

Theoretical characterization of temperature and density dependence of liquid water electronic excitation energy: Comparison with recent experimental data

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In a recent paper [Aschi *et al.*, *ChemPhysChem* **6**, 53 (2005)], we characterized, by means of theoretical-computational procedures, the electronic excitation of water along the typical liquid state isochore (55.32 mol/l) for a large range of temperature. In that paper we were able to accurately reproduce the experimental absorption maximum at room temperature and to provide a detailed description of the temperature dependence of the excitation spectrum along the isochore. In a recent experimental work by Marin *et al.* [*J. Chem. Phys.* **125**, 104314 (2006)], water electronic excitation energy was carefully analyzed in a broad range of density and temperature, finding a remarkable agreement of the temperature behavior of the experimental data with our theoretical results. Here, by means of the same theoretical-computational procedures (molecular dynamics simulations and the perturbed matrix method), we investigate water electronic absorption exactly in the same density-temperature range used in the experimental work, hence, now considering also the absorption density dependence. Our results point out that, (1) for all the densities and temperatures investigated, our calculated absorption spectra are in very good agreement with the experimental ones and (2) the gradual maxima redshift observed increasing the temperature or decreasing the density has to be ascribed to a real shift of the lowest $\tilde{X} \rightarrow A$ electronic transition, supporting the conclusions of Marin *et al.* © 2008 American Institute of Physics. [DOI: [10.1063/1.2826325](https://doi.org/10.1063/1.2826325)]

Despite a huge number of theoretical and experimental works¹⁻⁵ concerning the optical absorption of water, only recently, a clear consensus picture of the temperature and density dependence of the absorption spectrum is emerging. In fact, recently, Marin *et al.*⁶ (hereafter referred to as paper I) presented arguments supporting the fact that the redshift of the absorption maximum observed increasing the temperature is entirely due to a true shift in the water electronic transition energy. The experimental evidence presented in that paper unequivocally excluded the fact that the observed redshift could be ascribed to the growth of the vibrational hot bands or to a scattering artifact.

In the most exhaustive and recent theoretical analysis of the photoabsorption of water,¹ where the general experimental trend was well reproduced, the authors pointed out the importance of the solvation effects on electronic excitation and spectrum broadening. Unfortunately, these calculations (published before the publication of paper I) mostly focused on the effect of density changes and, hence, no detailed com-

parison with the experimental data of paper I is really possible. Short before the publication of paper I, we reported a theoretical-computational study on liquid water absorption in a wide range of temperature along the 55.32 mol/l isochore.⁷ Our results not only accurately reproduced the absorption maximum at room temperature (about 300 K) but also predicted the maximum redshift for increasing temperatures later observed experimentally and reported in paper I. In that paper the authors pointed out the remarkable agreement of their data with our results for the temperature dependence and showed their disappointment for the lack of information on the absorption density dependence in our paper, making not possible to unambiguously compare their data with our results. The purpose of this letter is twofold: (1) to expand our previous study on electronic excitation of liquid water in order to provide a clear view on the temperature and density dependence of water absorption spectrum and (2) critically compare our results with the recent experimental measurements in a broad range of thermodynamic conditions presented in paper I. Therefore, we present here calculations on water electronic excitation, performed identically to the ones reported in our previous paper,⁷ within the same tem-

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perature (between 25 and 400 °C) and density (between 0.1 and 0.358 g/cm³) ranges used in the experiments of paper I.

The theoretical-computational procedure used, the perturbed matrix method (PMM) combined with molecular dynamics (MD) simulations, has been extensively described in a number of previous works.^{7–10} Briefly, PMM is a recent statistical mechanically based method able to provide the electronic properties of a chemical system embedded in a complex molecular environment. This mixed quantum/classical method is in line with usual quantum mechanics/molecular mechanics (QM/MM) procedures: a part of the system considered is described quantum mechanically (quantum center, QC) whereas the rest acts as semiclassical molecules providing the perturbation (i.e., the electric field). The main novelty in PMM is the way used to obtain the coupling between the QC electronic states and the (moving) atomic environment. In fact, indicating with \mathbf{r}_n the QC nuclear coordinates (in the present case the QC is a single water molecule) and with \mathbf{x} the atomic environment coordinates providing the (classical) perturbing field (here the coordinates of the remaining water molecules), we can write, within certain approximations,^{8,9,11,12} the (electronic) perturbed Hamiltonian matrix for the QC as

$$\begin{aligned} \tilde{H}(\mathbf{r}_n, \mathbf{x}) \cong & \tilde{H}^0(\mathbf{r}_n) + q_T \mathcal{V}(\mathbf{r}_0, \mathbf{x}) \tilde{I} + \tilde{Z}_1(\mathbf{E}(\mathbf{r}_0, \mathbf{x}), \mathbf{r}_n) \\ & + \Delta V(\mathbf{r}_n, \mathbf{x}) \tilde{I}, \end{aligned} \quad (1)$$

where q_T is the QC total charge, $\tilde{H}^0(\mathbf{r}_n)$ is the unperturbed Hamiltonian matrix which can be built by a standard isolated water molecule electronic-structure calculation, $\mathcal{V}(\mathbf{r}_0, \mathbf{x})$ and $\mathbf{E}(\mathbf{r}_0, \mathbf{x})$ are the (perturbing) electric potential and electric field at a given QC \mathbf{r}_0 position (typically the geometrical or mass center), respectively, $\tilde{Z}_1(\mathbf{E}, \mathbf{r}_n)$ is a perturbation energy matrix which is given by the electric field and transition dipole moments, i.e. $[\tilde{Z}_1]_{l,l'} = -\mathbf{E} \cdot \langle \Phi_l^0 | \hat{\boldsymbol{\mu}} | \Phi_{l'}^0 \rangle$, and $\Delta V(\mathbf{r}_n, \mathbf{x})$ approximates the perturbation due to all higher-order terms as a simple short-range potential. Moreover, Φ_l^0 are the unperturbed (electronic) Hamiltonian eigenfunctions and all the matrices used are expressed in this unperturbed basis set. If a MD simulation or—more in general—a configurational space sampling is carried out, a sequence of \mathcal{V} , \mathbf{E} is produced. Hence, the diagonalization of $\tilde{H}(\mathbf{r}_n, \mathbf{x})$, carried out along such a configurational sampling, will produce a trajectory of perturbed Hamiltonian eigenvalues (ε_i) and eigenvectors (\mathbf{c}_i) of the QC and, therefore, of whatever perturbed electronic property. Hence, calculating the perturbed electronic excitation energies and corresponding perturbed transition dipoles ($\boldsymbol{\mu}_{i,j}$), we may obtain the electronic spectrum (considering a unitary radiation energy density per unit frequency and neglecting the vibrational contribution) via the molecular absorption coefficient,

$$\epsilon_{i,j}(\nu) = \frac{B_{i,j}(\nu) \rho(\nu) h \nu}{c}, \quad (2)$$

TABLE I. Absorption maximum shift as a function of temperature.

Temperature (°C)	Density (g/cm ³)	ΔE_{\max} (eV) this work	ΔE_{\max} (eV) expt. ^a
25	1.000	0.81 (0.15)	0.90
150	0.930	0.50 (0.10)	0.67
275	0.785	0.40 (0.10)	0.44
400	0.358	0.31 (0.15)	0.29

^aReference 6.

$$B_{i,j} = \frac{|\boldsymbol{\mu}_{i,j}|^2}{6 \epsilon_0 \hbar^2}, \quad (3)$$

where $B_{i,j}$ is the Einstein coefficient (ϵ_0 is here the vacuum dielectric constant), $\rho(\nu)$ is the probability density in frequency (ν) space, i.e., the probability to find the chromophore within a given excitation frequency-energy interval divided by the corresponding ν interval, h is the Planck's constant ($\hbar = h/2\pi$) and c is the light speed. Note that the perturbed transition dipole squared lengths are obtained averaging over the distribution of the corresponding ν interval, provided by the sampling of the MD simulation. We used the QM calculations for the unperturbed water molecule [complete active space self-consistent field, CASSCF, calculations with 6-311+g(d,p) basis set] as described in details in our previous paper⁷ performing, identically to the simulations used in that paper, a new set of MD simulations of the simple point charge (SPC) water model¹³ at the same temperature-density conditions of the experimental work (paper I).

In Table I, we compare, at four temperature-density conditions, the absorption maximum shift with respect to the (ideal) gas phase excitation, provided by our theoretical/computational procedure with the corresponding values presented in paper I (note that, for our calculations, the error upper limit, resolution, is given by the numbers between parentheses while no information on the experimental noise is present in paper I). Our results match rather well, within the noise, the experimental data reproducing the redshift due to the temperature increase. Moreover, the calculated 0.5 eV variation of the absorption maximum between 25 and 400 °C temperatures quantitatively reproduces, within the noise, the experimental one (about 0.6 eV). Interestingly, the small deviation between theoretical (7.69 eV) and experimental (7.40 eV) (ideal) gas phase excitation energy seems the only significant variation between experimental and theoretical/computational data.

In Fig. 1 we show the (vertical) absorption spectra, as obtained by our calculations, at 25 and 400 °C corresponding to the temperature extremes of the investigated range. It is worthy to note that both theoretical/computational spectra presented, although narrower than the corresponding experimental spectra as a consequence of neglecting in our calculations the coupling with vibrational excitations, reproduce all the main features described in paper I: (1) the redshift of the maxima, presented in Table I, corresponds to a redshift of the whole absorption curve which, in particular, presents a large redshift in the low energy left tail (low energy absorption band edge, see the inset of the figure); (2) both spectra are reasonably well described by Gaussian curves with the

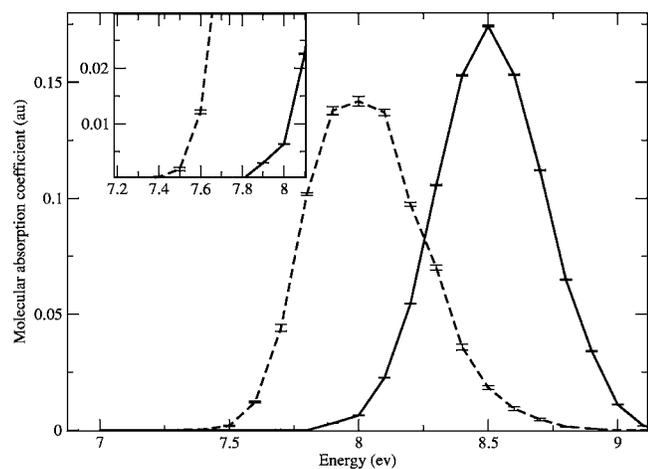


FIG. 1. The absorption spectra at 25 °C (solid line) and 400 °C (dashed line) temperatures as obtained by our calculations. The error bars correspond to one standard deviation.

400 °C one broadened and slightly asymmetric as a consequence of the increased water molecules fluctuations resulting in augmented perturbing field fluctuations. All the spectra we obtained for the other in between temperatures present a similar in between behavior (data not shown). Such results clearly indicate that the use of a single quantumlike molecule for vertical electronic excitations embedded in an electric field pattern, provided by classical molecular dynamics simulations, captures the essential physics characterizing liquid water electronic spectra. Therefore, the experimentally observed redshift due to temperature increase may be ascribed to the change of water-water interaction behavior affecting the electronic excitation rather than to vibrational or light scattering effects, confirming the conclusions of paper I.

Using the same theoretical/computational procedure, it is also possible to investigate the effect of density variation on the absorption spectrum. In Table II we report our calculated absorption maximum shift in the experimental range of 0.101–0.358 g/cm³ at 400 °C (see paper I). From this table the redshift with decreasing density is clear due to the expected emerging gaslike behavior of the water molecules and in agreement with previous simulation data by Bursulaya *et al.*¹ based on a different computational approach. Interestingly, the absorption spectra we obtained at the density extremes, Fig. 2, show that the density change provides a rather different effect that temperature change: (1) the redshift of the maxima does not really correspond to a shift of the entire curve and, in particular, the low energy tail (see inset of the figure) is virtually the same at both densities;

TABLE II. Absorption maximum shift as a function of density.

Temperature (°C)	Density (g/cm ³)	ΔE_{\max} (eV) this work
400	0.101	0.06 (0.10)
400	0.167	0.16 (0.10)
400	0.219	0.21 (0.15)
400	0.259	0.21 (0.15)
400	0.310	0.26 (0.10)
400	0.358	0.31 (0.10)

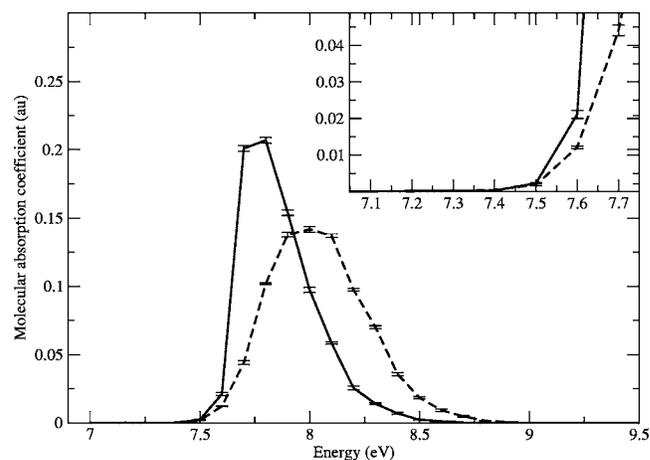


FIG. 2. The absorption spectra at 400 °C for 0.101 g/cm³ (solid line) and 0.358 g/cm³ (dashed line) densities as obtained by our calculations. The error bars correspond to one standard deviation.

absorption curve at 0.358 g/cm³ is reasonably well described by a Gaussian, at the lowest density (0.101 g/cm³), an asymmetric shape is present, with the latter curve significantly narrower as a consequence of the decreased water-water interactions resulting in decreased perturbing field fluctuations. All the spectra we obtained for the other in between densities present a similar in between behavior (data not shown).

In paper I no evaluation of the absorption maxima variation due to the density change at 400 °C is given and only a slight blueshift of the low energy absorption band edge (low energy tail) is described for decreasing densities. The authors of that paper argued that such a result is probably due to the line narrowing covering, in the low energy tail, the expected redshift. Our results, showing that for decreasing densities the clear absorption maximum redshift is associated to a fixed low energy absorption band edge (low energy tail) as a result of the spectrum narrowing and increasing curve asymmetry, seem to confirm such an idea pointing out the major relevance of the electrostatic interactions in determining the absorption line shape. In fact, in our model, the QM electronic description is limited to a single molecule, hence neglecting excitonic effects, e.g., wavefunction overlap. The remarkable reproduction of the experimental data by our calculations also reveals the reliability of the SPC water model in providing the perturbing electric field pattern determining the absorption line shape. However, given the importance of accurate liquid state absorption modeling, we are currently collecting detailed information on the electronic wavefunction of perturbed quantum centers, as revealed by our calculations, which will be outlined in a forthcoming paper.

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