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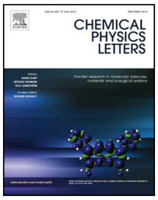

Solvent effects to compute UV–vis spectra for ionic metal complexes[☆]

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ABSTRACT

The correct representation of the solvent is a crucial issue for the computation of molecular properties in solution, especially UV–vis spectra.

This Letter shows that for mainly ionic complexes involving intra-ligand electronic transitions, the use of a hybrid model (microsolvation and PCM) leads to a good reproduction of the experimental electronic spectra. The use of smaller molecules (water instead of methanol) in the first coordination sphere did not change the optical absorption computation, saving by this way computation time. A tentative explanation based on the nature of the solvent–metal cation bonds is then presented.

1. Introduction

Solvent description is a crucial point for the good reproduction of many physical or chemical properties with quantum-chemistry-based methods. Among them, solubility [1], pK_A [2] and redox potential [3] computations have been deeply investigated due to the explicit involvement of the solvent. Nevertheless, many other properties are influenced by the solvent and need a careful representation of its properties. It is especially the case of spectroscopic properties such as UV–vis absorption. Indeed, the solvatochromism is quite important on many molecules, which prevents one from neglecting the solvent in this case.

The computation of UV–vis spectra has drawn attention in the last decades and many methods are now well-suited to reproduce and predict the absorption properties of molecules [4]. These methods are crudely grouped in two categories: wave-function or electron-density based. The former category is represented by methods such as CIS, CASSCF, CASPT2 [5], EOM-CC [6], CC-LRT [7], SAC-CI [8] or ADC(2) [9]. The latter one is mainly represented by TD-DFT methods [10]. TD-DFT methods have been shown to give accuracy comparable to post-Hartree–Fock methods with a suitable functional [11], it is therefore often regarded as a good compromise between accuracy and CPU time for metal complexes [12,13]. Then, this Letter will be limited to the application of TD-DFT to compute electronic excitations.

Several models are possible for the solvent in quantum chemistry and most of them are applicable to TD-DFT computations. This issue has been deeply studied by many groups on several molecules families. First the solvent can be represented by a continuum [14]. In this case, no individual solvent molecule appears, but their bulk properties are replaced by some macroscopic (dielectric constant for instance) and microscopic (solvent radius for instance) quantities. The formalism to use this model with TD-DFT is now developed and implemented in some computation codes [15] with some variants whose influence has been studied in details [16–18]. Second the solvent molecules can be represented individually, that is generally processed by the use of molecular dynamics based methods: many examples are now given were geometries are obtained by any computational method; some snapshots are then extracted and the low-lying excitations are computed and summed up to obtain a spectrum accounting for a large subset of the possible conformations [19,20]. These two approaches possess both strengths and weakness. The explicit representation is a better microscopic representation of the system but taking into account enough solvent molecules can be quite CPU-expensive. The computation time needed by the dynamics can be diminished by the use of molecular mechanics or QM/MM methods. The implicit representation is faster as less electrons are taken into account, but the parameters chosen to represent the solvent and the variety of implementations is wide that can lead to more empiricism in its application.

Another approach is to mix explicit and implicit methods to try to obtain advantages from both methods. A first way to apply this method is from the explicit method: once the structures obtained with the explicit solvent obtained, molecular structures are extracted but the solvent molecules are removed and replaced (without geometry re-optimization) by an implicit solvent to

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[☆] Cartesian coordinates for species labeled CA and CA-2H and complexes **1**, **2**, **3** and **4** (2 flavors) are reported in SI.

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compute the excitations [21], saving by this way CPU time in the last step. A second way roots in the implicit method: instead to take account of each solvent molecule, only a few chosen ones are added on the most important part of the molecules (microsolvation); around this structure, a continuum model is added to fully account for the solvent [22,23]. This last semi-implicit method is chemically appealing: the CPU time is reduced in comparison with a fully explicit model while the significant microscopic parameters are kept. However, it needs a good knowledge of the studied system to avoid to skip some important molecules or to add non useful ones that would lengthen computations without increasing the precision of obtained results [24–26].

The purpose of this Letter is to advocate that in the case of ionic metal complexes, explicit solvent molecules need to be added to correctly account for the solvent influence on UV–vis parameters. For metal cations whose solvation sphere is non-isotropic, such as copper(II) or lead(II), some elements to prove it have yet been given in our previous works [27] but in the case of more symmetrical coordination sphere, the proof is still needed. This will be illustrated by the study of an example: the complex (CA–Al) formed by the complexation of $\mathrm{Al^{III}}$ cation with caffeic acid (CA) (see Figure 1) in methanol solution. CA is a naturally occurring molecule released by some plants to form complexes with nutriments and stabilize them in an oxidation state assimilable by plants [28]. Therefore, its complexation is a subject of importance that has been studied in our team and the structure of its complex with $\mathrm{Al^{III}}$ cation (chelation to the fully-deprotonated catechol group) has been determined by an approach comparing measured and computed UV–vis data [29,30]. Then, we focused only on the nature of the solvent model used.

The importance of adding some solvent molecules will be emphasized by showing that it leads to a good reproduction of the experimental data that a purely implicit solvent model cannot achieve. Then, the possibility to replace the solvent molecules by smaller ones will be emphasized. Last, a tentative explanation of these features will be proposed based on the nature of the bonds implied in the studied complex.

2. Computational details

All calculations were carried out with the Gaussian 09 set of programs [31]. DFT-based methods, including its time-dependent version (TD-DFT) were used throughout. More specifically, B3LYP global hybrid functional [32–35] was used due to its ability to compute absorption properties in the UV–vis domain [11]. The $6\text{-}31+G^{**}$ basis set was used to represent all atoms [36–38]. Structural optimizations were processed using standard algorithms without any symmetry constraint. The nature of minima was checked by subsequent vibrational analysis. TD-DFT formalism was used in the adiabatic approximation to compute excitation energies and associated oscillators strengths. The lowest excited states were taken into account to compute vertical excitation energies (the number of states taken into account was chosen for each complex to obtain all excitations below 200 nm (6.20 eV)).

The model for the solvent is studied below, but when a continuum represents the solvent (methanol), PCM, as implemented in Gaussian with the internal parameters for methanol, is used [14,39]. More precisely, the Integral Equation Formalism (IEF) was used in the linear response approach. Some tests (not detailed in this Letter) have been performed with state-specific solvation, but no significant change was observed on the studied systems. The study reported here focused on absorption properties so non-equilibrium solvation was used throughout.

Atoms-in-molecules (AIM) computations [40] were carried out to give some insight about the bond nature in the studied complexes. Bond critical points (BCPs) and ring critical points (RCPs) were located, and local and integrated properties were computed using the AIMAll software [41].

Table 1
Main characteristics of the models introduced for the study of the solvation (Y and N mean yes and no, respectively).

Model	Explicit molecules?	Continuum?	Energetic minimum?
1	N	N	Y
2	N	Y	Y
3	Y	N	Y
4	Y	Y	Y
3′	N	N	N, obtained from **3**
4′	N	Y	N, obtained from **4**

3. Presentation of the models used

The absorption electronic spectrum of CA–Al has been recorded in methanol solution [29] so the best representation of this solvent to reproduce the experimental results is the purpose of this Letter. Several models involving microsolvation and/or continuum model were therefore used. Starting from the simplest model (**1**, no solvation of any kind), two directions were explored. The addition of a continuum (characterized, among other parameters, by $\varepsilon = 32.613$ for methanol) leads to model **2** while the addition of explicit molecules (methanol) around the complex leads to model **3**. When these two approaches are mixed, a fourth model (labeled **4**) is obtained. In each case, optimizations have been carried out and electronic transitions were computed. To fulfill a good understanding of the underlying phenomenons, two unusual models were introduced from **3** and **4** by removing the explicit solvent molecules and recomputing the electronic transitions without re-optimizing the structure of the complexes. These last two models are labeled **3′** and **4′**. The main characteristics of those models are recalled in the synthetic Table 1.

Models involving explicit molecules of methanol (**3** and **4**) imply a choice on the position of the solvent around the molecules. Preliminary studies on CA have been carried out. Several structural hypotheses were computed involving interaction between solvent and the two main functional groups located on CA (catechol and carboxylic acid) and the electronic transitions were computed. When comparing the computed value for the lowest-energy electronic transition with the experimental value obtained in methanol (314 nm, 3.95 eV), the best compromise between accuracy and precision of the computed transition was obtained using the continuum model only whose result (324 nm, 3.83 eV) is in line with the accuracy of TD-DFT methods, while adding solvent molecules did not improve the result or even deteriorate it (for instance, the addition of two molecules on the catechol and two on the carboxylic acid gives a computed value of 337 nm (3.68 eV) for the equivalent transition). This has been confirmed for CA–Al by some computations carried out with more explicit molecules: additions on other functional groups did not lead to any improvement while addition in the second coordination sphere of the cation results in delicate structural optimizations without accuracy benefit. Therefore, in the following, the explicit interaction between the solvent and CA–Al in models **3** and **4** will only be considered by the interaction of the $\mathrm{Al^{III}}$ cation and methanol molecules.

4. Study of these different models for CA–Al

4.1. Geometrical investigation

The six models have been applied to the study of CA–Al and structural optimizations were carried out. Some significant geometrical parameters for CA, CA-2H (a formal structure where the two protons of catechol have been removed from CA) and the six