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An SC-MEH Molecular Orbital Study of $HCo(CO)_4$ and $Co(CO)_4$

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The Self Consistent Modified Extended Hückel (SC-MEH) molecular orbital method has been applied to the $HCo(CO)_4$ and $Co(CO)_4$ molecules. The results show that the highest occupied orbitals are predominantly ligand in character, which is at variance with other published calculations. Computation of the UV and photoelectron spectra, bond energy and some associated parameters, and magnetic hyperfine parameters of $Co(CO)_4$ have been carried out and found to be in exceptionally good agreement with experiment. The reported results also provide an acceptable rationalization for the observed photolysis and homolytic activity of the $HCo(CO)_4$ molecule.

Introduction

The Self Consistent Modified Extended Hückel (SC-MEH) molecular orbital method has thus far been applied to a number of transition metal halocomplexes and related systems, in both its normal and pseudorelativistic formalisms [1–4]. As a further test of the general applicability of the method, the SC-MEH calculations reported in this work apply to a case in which metal–ligand interactions involve a large degree of electron delocalization.

Because of its importance in hydroformylation reactions and a need for further chemical characterization, as demonstrated in a previous paper [5b], the $HCo(CO)_4$ molecule has been selected as a desirable point of focus. There have already been several molecular orbital studies of this molecule, ranging from semi-empirical to ab initio SCF treatments [6–10]. As will be demonstrated, the present SC-MEH results differ from these previous studies. The agreement between our present calculated and experimental properties for both $HCo(CO)_4$ and $Co(CO)_4$ is good, yet the interesting feature is that the SC-MEH results yield a manifold of highest occupied MO's which are predominantly ligand in character. This is a direct contrast to previous calculations in which the bonding MO's were calculated to be largely of metal character.

Method of Calculation

Specific features and full development of the SC-MEH method have already been detailed elsewhere [1–4, 11], and hence need not be repeated here. Only the essential features will be pointed out as follows. The one-electron operator approximation to the extract molecular HF-SCF Hamiltonian is factored into single and multicenter terms. The single center atomic terms are expressed as 'bonding orbital ionization energies' (BOIE), which are derived from valence orbital ionization energies adjusted for electron affinities and neighboring atom electrostatic effects [4]. All interatomic electrostatic interactions are treated in an effective point-charge approximation. The well-known Mulliken approximation is applied to all multicenter integrals except for exchange. A correction for interatomic exchange effects is independently incorporated, as will be subsequently explained. All overlaps are calculated explicitly with Slater type orbitals (STO) derived from the best free atom or ion HF-SCF wave functions. The analytic form of these may be either multiexponential or overlap-matched, single exponential. In the latter case, the radial moments $\langle r\rangle$ and $\langle r^2\rangle$ for the A. O. functions are solved simultaneously to obtain optimized values of n and ζ which are properly overlap matched [4]. This procedure has already been described in detail by Cusachs and co-workers [12]. Löwdin orthogonalization is applied with rotational invariance preserved, and the entire calculation is iterated to self-consistency in orbital populations and atomic charge. In the case of a complex ion or ionized molecule an external stabilizing potential, equal in magnitude but opposite in sign to that of the molecular cluster, is superimposed on each of the bonding atoms at a distance equal to the calculated average molecular center of charge. Hence all MOs are not merely shifted by a constant energy, but all are altered as an implicit function of the atomic charge distribution.

Finally, since the one electron M.O. eigenvalues are deficient in the interatomic electron exchange [11], any attempts to correlate spectra or any energy dependent properties must account for this. As has

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already been shown [11], it is possible to define the 'effective' electron spin in the i^{th} A. O. of any L.C.A.O-M.O. as $S_i^{eff} = C_i^2|1/2| = C_i^2 S_i$, where C_i is the Löwdin eigenvector. Thus by proceeding in a manner similar to that of Jϕrgensen for the free atom case [13], it is possible to derive the M.O. average spin pairing energy equation

$$E_{sp}^{ave} = 1/2\ \Sigma\ C^2_{i,j}D_{i,j}[\bar{S}_{i,j}(\bar{S}_{i,j} + 1) - S_i(S_i + 1) - S_j(S_j + 1)] \quad (1)$$

where $D_{i,j}$ is the atomic spin-pairing energy parameter for the i^{th} or j^{th} orbital, and the effective average spin is

$$\bar{S}_{i,j}(\bar{S}_{i,j} + 1) = \frac{P_{ij}(P_{ij} + 2)}{4}\left[\frac{2l_{ij} + 1}{4l_{ij} + 1}\right]\frac{(P_{ij}(P_{ij} - 1))}{2} \quad (2)$$

for a pure atomic l^n configuration, where $P_{i,j}$ is given by the Löwdin populations of the A.O.s comprising the L.C.A.O.-M.O.

The monatomic orbital energy inputs (BOIE) [11] are derived from the best theoretical and/or experimental atomic data available. For the $HCo(CO)_4$ calculation, the BOIE's of the Co atom were derived from the q = −1, 0, +1 and +2 ionized states, having the configuration $3d^8 4s^2$, $3d^7 4s^2$, $3d^7 4s^1$, $3d^8$ and $3d^7$. While not a requirement of the SC-MEH method, for the present calculation it was most convenient to describe the average energy for each charged configuration by the relation $Aq^2 + Bq + C = BOIE$. The necessary orbital ionization energies and electron affinities were derived from published theoretical calculations [15a–c], as available. In those cases for which data were lacking (as with 4p and some 4s configurations), monotonic extrapolation of the 3d–4s and 4s–4p energy differences as a function of charge was invoked.

The data for H, C and O were derived in an analogous manner. Two sets of BOIEs were derived for H with q = −1 and 0; one involving only the 1s orbital, and a second including 1s, 2s and 2p. As will be shown later, the additional configurational interaction afforded by the latter set is favorable for providing a more complete description of the binding, and also leads to a Co–H bond energy and net H charge in good agreement with experiment. The BOIE's of C and O were fitted for q = −1, 0 and +1, and confined to 2s and 2p configurations.

The rationale for including H2s, 2p functions and not 3s, 3p for C and O in the basis sets, is as follows. Considerations of electron affinity, electronegativity, and infra red spectral data [5], and other theoretical calculations [6–10], imply that in $HCo(CO)_4$ the net distribution of fractional atomic charges on H, C and O, should be negative, positive and negative respectively. For C^+ the 3s and 3p levels lie some 23 and 26 ev higher than the ionization energies of the 2s, 2p valence levels of the C ground state. Even if the fractional charge acquired by carbon were only of the order of +0.2, for example, these 3s and 3p virtual levels would still be some 5 ev above the neutral atom ground state. Similarly, the 3s and 3p levels of O^- are the order of 15 ev higher than the ionization energy of the neutral atom ground state. If it were assumed that the oxygen fractional charge were only −0.2, these 3s, 3p levels would still be at least 3 ev above the oxygen atom ground state. However, the 2s, 2p levels of H^- should be no more than about 0.5 ev higher than the energy to ionize from the $H(1s^1)$ ground state. Hence there is no logical reason for excluding them in the basis sets, particularly if the H is likely to acquire a negative charge, which as shown later are the conclusions drawn from both experimental and theoretical studies.

Furthermore, it has been shown by Facelli and Cantreras, that the 2p functions of H must be included as polarization functions if satisfactory agreement between calculated and observed NMR parameters is to be attained [14]. Also, the results obtained in the present calculation on $HCo(CO)_4$ yield a negative charge on H regardless of whether or not the 2s, 2p functions are included. Thus there is no basis from which it could be logically concluded, that expanding the H basis set to 1s, 2s, 2p orbitals might prejudice these calculations in any way. On the contrary, it is more likely that the reverse may be true.

STO Exponents and Coordinates

Single overlap-matched STOs were employed in these calculations. As stated above, optimal principal quantum numbers, n_{eff}, and the ζs were derived via simultaneous solution of the radial moment equations for $\langle r \rangle$ and $\langle r^2 \rangle$. The required expectation values were in turn obtained from HF-SCF atomic calculations [15a–c]. Virtual orbital parameters for Co (*i.e.* 4p and 4s in some changed configurations) were derived by graphical extrapolation, as described elsewhere [4]. It is to be noted that the optimal values of n_{eff} are always less than n, in cases were $n \geq 4$. For n = 4, $n_{eff} = (n - 1)$.

The ζ s for the H 2s and 2p orbitals were derived by setting the average energy differences of 1s–2p and 1s–2s equal to $Ze^2/\Delta\bar{r}$, where $\Delta\bar{r} = \langle r \rangle - a_0$. Having obtained $\langle r \rangle$, the ζ was calculated for $n_{eff} = 2$.

The internuclear distance in the CO molecule was set at 2.132 a.u., while the coordinates for the $HCo(CO)_4$ and $Co(CO)_4$ calculations were obtained from the data of McNeill and Scholer [16]. The bond distances are (au): H–Co (2.948), Co–C(ax) (3.334), Co–C(eq) (3.386), Co–O(ax) (5.490), and Co–O(eq) (5.446).

TABLE I. Valence Orbital Energies of CO.

Investigator(s) (reference)	Method	M.O.	E_{calc}	$E_{obs}{}^a$	$E_{obs}{}^b$
Ransil [18]	STO-SCF	5σ	–13.08	13.98	14.5
		1π	–15.86	16.58	17.2
Nesbet [19]	Expanded	5σ	–15.52		
	basis-SCF	1π	–17.77		
McLean and Yoshemine [20]	Double Zeta	5σ	–15.11		
	GTO-Ab initio	1π	–17.42		
Neumann and Moskowitz [21]	HF-SCF	5σ	–15.08		
		1π	–17.35		
Fenske and DeKock [22]	Fenske–Hall	5σ	–13.81		
		1π	–20.99		
Mintmire and Sabin [23]	LCAO-Xα	5σ	–15.2		
		1π	–17.6		
This work	SC-MEH	5σ	–13.32[c]		
		1π	–17.31[c]		

[a] All data in ev PES from reference 24. [b] XPS from reference 25. [c] After application of spin-pairing energy correction.

TABLE II. U.V. Singlet Excitation of CO.

Author(s) (reference)	Method	MO	$E_{calc}{}^a$	$E({}^1\pi\rightarrow\Sigma)^a$
Nesbet [19]	Expanded basis-SCF	–	–	10.5[b]
McLean and Yoshimine [20]	Double Zeta	5σ	–14.886	
	GTO-Ab initio	2π	3.992	10.894
Fenske and DeKock [22]	Fenske–Hall	5σ	–13.806	
		2π	0.366	13.440
Copper and Langhoff [26]	SCF-CI	–	–	9.1[b]
This work	SC-MEH	5σ	–13.695[c]	
		2π	–6.384	7.311
Observed				8.07[d]

[a] All energies are in units of ev. Excitation energies are relative to the fixed internuclear distance 2.132 au. [b] These values were interpolated from Fig. 1 in each of the respective references [19, 23]. [c] The spin pairing energy was applied to the excited configuration $(2\pi)^1$ $(5\sigma)^1$ relative to the $(5\sigma)^2$ ground state. [d] Herzberg, 'Molecular Spectra and Molecular Structure. I. Spectra of Diatomic Molecules'. D. Von Nostrand, New Jersey (1965) p. 522.

Results and Discussion

CO Molecule

Calculated photoelectron and U.V. spectra

As can be seen in Table I, the SC-MEH calculated energies of the 5σ and 1π levels, corrected for spin-pairing energy, are in as good agreement with experiment as those calculated by other methods [16–25].

For reasons stated above, no attempt has been made however to correlate the calculated energies of the 3σ and 4σ levels. However, it is to be noted that other calculations invariably place these at some 2–3 ev above the observed data, unless relaxation effects are accounted for in a Δ SCF calculation.

Those calculations of CO that have reported the lowest unoccupied 2π level in addition to the occupied levels of the ground state, are given in Table II together with the calculated ${}^1\pi \leftarrow {}^1\Sigma$ electronic transition. The SC-MEH results yield a singlet transition that is some 0.8 ev lower than the observed, while all other calculations with the exception of Cooper and Langhoff [26] are more than 2 ev higher than the observed value [19, 20, 22, 26]. Cooper and

Langhoff point out that if the $^1\pi$ excited state wave functions are used rather than the ground state functions, the $^1\pi \leftarrow {}^1\Sigma$ transition is calculated to be 8.07 ev, in perfect agreement with experiment. It may be inferred from Fig. 1 of reference [26], that in the $^1\Sigma$ excited state R is some 0.39 au longer than in the $^1\pi$ ground state. While we have not made any detailed SC-MEH calculations for CO at this increased bond distance (since our primary focus is not on CO per se, but on $HCo(CO)_4$), a rough estimate yields energy increases of some 0.5 to 0.8 ev and 1.0 to 1.5 ev for the 5σ and 2π levels respectively at $R \sim 2.4$ au. This too would then be in excellent agreement with experiment.

Bond energy

It is usually difficult to infer an adequate description of bond energy from only ground state MO calculations, unless the complete potential energy cuve is calculated. However, there are some features unique to the SC-MEH method which allows ready access to a reasonable estimate of bond energies, from the ground state equilibrium calculation.

The calculated SC-MEH eigenvalues provide a manifold of levels, both occupied and unoccupied virtuals, which fall into the negative energy region of the total molecular potential well. The critical threshold for the bond breaking process should be associated with the primary bonding M.O. levels, but these will be augmented via perturbations resulting from excited interactions with the appropriate virtual MOs lying in the negative region of the potential well.

The primary valence MOs can be defined as those bonding MOs which contain an appreciable admixture of A.O. character from both of the bonding atoms, and are confined to only those MOs whose energies do not exceed the lowest ionization threshold of the molecule. The average weighted bonding contributions from these primary valence MOs are accessed from the square of the LCAO-MO coefficients, c_i^2. It is defined that $c_i^2 = 0.50$ for a given A.O. on either one of the atoms in the bonded pair is the criterion for maximum bonding. Thus each of the calculated c_i^2 for each A.O. in a primary valence M.O. is weighted $c_i^2/0.50 = c_{iw}^2$, from which the sum, $c_{iwt}^2 = \sum\limits_i c_{iw}^2$, is obtained. Hence the ratios c_{iw}^2/c_{iwt}^2 provide the fractional weights by which the energy contribution of each primary valence M.O. must be multiplied. These are summed to give the total weighted energy. The same weighting factors are also applied to the number of electrons within each primary valence M.O., and these are summed to provide the total weighted number of bonding electrons, $\bar{e}$. From these data the weighted total energy per electron, $\bar{E}/\bar{e}$, is calculated.

The net interatomic overlap population (IOP) is outputed as a direct result of the Löwdin orthogonalization, and may be described as the average number of bonding electrons per bond type (#e/b.T.). Thus the product of $\bar{E}/\bar{e}$ with the IOP(#e/b.T.) and the number of bond types, (b.T.), *i.e.* the MO degeneracy per bonding pair of electrons, should provide the first part of the bonding energy relation.

The second part is derived from the average excitation energy for primary valence electrons promoted to vacant virtual MOs. This may be expressed as $\Delta\bar{E}_{ex}/n$, where $\Delta\bar{E}_{ex}$ is the average energy difference for n average electrons in symmetry allowed electronic transitions E_i virtual (unocc.) $\leftarrow$ E_i primary (occ.). In calculating $\Delta\bar{E}_{ex}/n$, the c_{iw}^2/c_{iwt}^2 must be determined including those symmetry allowed transitions to excited states which involve only the specific bonded atoms in question. In the CO molecule, for example, these transitions include the occupied 4σ, 5σ and 1π to the unoccupied $2\pi^*$ levels, for which E = 20.42, 6.92 and 10.91 ev respectively. When each of these transition energies is multiplied by the fraction of ground state character (*i.e.* the c_{iw}^2/c_{iwt}^2 in each case), the energy contributions appearing in the row headed by $\Delta\bar{E}_{ex}/n$ in Table V are obtained. The sum of these contributions divided by the weighted number of bonding electrons gives the value of $\Delta\bar{E}_{ex}/n$. Hence the final expression derived for bond energy via the SC-MEH method is

$$\text{B.E.} + (\bar{E}/\bar{e})\dot{x}\,\text{IOP}(\#e/\text{b.T})\dot{X}(\#b/T) - \Delta\bar{E}_{ex}/n \qquad (3)$$

Application of eqn. 3 to the CO molecule is given in detail in Table III. Also presented in Table III are bond energies calculated according to eqn. 3 for: Cl_2, HCl, NO, XeF_4, $CuF_{2(g)}$, $CuCl_4^{2-}$ and $FeCl_4^{2-}$ and $PtCl_4^{2-}$; so as to demonstrate the general utility of the method. In those cases involving unpaired electrons, stabilization via configuration interaction with core electrons must also be included in $\Delta\bar{E}_{ex}/n$. It is interesting that this computational procedure is similar to that derived from SCF-Xα calculations by Ziegler [27]. A more extensive investigation of this proposed method for bond energy calculations is currently underway, and will be presented in a future publication.

$HCo(CO)_4$ and $Co(CO)_4$

Orbital characteristics

SC-MEH calculations on the $HCo(CO)_4$ molecule were carried out utilizing the nine valence electrons of Co (3d, 4s and 4p basis), one of H (1s and 1s, 2s, 2p bases) and ten for each CO ligand (2s, 2p basis). These fifty electrons were placed in $1A_1$ through $8A_1$ and $1A_2$ and 1E through 8E molecular symmetry orbitals, consistent with the C_{3v} symmetry point group of the molecule. The coordinate system adopted placed Co at the origin, H and CO(1) ligands

TABLE III. SC-MEH Bond Energy Calculations.

A. *CO Molecule*

Orbital	$^5\sigma$	$^1\pi$	$^4\sigma$
c_i^2	0.42	0.24	0.35(s), 0.18(p)
$c_i^2{}_w$	0.84	0.48	0.70(s), 0.36(p)
$c^2{}_{iwt}$	–	–	– = 2.38
$c^2{}_{iw}/c^2{}_{iwt}$	0.35	0.20	0.29(s), 0.15(p)
$\bar{E}$(ev)	$(13.32 \times 0.35) + (17.31 \times 0.20) + (26.82 \times 0.29) + (26.82 \times 0.15)$		= 19.92
$\bar{e}$	$(2 \times 0.35) + (4 \times 0.20) + (2 \times 0.29) + (2 \times 0.15)$		= 2.38
$\bar{E}/\bar{e}$			= 8.37
IOP(e/b.T.)			= 1.20
b.T.	$(1 \times 0.35) + (2 \times 0.20) + (1 \times 0.29) + (1 \times 0.15)$		= 1.19
$\Delta\bar{E}_{ex}/n$(ev)	$(0.34 + 0.31 + 0.84 + 0.43)/2.38$		= 0.81
B.E. (calc)	8.37(ev/e) × 1.20(e/b.T) × 1.19(b.T.) – 0.81 ev		= 11.14 ev
B.E. (obs)			= 11.23 ± 0.03 ev (ref. 26)

B. *Molecular Unit*

	Cl_2	HCl	NO	XeF_4	$CuF_2(g)$	$CuCl_4{}^{2-}$	$FeCl_4{}^{2-}$	$PtCl_4{}^{2-}$
$\bar{E}/\bar{e}$	5.57	7.00	8.55	3.20	5.36	7.76	4.64	4.46
IOP(e/b.T)	0.352	0.637	0.691	0.861	0.435	0.465	0.734	0.488
b.T.	2.00	1.00	1.10	2.00	1.75	1.54	1.80	2.00
$\bar{E}_{ex}/n$(ev)	1.25	0	−0.27	4.12	0	−1.05	−0.22	0.22
B.E. (calc)(ev)	2.67	4.46	6.77	1.39	4.08	6.61	6.35	4.13
B.E. (obs)(ev)	2.49	4.45	(6.56–7.04)	1.36	(3.43–4.22)	6.66	6.25	(3.96–4.39)
Reference	29	29	29	29	29	30	30	31

along the Z axis and CO(2)–CO(4) in the equatorial plane. Table IV contains the pertinent data for some of the highest occupied MO s accounting for fourteen of the total fifty electrons in the molecule, and the unoccupied virtual orbitals up to the lowest positive 13E*.

A comparison of the present results with other calculations is presented in Table V. Unfortunately there is not much detailed information available in the published literature with which to make systematic comparisons. The data of Fonnesbeck, *et al.* [10], for example, provides the calculated energy levels but is lacking in orbital populations and atomic charges. Grima, Chaplin and Kaufmann [8], on the other hand, present detailed populations and charges but no orbital energies. Furthermore, the GCK publication is the only one which mentions any details as to the choice of basis functions. Yet their choice of a single 4p function with orbital exponent of 0.25 appears to be a rather poor representation for a well behaved gaussian orbital.

The FHJ calculations [10] give the HOMO as an A_1 orbital at −10.63 ev. While our results are in agreement with this symmetry assignment, the calculated energy is −13.51 ev. With the exception of the CNDO calculation [8], the data presented in Table V are all in agreement as to the symmetry of the HOMO. There are considerable differences, however, regarding the A.O. character of the HOMO. While the FHJ results suggest this to be an orbital of primarily Co $4P_z$, $3d_{z^2}$ and H1s character, the GCK ab initio data indicate that it is primarily Co 3d–H1s with smaller contributions from the Co 4s and 4p. The CNDO results also agree essentially with the FHJ. However, the SC-MEH results presented in Table IV suggest that the HOMO is primarily H1s and CO ligand, with a small degree of Co 4pz character and only very small $3d_{z^2}$ and 4s contribution.

A separate SC-MEH calculation on the $Co(CO)_4$ radical, shows that the unpaired electron resides in the $7A_1$ orbital at an energy of −11.08 ev. The relative percent A.O. character of this orbital is 8.5

TABLE IV. SC-MEH Results for $HCo(CO)_4$.

M.O.	Occup.	E_{calc}	Co 3d	Co 4s	Co 4p	H 1s	H 2s	H 2p	CO[c] 4σ	CO[c] 5σ	CO[c] 6σ*	CO[c] 1π	CO[c] 2π*
			Percent A.O. Composition per M.O.[a]										
13E*	0	+3.49											
$10A_1$	0	−2.09											
$9A_1$	0	−3.78											
12E	0	−6.39											
11E	0	−7.44											
10E	0	−7.78	0.9	0.7	0.3	31.4	10.7	1.3	0.2	40.8	5.2	–	8.0
9E	0	−8.44	7.4	–	0.2	–	–	3.8	0.6	46.5	4.1	0.1	36.8
$8A_1$	2	−13.51	0.6	0.3	6.4	31.4	0.3	–	2.4	45.7	0.8	2.8	8.5
8E	4	−13.90	5.9	–	6.5	–	–	2.9	0.4	10.0	0.3	12.2	61.6
$7A_1$	2	−16.08	–	3.2	–	2.3	0.5	0.4	0.6	28.6	1.3	16.6	46.0
$6A_1$	2	−16.84	9.3	–	–	–	–	–	5.9	2.3	7.8	74.0	0.7
$5A_1$	2	−17.05	2.1	–	–	–	–	–	24.4	6.3	3.3	62.9	1.0
$4A_1$	2	−17.32	2.2	–	0.5	–	–	0.2	1.9	1.4	0.6	87.8	5.2

[a] Relative percent A.-O. character within each M.O. [b] All in units of ev with spin pairing correction included. [c] The small contributions for 3σ have been omitted.

TABLE V. Molecular Orbital Parameters of $HCo(CO)_4$.

Reference: (Method)	FHJ[a] (restricted HF) ev	GCK[b] (ab initio)	(CNDO)	This work (SC-MEH) ev
E(Occupied MOs):	(A_1) −10.63	(A_1)	(E)	(A_1) −13.51
	(E) −10.70	(E)	(A_1)	(E) −13.90
	(E) −14.40	(E)	–	(A_1) −16.08
	(A_1) −17.23	(A_1)	–	(A_1) −16.84
	(E) −17.55	(E)	–	(A_1) −17.05
	(A_1) −17.73	(A_1)	–	(A_1) −17.32
Total Population:				
Co 3d	–	7.54	6.79	8.55 (8.51)[c]
4s	–	0.43	0.49	0.29 (0.31)
4p	–	0.55	1.49	0.59 (0.71)
H 1s	1.18	1.29	1.23	0.92 (1.04)
2s	–	–	–	0.06 (–)
2p	–	–	–	0.25 (–)
C_{ax} 2s	–	1.39	1.17	1.37 (1.38)
2p	–	2.36	2.60	2.29 (2.27)
O_{ax} 2s	–	1.79	1.17	1.58 (1.58)
2p	–	4.49	4.47	4.64 (4.65)
C_{eq} 2s	–	1.46	1.19	1.37 (1.41)
2p	–	2.33	2.64	2.26 (2.24)
O_{eq} 2p	–	4.51	4.48	4.61 (4.62)
Net Atomic Charges:				
Co	–	+0.59	+0.23	−0.43 (−0.52)
H	−0.31	−0.29	−0.23	−0.23 (−0.04)
C_{ax}	–	+0.25	+0.23	+0.34 (+0.35)
O_{ax}	–	−0.28	−0.18	−0.22 (−0.23)
C_{eq}	–	+0.21	+0.17	+0.37 (+0.35)
O_{eq}	–	−0.30	−0.19	−0.19 (−0.21)

[a] See reference 10. [b] See reference 8. [c] Values in parenthesis are for H1 s basis only.

Co($3d_{z^2}$), 1.2 Co(4s), 12.4 Co($4P_z$) and 77.9 CO(σ). Hence the result obtained when H is bonded, namely that the $8A_1$ HOMO is primarily of H and CO character (with electron density shifted away from cobalt, since H because negative in charge), is not surprising.

The fact that the highest valence MOs in $HCo(CO)_4$ are calculated to be largely ligand in character (see (Table IV) is admittedly out of line with other calculations both on this molecule and metal carbonyls in general. However, it is also to be noted that recently both ab initio and high quality semi-empirical calculations (INDO) on transition metal chloro complexes, show very much the same features of substantial ligand character in the higher occupied valence MOs [32–34]. Yet, these findings are also at odds with most previous conventional calculations on transition metal chloro complexes, but do indeed provide the best agreement with observed photoelectron spectra. In fact, in their work on tetrachloro complexes of Fe, Co and Cu, Bacon and Zerner make the following statement [35]: *"In our results the 3d MOs are not the HOMOs but lie well below the ligand 3p MOs".*

Of course we do not presume that Cl^- ligands would necessarily behave with the same bonding characteristic as CO, but SC-MEH calculations on complexes with Cl^- ligands have already been shown to provide good agreement with experimental data [2–4]; hence, there is no reason to expect that our results obtained on carbonyl or carbonyl hydride complexes should be any less reliable. On the contrary, the data presented below clearly vindicate the case in point.

UV spectra

The UV spectrum of $HCo(CO)_4$ has been measured by Sweany in an argon matrix [5a]. There is observed an intense shoulder at 227 nm and a broad intense band about 187 nm. There is no evidence whatever for any bands at longer wavelengths. Both bands appear to be charge transfer in character.

From the data given in Table IV, and upon considering spin pairing corrections in the ground *vs.* excited state, the allowed single $E \leftarrow A_1$ and $A_1^* \leftarrow A_1$ transitions are calculated. Assuming there is no appreciable geometry change or differences in net relaxation between ground and excited states, the relationship derived is

$$E_h \leftarrow E_l = E^h_{corr.} - E^l_{corr.} - \bar{E}s.p.(ex)/2(\Lambda + 1) \qquad (4)$$

where h and l refer to the higher and lower states respectively, $\bar{E}$ s.p. (ex) is the average spin pairing energy for the excited configuration calculated according to eqns. 1 and 2, and $(\Lambda + 1)$ is the maximum multiplicity of the MO 'spin orbital' (M.O. degeneracy/Λ = 0/0, 2/1, 3/2). The third term in eqn. 4 is calculated to be 0.53/4 ev for singlet transitions from the $8A_1$ to 9E, 10E, 11E and 12E levels respectively. The only allowed $A_1^* \leftarrow A_1$ transitions involve the $9A_1$ and $10A_1$ levels appearing at −3.70 and −2.09 ev. But these are too high in energy by comparison to the upper limits of the currently observed spectrum.

In C_3 symmetry $E \leftarrow E$ transitions are allowed in both Z and X, Y polarization. Hence it is conceivable that transitions from the 8E to 9E, 10E, 11E and 12E levels may be competing with the $E \leftarrow A_1$ transitions. For these singlet transitions the third term in eqn. 4 is calculated to be 1.132/16 ev. However, it is to be noted that the 8A and 8E levels differ by only 0.39 ev and are hence likely to be highly mixed upon excitation. Other consideration for mixing include the 9E, 10E and 10E, 11E levels, which differ by only 0.66 and 0.34 ev respectively.

As shown in Fig. 3 of reference 5a, there are two bands in the observed spectrum at 5.46 and about 6.6 ev respectively, but the actual position of the latter is less certain since it appears just at the lower wavelength cut-off limit of the spectrometer. However it is observed to be significantly even more intense than the other intensed, rather sharp band at 5.46 ev. None the less, both bands are clearly contained within an envelope of intense absorption having its on-set at less than 300 nm.

Both calculated and observed bands in the U.V. spectrum of $HCo(CO)_4$ and $Co(CO)_4$ are presented in Table VI. It is to be noted that all calculated bands appear well within the observed absorption envelope, and there are no bands calculated at lower energies. Thus the agreement with the observed spectrum is good in this respect. It may further be inferred from Table IV and VI that the orbital characteristics of the pertinent levels involved in the symmetry allowed transitions (*i.e.* $E \leftarrow A_1$ and $E \leftarrow E$) are such, that even spin-forbidden triplet transitions should have comparably large oscillator strengths and thus be of relatively high intensity. If such is the case, then the lower energy observed band (which is less intense) might be $9^3E \leftarrow {}^1(8A_1, 8E)$, which according to eqn. 4 would have the calculated energy: (−8.44) + (13.51 + 13.90)/2 + (0.53 + 1.132)/8 (ev) = 5.47 ev. This would obviously be in excellent agreement with the observed value. However, confirmation of this proposal will have to await a further detailed experimental spectral investigation.

Furthermore, the relative AO characteristics of the MO s indicate that a $9E \leftarrow (8A_1, 8E)$ transition would have the effect of displacing all the electron density from the strongly bonding H 1s orbital. Such would not be the case if the 10E orbital were comparably involved in the photolysis mechanism. A similar effect would also occur with transitions to the higher 11E and 12E orbitals. Thus it may well be that both bonds in the observed spectrum are photoactive.

The observation that upon photolysis the ratio of CO to H loss is about 8:1 (neglecting the cage effect

TABLE VI. U.V. Spectrum of $HCo(CO)_4$ and $Co(CO)_4$.

A. $HCo(CO)_4$

$E(h \leftarrow l)$ (calc; ev)	M.O.[a] (h)	Percent A.O. Character (h) ($\geq 1\%$)	Assignment[b]	ΔE[c] (obs., ev)
4.94	9E	7.4Co(3d), 3.8H(2p), 88.9CO	$9^1E \leftarrow 8^1A_1$	
5.39			$9^1E \leftarrow 8^1E$	
5.47			$9^3E \leftarrow {}^1(8A_1, 8E)$	5.46
5.60	10E	1.0Co(3d), 1.0Co(4s, 4p), *31H(1s)* 11H(2s), 1.3H(2p), 54.7CO	$10^1E \leftarrow 8^1A_1$	
6.05			$10^1E \leftarrow 8^1E$	
5.94	11E	1.0Co(3d), 1.0H(2p), 98CO	$11^1E \leftarrow 8^1A_1$	
6.39			$11^1E \leftarrow 8^1E$	
7.06	12E	12Co(3d), 2.0H(2p), 86CO	$12^1E \leftarrow 8^1A_1$	
7.51			$12^1E \leftarrow 8^1E$	~6.6 (est.)[d]

B. $Co(CO)_4$

ΔE(calc.)[e]	ΔE(obs.)[e,f]		Assignment
	Ar matrix	CO matrix	
28,316	29,410	28,090	$10^2E \leftarrow 7^2A_1$
32,913	33,780	31,650	$11^2E \leftarrow 7^2A_1$
41,706	41,670	39,120	$12^2E \leftarrow 7^2A_1$

[a] The 9E, 10E and 11E levels differ by only 0.66 and 0.34 ev respectively. Hence both energy and symmetry dictate that these should be heavily mixed in the excited state. [b] All must be either $E \leftarrow A_1$ or $E \leftarrow E$ transitions, since $A_1 \leftarrow A_1$ are much too high in energy. [c] See reference [5a]. [d] See Conclusions. [e] cm^{-1}. [f] Data from ref. [44]. Two unresolved shoulders *ca.* 39,000–29,000 cm^{-1}, not included here.

for hydrogen atom loss) can also be rationalized from these calculated results. As can be noted from Table IV, those bonding MO s having a large degree of H character contain about twice as much CO character as well, and there are four times as many CO s per mol as H. Furthermore, there are other transitions in the 6–7 ev range for which the amount of CO character in the vacant MO s is greater than the occupied, which can reasonably be expected to cause metal–carbonyl bond weakening. Hence, a sizable CO to H loss ratio is not unexpected on the basis of this calculated electronic structure.

Photoelectron spectrum of $HCo(CO)_4$

It has been clearly demonstrated by the work of Bacon and Zerner [33], Tse [34], Tossell [35], Bohn [36a], Larsson [37], Guest *et al.* [9], and Calabro and Lichtenberger [37], to cite a few among many, that the application of Koopman's theorem to the photoionization of transition metal complexes gives rise to enormous errors, owing to large relaxation effects accompanying the ionization of metal orbitals. In fact, Guest and co-workers have made the explicit comment that their ab initio SCF calculation of the $HCo(CO)_4$ ground state gives an incorrect order (as far as correlation with the observed P.E. spectrum via Koopman's theorem is concerned) for those MO s which have been assigned Co–3d and Co–H bonding [9].

A ΔSC-MEH calculation analogous to ΔSCF calculations has been carried out in the following manner. The energy of the $HCo(CO)_4^+$ ion is calculated for each occupied MO from which a hole has been created for the $(0) \rightarrow (+)$ orbital ionization. These calculations were made by considering the net atomic changes (q) calculated for the $HCo(CO)_4$ unionized state to be increased by $(q + 1)$ in the ionized state. The atomic inputs for the ion calculation were determined for the $(q + 1)$ ionized atoms with relaxation included. The latter correction was computed from the relation given by Calabro and Lichtenberger [38]:

$$E_R = \sum_{n,l} (N^+_{n,l}/n^2)[S^+_{n,l} - S_{n,l}]^2$$

where E_R is the relaxation energy, $N_{n,l}^+$ is the number of elections in the ionized atom having quantum numbers n and l, and $S^+_{n,l}$ and $S_{n,l}$ are the net shielding factors for ionized and unionized atoms respectively.

TABLE VII. SC-MEH Calculation for Ionization of $HCo(CO)_4$.

$HCo(CO)_4$			$HCo(CO)_4^+$	
Ionized M.O.	Percent A.O. Character^a	E^b	Percent A.O. Character^a	SC-MEH^b
3E	82(3d), 18(CO)	−23.55	97(3d), 3(CO)	8.57(8.84)^c
4E	55(3d), 45(CO)	−20.87	98(3d), 2(CO)	9.19(7.37)
$5A_1$	52(3d), 11(H, 1s), 37(CO)	−17.32	69.5(3d), 9.6(4s), 7(H, 2p), 11.9(CO)	9.92(4.81)
$8A_1$	6(4p), 31(H, 1s), 63(CO)	−13.51	43(4p), 13(H, 2p), 44(CO)	11.32(1.71)
8E	6(3d), 6.5(4p), 5.4(H, 2p), 82.1(CO)	−13.90	4(3d), 18(4p), 75.7(H, 2p), 2.3(CO)	13.88(0.92)
$7A_1$	3.2(4s), 2.3($H_1$1s), 94.5(CO)	−16.08	1(4s), 99(CO)	16.42(0.34)
$6A_1$	2.4(3d), 0.5(4p), 97.1(CO)	−16.84	100(CO)	17.19(0.35)
$5A_1$	2.4(3d), 1(4p), 0.5($H_1$1s), 96.1(CO)	−17.05	100(CO)	17.40(0.35)
7E	4(3d), 0.8(4p), 95.2(CO)	−17.48	1.6(3d), 98.4(CO)	18.21(0.73)
5E	2(3d), 98(CO)	−17.76	100(CO)	18.46(0.70)
6E	9.2(3d), 90.8(CO)	−17.68	6(3d), 94(CO)	18.48(0.80)

[a] Only those A.O.s contributing ⩾1.0 percent are included. [b] All in ev, including spin-pairing interaction, *etc.* [c] Only the relaxation contribution.

TABLE VIII. Calculated *vs.* Observed Photoelectron Spectrum of $HCo(CO)_4$.

MO	Primary A.O. Composition	$E_{(+)\leftarrow(0)}$ (calc)	P.E.S. (obs.)	Band	Character^a
				predicted	obs
$8A_1$	H and CO	11.32	11.5	S-NS (H, CO)	S-NS (CO–H)
$5A_1$	Co and CO	9.92	9.90	B-WS (Co, CO)	B-WS (Co)
4E	Co and CO	9.19			
3E	Co	8.57			
		(ave. = 8.88)^b	8.90	B-WS (Co)	B-WS (Co)
$7A_1$	CO	16.42			
$6A_1$	CO	17.19			
$5A_1$	CO	17.40			
		(ave. = 17.00)^b	17(tail)	B-NS (CO)	B-NS (CO)
8E	CO(Co)	13.88	13.8(onset)	B-SS (CO, Co)	B-FS (Co–C)
7E	CO	18.21			
6E	CO	18.48			
5E	CO	18.46			
		(ave. = 18.38)^b	18.2	B-NS (CO)	? (CO)

[a] S = sharp; B = relatively broad; NS = no splitting; WS = with splitting; SS = some splitting; FS = fine structure. [b] Orbital characteristics suggest these excited states should be thoroughly mixed.

The results of this ΔSC-MEH computational procedure are presented in Table VII. All occupied MO s in the −19 ev range were considered in the calculation. Since the unionized HOMO ($8A_1$) appears at −13.51 ev there are no occupied MO s at energies higher than this. The only other occupied MO s which were not included are those that appear lower than −20 ev, for which even relaxation corrections would not bring them into the 8–19 ev range of the observed photoelectron spectrum of $HCo(CO)_4$ [39]. A comparison of the calculated and observed photoelectron spectrum is presented in Table VIII.

Atomic charges and bond energies

Core shifts in the XPS spectra of metal carbonyl and carbonyl hydrides have been interpreted by Jolly and co-workers to imply a substantial negative charge on the H atom in $HCo(CO)_4$ [40]. While it may not be agreed that the H charge –0.799 assigned by these investigators is numerically accurate, because of the assumed metal charge, the trends in experimental data do none the less indicate that the H should be negatively charged. Similarly, shifts in the IR spectrum of $HCo(CO)_4$ have led Sweany to conclude that the H atom must indeed bear a negative charge, since the average force constant for the CO modes of $HCo(CO)_4$ is greater than that of $Co(CO)_4$, thus indicating a shift of electron density from the metal to H [5a]. The NMR data for $HCo(CO)_4$ have been interpreted by Lohr and Lipscomb with H having a charge between –0.1 and –0.3 [41].

The fact that the $pK_a \approx 1$ for $HCo(CO)_4$ is not so much a consequence of the H partial charge as it is a reflection of the weakness of the Co–H bond. The insolubility of $HCo(CO)_4$ in water is well known and an ion as large as $Co(CO)_4^-$ resulting from $HCo(CO)_4 \rightarrow H^+ + Co(CO)_4^-$ cannot be highly solvated. Thus the acidity of $HCo(CO)_4$ is clearly related to the facility of cleaving the Co–H bond and the associated solvation of H^+.

The results obtained by FHJ [10] and GCK [8] assign Co charges of +0.59 and +0.23 respectively. This no doubt has much to do with the quality of the basis functions employed in the calculations.

In first row transition metals the 4p orbital is particularly sensitive to this charge factor.

In an ab initio SCF-CI calculation on $Cr(CO)_5$ incorporating a reasonably good gaussian 4p basis Hay obtained a charge of –0.92 on Cr [42]. Similarly, Kirschenbaum and coworkers have made a critical examination of variation in bond properties and charges with the choice of 4s, 4p bases for Ni in $Ni(CO)_4$ [43]. The best optimized STO exponents provided a charge on Ni of –0.21, whereas other ab initio calculations utilizing inferior basis sets yielded positive charge on Ni. In view of these findings, we feel confident that the SC-MEH results are equally reliable in providing acceptable net atomic charges.

As has already been demonstrated with the CO molecule, the SC-MEH data provide a convenient method for calculating bond energies. Application of eqn. 3 to the calculated data for the $HCo(CO)_4$ molecule gives the results presented in Table IX. In the H–Co bond energy calculation, the net excitation energy contribution is averaged over two A_1 to A_1^* orbitals. Since the net charges on both H and Co atoms are negative, further stabilization can only be imparted via a shift of electron density away from either atom. In effect, this means that the excitation energy term in eqn. 3 will be a stabilizing factor rather than a destabilizing one, and hence its sign is negative.

In the calculation of the ligated CO bond energy, the excited state contribution is averaged over five orbital transitions (*i.e.* ΔE_{ex} between 2.70 and 5.70 ev). No distinction is made between axial and equatorial ligands, in so far as the average excitation energy term is concerned. Similarly in the Co–CO bond energy computation, $\Delta\bar{E}_{ex}$ is an average over two transitions with no distinction between axial and equatorial positions.

McKinney and Pensak have utilized MEHT calculations of total energies to arrive at bond energies of metal carbonyls [7]. As can be seen in Table IX, the value obtained by both SC-MEH and MEHT calculations are in close agreement for the $Co–CO_{(ax)}$ bond energy. However, the MEHT method for obtaining bond energies is not capable of distinguishing bond anisotropy, and hence is not in close agreement with

TABLE IX. Bond Energies in $HCo(CO)_4$ [a].

Bond	$(\bar{E}/e)$	(IOP)	(b.T.)	$(\bar{E}_{ex}/n)$	B.E. (ev) (calc)	B.E. (ev) (accepted value)
H–Co	$8.38/_4$	0.156	1	–1.12 (ev)	2.42 (2.77)[b]	2.5[c]
$CO_{(eq)}$	$37.10/_6$	1.296	2	5.68	10.55 (–)	–
$Co_{(ax)}$	$37.10/_6$	1.287	2	5.68	10.23 (–)	–
$Co–CO_{(eq)}$	$61.47/_6$	0.134	2	1.30	1.44 (1.70)	1.39[d]
$Co–CO_{(ax)}$	$61.47/_6$	0.163	2	1.30	1.75 (1.70)	1.39[d]

[a] See eqn. 3 and associated discussion for explanation of data. [b] Data in parenthesis taken from reference 7. [c] See reference 43. [d] These data are for $Co_2(CO)_8$ and $Co_4(CO)_{12}$, taken from J. A. Connor, *Topics in Current Chem.*, *71*, 71–110 (1977).

the SC-MEH result for the Co–CO$_{(eq)}$ bond. A comparative discrepancy is also observed for the Co–H bond, but the SC-MEH result is in close agreement with the accepted value [44]. Unfortunately, there are no reported experimental or calculated data with which to compare the ligated CO bond energy.

The ligated CO bond energy is computed to be on the average some seven percent lower than that of the free CO molecule, which is certainly not beyond expectations. The fact that the calculated axial ligated CO bond energy is three percent higher than the equatorial might also have been anticipated, since the Co–C$_{(ax)}$ bond length is about 0.06 Å shorter than the equatorial.

Magnetic hyperfine A and g tensors of Co(CO)$_4$

The basic definitions of magnetic hyperfine A and g tensors may be found in any standard text [45]. In an axially symmetric geometry the anisotropic components of the A tensor for ^{59}Co in Co(CO)$_4$ (C_{3v}-z totally symmetric axis) are given as

$$A_{\parallel}(^{59}\mathrm{Co}) = A_{F.C.} + Azz(DIP)_1 + Azz(DIP)_2 \qquad (5a)$$

$$A_{\perp}(^{59}\mathrm{Co}) = A_{F.C.} + Axx(=Ayy)(DIP)_1 + + Axx(=Ayy)(DIP)_2 \qquad (5b)$$

where only the diagonal components of A_{qq} (q = x, y, z) are non-vanishing. $A_{F.C.}$ is the Fermi contact term given by

$$A_{F.C.} = \frac{8\pi}{3} g_e g_n \beta_e \beta_n \underset{k,i}{} C^2{}_{ki} |\psi(0)|^2{}_{ki}(P_{ki}) \qquad (6)$$

where g_e β_e and g_n β_n are electron and nuclear 'g factors' and magnetic moments respectively (β_e is given a negative sign); C_{ki} are the Löwdin A.O. coefficients for each orbital in the molecular orbital containing the unpaired electron; $\psi(0)_{ki}$ is the electron density per electron for the ith orbital at the nucleus of the kth atom, and P_{ki} the Löwdin population per orbital per atom. A(DIP)$_1$ and A(DIP)$_2$ are the first and second order dipolar contributions given by

$$\begin{aligned} A(DIP)_1 &= Tqq(q = x, y, z) \\ &= g_e g_n \beta_e \beta_n \sum_{k,i} C^2{}_{k,i}(\alpha^{qq}_{m,ml\,k,i})\langle r^{-3}\rangle_{k,i}(P)_{k,i} \end{aligned} \qquad (7a)$$

$$\begin{aligned} A(DIP)_2 = {} & \\ -2g_e g_n \beta_e \beta_n & \sum_{n,q} \sum_{k,i} C^2{}_{k,i}(\alpha^{qq}_{m,ml})_{k,i}\langle r^{-3}\rangle_{k,i}(P)_{k,i} \\ & \times \frac{\langle\psi o|\zeta_l Lq|\psi n\rangle\langle\psi n|\tilde{L}q|\psi o\rangle}{E_n - E_o} \end{aligned} \qquad (7b)$$

where, in addition to the terms already defined $\alpha^{qq}_{l,ml}$ is the orbital angular factor for the alignment of the electron spin according to a (3 cos^2 – 1) dependence; $\langle r^{-3}\rangle$ is the one-electron orbital expectation value for kth atom in the calculated charge state; ζ_l is the one-electron spin–orbital coupling constant for each of the k atoms comprising the LCAO-MO containing the unpaired electron, and $\tilde{L}q$ is the qth (x, y, z) component of the orbital angular momentum correcting the ground, ψo and excited, ψn, states, having the energies E_o and E_n respectively.

It is to be noted that in the present case, the effective radial distribution of the cobalt 3d, 4s and 4p orbitals is 3.09 au (weighted average) which is to be compared with the cobalt–ligand bond distance of 3.33 au. Since the radial distributions of the carbon and oxygen 2p orbitals are about 1.5 and 1.3 au respectively, the unpaired electron in the Co(CO)$_4$ radical has its spin density well localized onto the CO ligands. Hence it is appropriate to evaluate the tensors of eqn. 6, 7a and7b by summing over i orbitals of the k atoms comparing the LCAO-MO in which the unpaired electron resides. The associated $\langle r^{-3}\rangle$ terms are evaluated as projected onto the Co nucleus, which of course for the CO ligands turn out numerically to be essentially the same as those for free C and O atoms appropriately adjusted for their respective net charges in the molecule.

TABLE X. 'A' and 'g' Tensors for Co(CO)$_4$.

^{59}Co	^{13}C	Calc. (10^{-10} au)	Obs.[a] (10^{-10} au)
$A_{F.C.}$	–	–145.05	–141
A(DIP)$_1$			
A_{zz}	–	409.56	–
A_{xx}	–	–163.73	–
A_{yy}	–	–163.49	–
A(DIP)$_2$			
A_{zz}	–	2.86	–
A_{xx}	–	59.29	–
A_{yy}	–	–60.95	–
$A_{\parallel}$	–	261.6	264 ± 5[b]
$A_{\perp}$	–	–248.4	250 ± 5[b]
	$A_{\parallel}$	122.4	119 ± 9[b]
	$A_{\perp}$	–112.8	109 ± 5[b]
	$g_{\parallel}$	2.0092	2.007 ± 0.010
	$g_{\perp}$	2.1356	2.128 ± 0.010

[a] Data from reference [32]. [b] Only absolute values are reported.

The data for $A_{F.C.}$ of ^{59}Co in Co(CO)$_4$ obtained from the SC-MEH calculation of $A_{F.C.}$ are presented in Table X. Since only s orbitals give non-vanishing contributions to $|\psi(0)|^2$ for a non-relativistic basis, these were the only contributions to $A_{F.C.}$ considered according to eqn. 6. Similarly, the calculated

$A(DIP)_1$ and $A(DIP)_2$ terms of ^{59}Co, are presented in Table X.

The ligand hyperfine ^{13}C A tensors may be written as

$$A_{\parallel}(^{13}C = A_{F.C.} + 2[A_L(DIP)_0 + A_L(DIP)_1 + +A_L(DIP)_2] \quad (8a)$$

$$A_{\perp}(^{13}C) = A_{F.C.} - [A_L(DIP)_0 + A_L(DIP)_1 + + A_L(DIP)_2] \quad (8b)$$

where the zeroth order ligand dipolar term is

$$A_L(DIP)_0 = -g_e g_N \beta_e \beta_N [1/\langle r_{MO}\rangle_{eff})^3] \quad (9)$$

with $\langle r_{MO}\rangle_{eff}$ is taken as the weighted average of all ith A.O.'s over k atoms in the M.O. containing the unpaired electron. All other terms in 8a and 8b are as defined in 7a and 7b but referred to the carbon rather than the cobalt nucleus.

The g tensors are affected only by spin–orbit coupling and the extent to which the orbital angular momentum mixes ground and excited states via second order perturbation. The appropriate equations for the axially symmetric case are

$$g_{\parallel} = g_e + 2\lambda_{eff} \sum_{n\neq 0} [\langle\psi o|\tilde{L}_z|\psi n\rangle\langle\psi n|\tilde{L}_z|\psi o\rangle](E_n - E_o)^{-1} \quad (10a)$$

$$g_{\perp} = g_e + 2\lambda_{eff} \sum_{n\neq 0} [\langle\psi o|\tilde{L}_x|\psi n\rangle\langle\psi n|\tilde{L}_x|\psi o\rangle + + \langle\psi o|L_y|\psi n\rangle\langle\psi n|\tilde{L}_y|\psi o\rangle](E_n - E_o)^{-1} \quad (10b)$$

where λ_{eff} is the spin orbital coupling constant for all the electrons in a specific configuration, which is taken as $\zeta_1(Pl)$, *i.e.* the one-electron spin–orbital coupling constant for the atom in the specific charge state in the molecule, times the Löwdin orbital population. The other terms bare the same significance as those defined in eqns. 7a and 7b.

The final results of the SC-MEH calculation of A and g tensors for $Co(CO)_4$ are presented in Table X, together with the observed values reported by Ozin, *et al.* [32].

Conclusion

The SC-MEH-MO method has been applied to $HCo(CO)_4$ and $Co(CO)_4$. While the calculated bonding scheme does differ from the conventional description deduced by other MO techniques, the agreement obtained between the calculated and observed U.V. and photoelectron spectra, magnetic properties, and bond energies is exceptionally good. These results are in line with those obtained previously on first row transition metal halo complexes, xenon fluorides and Pt(II) complexes, all of which were also studied by the SC-MEH-MO method. Hence it must be concluded that the quality of these results cannot be merely accidental in nature.

More specifically, the present results show that ligand field concepts restricted to a manifold of d orbitals alone have little or no true validity in characterizing these molecules. It is also shown that the H–Co bond gains its stability at the expense of weakening the Co–CO bonds, via a drift of electron density away from the Co metal center and CO groups (see Table IV and section 'Atomic charges and bond energies').

Calculated bond energies also confirm the fact that the H–Co bond is substantially stronger than the Co–CO bond. Hence selective homolysis of the H–Co bond can only be achieved via radiation of specific excited states, as is found experimentally and supported theoretically.

Finally, the rather strongly acidic nature of $HCo(CO)_4$ does not necessarily have to be interpreted as indicative of the H atom bearing a positive charge. On the contrary, both experimental and theoretical data strongly suggest that such is in all probability not the case, as discussed in Section B.4.

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