### Theoretical Characterisation of the Electronic Excitation in Liquid Water

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Because of its central role in basically all aspects of science, water is certainly one of the most extensively investigated substances, from a theoretical point of view. Many properties have been, in fact, theoretically addressed both in the isolated and condensed phases. Nevertheless, many aspects are still not completely understood and represent the focus of active theoretical interest. Among them, one of the most appealing is certainly the understanding of the electronic properties, in particular the photoabsorption features, in condensed phase. Liquid water experimentally shows, under ambient conditions, the 0–1 absorption maximum at 147 nm, that is, 88 kJ mol<sup>-1</sup> shifted toward the blue with respect to the corresponding absorption in vacuum.<sup>[1-3]</sup> This blue-shift is known to be more pronounced in ice than in liquid water,<sup>[4]</sup> and it is also present in small water clusters.<sup>[5]</sup> From these observations, it is well-established that such a blue-shift is to be mainly ascribed to the short contacts of the excited molecule with its solvation shell (the water dipole moment undergoes an inversion upon 0–1 excitation<sup>[6]</sup>). However, only a few theoretical studies have been so far devoted to modelling water photoabsorption in the condensed phase.<sup>[7-9]</sup> The computational methods available nowadays are, in fact, able to provide extremely accurate information about the photoexcitation of isolated molecules. However, there are still many difficulties in modelling the same phenomenon in the condensed phase. The inclusion of electronic degrees of freedom (necessary for studying an electronic excitation) into a simulation of a large number of molecules (necessary for a reliable modelling of a condensed phase) is, in fact, still challenging from a computational point of view. In this context, we recently proposed a theoretical computational approach, the perturbed matrix method (PMM),<sup>[10,11]</sup> whose main computational feature is the possibility of including, into a classical simulation algorithm, electronic degrees of freedom. In a number

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of recent applications, which were carried out both on large biomolecular systems<sup>[12,13]</sup> and on a small solute in solution,<sup>[14]</sup> PMM actually revealed to be a rather reliable computational tool for evaluating the spectroscopic (absorption) properties in the condensed phase. Herein, we wish to address—via PMM the modelling of the photoabsorption spectroscopy of liquid water, with the precise aim of better understanding this phenomenon and, at the same time, of further evaluating PMM accuracy. Moreover, and similarly to our previous studies on formaldehyde in water,<sup>[14]</sup> we also evaluate the excitation thermodynamics by combining PMM calculations with the quasi-Gaussian entropy (QGE) theoretical approach.<sup>[15, 16]</sup>

### **Theory and Computational Methods**

The theoretical basis of PMM has been widely described elsewhere.<sup>[10,11,14]</sup> Here, only the main features of the computational strategy will be outlined. The underlying philosophy of PMM is essentially in line with all currently employed quantum mechanical/molecular mechanical (QM/MM) procedures. In other words, a portion of a complex molecular system-hereafter called quantum centre (QC)-such as a solute, a part of a biomacromolecule, a molecular cluster, etc. is treated quantum mechanically with the rest of the system, for example, the solvent and/or the protein, acting as a perturbation. The novelty, in PMM, is the way in which such a perturbation is dynamically coupled with the QC. In fact, with  $\mathbf{r}_n$  being the nuclear coordinates of the QC (i.e., a single water molecule) and x being the coordinates of the atoms that provide the (classical) perturbing field (i.e., all remaining water molecules), we can write, within certain approximations,<sup>[11, 14]</sup> the (electronic) perturbed Hamiltonian matrix for the QC as Equation (1):

$$\tilde{\mathscr{H}}(\mathbf{r}_{n},\mathbf{x}) \cong \tilde{\mathscr{H}}^{0}(\mathbf{r}_{n}) + q_{\mathsf{T}}\nu(\mathbf{r}_{0},\mathbf{x})\tilde{l} + \tilde{Z}_{1}[\mathbf{E}(\mathbf{r}_{0},\mathbf{x}),\mathbf{r}_{n}] + \Delta V(\mathbf{r}_{n},\mathbf{x})\tilde{l}$$
(1)

where  $\tilde{\mathscr{H}}^{0}(\boldsymbol{r}_{n})$  is the unperturbed Hamiltonian matrix, which can be built by a standard "isolated water molecule" electronic-structure calculation;  $v(\mathbf{r}_0, \mathbf{x})$  and  $\mathbf{E}(\mathbf{r}_0, \mathbf{x})$  are the (perturbing) electric potential and the electric field at a given QC  $\mathbf{r}_0$  position (typically the geometrical centre), respectively;  $\tilde{Z}_1(\mathbf{E},\mathbf{r}_n)$  is the perturbation energy matrix, which is explicitly given by  $[\tilde{Z}_1]_{ll} =$  $-\mathbf{E} \langle \Phi_l^0 | \hat{\boldsymbol{\mu}} | \Phi_l^0 \rangle$ ; and  $\Delta V(\mathbf{r}_n, \mathbf{x})$  approximates the perturbation due to all higher-order terms as a simple short-range potential. Moreover,  $\Phi_{l}^{0}$  are the unperturbed (electronic) Hamiltonian eigenfunctions, and all the matrices used are expressed in this unperturbed basis set. If a molecular dynamics (MD) simulation or-more general-a configurational space sampling is carried out, a "sequence" of **E** and  $\nu$  is produced. Hence, the diagonalisation of  $\mathscr{H}(\mathbf{r}_{n},\mathbf{x})$ , carried out along such a configurational sampling, will produce a "trajectory" of perturbed eigenvalues ( $\varepsilon$ ) and eigenvectors (c) of the QC and, therefore, of whatever perturbed electronic property. In the case of liquid water, the choice of using a single water molecule, instead of a molecular cluster, as QC might result-although it allows a straightforward computational application of PMM-in an oversimplified model. However, the use of a molecular cluster as QC would imply the simulation of such a cluster embedded into the solvent molecules, and such a simulation, although possible, requires the design of the cluster force field and the statistical sampling of the cluster's internal configurational space. Moreover, it should be noted that, when MD simulations based on non-polarisable force fields are utilized, as usual, the definition of a single molecule as QC interacting with the molecular environment is probably statistical-mechanically more coherent with the physics of the simulated system.

By extracting the perturbed excitation energies and the related perturbed transition dipoles,  $\boldsymbol{\mu}_{i,j} = \langle \Phi_i | \hat{\boldsymbol{\mu}} | \Phi_j \rangle$ , where [Eqs. (2)–(5)]:

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

$$[\tilde{\Lambda}_{x]l,l}^{0} = \langle \Phi_{l}^{0} | \hat{\mu}_{x} | \Phi_{l}^{0} \rangle \tag{3}$$

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

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

we can readily obtain, by a straightforward statistical averaging, the electronic vertical excitation distribution corrected by the transition probability, that is, the electronic spectrum without the internal quantum vibrational contribution. Such a curve for the  $i \rightarrow j$  transition, denoted by  $l_{i,j}(\lambda)$ , can be obtained by using the corresponding Einstein coefficient  $B_{i,j}$  combined with the probability density  $p(\lambda)$  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 [Eqs. (6a) and (6b)]:

$$I_{i,j}(\lambda) = B_{i,j}\rho(\lambda) \tag{6a}$$

$$B_{ij} = \frac{|\boldsymbol{\mu}_{ij}|^2}{6 \in {}_0\hbar^2} \tag{6b}$$

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

From the previous equations, we can also express the freeenergy exchange, for an electronic excitation of the quantum centre, with all the neighbouring molecules in their electronic ground state<sup>[14]</sup> [Eq. (7)]:

$$\begin{split} \Delta A &= -kT \ln \left[ \frac{\int e^{-\beta u_{i}} d\xi dx d\pi_{\xi} d\pi_{x}}{\int e^{-\beta u_{0}} d\xi dx d\pi_{\xi} d\pi_{x}} \right] - kT \ln \frac{Q_{v,i}}{Q_{v,0}} \\ &= -kT \ln \langle e^{-\beta (u_{i}-u_{0})} \rangle_{u_{0}} - kT \ln \frac{Q_{v,i}}{Q_{v,0}} \\ \langle e^{-\beta (u_{i}-u_{0})} \rangle_{u_{0}} &= \frac{\int e^{-\beta (u_{i}-u_{0})} e^{-\beta u_{0}} d\xi dx d\pi_{\xi} d\pi_{x}}{\int e^{-\beta u_{0}} d\xi dx d\pi_{\xi} d\pi_{x}} \\ u_{i} &= \varepsilon_{i} + \kappa_{\xi} + u_{env,i} \end{split}$$
(7)

where  $\xi$  are the classical nuclear degrees of freedom of the QC,  $\pi$  the conjugated momenta,  $\kappa_{\xi}$  the (classical) kinetic energy of the QC and  $u_{\text{env,i}}$  the internal energy of the environment (excluding the interaction with the quantum centre and the possible environmental quantum vibrational terms) ob-

tained when the quantum centre is in the *i*th electronic state and all the environment molecules are in their electronic ground states. Moreover,  $Q_{v,0}$  and  $Q_{v,i}$  are the quantum vibrational partition functions for the ground and *i*th electronic states of the quantum centre (we assume that such an usual factorisation is always possible). Note that, in the definition of  $u_{i}$ , we disregard the contribution due to the shift in the vibrational energy of the ground state with respect to the reference value defining the corresponding vibrational partition function. Here, this term is considered to be negligible (i.e. we assume that the vibrational frequencies are virtually independent of the coordinates). Note also that the eigenvalue  $\varepsilon_i$  of the perturbed Hamiltonian matrix should be obtained at the minimum energy configuration of the corresponding electronic state. However, even when the excited electronic state has a minimum energy position which is different from that of the ground state, vertical excitations can be used to correct the excitation energy with the energy shift due to the position relaxation, that is, the energy exchange between the vertical excited state and the corresponding excited state in its minimum energy configuration. A computationally convenient approximation for rigid molecules, which was used both in a previous work<sup>[14]</sup> and in the present one, considers this correction as a constant that is independent of the perturbation (i.e. its value can be obtained in the unperturbed condition) and, hence, irrelevant when subtracting the unperturbed excitation energy (which is also a constant for rigid molecules) from the excitation free energy. This approximation is typically valid for QC, where the minimum energy positions of the ground and (considered) excited states are rather close, as we have assumed herein to simplify our calculations. Note that, in the case in which the environmental energy is basically independent of the electronic state of the quantum centre, as we assume neglecting atomic polarisation,  $u_i - u_0 = \varepsilon_i - \varepsilon_0$ , this last equation, together with the assumption that  $Q_{v,i} \cong Q_{v,o}$  (i.e., assuming that the free-energy term due to the quantum vibrational partition functions can be neglected), was used for the calculation of the excitation free energy, which is hence equivalent to the vertical excitation free energy. The values obtained at different temperatures were then used to parameterise a theoretical model for the excitation thermodynamics based an the quasi-Gaussian entropy theory, as described in a previous paper.<sup>[14]</sup>

For the PMM procedure, an adequate description of the electronic properties of the isolated (unperturbed) solute molecule (in this case a water molecule) and a reliable and statistically meaningful MD simulation providing the solute–solvent interaction are necessary. We performed MD simulations over a wide temperature range (300–800 K), using a cubic box of 256 simple-point-charge (SPC)<sup>[17]</sup> water molecules at 55.32 mol L<sup>-1</sup> density. All simulations were performed using the Gromacs software package,<sup>[18–20]</sup> which was modified to use the isokinetic temperature coupling<sup>[21]</sup> for obtaining results that were fully consistent with statistical mechanics.<sup>[22, 23]</sup> For all simulations, the number of steps was 2500 000, with two different time steps: 2 fs for simulations in the range 300–500 K and 1 fs in the range 600–800 K. Hence, the corresponding simulationtime lengths were about 5 and 2.5 ns. The long-range electro-

statics was calculated using the particle mesh Ewald (PME) method,<sup>[24]</sup> with 34 wave vectors in each dimension and a fourth-order cubic interpolation. We also used roto-translational constraints to stop the water "solute" in the simulation box.<sup>[22]</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. Different sets of quantum chemical calculations for the isolated water molecule were carried out using two complementary high-level-of-theory computational approaches: the complete active space self-consistent field (CASSCF) and the coupled-cluster (CC) linear-response calculation<sup>[25]</sup> including the single and double excitations (CCSD). The active space used in the CASSCF calculations consisted of eight electrons in 12 orbitals, and the 6-311++ g(d,p) basis set, hereafter named BSI, was used. For the CC calculations, we used the 6-311 + + g(3df, 2pd) basis set (hereafter called BSII). For comparison with literature data,<sup>[7]</sup> we also performed a few test calculations using the augmented cc-pVDZ basis of Dunning including polarisation and diffusion functions for each hydrogen atom and the Rydberg basis of Dunning and Hay for oxygen,<sup>[26,27]</sup> denoted herein as BSIII. For the calculation of the transition moments, to be used in conjunction with the CASSCF eigenvalues, a configuration interaction procedure was carried out using the natural orbitals obtained by a state-averaged CASSCF on the first ten electronic states. The quality of these quantum chemical calculations was checked by comparison with the available experimental and theoretical data.  $^{[7,\,28-31]}$  We also evaluated the vertical 0–1 excitation energy of water using time-dependent density functional theory calculations<sup>[32]</sup> (TD-DFT) combined with the polarisable continuum model (PCM)<sup>[33]</sup> to simulate the average effect of the water solvent. The hybrid B3 LYP<sup>[34]</sup> functional was used for this purpose with the BSI basis set. The Gamess,<sup>[35]</sup> Gaussian<sup>[36]</sup> and Dalton<sup>[37]</sup> packages were used for all these quantum chemical calculations.

#### **Results and Discussion**

The results of the calculations described in the methodological section are reported in Table 1.

From the table, it clearly emerges that CASSCF/BSI/PMM, which shows an energy maximum at 146 nm and a blue-shift

<b>Table 1.</b> Absorption maxima $(\lambda_{max})$ and related blue-shift (B-Sh) for the 0–1 rransition. BSI stands for 6-311 + + g(d,p), BSII for 6-311 + + g(3df,2pd)		
Method	$\lambda_{\max}$ [nm]	B-Sh [kJ mol <sup>-1</sup> ]
CASSCF/BSI/PMM 300 K	146	78
CC/BSII/PMM 300 K	150	64
CASSCF/BSI/PMM 400 K	146	
CASSCF/BSI/PMM 500 K	149	
CASSCF/BSI/PMM 600 K	151	
CASSCF/BSI/PMM 800 K	151	
TD-DFT (B3 LYP)/BSI/PCM	180	25
TAB/101) model 300 K <sup>7</sup>	150	65
experiment (liquid, 298 K) <sup>1</sup>	$147\pm1$	88±6

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of 78 kJ mol<sup>-1</sup>, provides excellent results (within the experimental noise).<sup>[1]</sup> Less satisfactory—even though still rather close to the experimental values-are the results from CC/BSII/ PMM, whose maximum is found at 150 nm with a blue shift of 64 kJ mol<sup>-1</sup>. Interestingly, our CC/BSII/PMM calculations are in very good agreement with the TAB/10D calculations from Kim and co-workers,<sup>[7]</sup> which were based on a methodology somewhat similar to PMM, and utilising CASSCF/BSIII quantum chemical calculations. We also tested, within our methodology, large atomic basis sets including the Rydberg functions, without obtaining any improvement in the results. Therefore, we decided not to use such computationally demanding basis sets any further. Such a finding is probably due to the fact that the presence of diffuse atomic basis set functions (i.e. BSII) in our unperturbed quantum chemical calculations, partially mimic the Rydberg effect. Moreover, the use of Rydberg functions in a single molecule QC is likely not to significantly improve the description of the possible molecular overlap taking place upon excitation, and the effective molecular Hamiltonian, optimised to reproduce the correct statistical mechanics of liquid water (SPC), correctly simulates macroscopic observables, which include—as is evidenced by our results—the absorption spectrum. This is probably due to the fact that the electric field fluctuations provided by SPC molecules satisfactorily mimic the real local field experienced by the chromophore.

In Figure 1, the first excitation spectrum (neglecting quantum vibrational effects) at 300 K is reported. It is worth noting that such vibrational effects in condensed phase, although im-



*Figure 1.* Excitation spectrum (excluding quantum vibrational effects) of liquid water at 300 K, as obtained by PMM calculations.

portant for an accurate and detailed modelling of the photoabsorption spectrum, typically provide an enlargement of the absorption curve without altering its maximum or its basic shape. However, we are presently extending PMM to explicitly include quantum nuclear vibrations to treat vibronic excitations. In Figure 2, we show such excitation spectra at three different temperatures: 300, 500 and 800 K. As already remarked in the previous section, all these profiles were obtained by



Figure 2. Excitation spectrum (excluding quantum vibrational effects) of liquid water at three temperatures, as obtained by PMM calculations.

combining the statistical probability of the excitation energy with the square length of the perturbed transition dipoles, both obtained by PMM. These curves show a rather large fullwidth-at-half-maximum (fwhm) of about 10 nm, although as the temperature is increased, an enlargement of the curve and a slight red-shift of the maximum are observed. Note that, in both figures, we only show data obtained by CASSCF/BSI/ PMM. Our results basically confirm previous findings on water photoabsorpiton,<sup>[7]</sup> showing that a sharp temperature increase (although poorly affecting the absorption maximum) systematically enlarges the distribution at the red-edge, while the blueedge remains essentially unaffected. Since no quantum vibrations are included in our model, the observed features of the excitation-energy-distribution width and shape must be entirely ascribed to the effect of the electric field fluctuation of the solvent.<sup>[7,13]</sup> Interestingly, the electric-field-fluctuation pattern is essentially determined by the combination of two independent components: a larger one occurring along the symmetry axis of the molecule, and another one-a rather dumped one-occurring orthogonal to the molecular plane. Considering that, upon the 0-1 excitation, the dipole moment decreases, these findings suggest that solvent electric field fluctuations are essentially given by molecular fluctuations within ground-state potential-energy minima, hence providing a blue tail close to the maximum absorption energy accessible to the system. Finally, in Figure 3 we show the excitation free energy (subtracted from the unperturbed excitation energy) as obtained by combining PMM data with the quasi-Gaussian entropy (QGE) theory, using the same procedure as in ref. [14], which is briefly described in the "Theory and Computational Methods" Section. In Figure 3, we show both the excitation free energies given by PMM at four temperatures and the curve provided by a QGE model (gamma state) parameterised fitting PMM data. The PMM values and the QGE model are in rather good agreement,<sup>[14]</sup> which confirms that also the excitation thermodynamics in a liquid can be well described by a relatively simple model (gamma state). From the QGE model, a rather characteristic thermodynamic behaviour emerges, which



**Figure 3.** Excitation free energy (subtracted from the unperturbed excitation energy) as obtained by PMM at four temperatures (•) and by QGE model (-----) parameterised fitting PMM data.

is due to a negative excitation heat capacity (e.g. at 300 K  $\Delta C_v = -62.7 \text{ Jmol}^{-1} \text{ K}^{-1}$ ). The decrease in temperature of the excitation free energy is associated to a strict temperature decrease of the excitation entropy (not shown), which occurs as a consequence of an energy fluctuation reduction of the entire system when an excited water molecule is added to the bulk water. Note that each excitation thermodynamic property for an infinitely diluted excited molecule (solute) corresponds to a change in the solute partial molar property due to electronic excitation and, hence, the QGE model provides a complete description of the partial molar properties of the excited state.

#### Conclusions

Herein, we used MD simulations and PMM calculations to obtain detailed information about electronic excitation in liquid water. The results clearly demonstrate the accuracy of this procedure and confirm the essential role that the dynamical coupling between the chromophore electronic states and the environment atomic motions plays in determining the electronic behaviour. When compared with other theoreticalcomputational procedures applied to liquid water, PMM turns out to be the most accurate, as obtained in the case of solvated formaldehyde.<sup>[14]</sup> Those methods using a mean-field approach are clearly inaccurate because of the too-rough approximation of treating the solvent as a macroscopic dielectric, while those based on explicit solvent interactions are typically missing the dynamical coupling, which can only be obtained with a rather extended configurational sampling. Finally, the combined use of PMM with QGE theory provided an analytical model for the complete thermodynamics of the excited state. Such information, which is essentially of theoretical interest for a water molecule, could be of great importance in other systems in which the excited state of a solvated molecule is involved in a chemical reaction. These results make PMM particularly interesting for studying quantum mechanical events in complex molecular systems and confirm its reliability and accuracy.

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