

How structural changes affect the parnitrophenol spectrum in aqueous solution: Insights from multiconfigurational calculations and the free energy gradient method

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[Abstract] A theoretical study of the solvatochromic shifts of parnitrophenol (pNP) and its deprotonated form, 4-paranitrophenolate anion (pNP⁻), in aqueous solution is presented using a QM/MM methodology with molecular dynamics simulation. The geometries optimized in aqueous solution are obtained using both the polarizable continuum and the free energy gradient methods. The calculated red-shifts of pNP at the CASPT2 (12,10) level are, respectively, 0.71 eV and 0.94 eV, in good agreement with the experimental ones (0.81-0.83 eV). For pNP⁻, the solvatochromism is minor but the neutral-anion difference in solution is calculated as 0.71 eV in good agreement with experiment (0.79-0.81 eV). These shifts are rationalized in terms of the geometry relaxation in solution, which is included legitimately by the present theoretical treatment.

[Introduction] Parnitrophenol (pNP) and its deprotonated form, 4-paranitrophenolate anion (pNP⁻) have been studied experimentally and theoretically. While the ultraviolet-visible (UV-Vis) absorption spectra of both molecules in gas and in aqueous solution have been measured, a number of theoretical calculations, limited to the gas phase, were performed to understand the experimental observations. However, the solvent effects on the excited states of these push-pull molecules influence also the hyperpolarizability that is essential to understand the non-linear optical behavior. Thus, in this work, we use QM/MM calculations to explain the origin of the experimentally observed solvatochromic shift of these molecules in order to clarify the difference between the spectral shifts of pNP and pNP⁻.

[Methods] The optimized geometries of pNP and pNP⁻ in gas were obtained at the B3LYP/aug-cc-pVDZ level, using the GAUSSIAN 09 package. For including solvent effects, geometry optimizations were also performed with both the polarization continuum method (PCM) and the Free Energy Gradient (FEG) method [1]. Electronic transitions were calculated with the multi-state CASPT2 method, performed using the MOLCAS 7.6 package. We included all the π orbitals in the active space, a total of 12 electrons in 10 orbitals, denoted as CASPT2(12,10).

To include the solvent effect in the electronic transitions, the sequential QM/MM methodology was used [2]. For this purpose, we use molecular dynamics (MD) simulations for sampling solute-solvent configurations and then select some of these configurations for performing electronic structure (ES) calculations. MD simulations were carried out using the Amber 09 package with the general AMBER force field (GAFF). The simulation cubic box, with one side of 27.5 Å, was composed by including 1 solute (pNP or pNP⁻) and 854 TIP3P water molecules. For each model system of pNP and pNP⁻ in aqueous solution, an equilibration NPT MD simulation was carried out for 100 ps at room conditions (300 K and 1 atm) with a time step of 1 fs. Then, a production NVT MD simulation was performed for 300 ps in the same room condition. From the simulation, an ensemble of configurations was prepared to construct an average solvent electrostatic configuration (ASEC) [3], used to

represent the solvent environment in the CASPT2(12,10) calculations (**Figure 1**).

[Results and Discussion] In our calculations, for the neutral form, pNP, the lowest π - π^* electronic transition is shown mainly as a HOMO-LUMO transition, involving a migration in the electronic density from the phenyl ring to the nitro group. Thus, an accurate description of these group geometries when interacting with the solvent should be very important to describe the electronic transitions. For obtaining the accurate geometry, we employed the FEG method to optimize the pNP geometry in solution (**Table 1**). On the other hand, for the deprotonated form, pNP⁻, the HOMO-LUMO transition does not show a clear characteristic. Consequently, the influence of the solute geometry change in solution is negligible (**Table 1**).

In Table 1, presented are the electronic transition energies of pNP and pNP⁻ obtained for 3 different geometries optimized in 3 different models. Using the geometry obtained with the PCM model, it yields an acceptable value, 4.22 eV, when compared with the experimental values (3.88[4], 3.90[5]). However, using the geometry obtained with the FEG model, it results in 3.99 eV, much closer to the experimental values. This fact corroborates our initial statement about the necessity of an accurate description of the pNP nitro group geometry in aqueous solution. As for the neutral-anion spectral shift (last column, Table 1), it is calculated as 0.61 eV by the FEG method with ASEC model. Further, the inclusion of some explicit water molecules in the pNP⁻ calculation improves drastically the shift value, in good comparison with experiment (0.79-0.81 eV, **Table 1**).

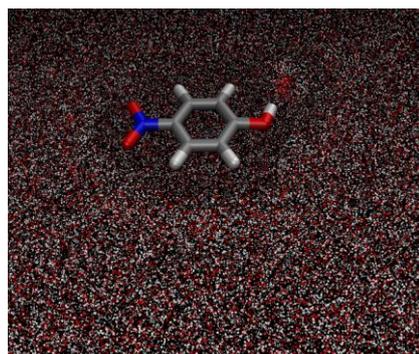


Fig. 1. The average solvent electrostatic configuration (ASEC) model used in the CASPT2 electronic transition energy calculations. While the pNP solute molecule is treated by a QM method, the surrounding solvent molecules are represented by the point charges localized in the atomic sites. Several snapshots are overlapped to construct an average configuration and the charge values are normalized by the number of snapshots used. Red points represent the O_{water} atoms, while white ones represent the H_{water} atoms.

Table 1: Lowest π - π^* transition energies of pNP and pNP⁻ in aqueous solution, calculated at the CASPT2(12,10) level, using geometries obtained with different models (GAS, PCM, FEG). Values in eV.

Model used in Solute Geometry Optimization		pNP	pNP ⁻	Spectral Shift (Neutral-Anion)
	GAS	4.51	-- ^a	--
	PCM	4.22	3.37	0.85
FEG	ASEC	3.99	3.38	0.61
	Explicit Water		3.28 ^{d)}	0.71 ^{d)}
EXP		3.88 ^{b)} , 3.90 ^{c)}	3.09 ^{b,c)}	0.79-0.81

^{a)} In gas phase, the geometry of pNP⁻ has symmetry C_{2v}, while in aqueous solution, the interaction with the water molecules breaks the symmetry to C₁; ^{b)} Ref. [4]; ^{c)} Ref. [5]; ^{d)} Including explicit water molecules in the electronic transition calculation.

In conclusion, our results provide an accurate and systematic atomistic explanation of the difference between the spectral shifts of pNP and pNP⁻, showing that the combination of multiconfigurational ES calculations and the microscopic geometry optimizations by the FEG method can be applied to understand the electronic spectra of solute molecules in solution.

[References]

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