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Theoretical studies of ground and excited electronic states of complexes $M(CO)_4(phen)$ (M=Cr, Mo, W; phen=1,10-phenanthroline)

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Abstract

Electronic absorption and emission data of $M(CO)_4(phen)$ complexes, where M= Cr, Mo or W; phen=1,10-phenanthroline are reported using density functional theory (DFT). Electronic absorption spectra of $[M(CO)_4(phen)]$ show a strong band in the visible region of the spectrum, whose metal to ligand charge transfer (MLCT) M → phen and M → CO_{ax} character is indicated by high molar absorptivity. This assignment is investigated by theoretical calculations, which differ from the early interplay of M → L metal to ligand charge transfer MLCT and ligand-field (LF) electronic transitions, occurring between d-orbitals. The phosphorescence of each complex was identified as a lowest, triplet metal to ligand charge transition (MLCT) around 740nm.

Keywords: Absorption, emission, DFT, excited states

1. Introduction

The photochemical and photophysical behavior of transition-metal complexes possessing low-energy metal toligand charge-transfer (MLCT) states have been the subject of many investigations [1-3]. Although luminescence has been observed for many complexes at low temperature, only a few complexes appear to luminescence at room temperature. In contrast to experimental studies so far, only a few theoretical investigations have been performed to study such transition-metal systems using theoretical calculations [4], in spite of the fact that density functional theory (DFT) successful at providing a means to evaluate a variety of ground-state properties with an accuracy close to that of post-HF methods [5, 6]. Furthermore, remarkable structural predictions have been obtained especially using the "hybrid" density functionals [7, 8] such as B3LYP and B3PW91 combining "exact exchange" with gradient-corrected density functionals. As a consequence, there is currently a great interest in extending DFT to excited electronic states [9]. For excited states of closed shell molecules, time-dependent DFT methods (TDDFT) have been developed. Applications of TDDFT approaches have recently been reported on transition metal complexes and get a considerably good result [10-13]. In this context, the time dependent DFT approach (TDDFT) offers a rigorous route to the calculation of vertical electronic excitation spectra [14-16]. Especially, the theoretical investigations on excited states are uncommon but necessary for the molecules used in organic light emitting diode devices (OLEDs), because the calculation of excited-state properties typically requires much more computational effort than that is needed for the ground states. In this study, the low-lying excited states are investigated at CIS level [17,18]. The rich electronic absorption spectra, photophysics and photochemistry of mixed-ligand group 6 transition metal carbonyls $[M(CO)_4(phen)]$ are usually interpreted in terms of low-lying M → L (MLCT) and high energy d-d transition, [19] whereas our calculations indicate that the electronic spectroscopy, photochemistry, and photophysics of $[M(CO)_4(phen)]$ is based on an interplay between M→ phen and M → CO_{ax} MLCT excited states.

2. Calculation methods

Calculations on the electronic ground states of $[M(CO)_4(phen)]$ (M = Cr, Mo or W and phen=1,10-phenanthroline) (as shown in Fig. 1), were carried out using B3LYP density functional theory. "Double-ξ" quality basis set LanL2DZ was employed as basis set. This B3LYP/ LANL2DZ level of theory has proven useful for other transition metal systems. McCusker

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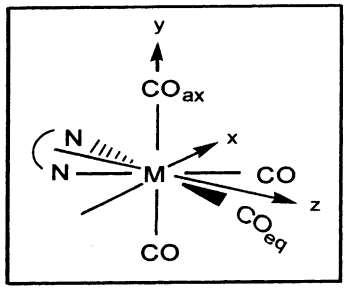
et al. employed B3LYP/LanL2DZ level of theory to study the excited-state electronic structures of $[RuL'_2(NCS)_2]^{4-}$ (where L'=4,4'-dicarboxylato-2,2'-bipyridine) [20]. Adamo and his co-leagues [21] present a combined DFT//B3LYP and TDDFT to predict absorption spectra of $[Ru(bpy)(tpy)dmso]^{2+}$ (bpy=2,2'-bipyridine, tpy=2,2':6',2"-terpyridine; dmso=dimethyl sulfoxide). A double-ζ quality LANL2DZ basis was used for all atom but oxygen and sulfur which were described by 6-31G*. The results show the good agreement between theory and experiment with errors within 0.2eV corresponding to the lowest allowed transition. Hay [22] well produced the low-lying excited electronic states in the Ir(III) complex $Ir(ppy)_3$ and the related complexes using B3LYP functional. "Double-ζ" quality basis sets were employed for the liangds (6-31G) and the Ir(LANL2DZ). The excited-state geometry was optimized at the CIS level of theory. The transition energies will be calculated at the ground-state and excited-state geometries with TD-DFT, and the results are compared with the available experimental data. All calculations are performed with Gaussian 03. The geometries were fully optimized with C_2 symmetry constraints.



N N = 1,10-phenanthroline (phen)

M = Cr, Mo, W

Fig. 1. The calculated structures for molecule $M(CO)_4(phen)$.

3. Calculation results and discussion

3.1 Ground-State Molecular Structures

The geometrical parameters are listed in Table 1. In fact, all complexes have distorted pseudo-octahedral structures that are typical of group 6 tetracarbonyls. We noted that the axial M-CO bonds in the three complexes were calculated to be significantly longer than the equatorial ones, this manifestation of the competition for M → L back-bonding of ligands with an equatorial configuration in the transition metal complexes.

Table 1. Selected DFT calculated bond lengths (Å) of ground states (S_0) and excited states (T_1) for complexes $M(CO)_4(phen)$ (M=Cr, Mo, W).

Bond (Å) lengthes	1 (M=Cr)		2 (M=Mo)		3 (M=W)	
	S_0	T_1	S_0	T_1	S_0	T_1
M-N	2.117	2.185	2.174	2.254	2.219	2.338
$M-CO_{eq}$	1.842	2.104	1.960	1.979	1.976	2.056
$M-CO_{ax}$	1.891	2.106	1.926	2.044	2.033	2.087

3.2 Molecular Orbitals and Excitation Energies

It will be useful to examine the highest occupied and lowest virtual orbitals for these transition metal complexes to provide the framework for the excited state TDDFT and CIS calculations in the subsequent section. Moreover, frontier orbitals play a relevant role in such systems, because they rule the electronic excitations and the transition character. The orbitals as well as the type of each MO are plotted according to their energies in Fig. 2 together with the major percent of the compositions on the right. In fig. 2, we pick up the most important five highest occupied orbitals and five lowest virtual orbitals. The three highest-lying occupied MO of the three complexes lie in an energetically narrow interval, ca. 0.1 eV wide. They can be approximately viewed as $d(\pi)$ orbitals, by the amount of metal 5d character about 60%. For example, the HOMO and HOMO-1 of $Cr(CO)_4(phen)$ contains 64% and 58% d_{xz} characters, admixed with about 28% CO character. The analogous HOMO-2 of $Cr(CO)_4(phen)$ has 57% $5d_{xz}$ (Cr) characters, respectively. The higher occupied orbitals, such as HOMO-3 and HOMO-4 are mainly phen π^* character. In fact, the three complexes have similar orbital character.

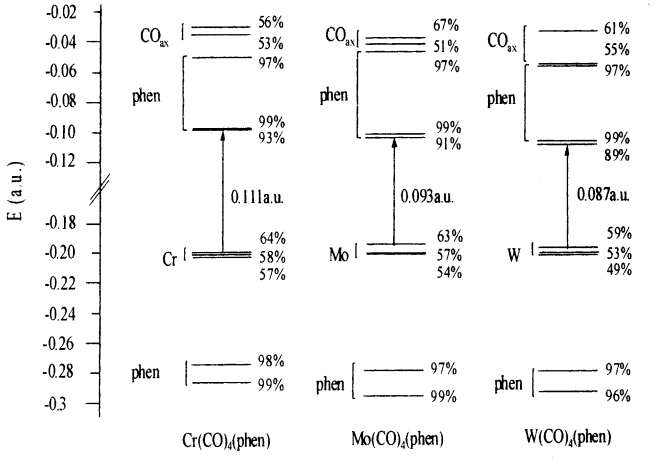


Fig. 2. Schematic drawing of orbital energies of frontier orbitals of complex $M(CO)_4(phen)$ from B3LYP calculation.