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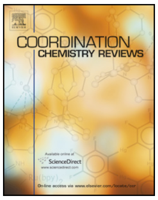

Review

Photochemistry and photophysics of transition metal complexes: Quantum chemistry

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ABSTRACT

Methodological aspects are highlighted in connection to three important theoretical issues in the field of transition metal complexes photochemistry and photophysics: (i) accuracy of electronic absorption spectra calculation and their interpretation; (ii) photo-induced isomerization and ultra-fast intersystem crossing processes in rhenium (I) α-diimine complexes; (iii) environment effects on absorption spectroscopy and photophysics of ruthenium (II) polypyridyl complexes. The results of recent applications provide an illustration of the role of spin–orbit coupling and environment effects in the photochemistry and photophysics of transition metal complexes and point to the limits of the methods for specific problems, such as accuracy, long-range charge-transfer excited states and biological environment modeling.

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1. Introduction

The accomplishment of density functional theory (DFT) [1–3], and it is extension to electronic excited states, the time-dependent DFT (TD-DFT) [4–6], has opened the route to a number of applications in various fields of chemistry from catalysis, to molecular properties and spectroscopies [7–11]. In parallel to this impressive

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success, more refined and costly quantum chemical methods based on wave function and perturbation theories and usually dedicated to small molecules have been developed in order to handle more ambitious chemical problems, either by size or by electronic complexity. Among the many challenges to theoretical chemists we can cite the modeling and interpretation of electronic absorption/emission spectra with accuracy, the simulation and understanding of complicated ultra-fast processes involving excited states and the modeling of environment effects on excited states properties and reactivity. For this purpose it is necessary to play with various methods of quantum chemistry able to provide appropriate tools for a diversity of systems and problematic.

Transition metal complexes cumulate most of the complexities inherent to theoretical studies: size, electronic delocalization, high density of electronic states of various characters, multi-reference nearly degenerate states, long-range charge transfer states, relativistic effects, especially spin–orbit coupling, dissociative states, states mixing and vibronic couplings. To this list we may add the difficulty at describing environment effects on excited metal complexes in biosystems. Typically, the more popular quantum chemical methods are based on four formalisms, namely density functional theory such as DFT [1–3], TD-DFT [4–6], Δ-SCF-DFT [12–14], the variational approaches based on self-consistent-field (SCF) formalism and its multi-configuration extension complete-active-space SCF (CASSCF) [15] or the variants restricted-active-space SCF (RASSCF) [16] or generalized-active-space SCF (GASSCF) [17], the configuration interaction (CI) [18,19] and its multi-reference extension (MR-CI) [20]. The multi-reference methods based on CAS formalism, taking into account non-dynamical electronic correlation, need to be completed by perturbative treatment in order to take into account dynamical electronic correlation effects and improve accuracy. The 2nd order perturbation theory based on CASSCF wave functions (CASPT2) [21,22] and its multireference extension MS-CASPT2 [23–25] are the methods of choice for achieving this task. Hybrid methods, which take the best of both worlds by combining DFT at short-range, and wave function or perturbative approaches at long-range, start to emerge [26]. Accurate structural and spectroscopic properties of transition metal complexes in the electronic ground state, or in the lowest excited state for highly symmetric molecules, can be obtained by most of the above methods. Nevertheless optimal balance between accuracy and computational effort characterize the user-friendly DFT based calculations. The performance of the wave functions based methods depends mainly on the quality of the reference wave function. For instance the cost and the slowness of the convergence of MR-CI methods to eigenstates limit their application to small systems (15 atoms). Despite of the efforts made in the past decade for improving the algorithms and taking advantage of the computer developments (parallel implementation, linear scaling, orbital's localization, etc.), this dependence to the reference is the limiting factor for handling large molecules with wave functions approaches. This is particularly dramatic in the case of excited states calculations due to the size of the basis sets generally needed and to the number of requested eigenstates. The use of cluster expansion "reference independent" methods [27,28] such as coupled cluster single double (CCSD) [29] and its extension to excited states, equation-of-motion-CCSD (EOM-CCSD) [30] is an alternative [31–34]. However these single-reference methods need to be developed beyond the single–double excitation scheme by introduction of triple (CCSDT) or even higher excitations [35], to describe properly excited states and dissociative processes. Consequently they become very expensive and are specifically developed for accurate spectroscopies and molecular properties in small molecules [36].

Recent reviews and articles will give to the reader an idea of the last developments and applications related to excited states in large molecules and/or transition metal complexes [8,37–44].

On the basis of recent applications based on TD-DFT, CASSCF/MS-CASPT2 as well as EOM-CCSD methods, three theoretical issues specific to transition metal complexes excited states will be discussed in the present review: (i) accuracy of electronic absorption spectra and their interpretation; (ii) processes in rhenium (I) α-diimine complexes; (iii) environment effects on absorption spectroscopy and photophysics of ruthenium (II) polypyridyl complexes. A first section is devoted to methodological highlights related to spin–orbit coupling (SOC), environment modeling and long-range charge transfer excited states. The three next sections report recent results of case studies illustrating the three issues described above.

2. Methodological highlights

2.1. Spin–orbit coupling

Most of light-induced processes in transition metal complexes involve a change of spin state and are not allowed in non-relativistic quantum formalism. A fully relativistic treatment based on Dirac equation [45] and a four-component Hamiltonian including scalar and spin–orbit contributions for many electrons systems is unrealistic and beyond the scope of the systems of interest in this contribution. The reduction of Dirac equation and its extension to many-electron problems has opened the route to several relativistic approaches based on approximate Hamiltonians applied with success to chemistry [46]. The scalar relativistic effects in molecules possessing heavy atoms are usually taken into account by relativistic atomic effective core potentials (ECP) included in widely distributed quantum chemistry software's or by perturbation theory. This level of approximation is usually satisfactory for ground state properties such as structure and energetic of transition metal compounds. As far as optical spectroscopy is concerned spin–orbit effects have to be included in order to determine the spin–orbit coupling (SOC) between states of different multiplicities and to compute the first-order splitting of the multiplets term energy into sub-levels, eigenstates of the spin–orbit operator. The spin–orbit coupling terms arise from one- and two-electron operators developed within the two-component formalism of the relativistic theory obtained by transformation of the four-component equation. The Douglas–Kroll (DK) [47,48] and the Breit–Pauli (BP) [49,50] forms are the most popular relativistic two-component operators. In most of the today applications the SOC effects in large transition metal complexes are included according to two approaches: (i) the RAS-state interaction (RASSI) including SOC [51] developed on the basis of a one-electron Fock-type spin–orbit Hamiltonian [52] within the atomic mean field approximation (AMFI) [53]; (ii) the zeroth-order regular approximation (ZORA) to the full relativistic Hamiltonian based on a one effective two-component regular Hamiltonian developed at the zeroth-order [54,55]. Both methods are derived from the Breit–Pauli spin–orbit Hamiltonian and are a good approximation to the Breit–Pauli theory. Whereas RASSI-SOC formalism has been developed for correlated wave functions, the ZORA operator is more adapted to perturbation and Kohn–Sham theories. Most of the ZORA applications are performed within the framework of DFT despite of some limitations [56,57].

The RASSCF wave functions computed with the scalar-relativistic Hamiltonian constitute the basis for the RASSI Hamiltonian matrix. This matrix is corrected for dynamic correlation (CASPT2) and includes the one-electron spin–orbit component as well as the dipole transition moment component. Its diagonalization leads to the spin–orbit eigenstates, associated oscillator strengths and spin–orbit coupling terms. Whereas in nonrelativistic theory the eigenstates form a basis for an irreducible representation

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