kohn−Sham orbital energies but not to Koopmans' theorem. See text for details.

can be identified. These parameters are best reproduced at the B3LYP/6-311G**, B3LYP/TZVP, and B3PW91/6-311G**

levels with average absolute differences of 0.17 ± 0.19, 0.19 ± 0.15, and 0.21 ± 0.08 eV, respectively.

The ordering of the Kohn−Sham orbitals (IE(e, Mn−CO(π^*)) < IE(b$_1$, Mn−CO(π^*)) < IE(a$_1$, Mn−H) < IE(b$_2$, Mn−CO(σ^*)) with all utilized functionals agrees well with the different studies on the electronic structure of HMn(CO)$_5$[33] and contradicts the obviously wrong ordering suggested by Koopmans' theorem (IE(a$_1$, Mn−H) < IE(e, Mn−CO(π^*)) < IE(b$_1$, Mn−CO(π^*)) < IE(b$_2$, Mn−CO(σ^*)).

However, BLYP proves to be a more efficient tool than the other functionals for the other hydrides. The average absolute difference is 0.27 ± 0.17 eV at the BLYP/6-311G** level. The statistics for the B3LYP/TZVP and B3PW91/6-311G** levels are 0.39 ± 0.21 and 0.33 ± 0.18 eV, respectively. The orderings of MOs are in line with published quantum chemical calculations and experiments.[33,34]

Halides ((η^5-C$_5$H$_5$)$_2$TiCl$_2$, (η^5-C$_5$H$_5$)$_2$TiBr$_2$, ClMn(CO)$_5$, BrMn(CO)$_5$). The highest differences in the predicted and measured vertical ionization potentials were found in the case of halides. From the statistics (Table 2) it can be seen that not only the averages (0.5−0.9 eV) but the standard deviations of the absolute differences (0.4−0.5 eV) are also significant, especially when compared with other types of compounds. The photoelectron spectrum of ClMn(CO)$_5$ is shown with the predicted ionization energies in Figure 3. The overall spectrum can be reproduced with the employed functionals, but the split of the peaks is smaller than in the experiment. The B3P86 functional with the 6-311G** basis set and the B3LYP functional with the LanL2DZ basis set overestimate the ionization energies. The overall structures of the spectra are well reproduced, but the individual peaks in the 9−11 eV region cannot be assigned unambiguously to the calculated ionization energies. The average differences are around 0.8 eV with standard deviations of around 0.7 eV. The most recent variable photon energy study[35] on XMn(CO)$_5$ (X = Cl, Br) confirms that the ordering of the molecular orbitals in the 9−11 eV region is IE(a$_1$, Mn−X) < IE(e, X) < IE(b$_2$, Mn) < IE(e, Mn). It is
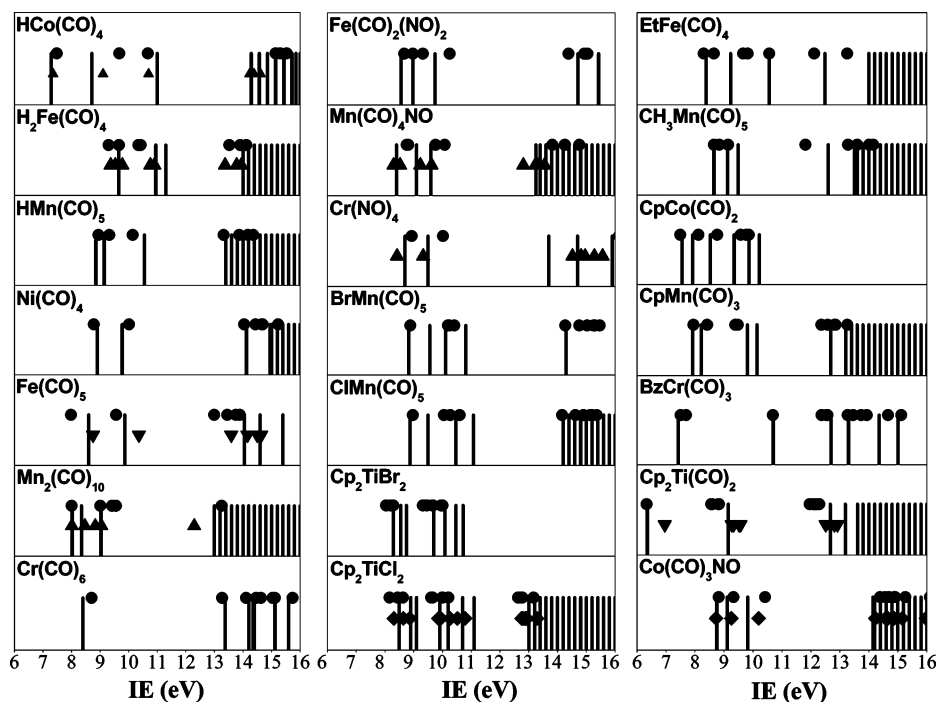

Figure 6. Experimental and predicted vertical ionization energies of the examined transition metal complexes (●, B3LYP/TZVP; ▲, BLYP/6-311G**; ▼, B3P86/6-311G**; ◆, B3PW91/6-311G**).

interesting to point out that our finding is that the ordering of the first two orbitals is the reverse of the published results: IE(e, X) < IE(a_1, Mn−X) < IE(b_1, Mn) < IE(e, Mn).

Nitrosyls ($Cr(NO)_4$, $Mn(CO)_4NO$, $Fe(CO)_2(NO)_2$, $Co(CO)_3NO$). The measured and predicted vertical ionization energies of $Co(CO)_3NO$ are shown in Figure 4. The structure of the spectrum is well reproduced at the B3LYP/6-311G**, B3LYP/TZVP, and B3PW91/6-311G** levels. The ordering of the molecular orbitals (IE(e, Co(d)) < IE(a_1,Co(d)) < IE(e, Co(d)) < IE(e, CO)) is in good agreement with the recently published He I/He II photoelectron study and CCSD-EOMIP calculations,[8] as well as the CI study of Lisini et al.[36] From the statistics (Table 2), it can be seen that the B3LYP and B3PW91 functionals provide the vertical ionization energies with a relatively high error of 0.5−1.0 eV in the case of $Cr(NO)_4$ and $Mn(CO)_4NO$, but the error is reduced to 0.2−0.3 eV in the cases of $Fe(CO)_2(NO)_2$ and $Co(CO)_3NO$. The average absolute difference obtained with the BLYP functional is 0.30 eV; that is, the BLYP functional is more efficient in the case of nitrosyl complexes than other functionals, similarly to the case of hydride derivatives.

Half-Sandwich Complexes ((η^5-C_5H_5)$_2$Ti(CO)$_2$, (η^6-C_6H_6)-Cr(CO)$_3$, (η^5-C_5H_5)Mn(CO)$_3$, (η^5-C_5H_5)Co(CO)$_2$). The structure of the He I photoelectron spectrum of (η^5-C_5H_5)Mn(CO)$_3$ along with the predicted ionization energies is shown in Figure 5. Although no exact match with any of the utilized functionals was obtained, the structure of the spectrum was reproduced well at the B3LYP/TZVP and B3PW91/6-311G** levels. The ordering of MOs is in line with the variable-energy photon source experiments[37] and high-level quantum chemical calculations,[38] as seen in Table 3.

From the statistics (Table 2), one can conclude that the B3LYP/TZVP level turned out to be the most efficient method for the half-sandwich complexes (with an average absolute difference of 0.39 ± 0.28 eV). The BLYP functional, which was also found to be efficient for some groups of complexes (see hydrides and nitrosyls), turned out to be a less promising choice here.

Alkyl and Alkene Derivatives ($CH_3Mn(CO)_5$, (η^2-C_2H_4)-Fe(CO)$_4$), (η^4-C_4H_6)Fe(CO)$_3$). The reproductions of the structure of the photoelectron spectra are characterized by the statistics in Table 2. B3LYP/6-311G**, B3LYP/TZVP, and B3PW91/6-311G** reproduce the spectral features with almost equal efficiency. The average absolute differences are 0.39, 0.34, and 0.35 eV, respectively. The averages of the standard deviations do not vary significantly either: 0.30, 0.29, and 0.29 eV for the three levels, respectively. On the other hand, with the BLYP functional, an average difference of 0.55 eV was found.

Conclusion

Based on the theoretical studies of Baerends et al., pointing out that negatives of Kohn−Sham orbital energies can be interpreted as vertical ionization energies, a method of predicting vertical ionization energies has been proposed and tested on a wide range of derivatives of transition metal binary carbonyls. The first vertical ionization energies were computed as the difference in the energy of the ground-state ion and neutral molecule at the equilibrium geometry of the latter. The calculated ionization energies differ from the experiment by 0.00 ± 0.22 eV when the B3LYP functional is used with the TZVP basis set. Vertical ionization energies of a wide range of transition metal complexes were calculated by shifting the negatives of the Kohn−Sham orbital energies so that the one
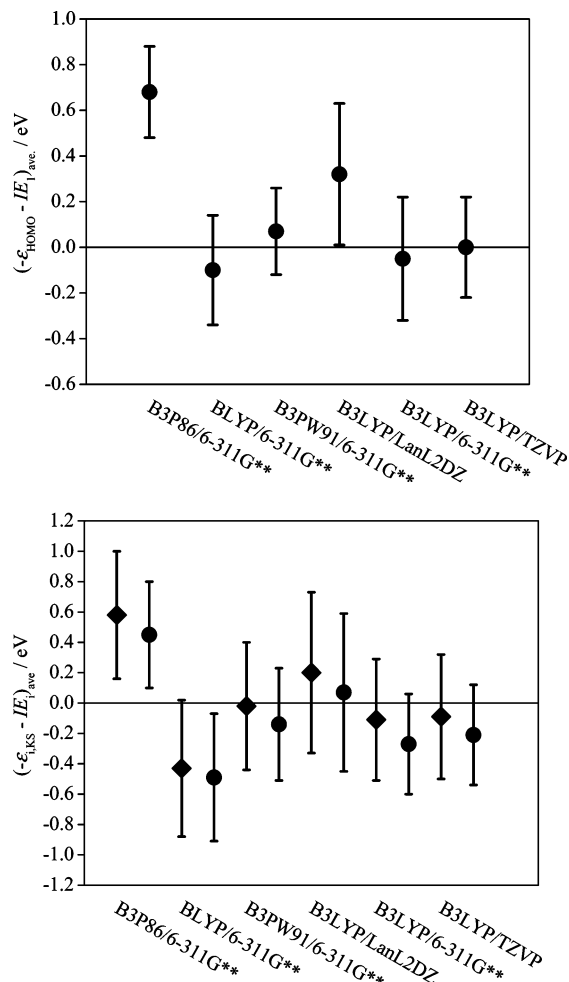

Figure 7. (a) Average differences in the calculated and experimental vertical ionization energies at each level functional and basis set. (b) Average differences in the calculated and experimental vertical ionization energies for the different functionals and basis sets: (◆) the average difference with the average standard deviation of the differences for all the studied compounds; (●) the average difference without the halides and nitrosyls. One can see that without the halides and nitrosyls the error of the predicted ionization energies is smaller.

corresponding to the HOMO matched with the calculated first vertical ionization energy. With the exception of halides, the photoelectron spectra were reproduced properly at the B3LYP/TZVP level for a broad choice of transition metal complexes. The photoelectron spectra and the predicted ionization energies are summarized in Figure 6. For each complex, the B3LYP/TZVP results are indicated. In five cases ($Mn_2(CO)_{10}$, $H_2Fe(CO)_4$, $HCo(CO)_4$, $Cr(NO)_4$, $Mn(CO)_4NO$), the BLYP/6-311G**, in two cases ($Fe(CO)_5$, $Cp_2Ti(CO)_2$), the B3P86/6-311G**, and in two cases (Cp_2TiCl_2, $Co(CO)_3NO$), the B3PW91/6-311G** levels did better than the B3LYP functional with the TZVP basis set. These results are also shown in Figure 6. It is interesting to point out that the BLYP functional with the 6-311G** basis set outdid the B3LYP and B3PW91 functionals in the case of hydrides and nitrosyls, but proved to be a much less efficient functional for all the other compounds. The average differences in the predicted and experimental first ionization energies with the average standard deviations are indicated in Figure 7a for the different levels of theory, and the overall average differences are shown in Figure 7b. One can see the same trend in the two figures; that is, the quality of the reproduction of the photoelectron spectrum strongly depends

on the precision of the first ionization energy. This way, an average difference of -0.09 ± 0.40 eV was found at the B3LYP/TZVP level. In Figure 7b, rectangles indicate the average differences calculated for all the investigated molecules, while dots show the average differences without the halides and nitrosyls, in which cases the method turned out to be less efficient. In this latter set of molecules, the average difference was found to be -0.21 ± 0.33 eV at the B3LYP/TZVP level. The orderings of MOs were in remarkable agreement with the experimental findings derived from the latest variable photon energy experiments and high-level quantum chemical calculations for all of the complexes studied except for the $XMn(CO)_5$ (X = Cl, Br) complexes, where a reverse order of the two highest energy molecular orbitals was found.

Considering the efficiency in reproducing the photoelectron spectra and the overall average differences, the B3LYP functional with the TZVP basis set can be recommended as a low-cost aid in the assignment of the photoelectron spectra of transition metal complexes. Since a successive ion single-point calculation starting from the B3LYP-optimized geometry is quite inexpensive, in some cases it may be helpful to repeat the calculations with a different functional to check whether these calculated absolute ionization energies produce a better match with the experimental IEs for the particular organometallic complex. Because the order of the calculated MO energies does not vary between the functionals, this may give additional confidence in the assignment of the spectrum.

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