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The Performance of the New 6-31G^{##} Basis Set: Molecular Structures and Vibrational Frequencies of Transition Metal Carbonyls

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Abstract: The performance of the newly proposed 6-31G^{##} basis set for calculating the equilibrium structure and vibrational frequencies of transition metal carbonyl complexes has been studied at the HF and DFT levels of theory. The 6-31G^{##} basis set has been constructed by augmentation of the 6-31G basis set by diffuse and polarization functions, which are generated from the corresponding 6-31G basis AOs response functions obtained in the frame of propagator approach. The predicted values of bond distances and vibrational frequencies for the title compounds are in good agreement with the experimental data. The relative energies and HOMO-LUMO gaps were also estimated for the series of MCO complexes.

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Key words: metal-carbonyls; *ab initio*; bond lengths; vibrational frequencies; basis set

Introduction

An *ab initio* study of the interaction of carbon monoxide with metal atoms is of considerable interest from both scientific and commercial points of view. Metal carbonyls are widely used for the production of metal powders, coating, catalyzing, and the initiation of a number of chemical processes.¹ Obtaining accurate data concerning such systems require the application of experimental techniques or reliable computational methods. The transition metal compounds still provide a challenge to computational techniques.

An ultimate goal of any quantum chemical approaches is compensating for any incompleteness of the used basis sets by inclusion of additional sets of diffuse and polarization functions. Here, it is necessary to mention the popular 6-31G basis set, which has been recently extended by addition of higher angular momentum basis functions to incorporate also the first-row transition metals.² However, the size and functional forms of such functions are being selected, as a rule, in an arbitrary way.

In this work, we present the results that were generated to investigate the general reliability of the new basis set proposed for the computation of geometric structures and vibration spectra of transition metal compounds. Mononuclear carbonyl complexes have been

selected for the present study. Most of such systems have been well characterized both theoretically^{2–6} and experimentally.^{7–14}

Construction of the Basis Set

Recently, we have proposed a new method for 6-31G basis set extension based on an analysis of the analytical expressions for the first-order correction functions $\chi^{(1)}$ to the unperturbed atomic functions $\chi^{(0)}$.^{15,16}

$$\chi^{(1)}(\vec{r}) = \int G_E(\vec{r}, \vec{r}') W(r') \chi^{(0)}(r') d\vec{r}'$$

where $G_E(\vec{r}, \vec{r}')$ is the Green's function and $W(r')$ is the perturbation operator. For the considered applications, we have chosen the

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dipole moment as a perturbation operator corresponding to the first-order perturbation theory in the presence of a weak homogeneous electric field, which could model the influence of the molecular environment. The latter could be important for reliable predictions of the properties of transition metal-containing complexes.

The proposed construction of the basis set is described below. Using the given perturbation operator, we have determined the response functions by the perturbation theory (the Green's function method) from the unperturbed functions. Then, these functions have been expanded over the functional set of the same type as the 6-31G basis set, according to the following scheme:

$$\begin{aligned} S^{(1)}(\xi) &\rightarrow p^{(0)}(\xi), \\ P^{(1)}(\xi) &\rightarrow s^{(0)}(\xi) + d^{(0)}(\xi), \\ D^{(1)}(\xi) &\rightarrow p^{(0)}(\xi) + f^{(0)}(\xi). \end{aligned}$$

As a result, the extension of the initial 6-31G basis set by its physically adapted augmentation resulted in the following 6-31G^{##} basis set:

$$\{s(6\xi_1), sp(6\xi_2, 6\xi_3, 3\xi_4, 1\xi_5), d(3\xi_6, 1\xi_7)\} \\ + \{p(6\xi_1, 3\xi_6, 1\xi_7), d(6\xi_2, 6\xi_3, 3\xi_4, 1\xi_5), f(3\xi_6, 1\xi_7)\},$$

which includes the d- and f-polarization and the diffuse p-functions. The notation $x(n\xi_i)$ denotes a set of n primitive Gaussians with a number of the orbital exponents ξ_i forming the basis x -type AO.

As a result, the response functions to the $s(6)$ basic functions are $p(6)$ functions with six primitives. Regarding the $sp(6)$, $sp(3)$, and $sp(1)$ functions, one requires the addition of four d-functions with six, three, and one primitives. The response functions generated from the $d(3)$ and $d(1)$ functions include two p- and two f-type functions with three and one primitives, respectively.

These additional "generated" functions significantly increase the flexibility of the new basis set compared to the 6-31G basis set. In addition, the described method of the basis set construction enables one to determine exactly the number and functional form of the necessary polarization and diffuse functions. It also removes the arbitrariness in selecting the orbital exponents. Moreover, in contrast to the method proposed in ref. 2, it is not necessary to carry out the additional procedure of optimizing the orbital exponents for additional basis functions since they are defined by the structure of the initial basis set.

Results and Discussion

To investigate the performance of the new basis set, we have performed geometry optimization and vibration frequency calculations with the suggested 6-31G^{##} and standard 6-31++G(3df,3pd) basis sets at the HF and DFT levels of theory for a set of metal carbonyls. On comparison, the parameters for the CO molecule have been calculated. All calculations have been carried out with the Gaussian 03 package.¹⁷ The obtained results are collected in Tables 1 and 2 and compared with other available theoretical and experimental results.

For all compounds presented in Tables 1 and 2, the HF approach gives a smaller R_{C-O} value and higher ω_{C-O} fre-

quency than those predicted at the DFT level. On comparison with the results for the CO molecule, it is clear that deficiencies in the HF approach arise from the description of CO and not from the description of the Me—CO bonding. In all cases, R_{C-O} is slightly shorter and ω_{C-O} is higher compared to the CO molecule. The frequency shift at the HF level is larger than that predicted by the DFT method. This effect combined with the longer Me—C bond and lower Me—CO frequency suggests that the HF approach underestimates the Me to CO d-electron transfer. This effect weakens the C—O bond and strengthens the Me—C bond.

For the $Fe(CO)_5$ complex (Table 2), agreement with the experimental data for the 6-31G^{##} basis set is achieved at the DFT approximation, which accounts for the electron correlation. Moreover, using the 6-31G^{##} basis set, it was possible to correctly reproduce differences between the values of the axial and equatorial Fe—C bond lengths.

Apparently, from the data for NiCO (Table 1) and $Ni(CO)_4$ (Table 2), the application of the proposed basis set results in predicted values of vibrational frequencies and geometrical parameters that are in good agreement with the experimental data. A comparison of the results obtained at the HF and DFT levels shows that inclusion of electronic correlation is necessary for a correct description of the 3d environment of the transition metals. The CrCO molecule was predicted to have a ${}^7A'$ ground state, which correlates with the ground state of the Cr atom and the CO ligand (${}^1\Sigma^+$). The ground-state geometry of the CrCO molecule adopts a bent conformation. It is known that, in carbonyl-metal complexes, the CO groups are connected to metal atoms through C atoms. As a result, the electron pair from a carbon atom transfers to a metal atom forming an σ -bond, and the metal d-electrons transfer back to the vacant loosen CO π -orbitals (π -bond). The 5σ orbital of CO does not point directly towards the metal in the bent CrCO, and the σ -repulsion can be reduced. This repulsion, coupled with the fact that $sd\sigma$ hybridization is not possible for the 7S state of the Cr atom due to the spin coupling of the s and $d\sigma$ orbitals, acts as a driving force for bending.

Comparing the Tables 1 and 2, the results of our calculations in the extended 6-31++G(3df, 3pd) basis set (built-in Gaussian package program) and the data obtained in²⁻⁵ at the MP2, DFT (BP86/6-311+G(2d), and B3LYP/6-311+G*) levels of theory are presented. As follows from the results displayed in Table 2, the addition of a single polarization f-function to the 6-31G basis sets for atoms from Sc through Zn,² even with the subsequent optimization the value of the polarization function exponent by minimizing the energy and application of the method of calculation that overestimates electronic correlation, do not give satisfactory agreement with experimental geometric data.

Recent studies³ now present an opportunity to further advance the prediction of properties and the formation of the $Zn(CO)_3$ molecule as well as the next members of the series of metal carbonyls: $Cr(CO)_6 \rightarrow Fe(CO)_5 \rightarrow Ni(CO)_4$. The antisymmetric stretching CO frequency calculated at the BP86/6-31G^{##} level of theory, 1974.5 cm^{-1} (Table 2), agrees well (within 1.3 cm^{-1}) with the experimental data obtained for the argon matrix.

The additional functions in the 6-31++G(3df,3pd) basis set are $s(1)$, $p(1,1)$, $d(1)$, $f(1,1,1)$, and $g(1)$ for transition metals and

Table 1. Calculated and Experimental Geometrical Parameters (Å, deg.) and Vibrational Frequencies (cm⁻¹) for Metal Carbonyls (MCO).

Molecule	Parameters	HF/6-31G ^{##}	HF/6-31++G (3df,3pd)	BP86/6-31G ^{##}	BP86/6-31++G (3df,3pd)	Other	Experiment ^a
CrCO (⁷ Σ ⁺) ∠Cr–C–O = 180	Number of basis function	114	148	114	148		
	R _{Cr–C}	4.582	5.740	2.117	2.120	2.206 ⁶	–
	R _{C–O}	1.108	1.107	1.156	1.155	1.133 ⁶	–
	ω _{Cr–C}	22	9	297	294	–	–
	ω _{C–O}	2426.1	2427.2	2014.1	2010.0	–	–
CrCO (⁷ A')	R _{Cr–C}	4.584	5.721	2.121	2.126	2.142 ⁵	–
						2.216 ⁶	
	R _{C–O}	1.108	1.107	1.165	1.164	1.162 ⁵	–
						1.143 ⁶	
	∠Cr–C–O	175.5	165.7	140.4	141.5	139.7 ⁵	–
						137.2 ⁶	
	ω _{Cr–C}	22.5	8.2	344.3	337.0	327.9 ⁵	–
FeCO (³ Σ [–]) ∠Fe–C–O = 180	R _{Fe–C}	1.736	1.969	1.697	1.699	1.774 ⁶	–
						1.149 ⁶	
	R _{C–O}	1.131	1.113	1.176	1.178		–
	ω _{bend}	402	266	369	365		330 ± 50 ⁷
	ω _{Fe–C}	607	303	585	576		530 ± 10 ⁷
	ω _{C–O}	2485.5	2273.8	1946.9	1923.3		1946.5 ⁷
							1933.7 ⁷
FeCO (⁵ Σ [–])	R _{Fe–C}	1.964	1.951	1.850	1.856	1.923 ⁶	–
						1.144 ⁶	
	R _{C–O}	1.118	1.119	1.168	1.167		–
	∠Fe–C–O	180.0	180	168.4	168.5	173.4 ⁶	–
	ω _{bend}	268	291	131	132		180 ± 60 ⁸
	ω _{Fe–C}	320	347	459	430		460 ± 15 ⁸
	ω _{C–O}	2231	2198	1968	1953		1990 ± 15 ⁸
NiCO (¹ Σ [–]) ∠Ni–C–O = 180	R _{Ni–C}	1.751	1.741	1.670	1.664	1.672 ⁶	–
						1.149 ⁶	
	R _{C–O}	1.116	1.115	1.170	1.169		–
	ω _{Ni–C}	463.4	477.0	609.0	611.5		–
	ω _{bend}	320.5	325.0	353.7	354.8		591.1 ⁹
							–
							409.1 ⁹
NiCO (³ A')	R _{Ni–C}	4.296	7.298	1.844	1.833	1.910 ⁶	–
						1.142 ⁶	
	R _{C–O}	1.108	1.107	1.165	1.155		–
	∠Ni–C–O	163.5	163.0	146.8	147.1	144.0 ⁶	–
	ω _{Ni–C}	35	3	458	412		–
	ω _{C–O}	2426.7	2426.9	1948.4	2033.3		2006.6 ⁷
							1994.4 ⁷
CO	R _{C–O}	1.109	1.107	1.144	1.143		1.128 ¹⁰
	ω _{C–O}	2422	2427	2108	2113		2170 ¹⁰

^aFrequencies; experimental data given in the gas phase, solid neon and solid argon, accordingly.

Table 2. Calculated and Experimental Geometrical Parameters (Å, deg.) and Vibrational Frequencies (cm⁻¹) for Metal-Carbonyls M(CO)_n.

Molecule	Parameters	HF/6-31G ^{##}	HF/6-31++G (3df,3pd)	BP86/6-31G ^{##}	BP86/6-31++G (3df,3pd)	Other	Experiment ^a
Cr(CO) ₆	Number of basis function	334	528	334	528		
	R _{Cr-C}	2.009	2.005	1.906	1.904	1.987 ²	1.914 ¹¹ 1.920 ¹¹
	R _{C-O}	1.114	1.113	1.159	1.158	1.119 ²	1.140 ¹² 1.160 ¹¹
	ω _{Cr-C}	630	640	688	692	—	—
	ω _{C-O}	2303	2309	1982	1984	—	2003 ⁷ 1998 ⁷ 1990 ¹⁰
Fe(CO) ₅	Number of basis function	290	452	290	452		
	R _{Fe-C(ax)}	2.058	2.045	1.800	1.803	2.035 ²	1.807 ¹³
	R _{Fe-C(eq)}	1.876	1.877	1.810	1.804	1.859 ²	1.827 ¹³
	R _{C-O(av.)}	1.113	1.116	1.159	1.158	1.117 ²	1.153 ¹³
	ω _{Fe-C}	563.5	569.3	630.5	635.1	—	—
	ω _{C-O}	2147.1	2185.4	2011.7	2016.0	—	2015.6 ⁷ 2010.5 ⁷ 2005.9 ⁷
Ni(CO) ₄	Number of basis function	246	376	246	376		
	R _{Ni-C}	1.914	1.902	1.827	1.818	1.866 ²	1.830 ¹² 1.838 ¹¹
	R _{C-O}	1.111	1.110	1.155	1.154	1.117 ²	1.141 ¹¹
	ω _{Ni-C}	265.3	282.1	455.5	458.0	—	—
	ω _{C-O}	2349.2	2355.3	2027.5	2030.0	—	2061.3 ⁷ 2056.3 ⁷ 2051.2 ⁷
Zn(CO) ₃	Number of basis function	202	300	202	300	315 ³	
	R _{Zn-C}	1.978	1.977	1.877	1.879	1.188 ³	—
	R _{C-O}	1.114	1.112	1.159	1.161	1.156 ³	—
	ω _{Zn-C}	381.4	368.0	464.2	460.0	—	—
	ω _{C-O}	2252.3	2266.1	1974.5	1972.3	1974.7 ³	1975.8 ³

^aFrequencies; experimental data given in the gas phase, solid neon, and solid argon, accordingly.

s(1), p(1), d(1,1,1), and f(1) for carbon and oxygen atoms. In the new basis set proposed here, the additional functions are p(6,3,1), d(6,6,3,1), and f(3,1) for metals and p(6) and d(3,1) for C and O atoms.

It should be emphasized that, in the 6-31G^{##} basis set, the additional orbitals contain more than one primitive Gaussian function, in contrast to the 6-31++G(3df,3pd), 6-311+G(2d), and 6-311+G* basis sets. In spite of the absence of orbitals with

Table 3. Relative Energies and HOMO-LUMO Gap for Different States of Metal Carbonyls (MCO).

Molecule	State	Relative energies (kcal/mol)		Band gap (eV)	
		BP86/6-31G ^{##}	BP86/6-31++G (3df,3pd)	BP86/6-31G ^{##}	BP86/6-31++G (3df,3pd)
		114 ^a	148 ^a	114 ^a	148 ^a
CrCO	⁷ A'	0.00	0.00	1.33	1.33
	⁷ Σ ⁺	2.51	2.51	0.65	0.65
FeCO	³ Σ ⁻	0.00	0.00	2.42	2.07
	⁵ Σ ⁻	9.41	8.72	1.22	1.14
NiCO	¹ Σ ⁺	0.00	0.00	1.65	1.63
	³ A'	36.77	36.40	1.47	1.39

^aBasis set size.

the highest value of angular moment (g- or f-functions) in the 6-31G^{##} basis set, the latter provides virtually identical values of vibration frequencies and bond distances (Tables 1 and 2) as much larger basis sets (it is ~35% smaller compared to the 6-31++G(3df,3pd)) basis set).

Table 3 contains the values of the relative energies and HOMO-LUMO gaps for the metal carbonyls: CrCO, FeCO, and NiCO at different electronic states calculated at the BP86/6-31G^{##} and BP86/6-31++G(3df,3pd) levels of theory. Compared to the larger standard 6-31++G(3df,3pd) basis set, the proposed 6-31G^{##} basis set predicts virtually the same values of the calculated parameters for the CrCO molecule. Also, in the case of FeCO and NiCO species, the results obtained with different basis sets are in good agreement. Thus, one can conclude that the 6-31G^{##} basis set could be used as an efficient and inexpensive basis set for calculations of geometric and energetic parameters of transition metal-containing molecules.

Conclusions

The main goal of this study was to test the newly developed 6-31G^{##} basis sets. A comparison of the experimental data, geometrical parameters, and vibrational frequencies predicted for the series of metal carbonyl complexes allows us to derive the following conclusions:

- Good agreement of the calculated results with experiment shows the efficiency of the proposed, physically justified, and middle-sized 6-31G^{##} basis set for considered metal carbonyls in the frame of the DFT approach.
- The way of basis set expansion under influence of an external electric field allows predictions of comprehensible values of frequencies and intensities IR- and the Raman-spectra dependent on derivatives from dipole moment and polarizability of molecules on internuclear distances.
- The BP86 functional has been used for the computation of molecules with transition metal atoms. It has been shown that, when combined with the proposed basis set, it provides reliable predictions for both the molecular structure and vibration frequencies.

It is concluded that the 6-31G^{##} basis set can be used for studying the structural and vibrational properties of transition metal complexes. The 6-31G^{##} basis set gives comparable results to those obtained with the existing, much larger basis sets.

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