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Environmental effects on electronic absorption spectra using DFT: An organic and positively charged fused polycyclic chromophore as a case study

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The benzo[1,2]quinolizino[3,4,5,6-*def*]phenanthridinium,-9-phenyl molecule (hereafter BQPT-ph$^+$) has been considered as a representative benchmark for simple organic and positively charged systems in solution to test the environmental effects on computed UV–Visible spectra. In particular the effects, both at geometric and electronic levels, related to the inclusion of bulk solvent, using a polarizable continuum model (PCM), and the explicit inclusion of the counterion (here BF_4^-) will be discussed. Electronic transitions were computed at TD-DFT level using a hybrid exchange correlation functional (PBE0) and a double zeta valence basis set. Effect of inclusion of diffuse and polarization function on the computed electronic spectra will also be discussed.

Finally, the importance of the vibronic structure to simulate the experimental band shape will be considered focusing on the first electronic transition, and computing ground and first excited states optimized structures together with harmonic frequencies at DFT and TD-DFT level, respectively. The good agreement obtained between computed and experimental spectra confirms the good quality of both the optimized geometries and the harmonic force fields.

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1. Introduction

Density Functional Theory (DFT) [1] and Time Dependent DFT (TD-DFT) [2] have become nowadays standard tools for investigating and predicting electronic properties of molecular chromophores in both the ground and the excited states [3–5], whether concerning purely organic species [6–13] or metal-containing complexes [14–21].

In particular, a rather extensive literature exists on the performances of TD-DFT for the calculation of UV–Visible spectra of organic dyes, [3–5,7–13] allowing for an exhaustive benchmark of the computational protocols. Well-performing and cheap computational approaches, mainly based on the use of hybrid exchange correlation functionals in conjunction with medium size basis sets (containing both diffuse and polarization functions on non-hydrogen atoms), have proven to provide valence excitations of organic dyes with an average error of a few tenths of eV [5], while slightly larger errors are expected for Rydberg bands [22].

Clearly a proper inclusion of solvent effects is also mandatory in order to reproduce or predict the experimental spectra with reasonable accuracy [5,8–10]. A simple yet efficient continuum model, such as the Polarizable Continuum Model (PCM), is normally more than proficient to simulate bulk solvent effects, while in the case of polar and protic solvents able to directly interact – i.e. through H-bonding – with the solute, the static inclusion of the first solvation shell or even only an *ad-hoc* solvation of selected molecular groups, seems to correctly reproduce the main solvatochromic effects [23]. Thus, the combination of the above-mentioned DFT-based protocols with PCM, for the inclusion of solvent effects, normally leads to a quantitative agreement with the experimental data in the case of standard organic dyes [5].

Besides well-known problematic systems displaying, for instance, an important charge transfer (CT) character of the transitions, which is not necessarily well reproduced by TD-DFT approaches [24–28], (highly) charged organic molecules likely to specifically interact either with the solvent, with the counterion or each other (for instance via π–π staking), also represent a good benchmark for current TD-DFT computational approaches.

One such a benzo[1,2]quinolizino[3,4,5,6-*def*]phenanthridinium,-9-phenyl molecule (BQPT-ph$^+$; Fig. 1) has been here considered as a test case. From an experimental viewpoint, even thought first reported by Katritzky and coworkers almost three

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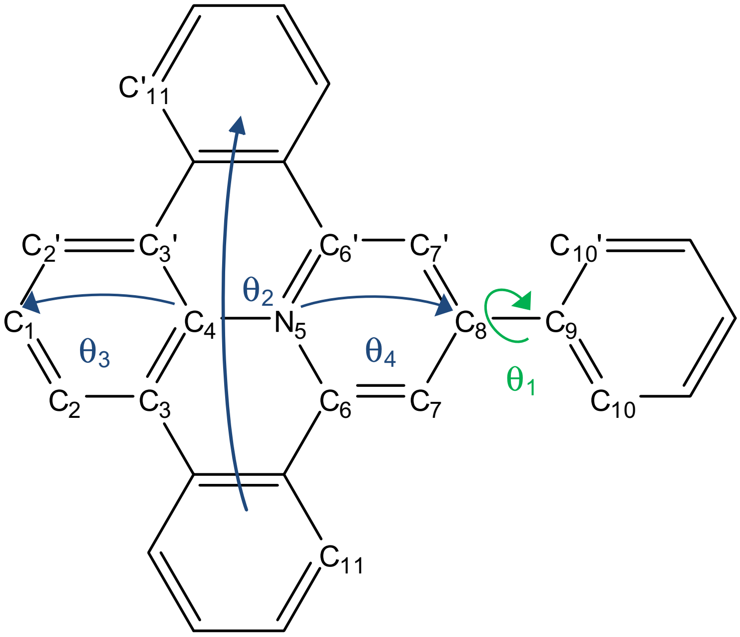

Fig. 1. Schematic drawing and labeling scheme of BQPT-ph$^+$.

decades ago [29,30], this compound deserves nowadays more attention in the framework of recent research related to polycyclic aromatic hydrocarbons (PAHs) [31] containing neutral [32,33] or positively charged nitrogen atom(s) [34,35] to tune their structural and physico-chemical properties as well as their supramolecular behavior.

From the computational standpoint, the BQPT-ph$^+$ represents a simple and well-characterized system to study the impact of solvent and counterion on the absorption spectra as well as the importance of vibronic coupling for a correct description of bands' shapes. As a matter of fact this fused molecule possesses a very characteristic and quite complex pattern of eight to nine bands (depending on the substituents) in the UV–Visible spectra, [30] thus representing a suitable benchmark for computational procedures aiming at reproducing both the energy and the band shape of UV–Visible absorption spectra.

To this end, excitation energies were computed at TD-DFT level using a hybrid, non-parameterized exchange-correlation functional (PBE0 [36]) and a medium quality basis set both in presence and absence of solvent and counterion (here BF_4^-). The band shape profile, related to the first electronic transition (S0 → S1), was then computed taking into account the harmonic vibrational nuclear motion for the ground and first excited states and their thermal population (at $T = 200$ K). The vibrationally resolved spectra was computed using a recently developed method based on a automatic selection of the relevant Franck–Condon factors through an a priori estimate of their values, thus allowing a drastic reduction of the computational burden and allowing the treatment of relatively large molecular systems [37–39]. Clearly, this approach requires both the optimization and the harmonic frequencies calculation of the molecule in its first excited state, recently made possible by the derivation – and implementation – of TD-DFT first and numerical second derivatives in gas phase and in solution [8–10,40,41].

The paper will be organized as follows. After a brief discussion on the structural effects (including purely geometrical and electronically-related contributions, whether separated or combined) induced by the presence of the solvent and of the counterion (Section 3.1), their impact on the computed spectra will be assessed (Section 3.2). Finally, the possibility of simulating band shapes for instance taking into account the vibrational – here harmonic – nuclear motions both in the ground and the excited states will be discussed.

2. Computational details

All calculations were carried out using a development version of the Gaussian code [42]. A hybrid Hartree Fock/Density Functional model, referred to as PBE0, was used [36]. The PBE0 was obtained by casting the PBE exchange and correlation functional [43] in a hybrid DFT/HF scheme, where the HF/DFT exchange ratio is fixed a priori to ¼ [44].

Both for the structural optimizations and the calculation of the electronic properties, all atoms were described by a valence double ς quality basis set (DZ [45]). The molecular structure of each compound has been fully optimized. Optical transitions were computed using the Time Dependent DFT approach [2,46] at the same level of theory. For clarity, only computed transitions with non-negligible oscillator strength ($f \geqslant 0.02$) are reported in the tables. In this paper only singlet–singlet (i.e. spin-allowed) transitions will be discussed. The transitions were computed at least down to 200 nm. While electronic absorption energies were computed as vertical excitations from the ground state, the S1 excited state structure was evaluated using analytical TD-DFT derivatives and characterized by computing numerical second derivatives [47].

Basis set effects on absorption spectra were tested using a larger Pople double ς quality basis set including one diffuse and one polarization functions (6-31+G(d)) for the most sophisticated model including both the counterion and bulk solvent. Such a basis set has been proven to provide valence excitations at convergence in organic molecules [5].

To simulate the solvent effect, an implicit solvation model is used: the Polarizable Continuum Model (CPCM) of Tomasi and co-workers was applied [48]. More specifically, we used the Conductor-like PCM model as implemented in Gaussian Development Version (CPCM) [49]. Water was considered as solvent in order to magnify the effect related to bulk polarity (highest dielectric constant).

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