Tailoring Transition Metal Complexes for Nonlinear Optics Applications. 2. A Theoretical Investigation of the Second-Order Nonlinear Optical Properties of $M(CO)_5L$ Complexes ($M = Cr, W$; $L = Py, PyCHO, Pyz, PyzBF_3, BPE, BPEBF_3$)

Maurizio Bruschi,[†] Piercarlo Fantucci,*,[‡] and Maddalena Pizzotti[§]

Department of Environmental Science, University of Milano-Bicocca, Piazza della Scienza 1, 20126 Milan, Italy, Department of Biotechnologies and Biosciences, University of Milano-Bicocca, Piazza della Scienza 2, 20126 Milan, Italy, and Department of Inorganic, Metallorganic and Analytical Chemistry of Milan University, Research Unit of INSTM of Milan University and CIMAINA Center of Excellence, Via Venezian 21, 20123 Milan, Italy

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In this work, we report an ab initio investigation of second-order nonlinear optical (NLO) properties and absorption electronic spectra of push−pull transition metal chromophores of the formula $[M(CO)_5L]$ ($M = Cr, W$; L = pyridine (Py), 4-formyl-pyridine (PyCHO), pyrazine (Pyz), *trans*-1,2-bis(4-pyridyl)ethylene (BPE)). Pyz and BPE are considered either with one nitrogen atom free or interacting with the strong acceptor BF_3. All of the molecular properties have been calculated using two different and methodologically independent approaches: the time dependent and coupled perturbed density functional theories (TDDFT and CPDFT) and the sum-over-states (SOS) approach, where the excited states are obtained via the single configuration interaction (SCI) ab initio method. DFT results are in acceptable agreement with the experimental energy values of electronic transitions (with the exception of chromophores with the large π-delocalization, like BPE); SCI calculations overestimate excitation energies and produce an inversion in the order of $d_M \rightarrow \pi^*_L$ and $d_M \rightarrow \pi^*_{CO}$ transitions. The SCI−SOS approach gives first-order hyperpolarizabilities, basically in agreement as trend and values with the experiments and seems to be a tool generally suitable for the evaluation of these properties also for transition metal complexes. On the other hand, the first-order hyperpolarizabilities computed using the CPDFT approach are consistently overestimated in comparison with the experimental results, especially in the case of a ligand with large π-delocalization. We also show that the "two-level" approximation taking into account only the lowest energy charge transfer excitation (e.g., $d_M \rightarrow \pi^*_L$) is not applicable to chromophores with the extended π-delocalized ligand (BPE) coordinated to a transition metal, due to significant contributions originating from intraligand $\pi_L \rightarrow \pi^*_L$ transitions. This study reports a detailed analysis and comparison of electronic NLO effects of transition metal complexes computed with DFT and ab initio SCI−SOS methodology.

Introduction

This is the second part of a series of papers[1] devoted to the theoretical investigation of the electronic and nonlinear optical (NLO) properties of some new push−pull asymmetrical transition metal (TM) complexes investigated experimentally by some of us,[2] based on the results of nonempirical quantum chemical calculations. The importance of TM complexes in the field of second-order NLO materials is now very well documented,[3−5] but a deep understanding of the underlying electronic features is still incomplete, because experimental NLO measurements are limited in number as are the theoretical investigations, so far carried out mainly at the empirical level.

Our previous paper[1] reported basic data for some of the title compounds such as best molecular geometries, charge distribution, and orientation of dipole moment, obtained from ab initio density functional theory (DFT) calculations.[6] In particular, information was obtained about the ground state electronic features of the asymmetrical complexes as functions of the donor−acceptor (acid−base) character of the monohapto nitrogen donor, π-conjugated ligand L bound to the $M(CO)_5$ moiety ($M = Cr, W$). In addition, general rules concerning the dependency of orientation and magnitude of dipole moment on the local coordination symmetry were discussed.

In the present study, the theoretical investigation is extended to the determination and analysis of the first-order hyperpolarizabilities of the title compounds, which are relatively simple systems containing only one TM atom. This set of complexes, however, is characterized by such pronounced differences in electronic features that it gives quite a broad spectrum of second-order NLO responses.[2] The complexes investigated are of the formula $[M(CO)_5L]$ ($M = Cr, W$; L = pyridine (Py), 4-formylpyridine (PyCHO), pyrazine (Pyz), *trans*-1,2-bis(4-pyridyl)-ethylene (BPE)). Pyz and BPE ligands have two nitrogen atoms: one coordinated to the metal center and the other free. We have also considered species generated by an acid−base interaction of the free nitrogen atom of Pyz and BPE with BF_3. Therefore, we considered 12 coordination compounds, all

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* Corresponding author. Phone: +39.02.64483477. Fax: +39.02.64483478. E-mail: piercarlo.fantucci@unimib.it.

[†] Department of Environmental Science, University of Milano-Bicocca.

[‡] Department of Biotechnologies and Biosciences, University of Milano-Bicocca.

[§] Research Unit of INSTM of Milan University and CIMAINA Center of Excellence.

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characterized by a metal atom in a d^6 configuration and zero oxidation state.

The aim of the present investigation is thus to analyze the electronic factors responsible for significant variations of second-order NLO properties using two complementary methodological approaches, as done, for example, by Varanasi et al.[7] for a class of push−pull organic chromophores. The adopted methods are the coupled perturbed density functional theory (CPDFT)[8,9] and the sum-over-states (SOS) methods.[10] As for the CPDFT approach, our study is parallel to other investigations of transition metal complexes already published.[11] However, the combined analysis of NLO properties based on the CPDFT and single configuration interaction (SCI)−SOS method is an original contribution of the present study. In both cases, calculations have been carried out at the "ab initio" level. The analysis of contributions entering the SOS, for each excited state, allows the conclusion that the "two-level" scheme[12] is not in general applicable to TM push−pull chromophores, different from the case of related organic species.

Computational Methods

NLO properties may be defined in terms of a power series of the molecular dipole moment in the presence of an oscillating electric field according to eq 1:

$$\mu(\mathbf{F})_i = \mu_i^0 + \sum_j \alpha_{ij} F_j + \frac{1}{2}\sum_{j,k}\beta_{ijk}F_jF_k + \frac{1}{6}\sum_{j,k,l}\gamma_{ijkl}F_jF_kF_l + ... \tag{1}$$

where $i, j, k, ... = x, y, z$; $\mathbf{F}(\omega)$ is the applied electric field with angular frequency $\omega = 2\pi v$; α_{ij}, β_{ijk}, and γ_{ijkl} are elements of the polarizability and of the first- and second-order hyperpolarizability tensors, respectively.

Among the theoretical approaches proposed for the calculation of the components of β and γ, we have applied the coupled perturbed (CP)[8] and the sum-over-state (SOS) methods.[10] The coupled perturbed method known as CPHF for the Hartree−Fock scheme[8] or CPDFT for the DFT variant[9] is based on the direct determination of the self-consistent first-order density matrix under the perturbation of a static or oscillating electric field. In this sense, the CPHF or CPDFT methods are approaches formally involving only the electron density of the ground state. On the contrary, the sum-over-states approach explicitly involves both ground and excited states, and it can be considered as an application of the time dependent perturbation theory of Orr and Ward.[10] The following SOS equations hold:

$$\alpha_{ij}(\omega) = \frac{1}{\eta}\sum_{l\neq 0}\left(\frac{\langle 0|\mu_i|l\rangle\langle 0|\mu_j|l\rangle}{\omega_{0l} - \omega} + \frac{\langle 0|\mu_i|l\rangle\langle 0|\mu_j|l\rangle}{\omega_{0l} - \omega}\right) \tag{2}$$

$$\beta_{ijk}(-\omega_\sigma;\omega_1,\omega_2) = \frac{1}{\eta^2}P(i,j,k;-\omega_\sigma,\omega_1,\omega_2) \times \sum_{l\neq 0}\sum_{m\neq 0}\frac{\langle 0|\mu_i|l\rangle\langle l|\bar{\mu}_j|m\rangle\langle m|\mu_k|0\rangle}{(\omega_{0l} - \omega_\sigma)(\omega_{0m} - \omega_2)} \tag{3}$$

$$\gamma_{ijkl}(\omega_\sigma;\omega_1,\omega_2,\omega_3) = \frac{1}{h^3}P(i,j,k,l;\omega_\sigma,\omega_1,\omega_2,\omega_3) \times (S_{ijkl}^{mnq} - V_{ijkl}^{mn}) \tag{4}$$

where

$$S_{ijkl}^{mnq} = \sum_{m\neq 0}\sum_{n\neq 0}\sum_{q\neq 0}\frac{\langle 0|\mu_i|m\rangle\langle m|\bar{\mu}_j|n\rangle\langle n|\bar{\mu}_k|q\rangle\langle q|\mu_l|0\rangle}{(\omega_{m0} - \omega_\sigma)(\omega_{n0} - \omega_2 - \omega_3)(\omega_{q0} - \omega_3)} \tag{5}$$

and

$$V_{ijkl}^{mn} = \sum_{m\neq 0}\sum_{n\neq 0}\frac{\langle 0|\mu_i|m\rangle\langle m|\mu_j|0\rangle\langle 0|\mu_k|n\rangle\langle n|\mu_l|0\rangle}{(\omega_{m0} - \omega_\sigma)(\omega_{n0} - \omega_3)(\omega_{n0} - \omega_2)} \tag{6}$$

In the above equations, the integrals $\langle l|\bar{\mu}_i|m\rangle$ concerning the l and m pairs of states are defined as $\langle l|\mu_i|m\rangle$ (the transition moment) when $l \neq m$ and as $\langle l|\mu_i|l\rangle - \langle 0|\mu_i|0\rangle$ (the difference between the dipole moment components of the excited and ground states) when $l = m$; ω_{0l} is the angular frequency associated with the $0 \rightarrow l$ transition; $\omega_\sigma = \omega_1 + \omega_2$ and $\omega_\sigma = \omega_1 + \omega_2 + \omega_3$ are the polarization frequencies for β and γ, respectively; P is a suitable permutation operator giving a sum over 6 and 24 terms for first- and second-order hyperpolarizabilities, respectively. The CPDFT calculations of the static second-order hyperpolarizabilites have been carried out using the B3LYP hybrid exchange-correlation functional[13] and the effective atomic core potential derived by Hay and Wadt[14] for metal atoms, with the associated double-ζ basis. All-electron double-ζ basis set of Dunning (D95V) has been adopted for all other atoms.[15] The excited states needed for SOS calculations have been obtained from ab initio configuration interaction (CI) including only single excited configurations (SCI).[16] The SCI and DFT calculations used the same basis set. For comparative purposes, optical absorption spectra have also been computed according to the random phase approximation (RPA)[17] within DFT (time dependent density functional theory (TDDFT)) and with the same basis set. As is well-known, in its original formulation, the RPA method implicitly considers correlation effects between ground and excited states (via double excitations), which are, on the contrary, absent in the SCI approach. This latter approach is acceptable only in the case that no excited states have double (or higher) excitation character and that correlation effects can be ignored for the ground state. CPDFT, SCI, and TDDFT calculations have been carried out using the Gaussian 98 suite of programs,[18] and SOS calculations were performed using a program written by us.

In the following, we will only discuss the first-order hyperpolarizability (β), in terms of β_{TOT} and β_{VEC} values, derived from "vector components" of β, $\bar{\beta}_i = \sum_{j\neq i}(\beta_{ijj} + \beta_{jij} + \beta_{jji})$, and respectively defined as $\beta_{\mathrm{TOT}} = [\sum_i \bar{\beta}_i^2]^{1/2}$ and $\beta_{\mathrm{VEC}} = \bar{\beta}\cdot\mu/|\mu|$, with μ being the dipole moment. Thus, β_{VEC} takes into account only the magnitude of the vector part of β projected along the direction of the dipole moment of the ground state. The β values are reported in units of $\beta\mathrm{u} = 10^{-30}\ \mathrm{cm}^{-5}\ \mathrm{esu}^{-1}$. To compare computed and measured β values, the theoretical values have been multiplied by factors derived from a phenomenological approach.[19] All of the results presented in this work refer to the DFT optimized geometries of TM complexes obtained in the previous[1] and the present work (data not reported for brevity). To validate the adopted methods, the first-order hyperpolarizability for two well studied prototypical push−pull organic chromophores, *p*-nitroaniline (PNA) and 4-amino-4′-nitrostilbene (ANS), has been calculated. It is well-known that measured β values of PNA and ANS are strongly affected by the polarity of the solvent;[20] as a consequence, some theoretical studies have been carried out taking into account solvent

TABLE 1: Dipole Moments (μ), Static First-Order Hyperpolarizabilities (β^0), First Allowed Excitation Energies (λ_{max}), and Oscillator Strengths (f) of PNA and ANS Computed at Different Levels of Theory[a]

	PNA			ANS		
	μ	β^0_{TOT}	β^0_{VEC}	μ	β^0_{TOT}	β^0_{VEC}
CPDFT/D95V	8.1	8.8	8.6	10.6	110.2	110.1
CPDFT/D95Vdp	7.7	8.7	8.6	11.7	106.4	105.9
CPDFT/6-31G(d,p)	7.4	6.8	6.6	9.9	87.4	86.7
CPDFT/6-311++G(d,p)	7.8	8.5	8.4	10.4	88.2	87.5
SOS−SCI/D95V	8.1	17.5	17.2	10.0	85.6	84.7
SOS−SCI/D95Vdp	7.8	15.5	15.3			
SOS−SCI/6-31G(d,p)	7.7	14.0	13.8	9.6	71.2	70.6
SOS−SCI/6-311++G(d,p)	7.9	15.1	14.9			
expt			15.5[b]			40[c]

	PNA		ANS	
	λ_{max}	f	λ_{max}	f
TDDFT/D95V	336	0.333	480	0.653
TDDFT/D95dp	338	0.342	478	0.717
TDDFT/6-31G(d,p)	322	0.324	454	0.713
TDDFT/6-311++G(d,p)	339	0.341	478	0.717
CIS/D95V	238	0.512	305	1.586
CIS/D95Vdp	248	0.504		
CIS/6-31G(d,p)	238	0.512	302	1.572
CIS/6-311++G(d,p)	249	0.505		
expt	365[c]		402[c]	

[a] μ in debyes; β_{TOT} and β_{VEC} in β units, βu = 10^{-30} cm^{-5} esu^{-1}; λ_{max} in nanometers. [b] From ref 20h: EFISH measurements in the gas phase with a wavelength of 1064 nm. [c] From ref 20d: EFISH measurements in CHCl$_3$ solution with a wavelength of 1907 nm.

effects.[21] In our work, the first-order hyperpolarizabilities of PNA and ANS have been calculated only in order to assess the reliability of computational schemes in predicting general trends of NLO properties. In this context, the exclusion of the solvent effects in the calculation of β does not seem to be an important limitation. In any case, for a more consistent comparison, our calculated β values are compared with EFISH (electric field induced second harmonic) measurements, obtained either in the gas phase with an incident radiation of 1064 nm for PNA[20h] or in CHCl$_3$ (a weakly interacting solvent) with an incident radiation of 1907 nm for ANS.[20d] All of the properties are computed on PNA and ANS considered in their best geometries. The geometrical structure of the NO$_2$-substituted phenyl ring is almost exactly transferable from PNA to ANS. Table 1 shows data for μ and static β_{TOT} and β_{VEC} (β^0_{TOT} and β^0_{VEC}) as well as data for the optical excitations. CPDFT β^0_{VEC} values of PNA are quite insensitive to the atomic basis set, up to the triple-ζ quality (D95V, D95Vdp, 6-31G(d,p), 6-311++G(d,p)) (see Table 1). Results from the rather inexpensive D95V basis are in good agreement with the experiment and comparable with those of more extended basis sets. SOS β^0_{VEC} values result in being slightly more dependent on the composition of the basis set. Indeed, the extension of the basis allows a more flexible description of the excited states included in the perturbation expansion. For example, the β^0_{VEC} value of PNA decreases from 17.2 to 13.8 βu upon going from the D95V basis to the 6-31G(d,p) basis. Both values are, however, in acceptable agreement with the experiment (15.5 βu). Some methodological problems may arise when dealing with more π-delocalized ANS species. In the framework of DFT, difficulties originate from its inadequacy to deal with the excited states and hyperpolarizabilities of highly π-conjugated molecules.[22] On the other hand, the SOS or SCI method may become inaccurate because of the existence of a dense optical spectrum composed of several low lying excitations, a case which strictly requires an extended treatment of correlation. With this in mind, calculations carried out with a limited basis and with severely truncated CI expansions on ANS are expected to give results less accurate than those concerning PNA. Accordingly, for all of the basis sets considered, the CPDFT β^0_{VEC} value of ANS is significantly overestimated: the addition of polarization and diffuse functions to the D95V basis does not improve the estimate of β^0_{VEC}, and also, the larger basis sets 6-31G(d,p) and 6-311++G(d,p) give a β^0_{VEC} value still too high with respect to the experiment. The SOS value of β^0_{VEC} is similar to the CPDFT one (at least for the 6-31G(d,p) basis set) but is in slightly better agreement with the experiment (Table 1). The general trend of CPDFT and SOS values can be considered as correct even taking into account that the frequency dependent values reported in Table 1 should be decreased (by about 10−20%) to give the corresponding static values.

In Table 1, the first allowed excitation energies (λ_{max}) and the corresponding oscillator strengths (f) of PNA and ANS, computed at different levels of theory, are also reported. The TDDFT method always gives slightly underestimated values of λ_{max} for PNA, while the corresponding values for ANS are always largely overestimated (about 50−80 nm), as expected.[22] The SCI method underestimates λ_{max} by about 100 nm for both PNA and ANS. In general, within a given methodology, the λ_{max} values appear to be quite independent of the composition of the basis set.

All of the above results clearly indicate limitations of both the CPDFT and SOS−SCI approaches. We would like to stress, however, that our choice of the computational frameworks is a necessary compromise between high accuracy and low computing time. The test calculations on PNA and ANS confirm that the CPDFT and SOS−SCI approaches are able to give complementary information, important for a correct analysis of the trends and order of magnitude of the molecular first-order hyperpolarizability. Furthermore, we are more interested in reproducing the general trends of the NLO properties than exact values because also the reference experimental data are known to be affected in general by non-negligible errors.

Results and Discussion

Second-Order NLO Properties of [M(CO)$_5$L] Species (M = W, Cr; L = Py, PyCHO, Pyz, PyzBF$_3$, BPE, BPEBF$_3$). Static first-order hyperpolarizabilities computed by the CPDFT and SOS approaches are shown in Table 2 together with the corresponding dynamic hyperpolarizabilities computed using the SOS method for a 1907 nm incident wavelength. Pyz and BPE ligands are centrosymmetric and therefore do not exhibit second-order NLO responses. The corresponding BF$_3$ monoadducts are asymmetric and show nonzero first-order hyperpolarizabilities with a β^0_{VEC} value significantly increasing in the case of the large π-delocalized BPEBF$_3$ ligand (see Table 2).

CPDFT Calculations on W Complexes. For all of the compounds investigated, the leading vector component of β and the dipole moment (μ) are directed along the charge transfer axes, and therefore, β^0_{VEC} is almost coincident with β^0_{TOT}. For the 16e [W(CO)$_5$] fragment, we computed $\beta^0_{\mathrm{VEC}} = -1.9$ βu: the negative sign indicates that the leading vector component of β is opposite the dipole moment direction. The coordination of Py and Pyz ligands to [W(CO)$_5$] enhances the computed β^0_{VEC} values to −11.6 and −17.3 βu, respectively, still with a negative sign. In both cases, the computed β^0_{VEC} values agree in sign but are about 3 times larger in absolute value than the experimental values.[2,23] A further strong enhancement of the absolute value of β^0_{VEC} (−49.8 βu) is observed for

TABLE 2: First-Order Hyperpolarizabilities (βu) of the Complexes Considered in This Study Using the CPDFT and SCI−SOS Approaches

	CPDFT		SOS				expt	
	static		static		SHG (ω_0 = 1907 nm)			
	β^0_{TOT}	β^0_{VEC}	β^0_{TOT}	β^0_{VEC}	β^0_{TOT}	β^0_{VEC}	β^0	β^λ
$\mathrm{PyzBF_3}$	0.9	−0.9	0.3	0.3	0.3	0.3		
$\mathrm{BPEBF_3}$	10.3	10.3	15.6	15.5	16.3	16.3		
$\mathrm{[W(CO)_5]}$	1.9	−1.9	14.2	−14.2	17.4	−17.4		
$\mathrm{[W(CO)_5Py]}$	11.6	−11.6	8.0	−8.0	8.5	−8.5		−4.4[e]
$\mathrm{[W(CO)_5PyCHO]}$	52.3	−49.8	25.8	−24.3	27.6	−26.0		−12[e]
$\mathrm{[W(CO)_5Pyz]}$	17.3	−17.3	12.8	−12.8	13.6	−13.6	−4.7[b,c]	−6[b,c]
$\mathrm{[W(CO)_5PyzBF_3]}$[a]	27.4	27.3	50.9	50.2	55.5	54.7	24[b,d]	38[b,d]
$\mathrm{[W(CO)_5BPE]}$	58.8	−58.8	11.4	−11.4	12.4	−12.4	−5.2[b,c]	−7[b,c]
$\mathrm{[W(CO)_5(BPE)BF_3]}$[a]	165.8	162.9	46.3	42.8	49.8	46.0	−36[b,d]	−49[b,d]
$\mathrm{[Cr(CO)_5]}$	1.8	−1.8	5.0	−5.0	6.7	−6.7		
$\mathrm{[Cr(CO)_5Py]}$	6.3	−6.3	0.1	0.1	0.1	0.1		
$\mathrm{[Cr(CO)_5PyCHO]}$	34.7	−31.7	6.1	−5.3	6.4	−5.6		
$\mathrm{[Cr(CO)_5Pyz]}$	11.1	−11.1	1.7	−1.7	1.8	−1.8		
$\mathrm{[Cr(CO)_5PyzBF_3]}$	26.7	26.5	11.4	11.3	12.1	12.1		
$\mathrm{[Cr(CO)_5BPE]}$	33.4	−33.4	4.9	4.8	5.1	5.0		
$\mathrm{[Cr(CO)_5(BPE)BF_3]}$	114.5	113.3	15.2	15.0	16.1	15.9		

[a] The values of the diagonal components of β (β_{xxx}, β_{yyy}, and β_{zzz}) for $\mathrm{[W(CO)_5PyzBF_3]}$ are 28.3, −0.4, and 0.0 βu (CPDFT) and 48.1, 0.0, and 0.0 βu (SOS) and for $\mathrm{[W(CO)_5BPEBF_3]}$ are −173.6, 0.1, and 0.0 βu (CPDFT) and −42.9, 0.4, and 0.1 βu (SOS), respectively, to be compared with solvatochromic data reported in the last column (see text for discussion). [b] Taken from ref 2. [c] From EFISH measurements. [d] From solvatochromic measurements. [e] Taken from ref 23: EFISH measurements at 1907 nm in toluene ($\mathrm{[W(CO)_5Py]}$) and $\mathrm{CHCl_3}$ ($\mathrm{[W(CO)_5PyCHO]}$). Theoretical β values for $\mathrm{[W(CO)_5Py]}$ and $\mathrm{[W(CO)_5PyCHO]}$ obtained at the ZINDO−SOS level are discussed in ref 25.

$\mathrm{[W(CO)_5PyCHO]}$; the value is about 4 times larger than the experimental value.[23] Note, however, that the experimental value was obtained from EFISH experiments working with an incident wavelength of 1907 nm:[2,23] under these conditions, β^0_{VEC} values are reliable only in the case that the γ contribution can be neglected. In addition, the experimental values are probably underestimated due to the reversible dissociation of the ligand L.[2] Theoretical β^0_{VEC} values calculated by the ZINDO−SOS approach[25] are in better agreement with the experiment, being equal to −5.91 and −15.5 βu for $\mathrm{[W(CO)_5Py]}$ and $\mathrm{[W(CO)_5PyCHO]}$, respectively. In the case of $\mathrm{[W(CO)_5PyzBF_3]}$, we computed $\beta^0_{\mathrm{VEC}} = 27.3$ βu: the increase in the value and the positive sign (in agreement with the experiment[2]) are entirely due to the inversion of the dipole moment caused by the coordination of the strong electron acceptor $\mathrm{BF_3}$ group. The leading component of β is almost unaffected by the presence of the $\mathrm{BF_3}$ group, being always almost parallel to the direction of the dipole moment axis and the charge transfer.[2] The replacement of Pyz with the more π-delocalized BPE ligand produces a strong effect on β^0_{VEC}. As shown in Table 2, the β^0_{VEC} value of $\mathrm{[W(CO)_5BPE]}$ is still negative but with an absolute value about 3 times larger than that of $\mathrm{[W(CO)_5Pyz]}$. Such a result for $\mathrm{[W(CO)_5BPE]}$ does not agree with the experimental value, which is negative but close in value to $\mathrm{[W(CO)_5Pyz]}$ (see Table 2).[2] Notably, coordination of $\mathrm{BF_3}$ to the free nitrogen atom of $\mathrm{[W(CO)_5BPE]}$ enhances considerably the computed β^0_{VEC} value, which also becomes positive.

A significant increase of the value of the first-order hyperpolarizability (still negative) associated with the presence of $\mathrm{BF_3}$ was obtained by the solvatochromic method.[2] It must be pointed out that solvatochromic measurement[24] can give a β value comparable only with the leading diagonal element of the tensor and not with β^0_{VEC}. In our case, since β_{yyy} and β_{zzz} are very small (Table 2), the leading element to be considered is β_{xxx}. The CPDFT of β_{xxx} for $\mathrm{[W(CO)_5PyzBF_3]}$ and $\mathrm{[W(CO)_5(BPE)BF_3]}$ is equal to 28.3 and −173.6 βu, respectively, and therefore in qualitative agreement with the solvatochromic results (24.0 and −36.0 βu, respectively, see Table 2).

CPDFT Calculations on Cr Complexes. The $\mathrm{[Cr(CO)_5L]}$ complexes exhibit a second-order NLO response systematically lower than that of the corresponding W(0) complexes (Table 2), a trend which can be ascribed to the reduced polarizability of the Cr(0) atom, with respect to W(0). In general, the calculated first-order hyperpolarizabilities for Cr(0) compounds are about 30−50% smaller than those for W(0) complexes. On the other hand, the general trend computed for various chromophores is confirmed in $\mathrm{[Cr(CO)_5L]}$ complexes: the absolute value of β^0_{VEC} increases by increasing the π-conjugation of the ligand and in the presence of the electron withdrawing $\mathrm{BF_3}$ group.

SCI−SOS Calculations on W Complexes. In the SCI−SOS calculations, the number of the CI roots considered (i.e., the number of excited states inserted in the summation) has been limited to 100, while the CI space is the full space for each complex. In Figure 1, the calculated β^0_{VEC} values of all of the chromophores investigated are plotted versus the number of states (ordered by increasing energy) included in SOS: 100 excited states lead always to converged values.

Some observation can be drawn when considering Figure 1: (i) In the case of $\mathrm{M(CO)_5}$ fragments, where only $\mathrm{M} \rightarrow \pi^*_{\mathrm{CO}}$ excitations are present, several excited states contribute to β^0_{VEC}, each of them to a small extent and, in general, with the same sign. (ii) $\mathrm{M} \rightarrow \pi^*_{\mathrm{L}}$ and $\pi_{\mathrm{L}} \rightarrow \pi^*_{\mathrm{L}}$ excitations contribute to β^0_{VEC} to a much larger extent than corresponding excitations involving carbonyl groups. (iii) A really dominant contribution cannot be observed in any of the examined cases. This is clearly in disagreement with expectations based on the two-level approximation. (iv) In the presence of π-conjugated ligands L, contributions of opposite sign came from low energy states as well as from higher energy ones. This fact further reinforces observation iii but underlines the possible occurrence of the cancellation of opposite contributions. (v) An oscillating behavior of β^0_{VEC} depending on the number of terms included in SOS is present with large amplitude in all cases of ligand L coordinated to $\mathrm{BF_3}$.

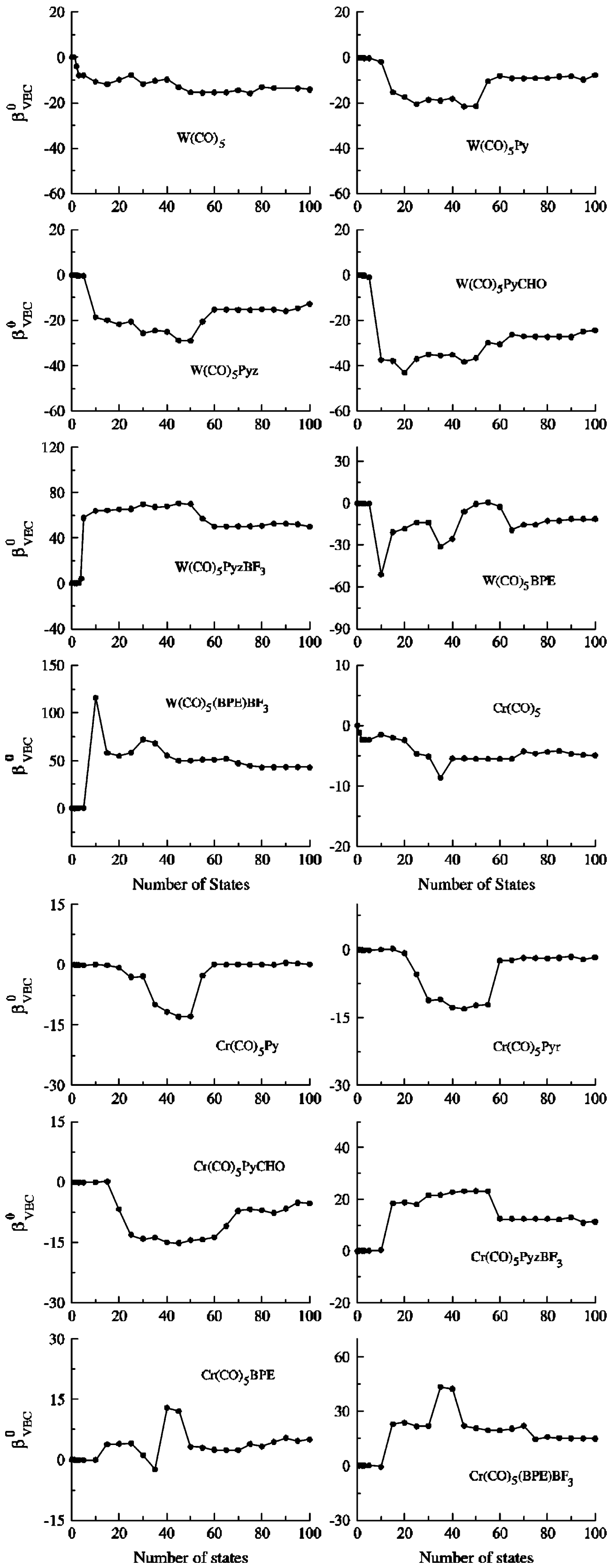


Figure 1. Static β_{VEC} (β^0_{VEC}) values of [M(CO)$_5$L] complexes (M = W, Cr; L = Py, PyCHO, Pyz, PyzBF$_3$, BPE, BPEBF$_3$) calculated using the SCI−SOS approach as a function of the number of excited states used in the SOS expansion.

The values of β^0_{VEC} computed according to SOS differ significantly (by a factor of 2.0−5.0) from the corresponding CPDFT values; however, the two methods agree as for the general trend (see Table 2). In particular, the important role played by the BF$_3$ group (increase in the absolute value of β^0_{VEC} and sign inversion) is common for SOS and CPDFT results: compare [W(CO)$_5$PyzBF3] and [W(CO)$_5$Pyz]. The substitution of Pyz with BPE ligand (characterized by a more extended π-delocalization) has little effect on SOS β values. This is due to the balance of a positive contribution of M → π^*_{L} excitation (twice larger in BPE than in Pyz complex) and of a negative contribution due to intraligand excitation in BPE (absent in the Pyz ligand, see Figure 1 and Table 2).

As commented above, solvatochromic data are available for [W(CO)$_5$PyzBF$_3$] and [W(CO)$_5$(BPE)BF$_3$]. The SOS β_{xxx} values for [W(CO)$_5$PyzBF$_3$] and [W(CO)$_5$(BPE)BF$_3$] are equal to 48.1 and −42.9 βu, respectively, which are closer to solvatochromic data than the CPDFT values. Therefore, our SOS calculations are able to reproduce nicely also fine differences between β_{ppp} and β^0_{VEC} values. The comparison with the solvatochromic experiment is satisfactory considering that such an approach is characterized by quite large uncertainties.

SCI−SOS Calculations on Cr Complexes. Also, the SOS approach predicts the first-order hyperpolarizability of the related Cr(0) chromophores to be much smaller, in general, than that of the corresponding W(0) chromophores (Table 2). As in the case of the W(0) complexes, calculated β^0_{VEC} values of [Cr(CO)$_5$BPE] and [Cr(CO)$_5$(BPE)BF$_3$] are quite different from those calculated by the CPDFT approach (Table 2).

Electronic Absorption Spectra of [M(CO)$_5$L] Species (M = W, Cr; L = Py, PyCHO, Pyz, PyzBF$_3$, BPE, BPEBF$_3$). Optical excitations of W and Cr complexes have been computed using the TDDFT and SCI methods (Table 3). In Figure 2, we report the simulation of experimental spectra obtained by broadening the computed excitation lines by means of a Lorentian function with a half-width equal to 30 nm.

For simplicity, in Table 3, only absorption wavelengths (λ), energies, and oscillator strengths (f) are reported concerning two low lying charge transfer transitions expected to contribute mostly to β values, namely, the $\text{d}_{\text{M}} \rightarrow \pi^*_{\text{L}}$ ($\lambda_{\text{M}\rightarrow\text{L}}$) and $\text{d}_{\text{M}} \rightarrow \pi^*_{\text{CO}}$ ($\lambda_{\text{M}\rightarrow\text{CO}}$) transitions. The relative intensity of the $\text{d}_{\text{M}} \rightarrow \pi^*_{\text{L}}$ transitions are always much higher than those of the $\text{d}_{\text{M}} \rightarrow \pi^*_{\text{CO}}$ ones (see the oscillator strengths of Table 3).

The SCI $\lambda_{\text{M}\rightarrow\text{CO}}$ values are in a reasonable agreement with the experiment, while the corresponding $\lambda_{\text{M}\rightarrow\text{L}}$ values are significantly underestimated. In addition, SCI calculations produce $\lambda_{\text{M}\rightarrow\text{L}}$ values lower than $\lambda_{\text{M}\rightarrow\text{CO}}$ values, in contrast with the experiment (see Table 3). However, the general trend of $\lambda_{\text{M}\rightarrow\text{L}}$ values for the different [M(CO)$_5$L] (M = W, Cr) complexes is well reproduced by our SCI calculations, when compared with the experimental data. In particular, the computed red shift of $\lambda_{\text{M}\rightarrow\text{L}}$ due to the coordination of BF$_3$ to the free nitrogen of Pyz in [W(CO$_5$)PyzBF$_3$] is about 90 nm (1.3 eV), a value not too far from that observed.[2] A shift to lower energies of $\lambda_{\text{M}\rightarrow\text{L}}$ may be easily correlated with the enhancement of the absolute value of β of [W(CO$_5$)PyzBF$_3$] with respect to [W(CO)$_5$Pyz], observed experimentally and confirmed by both CPDFT and SOS calculations. The replacement of Pyz with the more π-delocalized BPE ligand shifts $\lambda_{\text{M}\rightarrow\text{L}}$ to a higher value by about 35 nm (0.6 eV), while the coordination of the free nitrogen of BPE to BF$_3$ in [W(CO)$_5$BPE] produces a smaller increase of only 12 nm (0.2 eV), in good agreement with the experimental trend.[2]

The computed $\lambda_{\text{M}\rightarrow\text{L}}$ values for the [Cr(CO)$_5$L] complexes are systematically lower than those of the corresponding W(0) complexes. The red shift calculated when the free nitrogen of Pyz or BPE is coordinated to BF$_3$ is smaller than that for the

TABLE 3: Absorption Wavelengths and Energies for d → L and d → CO Transitions in Cr(0) and W(0) Complexes, Computed with Different Methods[a]

	SCI		TDDFT		expt	
	d → L	d → CO	d → L	d → CO	d → L	d → CO
$[W(CO)_5\,Py]$	234, 5.30, 0.134	347, 3.57, 0.036	401, 3.09, 0.071	419, 2.96, 0.012	332[b]	
$[W(CO)_5PyCHO]$	274, 4.53, 0.355	346, 3.58, 0.035	532, 2.33, 0.206	414, 2.99, 0.012	420−440[b]	
$[W(CO)_5Pyz]$	250, 4.97, 0.228	343, 3.62, 0.034	436, 2.84, 0.155	414, 2.99, 0.012	under $\lambda_{d\to CO}$[c]	398[c]
$[W(CO)_5PyzBF_3]$	336, 3.69, 0.279	338, 3.67, 0.034	526, 2.36, 0.256	401, 3.10, 0.011	528[c]	390[c]
$[W(CO)_5BPE]$	283, 4.38, 0.739	346, 3.58, 0.026	492, 2.52, 0.319	422, 2.94, 0.012	441[c]	403[c]
$[W(CO)_5(BPE)BF_3]$	295, 4.20, 0.984	346, 3.59, 0.034	603, 2.06, 0.324	418, 2.96, 0.012	449[c]	403[c]
$[Cr(CO)_5\,Py]$	199, 6.23, 0.078	370, 3.35, 0.006	368, 3.37, 0.035	387, 3.20, 0.012		
$[Cr(CO)_5PyCHO]$	231, 5.37, 0.246	370, 3.35, 0.005	502, 2.47, 0.150	390, 3.18, 0.013		
$[Cr(CO)_5Pyz]$	209, 5.94, 0.130	370, 3.35, 0.006	417, 2.81, 0.113	388, 3.19, 0.013		
$[Cr(CO)_5PyzBF_3]$	249, 4.98, 0.225	369, 3.36, 0.006	525, 2.36, 0.183	383, 3.24, 0.011		
$[Cr(CO)_5BPE]$	264, 4.70, 1.368	369, 3.36, 0.005	464, 2.68, 0.253	393, 3.15, 0.013		
$[Cr(CO)_5(BPE)BF_3]$	265, 4.67, 1.448	373, 3.33, 0.007	564, 2.20, 0.232	394, 3.15, 0.011		

[a] For each transition, the first, second, and third values are the wavelength (nm), the energy (eV), and the oscillator strength, respectively. [b] Taken from ref 23. [c] Taken from ref 2.

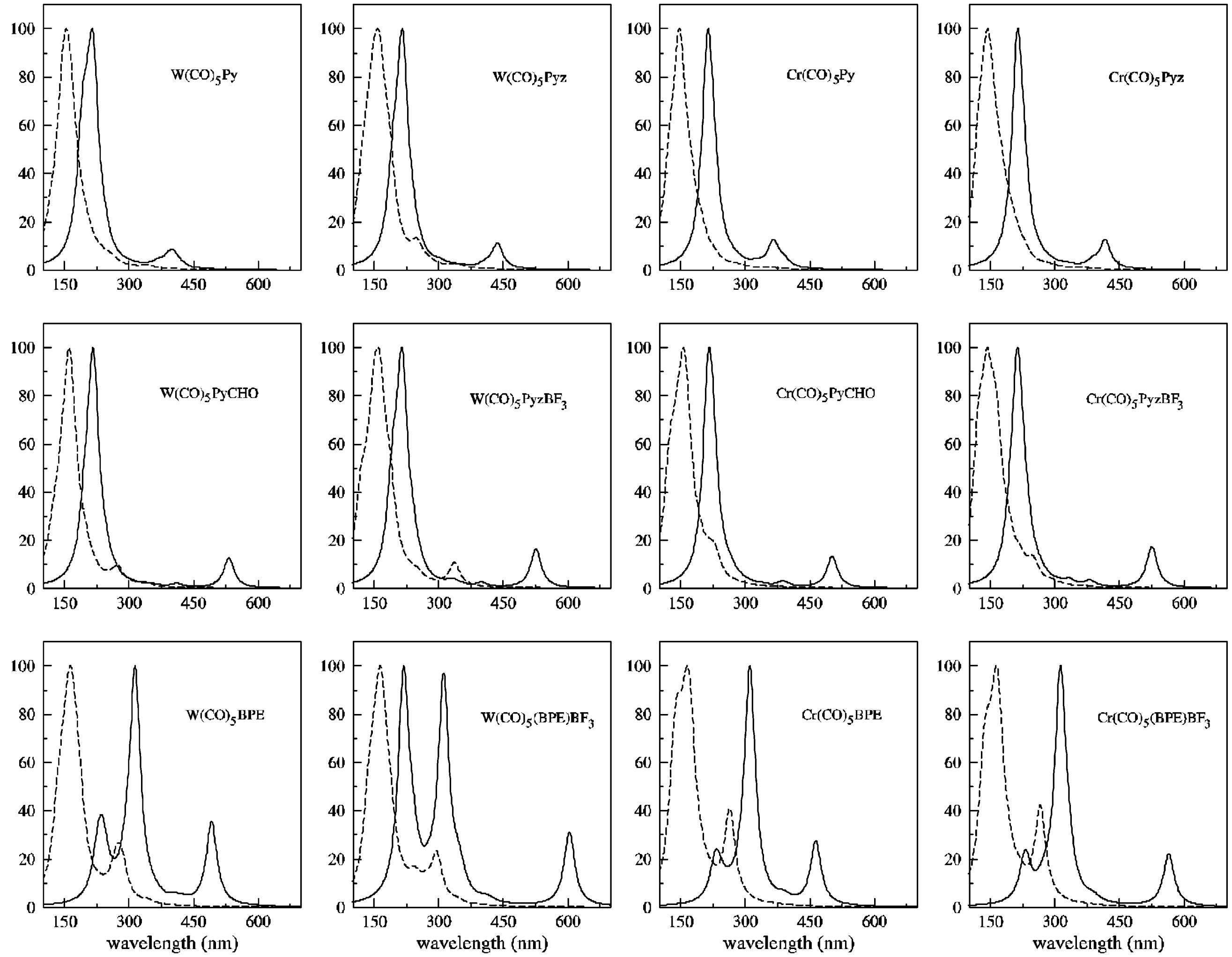


Figure 2. Simulated absorption UV−vis spectra of $[M(CO)_5L]$ complexes (M = W, Cr; L = Py, PyCHO, Pyz, $PyzBF_3$, BPE, $BPEBF_3$) calculated at the SCI/LANL2DZ (- - -) and TDB3LYP/LANL2DZ (—) levels of theory.

corresponding W(0) complexes. The extension of the π-delocalization of the organic ligand (e.g., $[Cr(CO)_5Pyz]$ vs $[Cr(CO)_5BPE]$) leads to a quite significant red shift of $\lambda_{M\to L}$ (Table 3).

The TDDFT value of $\lambda_{M\to CO}$ is red-shifted by about 50 nm (∼0.6 eV) with respect to the SCI one and is in fairly good agreement with the experiment. On the other hand, $\lambda_{M\to L}$ is remarkably higher than the SCI value and in general also red-shifted with respect to the experiment (Table 3). The trend of $\lambda_{M\to L}$ and $\lambda_{M\to CO}$, given by the TDDFT approach, is parallel to the experiment; in particular, $\lambda_{M\to L}$ is always predicted at a lower energy than $\lambda_{M\to CO}$. The red shift of $\lambda_{M\to L}$ due to the presence of the BF_3 group in $[W(CO)_5PyzBF_3]$ is equal to about 90 nm (0.5 eV), similar to the SCI value but smaller than the experimental one.[2] In the case of $[W(CO)_5(BPE)BF_3]$, $\lambda_{M\to L}$ increases by more than 100 nm (0.5 eV), similar to the corresponding Cr(0) complex, a result which disagrees with the SCI data and with the experiment. The very large enhancement

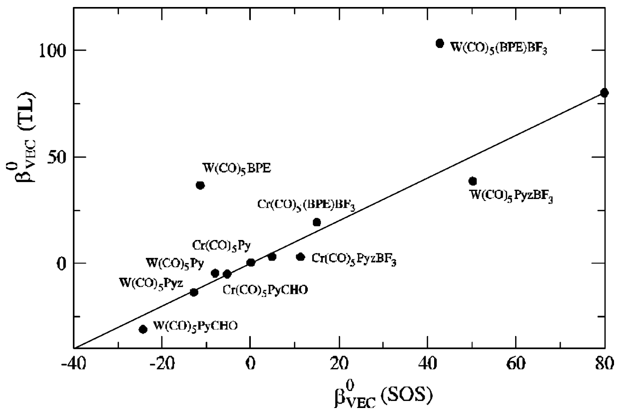


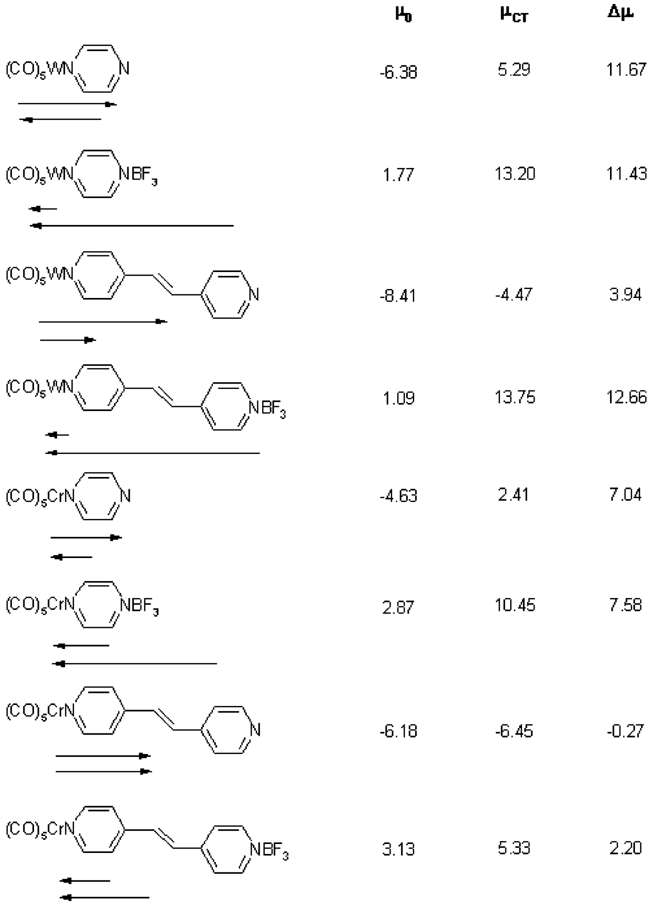
Figure 3. β^0_{VEC} from the two-level approximation (TL) versus β^0_{VEC} computed from the full SOS expansion.

of the CPDFT first-order hyperpolarizability in the case of $[M(CO)_5(BPE)BF_3]$ (M = W, Cr) chromophores, can be correlated to such a large red shift.

On the Validity of the Two-Level Approximation. For the chromophores investigated in this work, the SOS approach is a natural way to analyze the general reliability of the two-level approximation proposed by Oudar,[12] which has been very often applied to traditional push−pull organic chromophores. The approximation is based on the assumption that only the first charge transfer (in our case, the $d_M \rightarrow \pi^*_L$ excitation) may give a significant contribution to the first-order hyperpolarizability. Under Oudar's assumption, the SOS expansion for the calculation of β_{ppp} (p being the direction of the charge transfer) reduces to

$$\beta_{ppp} = \frac{3e^2}{2\eta} \frac{\omega_{0e} f_{0e} \Delta\mu_{e0}}{({\omega_{0e}}^2 - 4\omega^2) - ({\omega_{0e}}^2 - \omega^2)} \tag{7}$$

where f_{0e} and ω_{0e} are the oscillator strength and the angular frequency of the excitation from the ground state $|0\rangle$ to the excited state $|e\rangle$ and $\Delta\mu_{e0}$ is the variation of the static dipole between the $|e\rangle$ and $|0\rangle$ states. Some attempt of applying the two-level approximation for a qualitative analysis of experimental observations of organometallic push−pull chromophores has been done in ref 2. The two-level approximation can now be checked against our present full SCI−SOS calculations, by comparing full SCI−SOS β^0_{VEC} values with the values given by eq 7, considering only the $d_M \rightarrow \pi^*_L$ excitation. Note, however, that the $d_M \rightarrow \pi^*_L$ excitation is not the lowest energy transition in the considered complexes, different from the $\pi_L \rightarrow \pi^*_L$ transition occurring in conjugated organic systems. As shown in Figure 3, a fairly good correlation can be established between the two sets of values (full SCI−SOS and two-level) for all of the chromophores, with the exception of $[W(CO)_5BPE]$ and $[W(CO)_5(BPE)BF_3]$, for which the two-level β^0_{VEC} value is significantly larger than both the SOS and experimental values.[2] Analysis of the excited states (Figure 1) that significantly contribute to the β^0_{VEC} value in the SCI−SOS expansion easily explains such a drawback, due to the missing $\pi_L \rightarrow \pi^*_L$ excitation contributions which are naturally considered in the SOS but not in the two-level approach. These contributions act against those of the $d_M \rightarrow \pi^*_L$ transitions and seem to be specific for the BPE chromophore with high π-delocalization. An analogous effect is present also in the complexes of Cr(0) with BPE and $BPEBF_3$ and is responsible for the oscillating behavior of β^0_{VEC} as the number of excited states included in the SOS expansion increases (see Figure 1). However, due to a nearly complete cancellation of opposite contributions, the SOS β^0_{VEC} values are quite close to the two-level-approximation (TL) ones. In general, however, one should consider that such fine effects on β^0_{VEC} might be dependent on the specific nature of the ligand and of its substituents.[11a]



μ_0	μ_{CT}	$\Delta\mu$
-6.38	5.29	11.67
1.77	13.20	11.43
-8.41	-4.47	3.94
1.09	13.75	12.66
-4.63	2.41	7.04
2.87	10.45	7.58
-6.18	-6.45	-0.27
3.13	5.33	2.20

Figure 4. Variation of polarity upon MLCT excitation of $[M(CO)_5L]$ complexes. On the left, the upper and lower arrows represent μ for the ground state (μ_0) and excited state (μ_{CT}) dipole moments, respectively. On the right are the values of μ_0 and μ_{CT} as well as the difference $\Delta\mu = \mu_{CT} - \mu_0$.

In Figure 4, we report the direction and magnitude, along the charge transfer axis, of the dipole moments of the ground state (μ_0) and the $d_M \rightarrow \pi^*_L$ charge transfer state (μ_{CT}) as well as their difference $\mu_{CT} - \mu_0$ ($\Delta\mu$). In the presence of the BF_3 group in $[W(CO)_5PyzBF_3]$ and $[W(CO)_5(BPE)BF_3]$, μ_0 is reduced in magnitude and inverted in direction with respect to the corresponding BF_3 free complexes; the direction of μ_{CT} is conserved, and its magnitude is increased in $[W(CO)_5PyzBF_3]$, while its direction is inverted in $[W(CO)_5(BPE)BF_3]$. The modification of both μ_0 and μ_{CT} actually does not have a large effect on their difference, which remains quite comparable. Therefore, the large enhancement of β^0_{VEC} due to coordination of BF_3 is not caused by large differences in dipole moments in the excited and ground state but to a reduced excitation energy and to an increased oscillator strength. The behavior of $[M(CO)_5L]$ push−pull chromophores investigated in this work differs significantly from that of classical organic push−pull, π-conjugated chromophores, where an increased delocalization produces a large red shift of the λ_{max} value of the charge transfer state. On the contrary, as shown also by Marks et al. for para-substituted styrylpyridine $W(CO)_5$ complexes,[25] the $d_M \rightarrow \pi^*_L$ excitation is localized mainly on the pyridine ring coordinated to the metal and the extension of the π-conjugation of the ligand has only a minor effect.

Our ab initio calculations proved to give acceptable predictions of the trend and values of optical absorption spectra and the second-order NLO hyperpolarizability, for the set of new push−pull organometallic compounds considered here. The adopted computational framework, limited in sophistication by a necessary compromise between high accuracy and relatively low computing time, gives $\lambda_{M \rightarrow L}$ values calculated by the SCI approach largely underestimated with respect to the experimental values. However, the trend along the series of complexes and in particular the relevant effects due to binding of BF_3 to the free nitrogen atom ($PyzBF_3$ and $BPEBF_3$) is well reproduced. Despite the disagreement between SCI computed and observed $\lambda_{M \rightarrow L}$ values, the SCI−SOS β^0_{VEC} values are fairly close to the experiment, probably due to compensations internal to the method. All of the above commented examples allow one to conclude that the SCI−SOS approach is suitable in general to estimate second-order NLO properties and, unlike the semiempirical approaches, is of very broad applicability, including the case of transition metal complexes.

Conclusions

In the present investigation, we have shown that ab initio calculations of the static first-order hyperpolarizability of the push−pull organometallic chromophores $[M(CO)_5L]$ (M = Cr, W; L = Py, PyCHO, Pyz, $PyzBF_3$, BPE, $BPEBF_3$)[2] and of their electronic excitations give relevant information especially when two complementary computational approaches, such as CPDFT and SCI−SOS, are used.

The DFT approach gives correct trends and values of the major charge transfer transitions but overestimates first-order hyperpolarizabilities particularly in the case of chromophores with highly conjugated ligands. The SCI−SOS approach produces complementary results: electronic transitions calculated by the SCI approach deviate from the experiment, and only the main trend of $\lambda_M \rightarrow \pi^*_L$ energies is reproduced. However, the first-order hyperpolarizability calculated by the SCI−SOS approach is correct in trend and also in sign and magnitude with respect to the experiment.

The SOS approach allows also a detailed analysis of the electronic origin of the first-order hyperpolarizability. In this context, we have shown that in push−pull $[M(CO)_5L]$ organometallic chromophores the first-order hyperpolarizability is controlled by mechanisms different from those of traditional push−pull organic chromophores, due to the very particular role and spatial location of the $d_M \rightarrow \pi^*_L$ charge transfer transition. These findings confirm previous observations.[2,25] We have also shown that upon going from $[M(CO)_5Pyz]$ to $[M(CO)_5BPE]$ (and their BF_3 adducts) an intraligand transition must be taken into consideration for a correct prediction of β^0_{VEC}. Due to this latter effect, the observed and calculated increase of the first-order hyperpolarizability as the π-delocalization increases must be attributed not only to a larger increase of polarity upon excitation (Figure 4) but also (and mainly) to increased intensity and decreased excitation energy of the $d_M \rightarrow \pi^*_L$ transition.

Finally, our calculations have clarified, in a way more consistent than previously suggested,[2] the origin of β values experimentally found in solvatochromic investigation for $[W(CO)_5PyzBF_3]$ and $[W(CO)_5(BPE)BF_3]$.

In conclusion, our investigation has pointed out the opportunities and limitations of ab initio schemes when applied to rather simple organometallic chromophores, such as the push−pull $[M(CO)_5L]$ complexes, in the context of NLO and excited state properties. Furthermore, we stressed that the electronic mechanism of the first-order hyperpolarizabilities in organometallic chromophores may be quite different and more complicated from that usually accepted for classical push−pull linear organic chromophores. As a consequence, care must be used when dealing with oversimplified theoretical schemes for analysis, as the two-level approximation.

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