

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/230501566>

Improvement of scale factors for harmonic vibrational frequency calculations using new polarization functions

ARTICLE *in* INTERNATIONAL JOURNAL OF QUANTUM CHEMISTRY · JANUARY 2008

Impact Factor: 1.43 · DOI: 10.1002/qua.21574

CITATIONS

9

READS

74

4 AUTHORS, INCLUDING:



Anibal Sierraalta

Venezuelan Institute for Scientific Research

94 PUBLICATIONS 794 CITATIONS

SEE PROFILE



Elena Ehrmann

Simon Bolívar University

9 PUBLICATIONS 75 CITATIONS

SEE PROFILE



Rafael Añez

Venezuelan Institute for Scientific Research

43 PUBLICATIONS 187 CITATIONS

SEE PROFILE

Improvement of Scale Factors for Harmonic Vibrational Frequency Calculations Using New Polarization Functions

ANIBAL SIERRAALTA,¹ GUILLERMO MARTORELL,¹
ELENA EHRMANN,² RAFAEL AÑEZ¹

¹Laboratorio de Química Computacional, Centro de Química, Instituto Venezolano de Investigaciones Científicas, Apartado 21827, Caracas 1020-A, Venezuela

²Departamento de, Procesos y Sistemas, Universidad Simón Bolívar, Valle de Sartenejas, Baruta-Edo Miranda, Venezuela

Received 9 October 2007; accepted 29 October 2007

Published online 10 January 2008 in Wiley InterScience (www.interscience.wiley.com).

DOI 10.1002/qua.21574

ABSTRACT: Density functional calculations were carried to improve the calculated CO vibrational frequencies for transition metal carbonyls. Two types of density functionals were studied, hybrid and generalized-gradient methods. Using the simplex optimization method, new polarization functions for C and O atoms were obtained. With these new optimized functions, new scaling factors were obtained. The results reveal that, with the new polarization functions, the agreement between the calculated and the experimental values improves considerably. In general, the new scaling factors are very close to unit, with standard uncertainties close to $\pm 0.006 \text{ cm}^{-1}$. The use of the new polarization functions allows more precise calculations of the transition metal carbonyl CO vibrational frequencies. © 2008 Wiley Periodicals, Inc. *Int J Quantum Chem* 108: 1036–1043, 2008

Key words: scaling factors; DFT; vibrational frequencies; CO, AIM

Correspondence to: A. Sierraalta; e-mail: asierral@ivic.ve

Contract grant sponsor: FONACIT.

Contract grant number: G-2005000426.

This article contains supplementary material available via the Internet at <http://www.interscience.wiley.com/jpages/0020-7608/suppmat>.

Introduction

Presently, common computational quantum chemistry applications include calculations of minimum energy structures, activation energies, thermodynamic properties, and vibrational frequencies. These types of calculations aid scientists in their interpretation of experimental results. Vibrational frequencies are routinely calculated to verify if the calculated structure is indeed a minimum energy structure as well as to interpret infrared spectra and assign signals. Consequently, the accuracy of calculated frequency values is of utmost importance to adequately interpret experimental results. Typically, calculated harmonic vibrational frequency values are larger than the corresponding experimental values [1]. Two major error sources cause this disagreement: first, the theoretical treatment neglects anharmonicity effects, and second, calculated wavefunctions by present-day methods are, in general, only approximated; thus, they do not accurately describe the electron correlation. Relativistic effects, spin-orbit effects, the incompleteness of the basis sets, etc contribute to this problem. To overcome this problem, frequency scaling factors are often applied [2, 3]. The use of these scale factors leads to significant improvement in the calculated values by quantum chemistry methods.

Recently, the scaling factors have been revised to improve agreement between experimental and calculated values. According to Andreson and Uvdal [4], the optimal frequency scaling factors for B3LYP method with the basis sets 6-311+G(d,p) up to 6-311+G(3df,3pd), are: 0.9679 for high-frequencies, 1.0100 for low-frequencies, and 0.9877 for zero-point vibrational energies. Irikura et al. [5] reported scaling values for HF, MP2, QCISD, and some DFT methodologies such as BLYP, B3LYP, PBEPBE, among others. These authors state that the best value for B3LYP/6-311+G(d,p) method is 0.9669 with a relatively high standard uncertainty of ± 0.0205 . Tantirungrotechai et al. [6] obtained scaling factors for a set of density functionals such as OLYP, G96LYP, PBE0, B98, VSXC, etc. They found that the scaling factor is less affected by the basis set than by the exchange-correlation functional and that the G96LYP functional yields the calculated frequencies that are closest to the experimental frequencies. Unfortunately, this functional has the largest mean square error.

Usually, the scaling factors are obtained from a linear fit between the experimental and theoretical

frequencies, using available basis sets such as 6-31G(d,p), 6-311G(d,p), etc. However, these basis sets are not optimized to yield accurate frequency values; consequently, fitting deviations are around 7–10% [1, 3] with root mean square errors between 35–60 cm^{-1} [3–6]. A strategy to improve the correlation between the theoretical and experimental values is to perform a partial optimization of the basis sets to reproduce the experimental frequencies. In this work, we partially reoptimized the 6-31+G(d), 6-311G(d), 6-311+G(d), and D95V basis sets to improve the calculated frequencies values with the B3LYP functional, and the 6-31+G(d), 6-311G(d) basis sets for the BP86, B98, G97LYP, and PBEPBE functionals. The aim of this work is to show that a simple route to obtain more accurate vibrational frequencies is to reoptimize the polarization function (d function) of the standard basis sets.

In this study, only CO stretching frequencies were considered. These frequencies are very sensitive towards the CO adsorption mode on the transition metal, and their values allow to infer if the adsorption occurs at one or two metallic centers. The CO vibrational frequency is widely used by the experimentalist to determine the molecular aggregation state and the oxidation state of the metals in systems like metal-zeolites. To model these systems it is necessary to use many atoms therefore, small size basis sets are frequently used to calculate the interaction of the metals into zeolite with other molecules [7–9]. On the other hand, the main aim of our laboratory is to study and/or propose catalytic systems that are of environmental interest. Many of the pollutants with the largest greenhouse effects contain CO bonds. Finally, for the CO stretching frequency, there is a large amount of experimental data available; thus, these values are ideally suited to validate theoretical models. This work does not intend to solve or exhaustively analyze all the problems associated with frequency calculations. Instead of that it shows a way to obtain reasonable frequency values that could be helpful for the interpretation of IR signals. Thousand articles are published yearly where the CO stretching frequency is used to characterize the active site of the catalysts. It is not possible to give useful information about the characteristic of the adsorption site or active site, if the standard errors associated with the frequency calculations are high. Therefore, it is necessary to have methodologies or basis sets that are able to reduce the error in the calculations. The approach developed in this work is to reduce the uncertainty; that is, to reduce the error in the extrapolated value of

the vibrational frequencies in order deliver useful information to the experimentalist.

Methodology and Optimization Method

All geometry optimizations, energy, and frequency calculations were performed with Gaussian-03 program [10] at B3LYP, B98, PBEPBE, BP86, and G97LYP levels. Only polarization d functions were optimized because, according to previous studies [4] the polarization functions have a larger effect upon the vibrational frequency values than the diffuse functions. Simultaneous optimization of the C and O atom exponents (α_d) was achieved by minimizing the square error (Δ_{vib}) between the calculated and the experimental values.

$$\Delta_{\text{vib}} = \sum_i (\omega_i(\alpha_d) - \nu_i)^2 \quad (1)$$

where $\omega_i(\alpha_d)$ and ν_i are the i th calculated harmonic and i th experimental fundamental frequencies (in cm^{-1}), respectively. The search of the minima was performed using the Nelder-Mead simplex method. Our previous experiences with this method [11] show that it is adequate to minimize nonlinear functions without calculation of derivatives. The basis sets used for C and O were 6-31G+(d), 6-311G(d), 6-311+G(d), and the D95V (Dunning-Huzinaga valence double-zeta). The relativistic Stevens effective core potentials (CEP-121) as well as the Alamos pseudopotential (LANL2DZ) with its corresponding basis sets were employed for the second and third row transition metals; i.e., for Ag, Au, Os, Pd, Pt, Ir, Rh, and Ru atom. Sets of 29 frequencies for the optimization and 41 frequencies for the scaling were used (see supporting material). First, the molecules were optimized with the selected basis set and then, the vibrational frequencies were evaluated. The scaling factors for vibrational frequencies were determined through least-squares fits of the calculated frequencies versus the experimental values; i.e., minimizing the sum:

$$S = \sum_i^N (\lambda \omega_i - \nu_i)^2 \quad (2)$$

where N is the number of frequencies included in the optimization. The root-mean-square error (RMS) was calculated as

$$\text{RMS} = \sqrt{\frac{S}{N}} \quad (3)$$

and the standard uncertainty $u(\lambda)$ associated with the scaling factor λ was calculated according to Irikura et al. [5]

$$u(\lambda) = \sqrt{\frac{\sum_i^N (\omega_i(m_i - \lambda))^2}{\sum_i^N \omega_i^2}} \quad (4)$$

where $m_i = \nu_i/\omega_i$

The topological properties of the electronic density were calculated using AIM200 Windows version package from Büro für innovative software.

Results and Discussions

Table I shows the optimized as well the standard polarization (d) exponent values for B3LYP method and the 6-31+G(d), 6-311G(d), 6-311+G(d), and D95V basis sets. The basis sets used in this work are labeled as: A_I , B_I , C_I , and D_I for the standard basis sets, A_{II} , B_{II} , C_{II} , and D_{II} for the optimized basis sets to be used with CEP-121, A_{III} , B_{III} , C_{III} , and D_{III} for the optimized basis sets to be employed with LanL2DZ, etc. For example, A_I correspond to 6-31+G(d) with $\alpha_C = 0.800000$ and $\alpha_O = 0.800000$; B_I : 6-311G(d) with $\alpha_C = 0.626000$ and $\alpha_O = 1.292000$, A_{II} : 6-31+G(d) with $\alpha_C = 0.335884$ and $\alpha_O = 0.535903$ with CEP-121, A_{III} : 6-31+G(d) with $\alpha_C = 0.435120$ and $\alpha_O = 0.395156$ with LANL2DZ, etc (see Table I). In general, the optimized exponent values as well as their relative trends depend on the basis set and on the pseudopotential type used. For example, for CEP-121 with the 6-31+G(d) basis set (basis set A_{II}), the exponent value for oxygen (α_O) is larger than for carbon (α_C) while for LANL2DZ (basis set A_{III}), the trend is opposite; that is, $\alpha_C > \alpha_O$. Two factors may be responsible for these findings. (a) The pseudopotential basis set can penetrate into the region of the ligand basis set, affecting the C atom electronic distribution and therefore, changing the Metal—C distance as well as the C=O vibrational frequency (ν_{CO}). (b) The electron affinity and ionization potential depend on the pseudopotential type used, as well as on the associated basis set. Consequently, the charge transfer degree be-

TABLE I
Optimized and standard polarization (d) exponents for C (α_C) and O (α_O) on different basis sets and pseudopotentials for the B3LYP method.

Standard Values		
CEP-121/ LanL2DZ	Basis ^a	Set I ^b
A _I : 6-31+G(d)	0.800000	0.800000
B _I : 6-311G(d)	0.626000	1.292000
C _I : 6-311+G(d)	0.626000	1.292000
D _I : D95V ^c	—	—
Optimized Values		
CEP-121	Basis ^a	Set II ^b
A _{II} : 6-31+G(d)	0.335884	0.535903
B _{II} : 6-311G(d)	0.078153	0.547389
C _{II} : 6-311+G(d)	0.477442	0.233904
D _{II} : D95V	0.478099	0.036812
Optimized Values		
LanL2DZ	Basis ^a	Set III ^b
A _{III} : 6-31+G(d)	0.435120	0.395156
B _{III} : 6-311G(d)	0.474772	0.254267
C _{III} : 6-311+G(d)	0.429836	0.456263
D _{III} : D95V	0.635132	0.270553

^a Column of α_C values.

^b Column of α_O values.

^c The standard D95V basis set does not have polarization (d) functions.

TABLE II
Scaling factors (λ), standard uncertainties ($\pm u(\lambda)$), quadratic correlation coefficients (r^2), and root mean square errors (RMS) for the standard and optimized basis sets. B3LYP HGGGA Method.

Basis set/ECP	6-31+G(d)	6-311G(d)	6-311+G(d)	D95V
Standard basis sets				
CEP-121	0.9734 \pm 0.0052 r^2 = 0.9955 RMS = 11.0	0.9666 \pm 0.0055 r^2 = 0.9951 RMS = 11.5	0.9723 \pm 0.0050 r^2 = 0.9959 RMS = 10.5	1.0314 \pm 0.0091 r^2 = 0.9879 RMS = 18.0
LANL2DZ	0.9723 \pm 0.0030 r^2 = 0.9985 RMS = 6.3	0.9648 \pm 0.0044 r^2 = 0.9967 RMS = 9.4	0.9713 \pm 0.0060 r^2 = 0.9943 RMS = 12.5	1.0317 \pm 0.0079 r^2 = 0.9910 RMS = 15.7
Optimized basis sets				
CEP-121	0.9999 \pm 0.0027 r^2 = 0.9988 RMS = 5.7	1.0006 \pm 0.0046 r^2 = 0.9968 RMS = 9.3	1.0010 \pm 0.0040 r^2 = 0.9975 RMS = 8.1	1.0000 \pm 0.0047 r^2 = 0.9967 RMS = 9.5
LANL2DZ	1.0002 \pm 0.0030 r^2 = 0.9986 RMS = 6.1	0.9981 \pm 0.0050 r^2 = 0.9961 RMS = 10.2	0.9999 \pm 0.0039 r^2 = 0.9977 RMS = 7.9	0.9987 \pm 0.0055 r^2 = 0.9953 RMS = 11.5

HGGA stands for Hybrid Generalized-Gradient Approximation

tween the ligand and the metal will also depend on the pseudopotential type. The RuCO⁺ species exemplifies this behavior. For this species, the ground-state is ² Σ . When using 6-311+G(d) for C and O, the calculated vibrational frequencies and Ru—C distances change from 1,793.1 cm⁻¹ and 1.781 Å with B3LYP/CEP-121/6-311+G(d) to 1,781.7 cm⁻¹ and 1.760 Å, with B3LYP/LANL2DZ/6-311+G(d). The corresponding Ru net charges are -0.55e for B3LYP/CEP-121/6-311+G(d) and -0.78e for B3LYP/LANL2DZ/6-311+G(d). However, the calculated C—O distances are similar for both methodologies: 1.196 Å for B3LYP/CEP-121/6-311+G(d) and 1.200 Å for B3LYP/LANL2DZ/6-311+G(d). These results show how the pseudopotential type affects to some extent the properties of the ligand bonded to the metallic atom. However, it is noteworthy that the CEP-121 has a basis set with a triple zeta quality, while LANL2DZ is double zeta. Therefore, a direct comparison is not possible.

Table II compares the scaling factors for the standard (not optimized) and the optimized basis sets when the B3LYP method is used. The results indicate that, except for 6-311+G(d), the LANL2DZ/standard basis set combination behaves better than the CEP-121/standard basis combination, since the former yields lower RMS and $u(\lambda)$, and larger r^2 values. After optimization, the correlation between experimental and calculated values improves con-

siderably. Now, the scaling factors are quite close to unit. In general, after optimization the improvement for the CEP-121/basis set combination is better than for the LANL2DZ/basis set combination. For example, the RMS and $u(\lambda)$ values are reduced to almost a half for CEP-121/6-31+G(d), while for LANL2DZ/6-31+G(d) the values remain similar. With the new basis sets and scaling factors there is better agreement between theoretical and experimental values even in the cases where the reduction of the magnitude of $u(\lambda)$ is not significant. For instance, for $\text{Au}(\text{CO})_2^+$, the difference between the scaled theoretical and the experimental ν_{CO} values is 10.9 cm^{-1} at B3LYP level with the standard 6-311G(d) basis set and CEP-121(basis set B_I), while it is only -0.1 cm^{-1} with the optimized 6-311G(d) basis set (basis set B_{II}).

Irikura et al. [5] and Andreson and Uvdal [4] reported scaling factor values of 0.9669 and 0.9623, respectively, for 6-311G(d)/B3LYP. These values are similar to ours; 0.9666 and 0.9648 for CEP-121/6-311G(d) and LANL2DZ/6-311G(d), respectively. Nevertheless, our values for 6-31+G(d) (0.9734 and 0.9723,) and for 6-311+G(d) (0.9723 and 0.9713,) contrast with those found by Irikura et al. [5] for 6-31+G(d) (0.9632) and by Andreson Uvdal [4], for 6-311+G(d) (0.9613.) These results seem to indicate that for metallic carbonyls, the diffuse functions have more influence on the scaling factor than on pure organic compounds. It is worth to note that with the optimized functions this difference disappears; that is, the results obtained with 6-311G(d) and 6-311+G(d) are quite similar.

Bond energy (BE) calculation is a hard task because there is no variation theorem that allows calculation of an upper bound as in the case of the total energy. In general, goods values are obtained through error compensation between the left and the right side of a chemical equation. This balance depends on the method and the basis sets used. To investigate how this balance is affected by the optimized polarization functions, bond energy calculations that include the nonscaled zero-point vibrational energy correction (ZPVE) for the $\text{Pt}(\text{CO})_3^+$ and $\text{Pt}(\text{CO})_2^+$ species were performed. Table III shows that in some cases, the values calculated with the standard basis set fit experimental data better than those obtained with the optimized basis set, as occurs for the LANL2DZ/6-311G(d) combination. On the contrary, for the D95V basis set, the optimized function yields better BE values than the corresponding standard basis. For 6-311+G(d) both, the optimized and the standard basis yield similar values. The former results show

TABLE III
Calculated $(\text{CO})_2\text{Pt-CO}^+$ and COPt-CO^+ bond energies, in eV, including the ZPVE correction using B3LYP method.

Basis set/ ECP	6-31+G(d)	6-311G(d)	6-311+G(d)	D95V
<i>Pt(CO)₃⁺</i>				
CEP-121	1.04	1.06	1.02	1.32
	1.09	1.07	1.00	1.16
LANL2DZ	1.02	1.01	1.00	1.26
	1.00	1.11	1.02	1.10
<i>Pt(CO)₂⁺</i>				
CEP-121	2.02	2.00	2.00	2.27
	2.10	2.03	1.96	2.09
LANL2DZ	2.00	1.98	1.99	2.22
	1.97	2.14	1.99	2.01

Standard basis sets in italic. Optimized basis sets in plain.
Experimental bond energies: $(\text{CO})_2\text{Pt-CO}^+ = 1.02 \pm 0.05 \text{ eV}$;
 $\text{COPt-CO}^+ = 2.00 \pm 0.10 \text{ eV}$. [12]

that it is possible to obtain simultaneously good BE and vibrational frequency values without the need of scaling factors.

Table IV shows the scaling factors for the standard and optimized 6-31+G(d) and 6-311G(d) basis sets with different functionals. Comparison with the results of Table II reveals that the functional based on the HGGA approximation, B3LYP and B98, yields better results than those based on the GGA only. Even though that, in general, the linear correlation improvement is smaller for the GGA than for HGGA based functionals, the optimized basis set produces scaling factors close to unity without increasing the uncertainties associated with these scaling factors. According to Table IV, the scaling factor is less affected by the basis set than by the exchange-correlation functional. For example, the scaling factor for the standard 6-31G+ basis set changes from 0.9734 to 0.9645, to 1.0090 when going from B3LYP, to B98, to PBEPBE. While for B3LYP, the scaling factor changes from 0.9734, to 0.9666, and to 0.9723 for the 6-31+G*, 6-311G* and 6-311+G* basis sets, respectively. As expected, the use of the optimized *d* functions, not only affects the vibrational frequencies but also the geometrical and the electronic density topological parameters of the CO molecule.

To analyze the effect of the optimized functions on the properties of the CO molecule, quantum chemical calculations were performed using the op-

TABLE IV

Scaling factors (λ), standard uncertainties ($\pm u(\lambda)$), quadratic correlation coefficients (r^2), and root mean square errors (RMS) for the standard and optimized basis sets with different DFT approximations.

Basis set/ECP	B98 HGGA	PBEPBE HGGA	BP86 GGA	G96LYP GGA
Standard basis sets				
6-31+G(d) LANL2DZ	0.9645 ± 0.0032 $r^2 = 0.9982$ RMS= ± 6.8	1.0090 ± 0.0083 $r^2 = 0.9893$ RMS= ± 16.8	1.0134 ± 0.0076 $r^2 = 0.9910$ RMS= ± 15.4	1.0189 ± 0.0058 $r^2 = 0.9949$ RMS= ± 11.7
6-311G(d) LANL2DZ	0.9599 ± 0.0058 $r^2 = 0.9943$ RMS= ± 12.3	1.0019 ± 0.0106 $r^2 = 0.9822$ RMS= ± 21.7	0.9583 ± 0.0054 $r^2 = 0.9955$ RMS= ± 11.5	1.0107 ± 0.0073 $r^2 = 0.9916$ RMS= ± 14.9
Optimized basis sets				
6-31+G(d) LANL2DZ	0.9997 ± 0.0037 $r^2 = 0.9977$ RMS= ± 7.6	1.0050 ± 0.0073 $r^2 = 0.9917$ RMS= ± 14.8	1.0092 ± 0.0070 $r^2 = 0.9923$ RMS= ± 14.3	1.0148 ± 0.0053 $r^2 = 0.9957$ RMS= ± 10.6
6-311G(d) LANL2DZ	1.0014 ± 0.0057 $r^2 = 0.9948$ RMS= ± 11.6	0.9997 ± 0.0091 $r^2 = 0.9869$ RMS= ± 18.6	1.0035 ± 0.0102 $r^2 = 0.9890$ RMS= ± 17.0	1.0130 ± 0.0061 $r^2 = 0.9942$ RMS= ± 12.4

GGA Stands for Generalized-Gradient Approximation. HGGA Stands for Hybrid GGA.

timized polarization functions reported on Tables I and V. Table VI reports the C—O distance as well as the electronic density, ρ_{crit} , and the laplacian of the electronic density, $\nabla^2\rho_{\text{crit}}$, at the C—O bond critical point for free CO molecule. In general, two tendencies can be observed depending on the type of approximation used in the functional. For the HGGA methods B3LYP and B98, there is an increase in the C—O bond distance, $R_{\text{C—O}}$, around 0.011 Å and a decrease of the ρ_{crit} values, in comparison to the standard basis. On the contrary, in the cases of BP86 and G97LYP, which are GGA based methods, there is a decrease of $R_{\text{C—O}}$, around 0.0061 Å, and an increase of ρ_{crit} and $\nabla^2\rho_{\text{crit}}$ values. In spite of the fact that PBEPBE is a HGGA method, the trends are similar to BP86 and G97LYP; i.e., a

decrease in the $R_{\text{C—O}}$, and an increase of ρ_{crit} and $\nabla^2\rho_{\text{crit}}$. It is noteworthy that the PBEPBE method presents the highest percentage of Hartree-Fock exchange (25%) in comparison with B3LYP (20%) and B98 (22%) [14]. Consequently, this suggests that the trends in the geometrical as well as on the topological parameters depends not only on the functional type, HGGA or GGA, but also on the percentage of Hartree-Fock exchange in the functional. The same trend found for the 6-31+G(d) basis set was observed for the 6-311G(d) basis set, as shown in Tables VI and VII. This leads to the conclusion that the effect of the polarization (d) exponent optimization on the geometrical and topological parameters of the CO molecule depends more on the density functional than on the basis set.

TABLE V

Optimized polarization (d) exponents for C(α_{C}) and O(α_{O}) on different basis sets and functionals for the LANL2DZ pseudopotential.

Functional type/ Basis set	6-31G(d)		Functional type/ Basis set	6-311G(d)	
	α_{C}	α_{O}		α_{C}	α_{O}
B98 HGGA/A _{IV}	0.405813	0.291499	B98 HGGA/B _{IV}	1.678665	0.213084
PBEPBE HGGA/A _V	0.925813	1.530036	PBEPBE HGGA/B _V	1.055562	1.655424
BP86 GGA/A _{VI}	0.975040	1.353631	BP86 GGA/B _{VI}	1.012272	1.593480
G96LYP GGA/A _{VII}	0.982855	1.373071	G96LYP GGA/B _{VII}	0.748265	2.386883

GGA Stands for Generalized-Gradient Approximation. HGGA Stands for Hybrid Generalized-Gradient Approximation

TABLE VI

Values of distance C—O, $R_{\text{C—O}}$ in Å, vibrational frequency, $\nu_{\text{C—O}}$ in cm^{-1} , electronic density, ρ_{crit} in au, and the electronic density laplacian, $\nabla^2\rho_{\text{crit}}$ in au, at the bond critical point for the CO molecule calculated with the standard and the optimized 6-31+G(d) basis set.

Method/basis set ^a	$R_{\text{C—O}}$	$\nu_{\text{C—O}}^b$	ρ_{crit}	$\nabla^2\rho_{\text{crit}}$
B3LYP/A _I	1.137	2203.3	0.472	1.330
B3LYP/A _{II}	1.147	2140.8	0.441	0.892
B3LYP/A _{III}	1.148	2142.1	0.449	0.656
B98/A _I	1.137	2214.9	0.468	0.142
B98/A _{IV}	1.148	2135.4	0.446	0.653
PBEPBE/A _I	1.148	2120.8	0.459	1.120
PBEPBE/A _V	1.142	2129.0	0.469	1.434
BP86/A _I	1.149	2111.8	0.457	1.198
BP86/A _{VI}	1.144	2118.7	0.463	1.437
G97LYP/A _I	1.149	2107.0	0.458	1.199
G97LYP/A _{VII}	1.143	2113.3	0.469	1.450

Experimental values: $R_{\text{C—O}} = 1.128$ Å, $\nu_{\text{C—O}} = 2140.8$ cm^{-1} Ref. 13.

^a See Tables I and V, for definition of basis sets.

^b Unscaled values.

Regarding the effect of the exponent optimization on other than C—O bonds, Table VIII shows for the $\text{Rh}(\text{CO})_2^-$ molecule that, for any given functional and basis set, the use of optimized d exponent causes only a slight change in the Rh—CO bond while the trends for C—O bonds are as expected; i.e., an increases of $R_{\text{C—O}}$ distance for B3LYP and B98, and a decreases for BP86. The mayor impact is reflected on the calculated frequencies. The difference between the unscaled, at B3LYP/A_I, and the experimental C—O frequency is greater or equal to 50 cm^{-1} , while using the optimized 6-31+G(d) basis set for C and O (basis set A_{II}), this difference reduced to 2 cm^{-1} . On the other hand, using scaled factor the calculated C—O frequency is: for B3LYP/CEP-631+G(d) Std level $1,899.7 \pm 10.1$ and $1,823.3 \pm 9.7$ cm^{-1} and for the optimized 6-31+G(d) basis set $1,899.3 \pm 5.1$ and $1,818.3 \pm 4.1$ cm^{-1} . These last values are closer to the experimental values 1,900.4 and 1,816.7 cm^{-1} than the formers.

Even though the basis set were optimized for transition metal carbonyls, it is worthwhile to investigate the performances of these basis set in other bond types. Calculations for C—O stretching in acetone (exp. value 1,731 cm^{-1}) show that the optimized basis set B3LYP/A_{II}, and B3LYP/C_{III} give better values, 1,747 cm^{-1} and 1,750 cm^{-1} , re-

spectively, than those obtained with the standard basis sets B3LYP/A_I, 1,796 cm^{-1} and B3LYP/C_I, 1,789 cm^{-1} . On the other hand, for BP86 the value with B_{VI} 1,739 cm^{-1} is equal to the value obtained with B_I 1,739 cm^{-1} . For acetaldehyde, the C—O stretching (experimental value 1,743 cm^{-1}) showed similar trend. Results with B3LYP/A_{II} 1,769 cm^{-1} and B3LYP/C_{III} 1,771 cm^{-1} are better than those obtained with B3LYP/A_I 1,818 cm^{-1} and B3LYP/C_I 1,821 cm^{-1} . While for BP86 the results are quite similar, 1,766 cm^{-1} for BP86/B_{VI} and 1,764 cm^{-1} BP86/B_I. These results show that even thought, the basis sets were optimized for transition metal carbonyls they could be used in organic compounds.

Conclusions

We obtained new frequency scaling factors for fundamental frequencies calculated with various DFT methods and basis sets using least-squares fittings with optimized polarization (d) exponents to reproduce the experimental values. In general, the scaling factor is less affected by the basis set than by the exchange-correlation functional. The accuracy of the scaled vibrational frequencies is much higher for the

TABLE VII

Values of distance C—O, $R_{\text{C—O}}$ in Å, vibrational frequency, $\nu_{\text{C—O}}$ in cm^{-1} , electronic density, ρ_{crit} in au, and the electronic density laplacian, $\nabla^2\rho_{\text{crit}}$ in au, at the bond critical point for the CO molecule calculated with the standard and the optimized 6-311G(d) basis set.

Method/basis set ^a	$R_{\text{C—O}}$	$\nu_{\text{C—O}}^b$	ρ_{crit}	$\nabla^2\rho_{\text{crit}}$
B3LYP/B _I	1.127	2220.3	0.489	0.6475
B3LYP/B _{II}	1.139	2142.6	0.456	0.3179
B3LYP/B _{III}	1.142	2140.5	0.458	0.138
B98/B _I	1.128	2230.1	0.484	0.763
B98/B _{IV}	1.133	2135.6	0.504	−0.587
PBEPBE/B _I	1.139	2135.8	0.474	0.548
PBEPBE/B _V	1.134	2146.9	0.494	0.382
BP86/B _I	1.139	2127.6	0.473	0.533
BP86/B _{VI}	1.135	2139.1	0.491	0.395
G97LYP/B _I	1.138	2126.2	0.391	−0.171
G97LYP/B _{VII}	1.137	2127.7	0.396	−0.374

Experimental values: $R_{\text{C—O}} = 1.128$ Å, $\nu_{\text{C—O}} = 2140.8$ cm^{-1} Ref. 14.

^a See Tables I and V for definition of the basis sets.

^b Unscaled values.

TABLE VIII

Values of distances, CO vibrational frequency, electronic density and the laplacian at the Rh—CO and RhC—O bond critical points for the RhCO₂[−] molecule.

Method/Basis set	$R_{\text{Rh—CO}}$	$\rho_{\text{crit Rh—CO}}$	$\nabla^2 \rho_{\text{crit Rh—CO}}$	$R_{\text{C—O}}$	$\rho_{\text{crit C—O}}$	$\nabla^2 \rho_{\text{crit C—O}}$	$\nu_{\text{C—O}}^a$
B3LYP/CEP-121 A _I	1.851	0.165	0.453	1.181	0.425	0.795	1951.6 1873.1
B3LYP/CEP-121 A _{II}	1.857	0.164	0.481	1.193	0.398	0.441	1899.5 1818.5
B3LYP/CEP-121 C _I	1.859	0.163	0.469	1.172	0.436	0.308	1949.7 1870.7
B3LYP/CEP-121 C _{II}	1.854	0.164	0.476	1.188	0.415	−0.103	1898.4 1818.4
B98/LANL2DZ B _I	1.854	0.164	0.513	1.171	0.434	0.413	1984.1 1908.7
B98/LanL2DZ B _{III}	1.855	0.158	0.524	1.178	0.448	−0.750	1900.9 1825.5
BP86/LANL2DZ B _I	1.854	0.163	0.487	1.186	0.419	0.233	1891.5 1825.0
BP86/LanL2DZ B _{III}	1.857	0.160	0.492	1.183	0.434	0.093	1895.2 1829.3

Experimental values $\nu_{\text{C—O}}$ 1,900.4 and 1,816.7 cm^{−1} Ref. 15.

^a Unscaled values.

new basis sets than for the standard ones. The uncertainties presented in Tables II and 5 reveal that the scaling factors are accurate to only three significant figures except for BP86/6-311G(d). Even though, on average, these optimized basis sets perform equally well, the deviations in the geometrical parameters for the each functional differ. This reflects the difficulty in describing the whole spectrum, geometries, binding energies and vibrational frequencies using one basis set and a given functional. In summary, the relevant feature in this work is the demonstration that optimized polarization d functions reduce the uncertainty $u(\lambda)$, (improve the accuracy and precision) associated with the calculation of vibrational frequency values.

References

1. Hehre, W. J. L.; Radom Schleyer; P. V. R.; Pople, J. A. Ab Initio Molecular Orbital Theory; Wiley: New York, 1986.
2. Rauhut, G.; Pulay, P. J Phys Chem 1995, 99, 3093.
3. Scott, A. P.; Radom, L. J Phys Chem 1996, 100, 16502.
4. Andreson, M. P.; Uvdal, P. J Phys Chem A 2005, 109, 2937.
5. Irikura, K. K.; Johnson, R. D., III; Kacker, R. N. J Phys Chem A 2005, 109, 8430.
6. Tantirungrotechai, Y.; Phanasant, K.; Roddech, S.; Surawatana-wong, P.; Sutthikhum, V.; Limtrakul, J. J Mol Struct (THEOCHEM) 2006, 760, 189.
7. Pidko, E. A.; van Santen, R. A. J Phys Chem C 2007, 111, 2643.
8. Pidko, E. A.; Hensen E. J. M.; van Santen, R. A. J Phys Chem C 2007, 111, 13068.
9. Joshi, A. M.; Delgass, W. N.; Thomson, K. T. J Phys Chem C 2007, 111, 11424.
10. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. Gaussian 03, Revision D. 02; Gaussian, Inc.: Wallingford CT, 2004.
11. Ruetter, F.; Sanchez, M.; Mendoza, C.; Sierraalta, A.; Martorell, G.; Gonzales, C. Int J Quantum Chem 2004, 96, 303.
12. Zhang, X.; Armentrout, P. B. Organometallics 2001, 20, 4266.
13. Linag B, Andrews L. J Phys Chem A 2000, 104, 9156.
14. Schultz, N. E.; Zhao, Y.; Truhlar, D. G. J Phys Chem A 2005, 109, 11127.
15. Zhou M.; Andrews L. J Phys Chem A 1999, 103, 7773.