

Electron momentum spectroscopy of the valence orbitals of the water molecule in gas and liquid phase: A comparative study

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Abstract

We present a comparative study of the electron momentum spectroscopy (EMS) of the valence orbitals of the water molecule in gas and liquid phases. The molecular properties of the water molecule in liquid water have been computed within the framework of the polarizable continuum model. Surprisingly, we find that, although most of the molecular properties of the water molecule do show significant differences between gas and liquid phases, the shape of the EMS profiles are almost insensitive.

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1. Introduction

For gas phase molecules, a large body of data exists from EMS studies. EMS uses the electron–electron coincidence technique to probe the electronic structure of the molecular gas target [1] and has long been shown to provide stringent tests for quantum chemistry calculations performed at different level of sophistication such as for instance, Hartree–Fock (HF), configuration interaction (CI), Kohn–Sham (KS) formulation of the density functional theory (DFT). Most of the experimental works reported in the literature have been carried out in gas phase.

In particular, gas water molecule has been intensively studied since the pioneer works of Cambi et al. [2] and Bawagan et al. [3]. This molecule which is essential for life and many living organisms constitutes a very interesting

target. Indeed, as liquid water constitutes 80% of biological material, there is considerable interest in cross sections for electron-impact ionization of water for use in charged particle track structure analysis. The latter was therefore commonly used in radiation damage models in biological samples [4]. However, in most computational studies devoted to this issue, for the sake of simplification, water molecules in living cells which are normally present in the liquid state are replaced by gas water molecules. So far, this assumption has not been validated. Moreover, it is not based on physical grounds since most of the molecular properties of water in liquid and gas phases (e.g., electric dipole moment, ionization potential...) exhibit significant differences between them (see Section 2.1).

In this work, we want to address the following question: is EMS a suitable method to investigate the electronic properties of a water molecule in the liquid phase? As far as we know, no work on this issue has yet been published.

The letter is organized as follows. In the next section a summary of the theoretical methods is given. In Section 3

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the results are presented and discussed. Finally, the letter is ended with concluding remarks. Atomic units (a.u.) are used unless otherwise specified.

2. Theoretical methods

2.1. Quantum chemistry calculations

All the computations have been carried out using the Gaussian 03 program [5]. The wave function has been computed at the Hartree–Fock level of theory using the augmented, correlation-consistent, polarized-valence quadruple-zeta basis set (aug-cc-pvQZ) of Dunning and co-workers [6]. This basis set consists of Gaussian-type orbitals with contraction (13s 7p 4d 3f 2g)/[6s 5p 4d 3f 2g]. For convenience, we use Cartesian d, f and g functions. The total number of atomic orbitals for water is 215 with 241 primitive Gaussians. The water geometry in gas phase is experimentally known but measured values in the liquid state are incomplete and not very accurate. For this reason, we have carried out geometry optimization calculations in the liquid phase and, for consistency, also in gas phase. Geometry optimization has been done including electronic correlation energy at the second-order Møller–Plesset perturbation theory (MP2) [7]. This theoretical scheme is expected to provide very accurate results. Comparison with available experimental data confirms this point as we discuss below.

For the computations in the liquid phase we use the polarizable continuum model (PCM) developed by Tomasi and co-workers [8,9]. It is based on the representation of the liquid by a polarizable dielectric continuum having the static dielectric constant of water ($\epsilon = 78.39$). A cavity is created in this continuum and a water molecule is placed in it. The molecule is described quantum mechanically and its Hamiltonian includes the electrostatic interactions with the surrounding dielectric medium. Since the continuum is polarized by the molecular charges, it creates a reaction potential inside the cavity, which in turn polarizes the molecule. The wave function must therefore be obtained by an iterative computation using the so-called self-consistent reaction field approach. PCM and related continuum methods are very efficient to predict molecular properties in the liquid state and lead to computations that are not much costly than equivalent calculations for an isolated molecule. A critical evaluation of these methods can be found in several reviews [8–11].

Let us make a few comments on the quality of our computational level. In Table 1, we have summarized the results obtained for some molecular properties and compared them with available experimental data. As shown, the agreement between theory and experiment is very good. The OH bond is elongated by the effect of the liquid. The length variation is correctly predicted by the calculation, as well as the variations of the dipole moment and ionization potential. Note that accurate prediction of the gas-phase dipole moment of water requires taken into account

Table 1

Computed and experimental geometry, dipole moment and ionization potential for the water molecule in gas and liquid phase. Computed dipole moments are given using Hartree–Fock densities (in parenthesis) or the generalized MP2 densities

	d_{OH} (Å)	α_{HOH} (deg.)	μ (D)	IP (eV)
<i>Gas</i>				
Calc	0.959	104.3	1.86 (1.98)	12.9
Exp.	0.957 [16]	104.5 [16]	1.85 [14]	12.6 [18]
<i>Liquid</i>				
Calc	0.969	103.6	2.32 (2.42)	9.1
Exp.	0.970 [17]		≈ 2.6 [15]	≈ 9.9 [18]

correlation effects, as shown before [12]. Note also that the computed dipole moment in the liquid phase is slightly smaller than the estimated experimental quantity. This can be explained in part by the approximations made in the dielectric continuum model since more elaborated approaches usually predict slightly higher polarization effects. However, there is not unanimity on this point; further discussion can be found in Ref. [13].

2.2. Electron momentum spectroscopy

Electron momentum spectroscopy is based on the so-called binary (e,2e) reaction which is a high energy electron-impact ionization process. In a typical EMS experiment, a symmetric non-coplanar geometry is employed. A high energy incident electron ($E_0 = 1200$ eV) knocks out an electron from the target molecule and the two outgoing electrons are subsequently detected in coincidence at the same high energies ($E_1 = E_2 \approx 600$ eV) and the same polar angles ($\theta_1 = \theta_2 = 45^\circ$). Under such kinematical conditions, this scattering process can be viewed as a classical billiard ball-like collision between two free electrons.

In the plane wave impulse approximation (PWIA) the triple differential cross section (TDCS) for randomly oriented molecules is proportional to the spherically averaged momentum distribution of the Dyson orbital

$$\sigma = C \int |\langle \vec{p} \Psi_{N-1} | \Psi_N \rangle|^2 d\Omega, \quad (1)$$

where $|\vec{p}\rangle$ is a plane wave of momentum $\vec{p}$. Ψ_N and Ψ_{N-1} are, respectively, the many-electron wavefunction of the N electron initial state and the wavefunction of the $(N-1)$ electron final state describing the residual ion. The term C is a kinematic factor which is essentially constant. In most cases, the above expression may be simplified by using the so-called target Hartree–Fock approximation (THFA) in which the Dyson orbitals are replaced by the Hartree–Fock wavefunction of the initial state leading to

$$\sigma = C \int |\varphi_i(\vec{p})|^2 d\Omega, \quad (2)$$

where $\varphi_i(\vec{p})$ is the i th one electron momentum-space orbital. The suitability of Eq. (2) depends on the effect played

by relaxation effects on the final state wave function under the electron-impact ionization process. This effect can usually be neglected in gas phase calculations of EMS cross sections (the so-called frozen orbital approximation [19]). In the case of a solvated molecule, the THFA requires further comments since solvent relaxation might also play a role. For a fast process such as ionization, only the non-inertial component of the solvent polarization has to be considered. Its contribution may be represented by a final state interacting with an additional constant potential (the Born term) associated to the high-frequency dielectric constant of the solvent. This constant potential is therefore expected to shift the energy levels but not to polarize the molecular orbitals and, accordingly, its effect will be neglected here too.

Let us stress that correlation effects can be incorporated in the model either by using the configuration interaction description to compute the Dyson orbitals or by using the so-called target Kohn–Sham approximation (TKSA) in which the Kohn–Sham orbitals of the density functional theory are used in (2) instead of the Hartree–Fock ones [19].

Position-space wavefunctions are computed by using the Gaussian 03 program as already described in Section 2.1 and are subsequently converted to a single-center expansion

by using partial-wave expansion techniques [20,21]. The TDCSs are computed using a method recently developed for calculating the multiply differential cross sections for electron-impact ionization of molecules [22]. We neglect effects coming from molecular vibrations. This approximation is a common one in gas-phase EMS studies [23]. In the liquid phase, the intermolecular hydrogen-bond network is characterized by low frequencies of vibration (especially when compared to intramolecular modes) and therefore its effect will be neglected too.

3. Results

The EMS momentum profiles for the four valence orbitals of the water molecule in gas phase are depicted in Fig. 1. Since the experimental measurements are not absolute, they have been systematically adjusted in order to find the best agreement with the theoretical predictions. Furthermore, meaningful comparisons of EMS experimental data with theory can only be achieved by taking into account the effects of the instrumental momentum resolution caused by the finite acceptance angles of the spectrometer. Therefore, all the theoretical profiles have been folded with the instrumental momentum resolution employing the method described in full detail in [24,25]. Let us note that

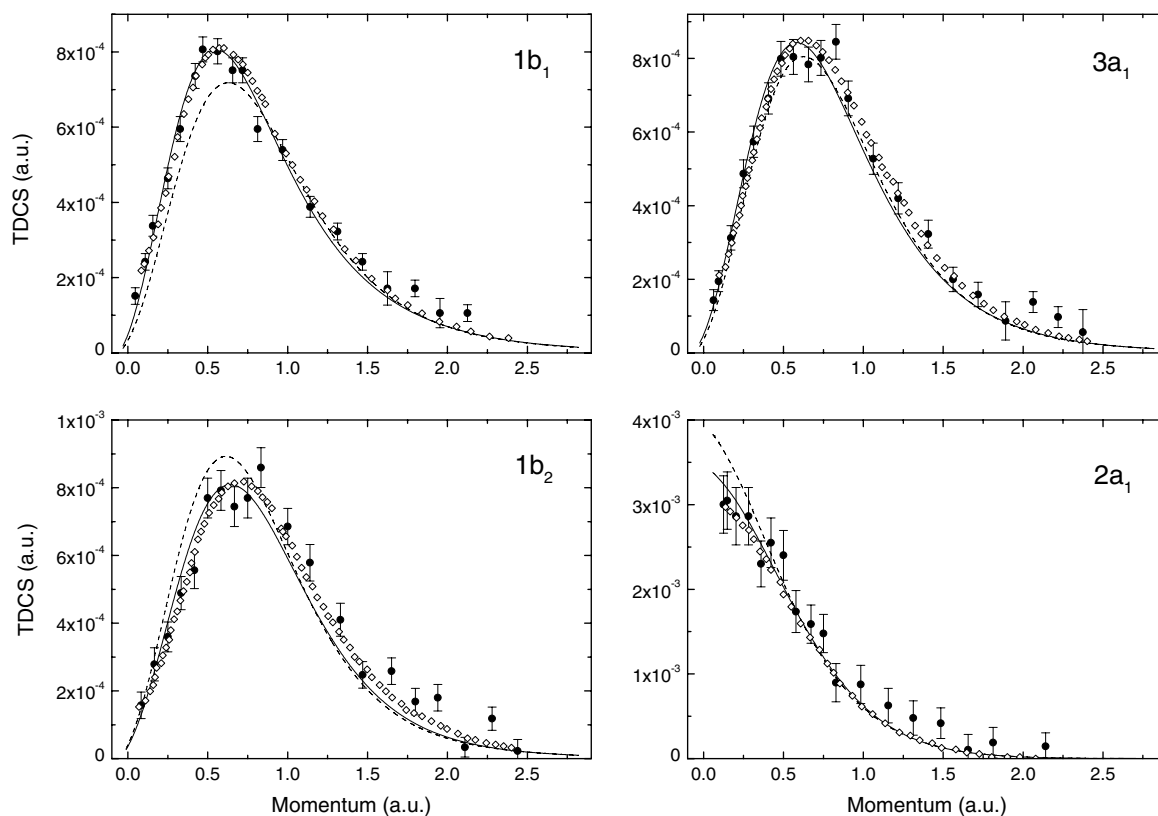


Fig. 1. EMS momentum profiles for the four valence orbitals of gas-phase water. Full dots with error bars are the experimental data taken from [3]. Full lines: present calculation using high level Hartree–Fock wavefunctions; dashed lines: SCF-LCAO-MO wavefunctions of Moccia [26]; open diamonds: CI Dyson wavefunctions taken from [19].

the main consequence of the folding is a shift in the momentum scale.

Good agreements are found between the experimental data of [3] and our theoretical predictions employing high level Hartree–Fock wavefunctions. It demonstrates that, in gas phase, the level of sophistication of our theoretical molecular modelling approach is sufficient. Furthermore, in order to assess the role played by the quality of the wavefunction in the comparison between theory and experiment we also show the EMS momentum profiles computed using less and more accurate wavefunctions. The former are the SCF-LCAO-MO wavefunctions obtained long time ago by Moccia [26] and the latter are CI Dyson orbitals given in [3].

An inspection of the figure clearly indicates that our results are very close to those obtained in [3] whereas calculations using a lower level [26] exhibit significant errors, in particular for the $1b_1$ and $1b_2$ valence orbitals.

A comparison of the EMS momentum profiles of water in gas and liquid phase is shown in Fig. 2. For the four valence orbitals very small differences are observed. The largest one is found for the HOMO orbital $1b_1$. In this case, the liquid phase cross section is almost everywhere larger than the gas phase cross section (except for $p > 1.35$ a.u. where the difference $\Delta \equiv \sigma_{\text{Liq}} - \sigma_{\text{Gas}}$ is slightly below zero). The fact that Δ has a positive value may be explained as

follows: in the liquid phase the outer valence orbitals are more diffuse (due to polarization effects originate from the surrounding water molecules) leading to a larger cross section. The difference, which is not exceeding 5%, is maximal at the maximum of the cross section at $p \approx 0.62$ a.u.. For the orbitals $3a_1$ and $2a_1$ the situation is rather similar except that the difference is now maximal in the region of small momenta. The $1b_2$ orbital exhibits a different behavior compared with the other ones investigated. Indeed, Δ has a negative value and is 10 times smaller. This last result must be put in relation with the conclusions of a recent experimental study on the photoemission from liquid water using synchrotron radiation [18]. In this work, it is found that the photoemission signal from $1b_2$ in liquid water is strongly reduced as compared to that from the gas phase indicating a specific sensitivity of this orbital to its surrounding. Finally, it worth noticing that today, no EMS experiment would be able to discern between the two phases.

In summary, a comparative study of the EMS of the valence orbitals of the water molecule in gas and liquid phases has been undertaken. For the gas phase, very good agreements are found between the experimental data of [3] and our theoretical predictions. In the liquid phase, though most of the molecular properties of the water molecule are substantially modified with respect to the isolated case, it is

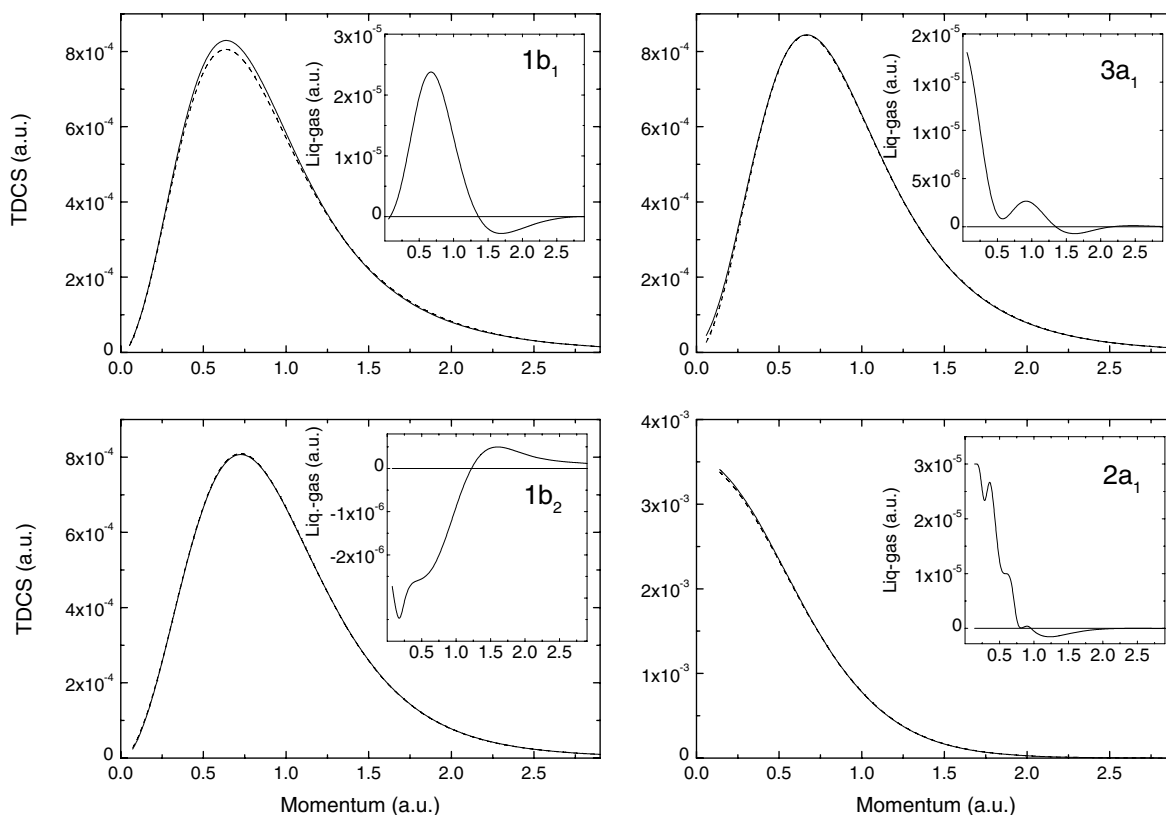


Fig. 2. EMS momentum profiles for the four H_2O valence orbitals in the liquid and gas phase. Liquid: full line; gas: dotted line. The difference between liquid phase and gas phase cross section is shown in the inset.

found that the shape of the EMS profiles are almost insensitive. This result suggests that electron momentum spectroscopy seems not to be a suitable technique for investigating the electronic structure modifications associated to solvation processes.

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