

On the role of solvent effects on the electronic transitions in Fe(II) and Ru(II) complexes



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ABSTRACT

Solvent effects on the vertical excitations of complexes with spin crossover are studied with CASPT2 and time-dependent DFT techniques. The geometry of the $[\text{Fe}(\text{phen})_3]^{2+}$ complex was optimized with DFT using the PBE0 functional, and subsequently, the absorption spectrum was calculated with CASPT2. The spectrum is in good agreement with experiment and the effects of the solvent were found to be small as long as the symmetry of the complex is maintained. The on-set of the MLCT band was found to be shifted by 0.4 eV, which we attribute to the lack of thermal motion in our treatment. The large solvent effects on some of the excitations in trans (Cl)-Ru (bpy) $\text{Cl}_2(\text{CO})_2$ are reproduced both with TD-DFT and CASPT2 through a COSMO or PCM treatment of the solvent.

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1. Introduction

Over the last decades important advances have been made toward the synthesis of systems with bistability under normal conditions for which the switching is fast and both states sufficiently long-lived to take profit of the bistability. A system capable of persistently changing its magnetic or electric properties upon some external stimulation has many potential technological applications, for example to make nano-switches or as memory devices. In this area of research, the compounds with an interconversion between two different spin states – spin crossover (SCO) – that can be triggered by a change in temperature, pressure or irradiation with light, form an important group. From the applicability point of view, the method that offers optimal control on the process is the light induced variant. This process, also known as light-induced excited spin state trapping (LIESST), was discovered in the 1980s [1,2] and the basic mechanism was elucidated shortly afterwards [3,4]. Important ingredients to explain the occurrence of LIESST are the energy difference between the high-spin (HS) and low-spin (LS) states; the vertical excitation energies of the metal-to-ligand charge transfer (MLCT) and ligand-field (LF) states; coordination degree of the ligand; cooperativity, among other factors [5–7].

Theoretical investigations have focussed on many of these aspects, but especially the determination of the energy difference between the HS and LS state has attracted much attention. The

pioneering work of Paulsen and co-workers [8] established that standard density functional theory calculations are not accurate enough to precisely predict the stability of the HS state with respect to the LS state (ΔE_{HL}) in mononuclear SCO complexes. Over the past decade, significant evidence has accumulated that even the best current DFT functionals can display large errors for specific types of transition metal energetics. In particular, standard pure functionals (like LDA, BLYP, or PBE) systematically overstabilize low-spin states, while hybrid functionals (like B3LYP, or PBE0) overstabilize high-spin states due to the inclusion of a portion of Hartree–Fock exchange. The B3LYP* and OPBE functionals have emerged as most likely candidates for use in SCO complexes. Reiher and co-workers [9] suggested a reduction of the amount of HF exchange to 15% in B3LYP functional, B3LYP*, but this change is not successful for all iron compounds. Swart and co-workers studied different combinations of the exchange and correlation functionals and found that the OPBE functional [10,11] which is the combination of Handy's optimised exchange (OPTX) with the PBE correlation (PBEc) correctly predicts the lowest spin state in many transition-metal complexes. Therefore it is *a priori* unknown which amount of HF exchange is appropriate to give good results for transition-metal complexes.

There are also several studies devoted to SCO based on post Hartree–Fock methodologies. These strategies are based on a multiconfigurational description of the electronic structure and make possible to consider spin eigenfunctions, to treat ground and excited states on an equal footing, and include spin–orbit coupling effects. A standard implementation of multiconfigurational self-consistent field (SCF) calculations is given by the complete active space (CASSCF) [12]. Combining CASSCF with multiconfigurational

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second-order perturbation theory (CASPT2) [13] results in a very successful computational scheme to treat transition metal complexes. The CASSCF wave function gives a good description of the electron distribution but lacks important dynamic electron correlation effects. This does not strongly affect the electron distribution but may give rise to rather large changes in the relative energies of the different electronic states. The complete active space second-order perturbation theory (CASPT2) accounts for dynamic electron correlation in the case of multiconfigurational wave functions of medium to large sized systems.

Since LIESST is intimately related to the local properties of the Fe(II) complex, especially to the first coordination sphere of the central metal, most theoretical studies take an isolated, *gas phase* molecule approach. The role of the environment (long-range electrostatic interactions, solvent effects) are less well-studied, although the study of Robert and co-workers for thermal SCO is a nice example how theory can quantify the effect of interactions that go beyond the simple isolated molecule description [14]. In the study of the SCO in Prussian-blue analogues it was found that the environment is actually the driving force for the HS–LS change [15]. One important ingredient of LIESST that is possibly strongly dependent on the description of the environment is the vertical excitation spectrum of the initial LS state. Actually, the study of the transient absorption spectroscopy study of Tribollet et al. on $[\text{Fe}(\text{phen})_3]^{2+}$ (phen = 1,10-phenanthroline) points to important solvent effects on the excitation energies [16]. This was based on the mismatch of approximately 0.3 eV between the relative energies measured in experiment and those calculated for the related compound $[\text{Fe}(\text{bpy})_3]^{2+}$ (bpy = 2,2'-bipyridine) with a multiconfigurational approach applied to the isolated complex [17,18].

To settle the importance of the solvent effects on the vertical excitation spectrum and explain the difference in calculated and observed transition energies, we investigate the electronic states of $[\text{Fe}(\text{phen})_3]^{2+}$, trans (Cl)-Fe (bpy) $\text{Cl}_2(\text{CO})_2$ and trans (Cl)-Ru (bpy) $\text{Cl}_2(\text{CO})_2$ (depicted in Fig. 1), comparing vacuum results with those obtained in a model that accounts for solvent effects. Furthermore, we compare time-dependent DFT to CASPT2 results in order to establish the viability of the simpler, and computationally more efficient DFT based method. The second and third complexes do not belong to the class of SCO materials, but were chosen as benchmark models. The Ru-compound has recently been studied

with TD-DFT and to some extent with CASPT2 [19] and shows important solvent effects, blue-shifting some specific MLCT states by approximately 1 eV.

2. Computational information

All geometries were optimized using the hybrid functional PBE0 [20], which adds 25% of exact Fock exchange to the standard PBE functional. This functional has been used previously, giving good results for the geometrical parameters for related SCO complexes [21,22]. The molecular orbitals are expanded with the default triple- ζ basis set with one polarization function (def2-TZVP) [23].

The optimal geometry of the HS and LS states of the three complexes was determined by optimizing all geometrical variables without symmetry constraints and characterized as minima by a vibrational frequency calculation. The geometries used to build the energy potential curves of the ground state around the LS DFT geometry were generated from restricted geometry optimizations fixing the Fe–N distances at different values in an interval of 1.8 to 2.0 Å. Time-dependent DFT calculations were performed with the PBE0 functional using the full random phase approximation (RPA) [24]. Additionally, calculations in solution were performed using H_2O or acetonitrile as solvent with the dielectric continuum model COSMO [25]. All DFT calculations were carried out using the TURBOMOLE package [26,27] version 6.3.

CASSCF/CASPT2 calculations were performed as implemented in the MOLCAS 7.4 package [28,29]. Atomic natural orbital (ANO) basis sets optimized for scalar relativistic effects and core correlation were applied for all atoms [30,31]. For complex **1** we used a (7s,6p,5d,4f,3g,2h) contraction for Fe, (4s,3p,1d) for N, (3s,2p) for C and (2s) for H. For complex **2**, the ANO basis is the same but for C and O, which is (4s,3p,1d) and the basis set for Cl is contracted to (5s,4p,1d). Complex **3** has the same basis set contraction. The Cholesky decomposition [32,33] was used to reduce the computational cost associated to the calculation of the two-electron integrals. Scalar relativistic effects were included using Douglas–Kross–Hess Hamiltonian [34]. Spin–orbit coupling and oscillator strengths of the electronic transitions were calculated with the state interaction approach [35,36].

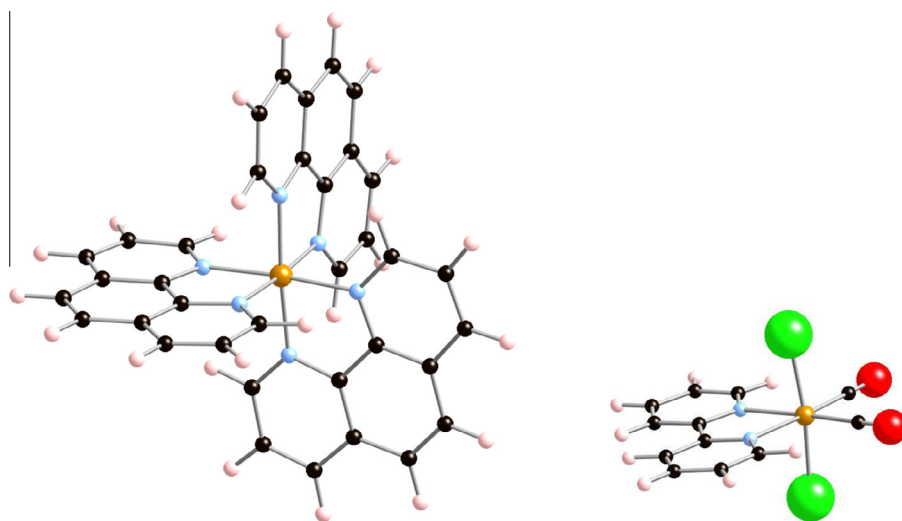


Fig. 1. Ball and stick presentation of the complexes studied in this paper: (left) $[\text{Fe}(\text{phen})_3]^{2+}$ (**1**), (right) trans (Cl)-Fe (bpy) $\text{Cl}_2(\text{CO})_2$ (**2**) and trans (Cl)-Ru (bpy) $\text{Cl}_2(\text{CO})_2$ (**3**). Color code: orange for Fe and Ru, red for O, green for Cl, black for C, blue for N and pink for H. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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