BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 49(4), 929—932 (1976)

Modified INDO Calculations of the Electronic Structure of Transition Metal Carbonyl Compounds

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(Received November 4, 1975)

An INDO molecular-orbital method developed for the treatment of systems involving 3d orbitals have been applied to transition metal carbonyl complexes $Ni(CO)_4$, $Cr(CO)_6$, and $Fe(CO)_3$(butadiene). The Koopmans-theorem values of ionization potentials are found to be in excellent agreement with the observed photoelectron-spectroscopic data, except for the cases where a considerable reorganization in electronic distribution accompanies the ionization process. The INDO molecular orbital functions compare well with those reported on the basis of *ab initio* calculations.

There appears to be an increasing necessity of devising reliable theoretical methods for use in the investigation of chemistry of transition metal complexes. Fortunately, recent advances in the He(I) photoelectron spectroscopy provide data useful for testing the validity of theoretical calculations.

We here report the results of INDO calculations for transition metal carbonyl compounds: $Ni(CO)_4$, $Cr(CO)_6$, and $Fe(CO)_3$(butadiene). The primary aim of this work is to examine the vertical ionization potentials of these compounds and thereby to assess the semiempirical procedure here adopted. It will be shown that our method is at least as useful an approximation as *ab initio* calculations hitherto reported.

Computational Method

Since the INDO procedure has already been described in detail elsewhere,[1] we will only give a brief outline here. The basis atomic orbitals consist of 3d, 4s, and 4p functions for central metals and of 2s and 2p functions for first row atoms. Zerner's single-parameter atomic orbitals[2] have been employed for Ni and Fe atoms, Burns' function[3] for Cr atom, and Clementi's functions[4] for ligand atoms. In evaluating one-center integral parameters, we have adopted the same method as described in Ref. 1 using the data compiled by Oleari *et al.*[5–7] and by Hinze and Jaffé.[8] Table 1 summarizes the orbital exponents of the basis set and the valence-orbital ionization potentials (VOIP), together with various two-electron integral values adopted for the transition metals.

Table 1. Atomic parameters[a] of the transition metals studied

	Cr	Fe	Ni
Exponents			
3d	2.450	2.722	2.960
4s	1.300	1.370	1.473
4p	0.775	1.370	1.473
VOIP (eV)	(d^4s^2)	(d^6s^2)	(d^{10})
I_d	11.64	12.64	5.02
I_s	6.11	6.73	7.19
I_p	3.23	3.24	3.10
Two-electron integrals (eV)			
J_{sp}	5.955	6.414	6.872
$J_{pp'}$	5.233	5.500	5.768
J_{sd}	8.948	9.509	10.088
$J_{z,zx}$	7.601	8.091	8.583
J_{x,z^2}	7.404	7.867	8.331
$J_{z,xy}$	7.295	7.755	8.215
J_{z,z^2}	7.709	8.203	8.699
$J_{z^2,xy}$	12.590	13.799	15.015
$J_{z^2,xz}$	13.124	14.383	15.644
J_{xy,x^2-y^2}	13.302	14.578	15.854
$J_{xz,yz}$	12.768	13.993	15.225

a) The other parameters, $U_{\mu\mu}$ and $g_{\mu\nu}$, are tabulated in Ref. 7. The exchange integrals $K_{\mu\nu}$ can be obtained from $K_{\mu\nu}=2(J_{\mu\nu}-g_{\mu\nu})$.

The molecular geometries used for calculations were taken from the experimental results. The interatomic distances and coordinate axes chosen are given in Figs. 1 to 3 for $Ni(CO)_4$,[9] $Cr(CO)_6$,[10] and $Fe(CO)_3$ (butadiene),[11] respectively.

Results and Discussion

$Ni(CO)_4$. The He(I) photoelectron spectrum for $Ni(CO)_4$ was recorded by Lloyd and Schlag[12]

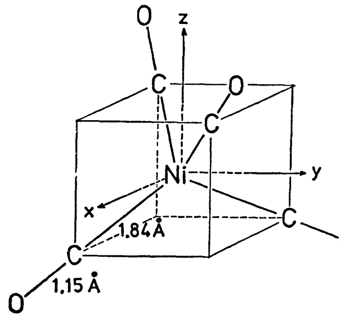

Fig. 1. Coordinate systems and structure for $Ni(CO)_4$ (T_d).

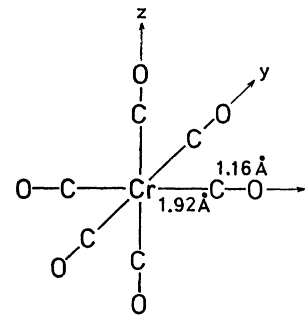

Fig. 2. Coordinate systems and structure for $Cr(CO)_6$ (O_h).

TABLE 2. COMPUTED AND EXPERIMENTAL IONIZATION POTENTIALS OF $Ni(CO)_4$ (in eV)

Symmetry[a)]	This calculation		*Ab initio*			SCF-X_α[e)]	Expt.[f)]
	$-\varepsilon$	Nature	$-\varepsilon$[b)]	$-\varepsilon$[c)]	ΔSCF[d)]		
$^2T_2$	9.00	$d_{xz},d_{yz},d_{x^2-y^2}$	11.67	10.75	7.0	9.3	8.8
^2E	9.72	d_{xy},d_{z^2}	13.49	12.82	7.8	10.7	9.7
$^2T_2$	14.09	σ(CO)	18.48	17.52		12.0(t_1) 12.2(t_2)	14.8

a) Irreducible representation of the point group T_d.
b) Ref. 15. c) Ref. 17. d) Ref. 16. e) Ref. 18. f) Refs. 12 and 13.

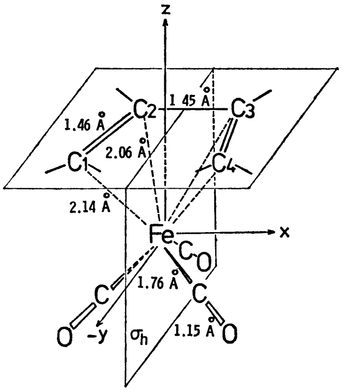

Fig. 3. Coordinate systems and structure for $Fe(CO)_3$-(butadiene)(C_s). The distances between C and H in the butadiene moiety are assumed to be 1.08 Å.

and by Green *et al.*[13)] The first three bands have been assigned to the ionizations from the t_2(Ni-d), e(Ni-d), and t_2(CO) orbital sets.

Table 2 shows the lowest three vertical ionization potentials (IP) obtained by the present calculation. The first two IP's correspond to the removal of an electron from the orbitals which have mainly a metal 3d character with $5t_2$[14)] (d_{xz}, d_{yz}, and $d_{x^2-y^2}$) and 2e (d_{xy} and d_{z^2}) symmetries. The third IP, on the other hand, is ascribable to the $4t_2$ orbital which is composed chiefly of the CO σ orbitals. The IP values calculated are in excellent agreement with the experimental data for ionization potential.

Also listed in Table 2 are the results of *ab initio* calculations by Hillier *et al.*[15,16)] and by Demuynck and Veillard,[17)] together with the IP values calculated by Johnson and Wahlgen[18)] using the SCF-X_α scattered-wave method. The *ab initio* calculations predict the same ordering of ionization orbitals as does our INDO treatment. However, the numerical values of IP do not agree well with observation; the Koopmans-theorem values are 2—4 eV higher than the observed IP while the ΔSCF values too low by *ca.* 2 eV. The SCF-X_α data are apparently more satisfactory than the results of *ab initio* calculations. They are yet no better than the IP values obtained by the present INDO approximation.

The excellent agreement of the INDO results with observation may perhaps be largely fortuitous. However, it appears that the semiempirical method used deserves credit as being a useful working tool.

$Cr(CO)_6$. The He(I) photoelectron spectrum for $Cr(CO)_6$[19)] has two peaks at 8.4 and 13.3 eV and a broad band in the range 14—16 eV. The first peak has been assigned to the ionization from the predominantly metal $2t_{2g}$ orbital. The second peak, which is much separated in energy from the first, might be due to the removal of an electron from either the $3e_g$ or (and) $4t_{1u}$ orbital; the assignment has not yet been settled. The order of the highest three occupied orbitals calculated by the self-consistent-charge-and-configuration(SCCC) method[20)] is $4t_{1u}<3e_g<2t_{2g}$, while *ab initio*[15)] and self-consistent-charge (SCC) molecular-orbital[21)] calculations result in the order $3e_g<4t_{1u}<2t_{2g}$.

In Table 3, the first three IP obtained by the INDO and *ab initio* calculations are compared with the experimental values. The assignment of the second and third IP is that predicted by Hillier and Saunders,[15)] who ascribe these two ionizations together to the second peak at 13.3 eV. The INDO calculations are successful in reproducing the experimental values for IP, in contrast to the considerable errors of the *ab initio* results. Although there is a disagreement in the ordering of $3e_g$ and $4t_{1u}$ orbitals between the two treatments, they show a common feature that the two orbitals in question are mutually very closely spaced.

For a further comparison between the two theoretical methods, we show in Table 4 the atomic populations in the molecular orbitals of our concern. Strictly speaking, it will be improper to directly compare the

TABLE 3. COMPUTED AND EXPERIMENTAL IONIZATION POTENTIALS OF $Cr(CO)_6$ (in eV)

Symmetry[a)]	This calculation $-\varepsilon$	*Ab initio*[b)] $-\varepsilon$	Expt.[c)]
$^2T_{2g}$	9.10	10.7	8.4
$^2T_{1u}$	12.68	17.5	13.3
^2E_g	12.62	17.9	

a) Irreducible representation of the point group O_h.
b) Ref. 15. c) Ref. 19.

TABLE 4. COMPARISON OF POPULATION ANALYSES FOR $Cr(CO)_6$ (in percent)

MO	Method	$-\varepsilon$(eV)	Cr(3d)	C	O
$2t_{2g}$	INDO	9.10	63	10	27
	Ab initio	10.7	75	8	17
$4t_{1u}$	INDO	12.68	0	37	59
	Ab initio	17.5	0	54	38
$3e_g$	INDO	12.62	19	42	38
	Ab initio	17.9	18	59	23

populations derived from the orthogonal (or Löwdin) basis set (INDO) with those reduced from the Mulliken analyses (*ab initio*). Nevertheless, the comparison will still have some significance in a qualitative sense. As Table 4 shows, the populations calculated by the INDO method are uniformly in harmony with the *ab initio* results. Of the highest three levels, the $2t_{2g}$ orbital consists of 60—80% Cr 3d orbitals (d_{xy},d_{yz}, d_{xz}) with an appreciable CO π^* orbitals. The $4t_{1u}$ orbital is predominantly CO π bonds, while $3e_g$ is about 20% Cr 3d ($d_{x^2-y^2}$, d_{z^2}) and 80% CO orbitals.

Fe(CO)₃(butadiene). Measurement of photoelectron spectrum for $Fe(CO)_3$(butadiene) was first made by Dewar and Worley[22] using a low-resolution spectrometer. Recently, Connor *et al.*[23] have recorded a preciser spectrum to achieve assignment of the bands with the aid of *ab initio* calculations.

In Fig. 4, we compare the observed spectrum with IP calculated by the INDO and *ab initio* methods. Aside from the 16a′ orbital, the sequence of the INDO orbital energies accords well with the *ab initio* results. However, neither set of these Koopmans-theorem values can rationalize the observed spectrum of $Fe(CO)_3$ (butadiene). The discrepancy in height between the filled orbitals and the valence ionic states is probably due to greater orbital relaxation on ionization. The ΔSCF results[22] show that the effect of the orbital relaxation is particularly great for the molecular orbitals 17a′, 15a′, and 11a″. For these orbitals, the breakdown of the Koopmans theorem is enormous. In this work, we have not attempted SCF calculations for the resulting ions, since our parametrization was originally aimed at best possible interpretations of the ground-state properties only.

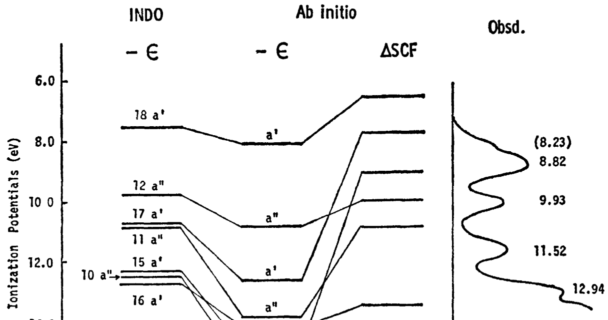

Fig. 4. Computed and experimental ionization potentials of $Fe(CO)_3$(butadiene). Symmetry designations of the molecular orbitals are based on the irreducible representation of the point group C_s.

Table 5 summarizes the results of population analysis of the molecular orbitals given in Fig. 4. It should be noted that the INDO calculation well reproduces the pattern of the *ab initio* populations. For the aforementioned three orbitals, for which the Koopmans theorem breaks down most seriously, the population on the central metal 3d orbitals is relatively large. Apparently, the orbital relaxation is most closely related with the 3d orbital population. With the orbitals 12a″ and 10a″, the 3d orbital populations are calculated to be small. Consistently, the INDO Koopmans-theorem values of IP due to these orbitals (9.75 and 12.45 eV) are in reasonable agreement with the observed ionization potentials (9.93 and 12.94 eV).

TABLE 5. COMPARISON OF POPULATION ANALYSES FOR $Fe(CO)_3$(butadiene) (in percent)

MO	Method	$-\varepsilon$(eV)	Fe(3d)	C_1+C_4	C_2+C_3
18a′	INDO	7.51	15	26	17
	Ab initio	8.1	33	34	9
12a″	INDO	9.75	11	45	20
	Ab initio	10.8	10	62	21
17a′	INDO	10.72	78	1	1
	Ab initio	12.6	51	12	20
11a″	INDO	10.74	84	3	2
	Ab initio	13.8	66	11	8
16a′	INDO	12.69	14	17	51
	Ab initio	14.1	34	12	48
15a′	INDO	12.31	90	2	1
	Ab initio	14.7	65	10	5
10a″	INDO	12.45	2	41	25
	Ab initio	15.4	13	32	18

Finally, we will briefly comment on the bonding character of the various molecular orbitals. The iron (3d)–butadiene (π) bonding is accomplished primarily through the d_{yz}–$1b_1$ and d_{xz}–$1a_2$ mixings in the orbitals 18a′ and 12a″, respectively. Both the orbitals 17a′ and 11a″ consist mainly of the iron 3d orbitals with an appreciable CO π orbitals. The orbitals 16a′ and 15a′ both have a slight iron–butadiene antibonding character. The 10a″ orbital is predominantly butadiene σ orbitals.

Concluding Remarks

The INDO calculations combined with Koopmans' theorem are found to be successful in interpreting the photoelectron spectra of transition metal carbonyl compounds, unless the orbital relaxation upon ionization is substantial. However, the results by no means indicate that Koopmans' theorem are indeed applicable to these compounds. In fact, the available results of *ab initio* calculations show that the effects of this relaxation are not negligibly small. It seems that our semiempirical treatment is just in effect allowing favorably for the effects of electron correlation. It follows that the resulting description of the ground states is probably reliable enough to discuss the bonding properties with. One obvious merit of semiempirical theories lies in the computational economy for the quality of the results they provide. One may thus anticipate immediate, though perhaps somewhat limited, usefulness of the present method for the investigation of various chemical problems[1] associated with transition metal complexes.

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