# Theoretical modeling of the valence UV spectra of 1,2,3-triazine and uracil in solution

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Assessment of the perturbed matrix method (PMM) ability in reproducing valence UV absorption spectra is carried out on two model systems: 1,2,3-triazine in methanol solution and uracil in water solution. Results show that even using the simplest definition of the quantum center, *i.e.* the portion of the system explicitly treated quantum mechanically, PMM provides rather good results. This paper further confirms the possibility of using PMM as a theoretical–computational tool, complementary to other methodologies, for addressing the electronic properties in molecular systems of high complexity.

# 1. Introduction

The explanation and prediction of solvatochromic shift on electronic transitions (absorption and emission) has been, in the last years, an active research area of theoretical and computational chemistry<sup>1-3</sup> which, despite the large number of theoretical models proposed and computational advances, still represents a rather complicated task even for relatively simple solutes. As a matter of fact, even though high level quantum chemical calculations can be nowadays carried out on increasingly large systems,<sup>4</sup> the high complexity of the configurational space encountered when a liquid phase is concerned,<sup>5</sup> makes this kind of calculations still challenging for theoretical and computational chemistry. Beyond the full quantum-mechanical (QM) treatment<sup>6</sup> several approaches have been proposed and successfully applied with this purpose in the last years. The most simple and, in many aspects, attractive approach is based on the implicit solvation model<sup>7-10</sup> which however, despite the huge number of improvements, usually needs the inclusion of explicit solvent molecules for reliable performances.

This inclusion may take place by means of an arbitrary selection of the dimension and the shape of the solvating shell or by selecting statistically relevant configurations from preliminary molecular dynamics (MD) or Monte Carlo (MC) simulations.<sup>11–13</sup> A valid alternative is the application of the quantum-mechanics/molecular-mechanics (QM/MM) schemes both based on empirical<sup>14–16</sup> or 'first-principle'<sup>17,18</sup> force fields. The above approach represents one of the most reliable methods for modeling spectroscopic properties. However, it must be noted that when the above scheme is employed it is always very important to ensure the statistical correctness of the procedure.<sup>19</sup> In other words the results may sometimes be affected by the limitations of the statistical sampling of the MD/MC simulations or by a not correct selection of the configurations to be treated at the QM level. In this respect, we have recently proposed a theoretical-computational approach, perturbed matrix method (PMM) whose main aim is the explicit inclusion of the electronic degrees of freedom into a configurational sampling procedure (MD or MC).<sup>20,21</sup> The main goal of PMM is the direct inclusion of the electronic degrees of freedom into the configurational space sampling in order to avoid any 'a posteriori' analysis. In a number of recent applications PMM has proved to be a very efficient tool for reproducing absorption (IR,<sup>22</sup> rotatory dispersion,<sup>23</sup> vertical valence-UV (VUV)<sup>24-26</sup>) spectra of molecular systems ranging from simple solutes in solution to rather complex species in protein environment. However, additional tests are necessary for definitely assessing PMM features in this respect. This is the aim of the present paper in which the vertical VUV absorption spectra, i.e. solvatochromic shifts, of small chromophores in solution are addressed. In particular we report theoretical results concerning two molecular species which have represented, very recently, benchmark systems for the modeling of UV-Vis spectra: 1,2,3-triazine (1,2,3-T Fig. 1a) and Uracil (Ur, Fig. 1b) in condensed phase. 1.2,3-T belongs to an interesting class of compounds,<sup>27</sup> which shows, in methanol, a very large peak in the region between 3.5-4.9 eV,<sup>28,29</sup> with a maximum blue-shifted of 0.47 eV with respect



Fig. 1 Schematic representation of 1,2,3-triazine molecule (1a) and uracil (1b).

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the lowest transition in gas-phase. The interpretation of 1,2,3-T solvatochromic shift, recently addressed computationally<sup>31,32</sup> in water, is based on the comparison between the lowest absorption bands in gas-phase and in solution (water). However, the presence of several transitions in this region<sup>28,29</sup> suggests that the large peak may arise from the merging of different signals and therefore a correct evaluation of the shift should take into account this possibility. Unlike 1,2,3-T, the Ur has been, on the other hand, at the center of a very active theoretical interest both in gas<sup>33-35</sup> and in condensed<sup>36-40</sup> phase. The experimental absorption spectrum of aqueous Ur predicts the existence of a large peak at 4.8 eV and a second one above 6.0 eV.<sup>41</sup> The first one has been assigned as the  ${}^{1}\pi \rightarrow \pi^{*}$  transition undergoing a red shift lower than 0.2 eV. On the other hand, the very weak  ${}^{1}n \rightarrow \pi^{*}$  transition is known to be shifted of about 0.5 eV. The above findings have been recently computationally addressed and successfully reproduced by Barone and Improta<sup>40</sup> using the polarizable continuum model (PCM)<sup>7,10</sup> approach with the inclusion of explicit solvent molecules. In this paper the VUV absorption ranges of 1,2,3-T (up to 5.0 eV) and Ur (up to 6.0 eV) have been reappraised by means of PMM procedure. As already remarked the underlying philosophy of PMM is perfectly in line with all the other QM/MM approaches, *i.e.* the predefinition of a quantum enter (QC) to be explicitly treated at the QM level, and the rest of the system acting as a perturbation. In this respect, it is of considerable interest to assess PMM performances even with the simplest definition of the OC, *i.e.* the uncomplexed chromophore molecule.

# 2. Theoretical and computational section

#### 2.1. Gas-phase calculations

Geometry optimizations of 1,2,3-T and Ur were performed using density functional theory at generalized gradientcorrected (GGA) nonlocal (NLDFT) approximation levels. At this end we adopted Becke's three-parameter hybrid method using the Lee-Yang-Parr correlation functional, B3LYP.<sup>42-44</sup> Becke's exchange functional and Lee-Yang-Parr correlation functional (BLYP),<sup>43,44</sup> and PBE0<sup>45–47</sup> with the 6-311++G(3df,3pd) basis set for 1,2,3-T and the triple-zeta Dunning's correlation consistent basis set<sup>48-50</sup> augmented with diffuse functions for all atoms, (Aug-cc-pVTZ)<sup>51</sup> for Ur. In order to evaluate the effects produced by the solvent molecules on the ground state geometries (vide infra) the same optimization procedures were also carried out including an increasing number of explicit water molecules (from 0 to 4 molecules) and embedding the cluster (or the naked solute) in a mean-field (PCM<sup>7</sup>) cavity.

The gas-phase VUV transitions were evaluated by performing two different sets of QM calculations: time dependent density functional theory (TD-DFT)<sup>52</sup> using the same functionals and linear response calculations as above, based on coupled cluster with the inclusion of the single and double excitations (CCSD)<sup>53</sup> with the Dunning's triple zeta (TZV) basis set. Note that both of the above calculations were carried out on the same B3LYP optimized geometries in vacuum (see the Results section). All calculations were run on a 4-way HP Proliant DL585 server with Dual-Core AMD Opteron (tm) Processor 850 running at 2.4 GHz. The GAUSSIAN 98<sup>54</sup> and DALTON 2.0<sup>55</sup> packages were used for density functional theory and coupled cluster quantum chemical calculations, respectively.

An estimation of the averaged solvation effect on the 1,2,3-T CCSD/TZV vertical excitation energies, was also evaluated using the self-consistent reaction field model (SCRF)<sup>56,57</sup> as implemented in the DALTON package.

#### 2.2 MD simulations and PMM calculations

In this study the single 1,2,3-T (Ur) molecule was considered as QC with all the remaining solvent molecules acting as classical perturbation. Note that the choice of including explicit solvent molecules in the definition of the QC would not represent a problem for the method. In this case one should carry out the simulation of such a cluster dipped into the solvent molecules. This calculation, although possible, would require the design of the cluster force field and the statistical sampling of the cluster internal configurational space. However, our recent studies<sup>24,25</sup> have clearly demonstrated that when a well balanced empirical force field is used, the choice of a single molecule as a OC provides excellent results for correctly simulating macroscopic observables such as excitation energy distribution at the equilibrium. Moreover, we wish to further point out that the main goal of the present study is precisely to analyze the actual accuracy of PMM theoretical procedure using the simplest definition of the QC, *i.e.* the single solute molecule. Therefore we denote with  $r_n$  the nuclear coordinates of 1,2,3-T (Ur) and with x the coordinates of the solvent atoms providing the (classical) perturbing field. Within certain approximations,<sup>21,24</sup> the electronic (perturbed) Hamiltonian matrix for 1,2,3-T (Ur) can be written as

$$\tilde{H}(\mathbf{r}_n, \mathbf{x}) \cong \tilde{H}^0(\mathbf{r}_n) + q_T V(\mathbf{r}_0, \mathbf{x}) \tilde{I} + \tilde{Z}_1 \left( E(\mathbf{r}_0, \mathbf{x}), \mathbf{r}_n \right) \\
+ \Delta V(\mathbf{r}_n, \mathbf{x}) \tilde{I}$$
(1)

where  $\tilde{H}^{0}(\mathbf{r}_{n})$  is the unperturbed Hamiltonian matrix which can be constructed carrying out standard electronic structure calculations on the isolated 1,2,3-T (Ur). In the above equation  $q_T$  is the total QC charge (in this case 0),  $V(\mathbf{r}_0, \mathbf{x})$  and  $E(\mathbf{r}_0, \mathbf{x})$  are the (perturbing) electric potential and electric field at a given QC  $r_0$  position (in this paper the solute geometrical center),  $\tilde{Z}_1(E_0, r_n)$  is the perturbation energy matrix explicitly given by  $[\tilde{Z}_1]_{l,l'} = -E\langle \Phi_1^0 | \hat{\mu} | \Phi_{l'}^0 \rangle$  and finally  $\Delta V(\mathbf{r}_n, \mathbf{x})$  approximates the perturbation due to all the higher order terms as a simple short range potential.<sup>20,21</sup> Constructing and diagonalizing such a perturbed electronic Hamiltonian at each step of the MD simulation, a 'trajectory' of perturbed eigenvalues  $(\varepsilon_i)$  and eigenvectors  $(c_i)$  of the QC can be, therefore, obtained. From such perturbed excitation energies and using the related perturbed transition dipoles  $\mu_{i,j} = \langle \Phi i | \hat{\mu} | \Phi_j \rangle$ where

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$$\mathbf{u}_{i,j} = \mathbf{c}_i^{*T} \tilde{\boldsymbol{A}}_x^0 \mathbf{c}_j \mathbf{i} + \mathbf{c}_i^{*T} \tilde{\boldsymbol{A}}_y^0 \mathbf{c}_j \mathbf{j} + \mathbf{c}_i^{*T} \tilde{\boldsymbol{A}}_z^0 \mathbf{c}_j \mathbf{k}$$
(2)

$$\left[\tilde{A}_{x}^{0}\right]_{l,l'} = \left\langle \boldsymbol{\Phi}_{l}^{0} | \hat{\mu}_{x} | \boldsymbol{\Phi}_{l'}^{0} \right\rangle \tag{3}$$

$$\left[\tilde{A}_{y}^{0}\right]_{l,l'} = \left\langle \Phi_{l}^{0} | \hat{\mu}_{y} | \Phi_{l'}^{0} \right\rangle \tag{4}$$

$$\left[\tilde{A}_{z}^{0}\right]_{l,l'} = \left\langle \Phi_{l}^{0} | \hat{\mu}_{z} | \Phi_{l'}^{0} \right\rangle \tag{5}$$

we can readily obtain, by a straightforward statistical averaging, the electronic vertical excitation distribution corrected by the transition probability, *i.e.* the electronic spectrum of 1,2,3-T (Ur) without the internal quantum vibrational contribution. Such a curve for the  $i \rightarrow j$  transition, denoted by  $I_{i,j}(\lambda)$ , can be obtained using the corresponding Einstein coefficient  $B_{i,j}$  combined with the probability density  $\rho(\lambda)$  of excitation in the wavelength ( $\lambda$ ) space (*i.e.* the probability to find the chromophore within a given excitation energy interval divided by the corresponding  $\lambda$  interval), both as obtained by MD and PMM

$$egin{aligned} & H_{i,j}(\lambda) \ = \ B_{i,j}
ho(\lambda) \ & B_{i,j} = rac{|m{\mu}_{i,j}|^2}{6\epsilon_0\hbar^2} \end{aligned}$$

Note that also the perturbed transition dipole  $\mu_{i,j}$  is calculated, by averaging, within a given  $\lambda$  interval.

Two MD simulations (in two different solvents) were performed at isochoric/isothermal conditions (canonical ensemble). In the case of 1,2,3-T, we used the Gromacs simulation software package<sup>58–60</sup> implemented in parallel execution and modified to use the isokinetic temperature coupling<sup>61</sup> for obtaining results fully consistent with statistical mechanics.<sup>62,63</sup>

Few computational studies have been reported in the literature to investigate the 1,2,3-T system in water,<sup>31,32</sup> but the lack of experimental results in water solutions prompted us to first attempt the study of the 1,2,3-T in methanol solvent (for which experimental data are available). To this end, MD simulations were carried out at 298 K, using a cubic box of 513 solvent methanol molecules and a single 1,2,3-T molecule, *i.e.* the QC. The force field parameters for 1,2,3-T were taken from the literature<sup>31</sup> and the Gromacs methanol model<sup>64</sup> was adopted thoroughly. The simulation was extended up to 4.0 ns and only 2.0 ns were used for evaluating the VUV spectra in conjunction with PMM. The long range electrostatics was calculated using the particle mesh Ewald (PME) method<sup>65</sup> with 34 wave vectors in each dimension and a 4th order cubic interpolation. We also applied roto-translational constraints to 1,2,3-T in the simulation box.<sup>62</sup> This procedure, which speeds up the solvent relaxation around the solute and allows a simple PMM application to simulation data, provides the correct statistical mechanics and thermodynamics of the system.

In the case of Ur, we used the AMBER simulation software<sup>66</sup> version 7. The Ur atomic charges were calculated by a resp (restrained electrostatic potential)<sup>67</sup> procedure from the electrostatic potential (ESP) at CIS/Aug-cc-pvtz level of theory using the AMBER antechamber program. The Ur molecule was immersed in a box of 513 TIP3P water molecules.<sup>68</sup> For constraining the roto-translational motion the Ur molecule was kept frozen in its ground state coordinates, and only the water molecules were allowed to move (belly run). For all the other simulation details we used the same protocol adopted for 1,2,3-T-methanol. In order to evaluate the unperturbed eigenvector and eigenvalues of 1,2,3-T and Ur, needed for PMM computational procedure, we used the same levels of theory employed for the transitions in gas-phase (see the Results section).

We wish to remark that if compared to PCM in its simplest application (naked solute in a continuum dielectric), PMM proves rather more expensive. On the other hand, if an 'embedded' complex is concerned, PMM and PCM do not show appreciable differences in terms of computational costs.

# 3. Results and discussion

# **3.1.** Vertical excitation energies of 1,2,3-triazine in the gas-phase

Our first goal is a proper evaluation of the basis set for constructing the Hamiltonian matrix of eqn (1). First of all, the proper selection of the geometrical parameters is of crucial importance as, within PMM scheme, the geometry adopted for deriving the unperturbed eigenstates should resemble as much as possible the situation in solution. The second aspect is the choice of the level of theory which, as already reported in our previous studies, must be driven essentially by two factors, *i.e.* reliable performances and relatively low computational costs.

In this respect, solvent effects on the ground state 1,2,3-T were found to be rather low.<sup>69</sup> At the same time different levels of theory did not produce appreciably different geometrical parameters in the gas-phase. This finding allowed us to consider all the geometries, optimized at different computational level, virtually identical for the purposes of the present study.

The unperturbed eigenstates were therefore calculated using two sets of *in-vacuo* calculations: (i) TD-DFT with different functionals; (ii) CCSD/TZV.

By comparing our results with experimental and high-level *ab initio* calculations (see Table 1) we can observe that the "pure" GGA functional (BLYP) strongly underestimates the experimental as well as the MRDCI transition energies. On the other hand, the two hybrid GGA functionals (PBE0 and B3LYP) provide similar description of the valence electronic excitations showing all the VUV transitions only slightly underestimated with respect to the experimental absorptions. This latter finding can probably be ascribed to the involvement of  $\pi$ -like orbitals whose over-stabilization produced by DFT calculations, is well documented.<sup>40</sup>

The comparison of TD-DFT with previous calculations<sup>29</sup> using CASSCF and CASPT2 approaches (also reported on Table 1), suggests that all the investigated VUV excited states are basically characterized by a single configuration character (which in fact turned out to account for more than 93% of all states investigated) and, most importantly, that the dynamical correlation plays a crucial role. For this reason we decided to reappraise the same transitions using a more correlated approach such as CCSD/TZV using the B3LYP/6-311++G(3df,3pd) optimized geometry. However, notwith-standing its documented performances,<sup>72–76</sup> CCSD performed quite similarly to GGA-based TD-DFT calculations (see Table 1).

Note also that at about 6.50 eV a Rydberg-like  $(R_y)^{1}n \rightarrow 3S$  transition, as already reported in the literature,<sup>29</sup> was also

	BLYP/B3	B3LYP/B3	PBE0/B3	CCSD/TZV//B3LYP/B3	Exp <sup>29</sup>
$S_0-S_1$	3.3 (0.0053)	3.7(0.0058)	3.7(0.005)	3.8(0.0067)	3.8
$S_0-S_2$	3.2 (0.00)	3.9(0.0)	4.0(0.0)	3.9(0.0)	
$S_0 - S_3$	3.5 (0.00)	4.0(0.0)	4.1(0.0)	4.1(0.0)	
$S_0-S_4$	3.7 (0.0064)	4.2(0.0047)	4.3(0.0)	4.4(0.0064)	4.7
	CASSCF <sup>30</sup>	MRDCI <sup>29</sup>	CASPT2 <sup>30</sup>		
$S_0-S_1$	4.5	4.1	3.3		
$S_0 - S_2$	4.8	4.2	2.6		
$S_0 - S_3$	5.6	4.6	2.9		
$S_0-S_4$	5.4	4.7	3.5		

Table 1Low-lying vertical transitions of gas-phase 1,2,3-triazine (eV); numbers in parentheses are oscillator strengths. B3 corresponds to 6-311++G(3df,3pd) basis sets

found at all levels of theory employed and also that further  $R_y$  states, known to be present at above 8.50 eV,<sup>29</sup> were disregarded in the present study, regarded essentially as not relevant for the evaluation of the VUV excitations with PMM. In conclusion, from the above analysis TD-DFT/B3LYP/6-311++G(3df,3pd) and CCSD/TZV//B3LYP/6-311++G(3df,3pd) turned out to provide sufficiently satisfactory results for evaluating low-lying unperturbed electronic states and were then selected for carrying out the PMM procedure by constructing, and diagonalizing at each MD step, a 9 × 9 Hamiltonian matrix<sup>77</sup> according to eqn (1).

#### 3.2. PMM on 1,2,3-triazine in methanol solution

In the previous section we have described the very low sensitivity of 1,2,3-T ground state geometry both to the level of theory and to the presence of the solvent. Based on the above findings MD simulation of 1,2,3-T (and subsequent PMM calculations) was therefore performed with the B3LYP/ 6-311++G(3df,3pd) geometry. In the Fig. 2 we report the radial distribution function, g(r), obtained from our simulation. The analysis of N–H(SOL) hydrogen bond (Fig. 2a) reveals a rather typical pattern characterized by two almost coincident sharp peaks centered at about 0.19 nm both for N1 and N3 (around each of two symmetric nitrogen atoms) and another peak at 0.21 nm for N2. Not surprisingly (inset b of

1.5 (a) g(r) 0.5 1.0 (b) 1 g(r) 0.5 0 0 0.2 0.6 0.4 0.8 r (nm)

**Fig. 2** Radial pair correlation function between 1,2,3-triazine nitrogen atoms and methanol hydrogen atoms (inset a), 1,2,3-triazine C–H groups and methanol oxygen atoms (inset b).

the same figure), we cannot detect the formation of any structured solvent organization around the C–H moieties of 1,2,3-T. The emerged picture, in analogy with the one in water,<sup>31</sup> describes 1,2,3-T as essentially interacting with methanol molecules, exerting an extremely narrow electric field distribution parallel to the ground state dipole moment (see Fig. 3).

In Fig. 4 we show the calculated VUV excitation energy distributions of 1,2,3-T in methanol whose maxima are reported in Table 2. As expected, from the result of Fig. 3, and considering the systematic dipole moments decrease upon all the investigated vertical excitations (Table 3), all the transitions are sharply shifted toward the blue in methanol. It is interesting to observe that the self-consistent reaction field approximation (SCRF) provides results systematically shifted toward the red with respect PMM. Note that the same calculations using PCM provided the same result. In order to qualitatively assess the effect of explicit solvent molecules we also carried out calculations using a complex of 1.2.3-T with an increasing number of solvent molecules embedded in a continuum dielectric. These calculations, for the sake of simplicity and for comparison with previous calculation,<sup>31</sup> were carried out using water as solvent and therefore they should be considered as only qualitative indications of the effect of an explicit solvation shell. The results reported in



**Fig. 3** Solvent electric field and unperturbed ground state dipole moment (see inset) not-normalized angle distribution function (F) as provided by MD simulation of 1,2,3-triazine in methanol.



**Fig. 4** PMM/CCSD/TZV//B3LYP/6-311++G(3df,3pd) calculated spectra (excluding quantum vibrational effects) of 1,2,3-T in methanol at 298 K.

Table 2 indicate the importance of the inclusion of these explicit molecules which greatly improve the computed shift.

Interestingly, for the second excited state, practically inaccessible from ground state in the gas-phase (neglecting higher order transition multipoles), PMM provides an unexpectedly high intensity. The analysis reported in Fig. 5 reveals, in fact, a strong similarity between the dipole moment expectation values and orientations of the first and second excited vertical electronic state. It is therefore plausible to explain the spectral change on the basis of a strong mixing of the electronic states induced by solvent electric field fluctuation.

By comparing the  $S_0$ - $S_1$  shift with the corresponding unperturbed result (Table 2), *i.e.* 0.33 eV, the shift apparently appears underestimated by 0.16 eV with respect to the experimental observation. However, as already pointed out, 1,2,3-T experimentally shows a very large peak, spanning the 3.5–4.9 eV range, and the absorption maximum experimentally detected should not be attributed only to  $S_0$ - $S_1$  transition but, rather, to the merging at all VUV signals. In this case PMM may be considered to reasonably reproduce the VUV absorption range even though the shape, for the lack of internal vibrations, is not well reproduced. A fully consistent and

**Table 2** Low-lying excited states shift (with respect to  $S_0$ – $S_1$  in gasphase/with respect to the corresponding transition in the gas-phase) of 1,2,3-triazine in methanol solution as provided by PMM/CCSD/ TZV//B3LYP/6-311++G(3df,3pd) and SCRF/CCSD/TZV//B3LYP/ 6-311++G(3df,3pd) at 298 K. Energies are reported in  $\Delta E$  (eV), numbers in parenthesis are oscillator strengths (non-dimensional). PMM energies and oscillator strengths refer to the absorption maximum (see Fig. 4).  $S_0$  and  $S_i$  stand for ground and *i*-th excited state, respectively. B3 corresponds to 6-311++G(3df,3pd) basis sets

	PMM/CCSD/ TZV//B3LYP/B3	SCRF/CCSD/ TZV//B3LYP/B3	CASSCF + MC (Water) <sup>31</sup>
$S_0 - S_1$	0.33(0.0055)	0.24(0.0094)	0.35-0.5
$S_0 - S_2$	0.41/0.31(0.0021)	0.26/0.16(0.00)	
$S_0 - S_3^2$	$0.5/0.2(\sim 0.0)$	0.49/0.19(0.00)	
$S_0 - S_4$	0.81/0.22(0.0133)	0.73/0.15(0.0152)	
• •	PCM/B3LYP/B3	$PCM + 3H_2O/$	$PCM + 4H_2O/$
	, ,	B3LYP/B3	B3LYP/B3
$S_0 - S_1$	0.25	0.34	0.38

**Table 3** Norm of unperturbed electric dipole (Debye) of the ground and first excited states (up to 6.0 eV) of 1,2,3-triazine (at CCSD/TZV// B3LYP/6-311++G(3df,3pd) level of theory) and uracil (at CCSD/ TZV//B3LYP/Aug-cc-pvtz level), in parenthesis is reported the angle (°) between  $S_i$  and  $S_0$ .  $S_0$  and  $S_i$  stand for ground and *i*-th excited state, respectively. There are no available experimental data on 1,2,3-triazine molecule in gas-phase

	Triazine	Uracil	Exp (Uracil) <sup>82</sup>
S <sub>0</sub>	5.7	4.4	4.3
$\mathbf{S}_1$	3.0 (0.0)	3.6 (131.1)	
$S_2$	3.1 (0.0)	5.7 (27.0)	
$\tilde{S_3}$	3.3 (0.0)	6.6 (149.7)	
$S_4$	3.6 (0.0)	~ /	

reliable description of 1,2,3-T would therefore require both the presence of explicit solvent fluctuating molecules (necessary for a correct reproduction of the transition energy range) and, most importantly, the inclusion of the vibronic coupling whose extension to polyatomic molecules is under study in our laboratories.<sup>22</sup>

## 3.3. Vertical excitation energies of uracil in the gas-phase

Following the same strategy used for 1,2,3-T, we initially addressed the choice of the unperturbed set of eigenvalues and eigenvectors, as well as the geometrical parameters, for carrying out the PMM study of the low-lying transition in the case of aqueous Ur. Similarly to 1,2,3-T, and as already emerged by previous studies<sup>40,78</sup> Ur geometrical parameters do not reveal dramatic changes upon hydration. Therefore, just like 1,2,3-T, for the present purposes (*i.e.* application of PMM) any good set of geometrical parameters may be considered virtually equivalent. In Table 4, we report the S<sub>0</sub>–S<sub>1</sub> ( $^{1}n \rightarrow \pi^{*}$ ), S<sub>0</sub>–S<sub>2</sub> and S<sub>0</sub>–S<sub>3</sub> (basically  $^{1}\pi \rightarrow \pi^{*}$ ) vertical transition energies, evaluated at different levels of theory, and compared to experimental and computational data available from the literature. In line with previous findings<sup>40</sup> our results confirm the good performance of TD-DFT



Fig. 5 PMM/CCSD/TZV//B3LYP/6-311++G(3df,3pd) normalized distribution function (F) of the angles between 1,2,3-T S<sub>1</sub> and ground state dipole moments (blue line) and S<sub>2</sub> and ground state dipole moments (red line). For the orientation of the ground state dipole moment see inset of Fig. 3.



**Fig. 6** Radial pair correlation function between: uracil carbonyl oxygen atoms and water hydrogen atoms (inset a), uracil ammide hydrogens groups and water hydrogen atoms (inset b), uracil C–H groups and water oxygen atoms (inset c).

calculations, in particular with use of the generalized gradientcorrected non local B3LYP and PBE0 functionals. Linear response theory with coupled cluster calculations, CCSD/ TZV//B3LYP/Aug-cc-pVTZ systematically slightly overestimates the result. In the light of these results for PMM calculation we used TD-B3LYP, TD-PBE0 and CCSD unperturbed calculations with the B3LYP/Aug-cc-pVTZ optimized geometry. In this case the Hamiltonian matrix of eqn (1) consisted of 10 states.<sup>77</sup>

# 3.4. PMM on uracil in water solution

In Fig. 6 we report the radial distribution function between uracil amide-hydrogen atoms and water molecules (6a) and between uracil carbonyl oxygen atoms and water molecules (6b). As far as the carbonyl groups are concerned, we obtained

**Table 4** Low-lying  $S_0-S_1$  ( $^{1}n \rightarrow \pi^*$ ) and  $S_0-S_2$  and  $S_0-S_3$  ( $^{1}\pi^* \rightarrow \pi^*$ ) transitions of gas phase uracil ( $\Delta E$ , eV); numbers in parentheses are oscillator strengths. BS1 and BS2 corresponds to Aug-cc-pvtz and TZV basis sets, while BS3 and BS4 to 6-311++G(2d,2p) and 6-31G(d), respectively

Level of theory	$S_0 - S_1$	$S_0 - S_2$	S <sub>0</sub> -S <sub>3</sub>
TD-B3LYP/BS1//B3LYP/BS1	4.62(0.0)	5.07(0.12)	5.81(0.03)
TD-PBE0/BS1//PBE0/BS1	4.80(0.0)	5.28(0.14)	6.11(0.03)
TD-BLYP/BS1//BLYP/BS1	3.93(0.0)	4.62(0.05)	5.05(0.03)
CCSD/BS2//B3LYP/BS1	4.90(0.0)	5.45(0.18)	6.40(0.05)
TD-PBE0/BS3//PBE0/BS4 <sup>40</sup>	4.80(0.0)	5.26(0.14)	
CASSCF <sup>80</sup>	4.78(0.0)	6.88(0.19)	7.03(0.08)
CASPT2 <sup>80</sup>	4.54(0.0)	5.00	5.82
MRCI(10,14) <sup>35</sup>	4.80(0.0)	5.79	6.57(0.03)
DFT/MRCI <sup>81</sup>	4.45(0.0)	5.48	6.06
Exp <sup>83–87</sup>	4.4	4.6-5.1	5.8-6.1

an excellent agreement with very recent Car–Parrinello MD results.<sup>79</sup> On the other hand, the agreement is less good concerning the distribution around amide–hydrogen atoms whose  $r_{\text{max}}$  is slightly overestimated (0.20 nm *vs* 0.18 nm<sup>79</sup>). Similarly to 1,2,3-T, such a water distribution produces a very narrow electric field distribution parallel to ground state dipole moment (see Fig. 7). The application of PMM, as reported in Table 5 and Fig. 8, provided rather good results if compared to previous theoretical and experimental investigations.<sup>40,41</sup> In particular, PMM basically reproduces CPCM results with explicit water molecules. In the same table, for comparison, we also report the same vertical electronic



**Fig.** 7 Solvent electric field and unperturbed ground state dipole moment (see inset) not-normalized angle distribution function (F) as provided by MD simulation of uracil in water.

**Table 5** S<sub>0</sub>–S<sub>1</sub> and S<sub>0</sub>–S<sub>2</sub> gas-phase/water shift (eV) of uracil in water as provided by TD-B3LYP/Aug-cc-pvtz//B3LYP/Aug-cc-pvtz, TD-PBE0/Aug-ccpvtz//PBE0/Aug-cc-pvtz and CCSD/TZV//B3LYP/ Aug-cc-pvtz at 298 K. Energies are reported in  $\Delta E$ (eV), numbers in parentheses are oscillator strengths (non-dimensional). BS1 and BS2 corresponds to Aug-cc-pvtz and TZV basis sets, respectively

Level of theory	$S_0 - S_1$	$S_0 - S_2$
PMM/TD-B3LYP/BS1//B3LYP/BS1	-0.18(0.19)	0.38(0.010)
PMM/TD-PBE0/BS1//PBE0/BS1	-0.10(0.22)	0.54(0.010)
PMM/CCSD/BS2//B3LYP/BS1	-0.12(0.13)	0.34(0.028)
SCRF/CCSD/BS2//B3LYP/BS1	-0.07(0.23)	0.21(0.0)
TD-PBE0-PCM <sup>40</sup>	-0.09(0.19)	0.29(0.0)
$TD-PBE0-PCM + 4H_2O^{40}$	-0.10(0.20)	0.48(0.0)
Exp <sup>41</sup>	$\sim -0.2$	$\sim +0.5$

transitions evaluated at the same level of theory, *i.e.* CCSD/ TZV//B3LYP/Aug-cc-pVTZ, in SCRF model.<sup>88</sup> The expected trend is reproduced even though the extent of the effect is slightly reduced, compared to PMM and PCM +  $(H_2O)_4$ results, respectively. Interestingly, as already found for 1,2,3-T, the first state of aqueous Ur is no longer 'forbidden' for the effect of the solvent perturbation which breaks the symmetry of the electronic wavefunctions and mix the states. In this respect, the resulting vertical excited states dipole moments are of extreme interest . In fact, looking at the distribution reported in Fig. 9 both for the first and the second excited states a sharp bimodal distribution can be appreciated. Note that in the present approach we indicate as 'ith excited state' the ith perturbed electronic state in terms of energy with respect to the ground state. The values of the maxima, roughly centered at 33 and 133°, respectively, closely resemble the values of the unperturbed  $S_1$  and  $S_2$  (see Table 3).

This result clearly indicates that, at least in the case of Ur, the 'first excited state' is actually a mixture of two distinct almost degenerate perturbed electronic states, both accessed during the phase-space sampling of the system.

A deeper insight into this result is presently under investigation in our laboratory.



Fig. 8 PMM/TD-B3LYP/Aug-cc-pvtz//B3LYP/Aug-cc-pvtz calculated spectra (excluding quantum vibrational effects)  $S_0$ - $S_1$  (a) and  $S_0$ - $S_2$  (b) of the first two transitions of Ur in water at 298 K.



Fig. 9 PMM/TD-B3LYP/Aug-cc-pvtz//B3LYP/Aug-cc-pvtz normalized distribution function of the angles between Ur  $S_1$  and ground state dipole moments (blue line) and  $S_2$  and ground state dipole moments (red dashed line). For the orientation of the ground state dipole moment see inset of Fig. 4.

# 4. Conclusions

In this paper the accuracy and reliability of PMM calculations in reproducing VUV absorption spectra in solution is further evaluated using two-model systems. Calculations of 1,2,3-T VUV transitions in gas-phase and in methanol solution were carried out at PMM/CCSD/TZV//B3LYP/6-311++ G(3df,3pd) level of theory. If compared to available experimental results (methanol) the calculated spectra reproduce, with a sufficient accuracy, the absorption interval as well as the solvatochromic shift. The major discrepancies can essentially be ascribed to the lack of the internal vibrations, not included in the model, which conceivably produce a strong enlargement of the experimental spectrum. The same computational strategy was also carried out for Ur in water solution. In this case we found a very good agreement with other computational methods and also with experiment. The present paper further points out the accuracy of PMM in reproducing electronic properties in condensed phase. In particular, even taking into account the simplest definition of the quantum center, we may expect PMM to reliably describe absorption VUV spectra in solution provided a sufficiently accurate empirical force field is used. In conclusion, our data confirm that PMM may represent a sufficiently accurate tool complementary to other well tested methodologies for addressing chemical problems of high configurational complexity.

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#### References

- M. Zaldini Hernandes, R. Longo, K. Coutinho and S. Canuto, Phys. Chem. Chem. Phys., 2004, 9, 2088–2092.
- 2 J. Karpiuk, Y. N. Svartsov and J. Nowacki, *Phys. Chem. Chem. Phys.*, 2005, **24**, 4070–4081.
- 3 J. Rejnek, M. Hanus, M. Kabela, F. Ryjaek and P. Hobza, *Phys. Chem. Chem. Phys.*, 2005, **9**, 2006–2017.
- 4 K. Morokuma, Philos. Trans. R. Soc. London, Ser. A, 2003, 360, 1149–1170.
- 5 M. P. Allen and D. J. Tildesley, *Computer Simulation of Liquids Oxford*, Oxford University Press.
- 6 L. Bernasconi, M. Sprik and J. Hutter, J. Chem. Phys., 2003, 119, 12417.
- 7 S. Miertus, E. Scrocco and I. Tomasi, J. Chem. Phys., 1981, 55, 177.
- 8 K. V. Mikkelsen, E. Dalgaard and P. Swanstrom, J. Phys. Chem., 1987, 91, 3081.
- 9 C. Curutchet, C. J. Cramer, D. G. Truhlar, M. F. Ruiz-Lopez, D. Rinaldi, M. Orozco and F. J. Luque, J. Comput. Chem., 2003, 24, 284–297.
- 10 J. Tomasi, B. Mennucci and R. Cammi, Chem. Rev., 2005, 105, 2999–3093.
- 11 R. Improta and V. Barone, Chem. Rev., 2004, 104, 1231.
- 12 C. Adamo and V. Barone, Chem. Phys. Lett., 2000, 330, 152.
- 13 C. Zazza, L. Bencivenni, A. Grandi and M. Aschi, J. Mol. Struct. (THEOCHEM), 2004, 680, 117.
- 14 A. Osted, J. Kongsted, K. Mikkelsen and O. Christiansen, J. Phys. Chem. A, 2004, 108, 8646.
- 15 K. Coutinho and S. Canuto, J. Mol. Struct. (THEOCHEM), 2003, 632, 235.
- 16 B. D. Bursulaya, J. Jeon, N. C. Yang and H. J. Kim, J. Phys. Chem. A, 2000, 104, 45.
- 17 U. F. Rohrig, I. Franck, J. Hutter, A. Laio, J. Vande Vondele and U. Rothlisberger, *ChemPhysChem*, 2003, 4, 1177.
- 18 O. Crescenzi, M. Pavone, F. De Angelis and V. Barone, J. Phys. Chem., 2005, 109, 445–453.
- 19 K. Coutinho, R. C. Guedes, B. J. Costa Cabral and S. Canuto, *Chem. Phys. Lett.*, 2003, 369, 345–353.
- 20 M. Aschi, R. Spezia, A. Di Nola and A. Amadei, *Chem. Phys. Lett.*, 2001, 344, 374.
- 21 R. Spezia, M. Aschi, A. Di Nola and A. Amadei, *Chem. Phys. Lett.*, 2002, **365**, 450.
- 22 A. Amadei, F. Marinelli, M. D'Abramo, M. D'Alessandro, M. Anselmi, A. Di Nola and M. Aschi, *J. Chem. Phys.*, 2005, **122**, 124506.
- 23 M. D'Abramo, M. Aschi, A. Di Nola and A. Amadei, *Chem. Phys. Lett.*, 2005, **402**, 559.
- 24 A. Amadei, C. Zazza, M. D'Abramo and M. Aschi, *Chem. Phys. Lett.*, 2003, 381, 187.
- 25 M. Aschi, M. D'Abramo, C. Di Teodoro, A. Di Nola and A. Amadei, *ChemPhysChem*, 2005, 6, 53.
- 26 M. Aschi, C. Zazza, R. Spezia, C. Bossa, A. Di Nola, M. Paci and A. Amadei, J. Comput. Chem., 2004, 25, 974.
- 27 E. Fos, J. Vilarrasa and J. Fernandez, J. Org. Chem., 1985, 50, 4894.
- 28 K. K. Innes, I. G. Ross and W. R. Moonmaw, J. Mol. Spectrosc., 1988, 132, 4894.
- 29 M. H. Palmer, H. McNab, I. C. Walker, M. F. Guest, M. MacDonald and M. R. F. Siggel, *Chem. Phys.*, 1998, 228, 39, and references therein cited.
- 30 G. Fischer, D. M. Smith and A. U. Nwankwoala, *Chem. Phys.*, 1997, **221**, 11–21.
- 31 J. Zeng and D. Xie, J. Comput. Chem., 2004, 25, 813-822.
- 32 D. Xie, X. Ma and J. Zeng, Chem. Phys. Lett., 2003, 368, 377-383.
- 33 N. Ismail, L. Blancafort, M. Olivucci, B. Kohler and M. A. Robb, J. Am. Chem. Soc., 2002, 124, 6818.
- 34 M. Merchan and L. Serrano-Andres, J. Am. Chem. Soc., 2003, 125, 8108.
- 35 S. Matsika, J. Phys. Chem. A, 2004, 108, 7584-7590.
- 36 M. Fulsher, L. Serrano-Andres and B. Roos, J. Am. Chem. Soc., 1997, 119, 6168.
- 37 M. K. Shukla and J. Leszczynski, J. Phys. Chem. A, 2002, 106, 8642.
- 38 A. Broo and A. Holmen, J. Phys. Chem. A, 1997, 101, 3589.

- 39 B. Mennucci, A. Toniolo and J. Tomasi, J. Phys. Chem. A, 2001, 105, 4749.
- 40 R. Improta and V. Barone, J. Am. Chem. Soc., 2004, **126**, 14320.
- 41 S. A. Williams, C. N. Renn and P. R. Callis, J. Phys. Chem., 1987, 91, 2730.
- 42 A. D. Becke, J. Chem. Phys., 1986, 84, 4524.
- 43 C. Lee, W. Yang and R. G. Parr, Phys. Rev. B, 1988, 37, 785.
- 44 A. D. Becke, J. Chem. Phys., 1993, 98, 5648.
- 45 J. P. Perdew and Y. Wang, Phys. Rev. B, 1992, 45, 13244.
- 46 J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, 77, 3865.
- 47 M. Ernzerhof and G. E. Scuseria, J. Chem. Phys., 1999, 110, 5029.
- 48 T. H. Dunning, Jr, J. Chem. Phys., 1970, 53, 2823.
- 49 T. H. Dunning, Jr and P. J. Hay, Methods of Electronic Structure Theory, ed. H. F. Schaefer III, Plenum Press, 1977, vol. 3.
- 50 R. A. Kendall, T. H. Dunning, Jr and R. J. Harrison, J. Chem. Phys., 1992, **96**, 6796.
- 51 T. H. Dunning, Jr, J. Chem. Phys., 1989, 50, 1007.
- S. Hirata and M. Head-Gordon, *Chem. Phys. Lett.*, 1999, **302**, 375.
   O. Christiansen, H. Koch, A. Halkier, P. Jorgensen, T. Helgaker and A. M. Sanchez de Meras, *J. Chem. Phys.*, 1996, **105**, 6921.
- 54 GAUSSIAN 98 (Revision A.7), Gaussian, Inc., Pittsburgh PA, 1998.
- 55 "Dalton, a molecular electronic structure program, Release 2.0 (2005), see http://www.kjemi.uni.no/software/dalton/dalton.html".
- 56 O. Christiansen and K. V. Mikkelsen, J. Chem. Phys., 1999, 110, 1365.
- 57 O. Christiansen and K. V. Mikkelsen, J. Chem. Phys., 1999, 110, 8348.
- 58 D. van der Spoel, R. van Drunen and H. J. C. Berendsen, *GRoningen MAchine for Chemical Simulations*, Department of Biophysical Chemistry, BIOSON Research Institute, Nijenborgh 4, NL-9717 AG, Groningen, 1994, gromacs@chem.rug.nl.
- 59 D. van der Spoel, A. R. van Buuren, E. Apol, P. J. Meulenhoff, D. P. Tieleman, A. L. T. M. Sijbers, R. van Drunen and H. J. C. Berendsen, *Gromacs User Manual Version 1.3*, 1996 Internet: http://www.gromacs.org/documentation/index.php.
- 60 W. F. van Gunsteren, S. R. Billeter, A. A. Eising, P. H. Hünenberger, P. Krüger, A. E. Mark, W. R. P. Scott and I. G. Tironi, *Biomolecular Simulation: The GROMOS96 Manual and User Guide*, Hochschulverlag AG an der ETH Zürich, Zürich, 1996.
  61 D. J. Evans and G. P. Morriss, *Statistical Mechanics of None-*
- 61 D. J. Evans and G. P. Morriss, *Statistical Mechanics of None-quilibrium Liquids*, Academic Press, London, 1990.
- 62 A. Amadei, G. Chillemi, M. A. Ceruso, A. Grottesi and A. Di Nola, J. Chem. Phys., 2000, 112, 9.
- 63 M. D'Alessandro, A. Tenenbaum and A. Amadei, J. Phys. Chem. B, 2002, 106, 5050.
- 64 It may be interesting, in this respect, to remark that the use of unpolarizable empirical force-fields (as the one adopted in the present and in previous PMM applications) is not an intrinsic limitation of PMM. Obviously, in this case only the orientational part in the ground state (equilibrium) condition is considered without taking into account the so called 'nonequilibrium' response for which a more advanced (and much more expensive) force field would be necessary.
- 65 T. A. Darden, D. M. York and L. G. Pedersen, J. Chem. Phys., 1993, 98, 10089.
- 66 AMBER, a package of computer programs for applying molecular mechanics, normal mode analysis, molecular dynamics and free energy calculations to simulate the structural and energetic properties of molecules, D. A. Pearlman, D. A. Case, J. M. Caldwell, W. S. Ross, T. E. Cheatham III, S. DeBolt, D. Ferguson, G. Seibel and P. A. Kollman, *Comput. Phys. Commun.*, 1995, **91**, 1–41.
- 67 C. I. Bayly, P. Cieplak, W. D. Cornell and P. A. Kollman, J. Phys. Chem., 1993, 97, 10269.
- 68 W. L. Jorgensen, J. Chandrasekhar, J. D. Madura, R. W. Impey and M. L. Klein, J. Chem. Phys., 1983, 79, 926.
- 69 Geometry optimizations of 1,2,3-T-(H<sub>2</sub>O)<sub>n</sub> cluster (with *n* from 0 to 4) embedded in continuum polarizable (PCM), were carried out at DFT levels (see methodological section) without showing appreciable differences with the gas phase.<sup>70,71</sup>.
- 70 C. Zazza, A. Amadei, N. Sanna, A. Grandi, L. Bencivenni and M. Aschi, submitted.
- 71 Selected distances (A) and angles (degree): N-N = 1.319, N-C = 1.341, N-N-N = 121.5.

- 72 H. Koch and P. Jørgensen, J. Chem. Phys., 1990, 93, 3333.
- 73 R. J. Rico, T. J. Lee and M. Head-Gordon, *Chem. Phys. Lett.*, 1994, **218**, 139.
- 74 R. J. Rico and M. Head-Gordon, Chem. Phys. Lett., 1993, 213, 224.
- 75 A. M. Graña, T. J. Lee and M. Head-Gordon, J. Chem. Phys., 1995, 99, 3493.
- 76 A. M. J. Sánchez de Merás, I. García Cuesta and H. Koch, Chem. Phys. Lett., 2001, 348, 469.
- 77 The dimension of the matrix was selected on the basis of the sensitivity analysis on the final result.
- 78 O. V. Shishkin, L. Gorb and J. Leszczynski, Int. J. Mol. Sci., 2000, 1, 17,27.
- 79 M. P. Gaigeot and M. Sprik, J. Phys. Chem. B, 2004, 108, 7458.
- 80 J. Lorentzon, M. P. Fulscher and B. O. Roos, J. Am. Chem. Soc., 1995, 117, 9265.
- 81 C. Neiss, P. Saalfrank, M. Parac and S. Grimme, J. Phys. Chem. A, 2003, 107, 140.
- 82 H. Basch, D. R. Garmer, P. G. Jasien, M. Krauss and W. Stevens, J. Chem. Phys., 1989, 163, 514.

- 83 D. Voet, W. B. Gratzer, R. A. Cox and P. Doty, *Biopolymers*, 1963, 1, 193.
- 84 L. B. Clark, G. G. Peschel and O. Tinoco, Jr, J. Phys. Chem., 1965, 69, 3615.
- 85 C. A. Sprecher and W. C. Johnson, *Biopolymers*, 1977, 16, 2243.
- 86 M. T. Fujii, T. Tamura, N. Mikami and M. Ito, *Chem. Phys. Lett.*, 1986, **126**, 583.
- 87 Excited States in Organic Chemistry and Biochemistry, ed. P. Vigny, J. P. Ballini, B. Pullman and N. Goldblum, Reidel, Dordrecht, 1997.
- 88 In this CCSCRF approach, the Ur molecule is assumed to be surrounded by a linear and homogeneous dielectric medium described in terms of two polarization vector fields, *i.e.* the optical one (always in equilibrium with the actual electronic structure) and the inertial one (which is slow in accompanying the changes in the electronic structure and introduces the contribution of the inertial modes of the solvent molecule to the electrostatic free energy of the total system).