Theoretical calculations of the structure and UV–vis absorption spectra of hydrated C_{60} fullerene

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Abstract

A combined Monte Carlo simulation with semiempirical quantum mechanics calculations has been performed to investigate the structure of hydrated fullerene (C_{60}HyFn) and the influence of hydration on its UV–vis spectra. The statistical information of the C_{60} fullerene aqueous solution (C_{60}FAS) is obtained from NPT ensemble including one C_{60} fullerene immerses in 898 water molecules. To obtain an efficient ensemble average, the auto-correlation function of the energy has been calculated. The analyzed center-of-mass pair-wise radial distribution function indicates that, on average, there are 65 and 151 water molecules around the first and second hydration shells, respectively, of a single C_{60} molecule. To calculate the average UV–vis transition energies of C_{60}HyFn, only the statistically uncorrelated configurations are used in the quantum mechanical calculations (INDO/CIS). These involve hundreds of supramolecular structures containing one C_{60} fullerene surrounded by the first hydration shell. The calculated average transitions at 268 and 350 nm are in very good agreement with the experimental prediction.
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1. Introduction

Preparing aqueous solutions of fullerenes has been a great challenge for biochemical, biophysical, and biological applications of these molecules [1–4] since the discovery of C_{60} 20 years ago [5]. Due to the hydrophobic interactions of fullerenes in aqueous environments [6], usually functionalized species are employed to obtain water-soluble forms [1,3]. Also, pristine fullerenes have been solubilized in aqueous acids by ultrasonic method [7]. Recently, the possibility of obtaining C_{60} fullerene aqueous solutions (C_{60}FAS) without the need of stabilizers or chemical modification has attracted attention in biomedical testing [4,8]. It has been shown [8] that, depending on concentration, C_{60}FAS are formed by spherical C_{60} aggregates containing since one C_{60} molecule up to larger clusters solvated by highly stable hydration shells. In particular, special attention has been directed at single hydrated C_{60} fullerene, namely, C_{60}HyFn or $C_{60}@\{H_2O\}_n$, in investigating the suspicious toxic effects of this hydrated system on both living organisms and environment [9].

The main properties and structure of fullerene solutions have successfully been investigated by using different techniques: electron microscopy [4], spectroscopy [2,8,10,11], and scattering [12]. However, the existence of clusters consisting entirely of single hydrated C_{60} molecules, i.e., $C_{60}@\{H_2O\}_n$, has been suggested to support some experimental data [4,8,11]. Also, the solubility of a single C_{60} fullerene is not completely understood by means of experimental studies. In this sense, many theoretical approaches have been proposed [2,6,8,13] to account for the water-soluble pure forms of fullerenes. One of the most important theoretical aspects is how to efficiently determine the number of water molecules in the hydration shells of the C_{60} molecule in aqueous solution [8,9,11,13]. An

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icosahedral water cluster[1] model, described by Chaplin [14], has been employed to explain the solubility of this fullerene via O–H$\cdots\pi$ hydrogen bonds [15]. In this geometrical model, 20 water molecules are first forming the hydrogen bonds with the π-orbital electron density of the 20 aromatic carbon hexagons of C_{60} [16]. Then, the next shell of the icosahedral is composed of 60 fully hydrogen bonded water molecules. Thus, a hypothetical cluster would be of the $C_{60}@\{H_2O\}_{80}$ type. On the other hand, Scharff et al. [8] have obtained, via semiempirical quantum-chemistry optimization, that $C_{60}@\{H_2O\}_{60}$ is the smallest energetically stable cluster of this hydrated fullerene.

It is known, however, that the solubility of apolar solutes depends on their physico-chemical properties and the thermodynamic conditions [17,18]. Furthermore, understanding the mechanism of solvent–solute interactions is important to complement the experiments made in solution. Here, we are interested in taking into account these aspects for $C_{60}FAS$. Hence, Monte Carlo (MC) simulation, combined with semiempirical quantum mechanics (QM) calculations [19–22], is performed aiming at obtaining reliable estimates of the structure and optical absorption spectra of $C_{60}HyFn$. The configurations of the aqueous solution are generated using MC simulation. Next, these are sampled on statistically relevant configurations for subsequent QM calculations. The auto-correlation function of the energy is calculated to ensure that statistically uncorrelated configurations are only used [21–25]. An advantage of this approach is that after performed the MC simulation the statistical information is available for efficiently running QM calculations [19,21–25]. The MC simulation is performed at atmospheric pressure and room temperature using the isobaric–isothermal (NPT) ensemble and the QM calculations are performed within the semiempirical INDO/CIS model [26–28], which includes dispersion interactions [20] between the two subsystems in the supramolecular hydrated cluster.

2. Computational details

Monte Carlo (MC) simulation has been performed at 298 K and atmospheric pressure for a solution of one C_{60} fullerene immerses in 898 water molecules. The C_{60} molecule was represented by an all-atom model fully optimized at B3LYP/6-311G* level [29–31]. The three-parameter SPC potential [32] was employed to describe the water–water interactions. For the interaction between C_{60} and water, an all-atom Lennard–Jones (LJ) potential was utilized. In this case, the 60-site pair-wise LJ potential of the carbon atoms in C_{60} ($\varepsilon_C = 0.076$ kcal mol^{-1}, $\sigma_C = 3.500$ Å) were based on OPLS-AA parameters development [33]. These have been combined with LJ SPC ones to generate the pair-potential parameters given by the rule $\varepsilon_{CO} =$

$(\varepsilon_C \varepsilon_O)^{1/2}$ and $\sigma_{CO} = (\sigma_C \sigma_O)^{1/2}$. Such an interaction model for C_{60}–water has efficiently been employed by Li et al. [6] in determining the solvent-induced repulsion between C_{60} fullerenes in aqueous solutions. The standard procedure for the Metropolis sampling technique [34] was carried out in the NPT ensemble using the simulation program DICE [35]. Beyond the cutoff radius of 15 Å, long-range water–water Coulomb interactions were evaluated by means of the reaction field method (using the dielectric constant of water equals to 78.5); while for the LJ potential the radial distribution function (RDF) was used. The simulation was carried out with periodic boundary condition in cubic cell using the minimum image method [34]. After thermalization of 1.4×10^7 MC steps, sampling was performed with an approximate running length of 9×10^7 MC steps in the NPT ensemble. The calculated average density was 1.017 g cm^{-3} corresponding to an average cubic cell of size 30.2 Å.

For the quantum mechanics (QM) calculations the statistics of $C_{60}FAS$ was optimized. A systematic procedure [19,21–25] to only select the relevant structures, without damaging the statistical averages, was utilized by calculating the auto-correlation function of the energy [21–25]. Such a methodology significantly reduces thousands of MC configurations of the aqueous solution to hundreds of configurations. Fig. 1 shows the calculated auto-correlation function of $C_{60}FAS$. As can be evaluated the correlation step number is approximately 300. This means that to obtain configurations less than 14% correlated [21,22], ca. 160 configurations should be sampled for the QM supramolecular calculations. These were carried out at the semiempirical INDO/CIS level [26] for each supramolecular system ($C_{60}HyFn$). The singly excited configuration interaction calculations from a Hartree–Fock ground state reference (CIS), performed to obtain the excitation energies of clusters containing solute and solvent, properly take into account the dispersion interaction [20] between the two
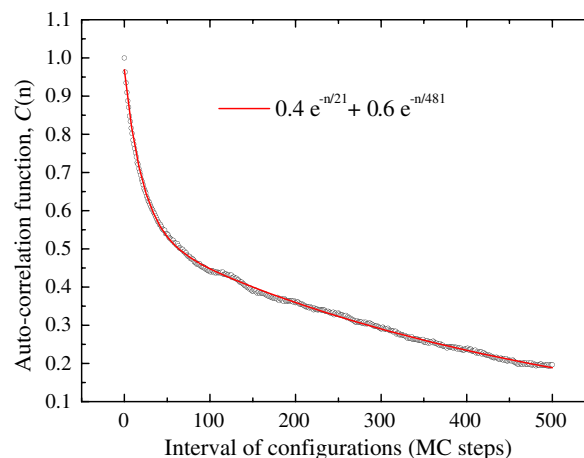

Fig. 1. Auto-correlation function of the energy for the MC simulation of $C_{60}FAS$ in NPT ensemble. For markovian processes the function $C(n)$ presents an exponentially decaying (the exponential best fit is shown) [19,21].

subsystems. It is also important to notice that CIS method satisfies the size-extensivity requirement in the supramolecular calculations [28]. This feature is rather important for calculating the spectroscopic properties of chromophores in solvents. Furthermore, it is well known that INDO/CIS often accurately produce the type of low lying excited states of molecular systems, which are dominated by single excitations [20,28]. Thus, this sequential MC/QM procedure becomes very efficient and yields statistically converged results in such a way that the average transition energies can be written as:

$$\langle \Delta E \rangle = \frac{1}{L} \sum_{i=1}^{L} \Delta E_i,$$

for which a chain of size L is obtained previously ($L = 160$) from the auto-correlation function [21,22].

3. Results and discussion

3.1. Structures

The hydration shells of C_{60} in aqueous solution were obtained using the pair-wise RDF. We show in Fig. 2 the calculated center-of-mass RDF, $G_{cm\text{-}cm}(r)$, between C_{60} and water. Comparing our profile with the RDF profile obtained via molecular dynamics simulations of C_{60} in water by Li et al. [6] we observe a good likeness. As indicated in Fig. 2, the first peak, corresponding to the first hydration shell, starts nearly at 6.0 Å and ends at the minimum value of 8.5 Å. This is formed by 65 water molecules, on average, as given by spherical integration of $G_{cm\text{-}cm}(r)$. The MC simulation gives hydrated aggregates of the $C_{60}@\{H_2O\}_{65}$ type, for which the thermodynamic aspects of the aqueous solution were properly considered. From the auto-correlation function ca. 160 nearly uncorrelated structures that represent $C_{60}HyFn$ have been obtained.

These structures show that preferential interactions between water and fullerene, such as O–H···π hydrogen bonds, are not expected to occur frequently in solution. Indeed, according to Andrievsky et al. [11], the stabilization of supramolecular $C_{60}@\{H_2O\}_n$ clusters should be explained by a weak C_{60}–water interaction, for which we have calculated classically an average value of -0.63 ± 0.27 kcal mol^{-1} with $n = 65$. Furthermore, these clusters present sphere-like hydrated shells around the fullerene, ordered due to water–water hydrogen bonding formation. Fig. 3 shows a representation of the first hydration shell for one of these structures. Considering all the $C_{60}@\{H_2O\}_{65}$ uncorrelated clusters, we have estimated an average number of 1.3 hydrogen bonds per water molecule, using a OH···O distance criterion of 2.4 Å [6]. Also, the calculated minimum distance between the carbon atoms in C_{60} and the atoms of water in this supramolecular cluster was 3.5 ± 0.6 Å considering all configurations.

Regarding the existence of larger supramolecular clusters, we have obtained from the center-of-mass RDF (Fig. 2) a second hydration shell starting approximately at 8.5 Å and finishing at 12 Å. In this case, we have found by spherical integration of $G_{cm\text{-}cm}(r)$ a total number of 216 water molecules, from the solute center-of-mass up to the limit of the second shell. Thus, ca. 151 water molecules are present in the second hydration shell. Now, the average number of water–water hydrogen bonds in the sphere-like hydration shell increases up to 1.5 per water molecules. This result indicates that the second shell is less ordered around C_{60} than the first one. Of course, the estimate of hydrogen bonding formation will depend on the type of interaction potential used in the simulation. For instance,
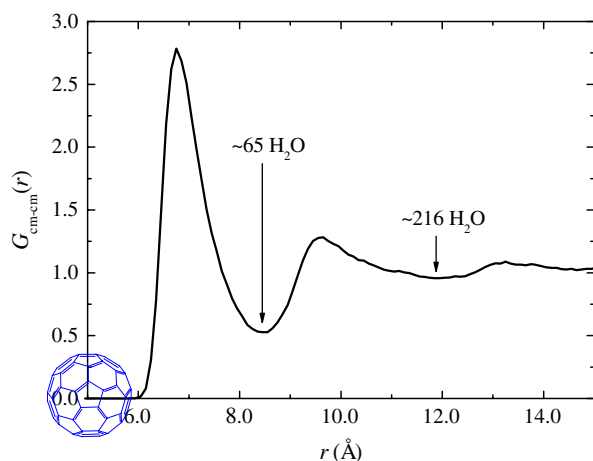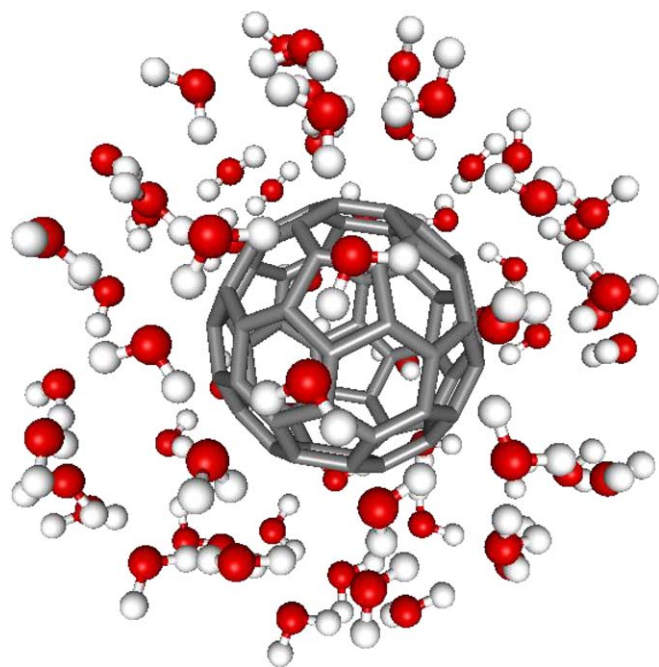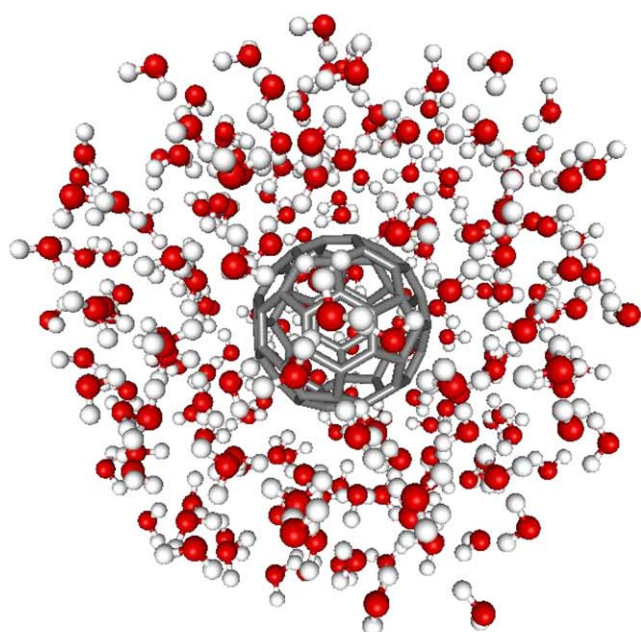

Fig. 2. Pair-wise RDF between the centers of mass of C_{60} and water. First peak shows the first hydration shell containing ca. 65 water molecules and second peak shows the second hydration shell containing ca. 151 water molecules. Integration of $G_{cm\text{-}cm}(r)$ gives a total of 216 water molecules from the solute center-of-mass up to the limit of the second shell.
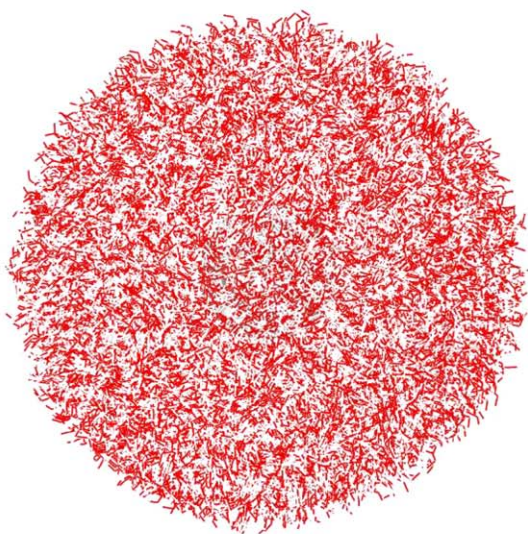

Fig. 3. Representation of one configuration in the first hydration shell of C_{60}. The calculated number of water molecules from RDF is ca. 65.

Li et al. [6] have found ~1.7 for this shell using the TIP4P model [36] to represent the water–water interactions. One of the MC supramolecular structures including the second hydration shell is represented in Fig. 4. According to our simulation, an intermediate shell formed by 80 water molecules around C_{60}, as modeled by Chaplin [14], is not well-defined. The calculated center-of-mass average distance between C_{60} and the second hydration shell limit was 9.5 ± 1.7 Å. As can be noticed, this leads to a diameter nearly within the predicted size [11] for a single $C_{60}HyFn$ in the range of 1.6–1.7 nm. Therefore, our result for aggre-

gates of the $C_{60}@\{H_2O\}_{216}$ type seems to be in accordance with the supposed existence of highly hydrated single fullerene aggregates, as obtained from electron micrograph [4]. Actually, these $C_{60}@\{H_2O\}_n$ clusters are expected to be formed by a large layer of water molecules [9] in comparison with the crystalline hydrates obtained in colloidal solutions of C_{60} fullerene.

3.2. UV–vis spectra

As discussed earlier, for calculating the optical absorption spectra of $C_{60}HyFn$, we have considered ca. 160 uncorrelated configurations of $C_{60}FAS$. This means that to obtain the statistical average values of the transition energies, 160 INDO/CIS supramolecular calculations were performed for the fullerene together with the first hydration shell. Using this procedure, the solvatochromic shift is evaluated by subtracting the calculated transition energy of the isolated C_{60} molecule from the average transition energy of the supramolecular cluster. This is a valid approach because CIS is known to be a size-extensive method [26]. Additionally, the semiempirical INDO/CIS approximation has been [21,22,24] a very successful method for spectroscopic shift in both polar and non polar solutes and solvents. Considering only one isolated C_{60}, two dipole-allowed transitions have been calculated at 266 and 331 nm. These values are in very good agreement with the UV–vis absorption spectra [8] of C_{60} fullerene in *n*-hexane (270 and 329 nm) [11] and toluene (269 and 335 nm) [8,37]. For the QM supramolecular calculations, we have used 60 water molecules in the hydration shell of each uncorrelated MC configuration. As shown in Fig. 5, this number of water molecules yields completely converged results for the spectra. Here, we should emphasize that our calculated absorption spectra of $C_{60}HyFn$ are consistent to explain the UV–vis spectra of $C_{60}FAS$ in a wide range of concentration. As noticed by Andrievsky et al. [11], the optical absorbance of C_{60}–water system has a linear behavior with the concentration.

Fig. 4. Representation of the first and second hydration shell of C_{60}: (a) one possible configuration containing a total of 216 water molecules and (b) superposition of all 160 configurations of $C_{60}@\{H_2O\}_{216}$ sampled from the simulation.
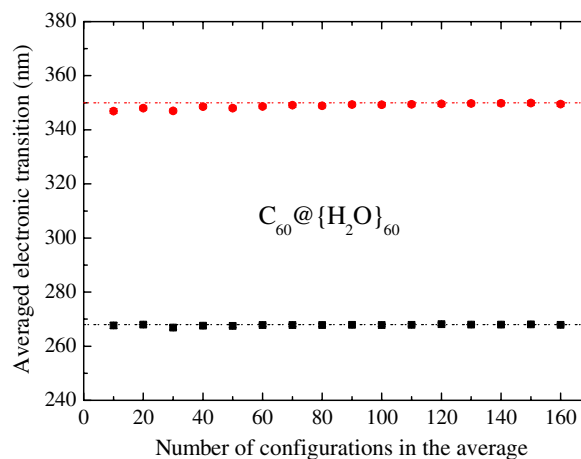

Fig. 5. Convergence of the calculated transition energies in the absorption spectra of C_{60} surrounded by 60 water molecules.

It is known that the intermolecular interaction between C_{60} and water is dominated by dispersion interactions, which are responsible for long-wavelength shifts in the optical spectra of fullerene in water, compared to the isolated form. Thus, from the theoretical point of view, it is very important including dispersion in the calculations. Indeed, this is satisfied in the INDO/CIS model for supramolecular systems, as demonstrated by Canuto et al. [20]. In this sense, our calculations for the $C_{60}@\{H_2O\}_{60}$ systems, as obtained from MC simulation, give average values slightly red-shifted of 268 ± 5 and 350 ± 9 nm, in comparison to the isolated C_{60}. Again, the theoretical results are confirmed by previous experimental values [8,11] of 265 and 345 nm. Despite the weak interactions between C_{60} and water, the spectra of isolated and hydrated fullerene differ slightly. Actually, the larger calculated red shift in $C_{60}HyFn$ is only ~19 nm (and 10 nm experimentally) [8]. In Fig. 5 it is shown the average electronic transitions of the hydrated fullerene over chains of different sizes. As can be seen, both calculated average values of transition energies are statistically converged results along the chains considered in the averages. This is not surprising, however, once these two transition energies of C_{60} are weakly changed by the surrounding water molecules. Also, if the sampling is efficient the average must converge rapid and systematically; i.e., the mean values are independent [19] of the particular choice of the set of MC configurations used in calculating the excitation energies.

At this point it is interesting to notice that we also have calculated transition energies into longer wavelengths, located at the visible region of the optical spectrum of $C_{60}HyFn$, as shown in Fig. 6. These spectral bands are not present in the isolated C_{60}, but only in the hydrated cluster. Experimentally, the absorptions of $C_{60}FAS$ in the visible region are also known [8,11] and can be connected with formation of weak donor–acceptor complexes of C_{60}–water [9,11]. Although Scharff et al. [8] have attributed these bands to the presence of possible solid aggregates of C_{60}, our QM calculations on the MC structures of
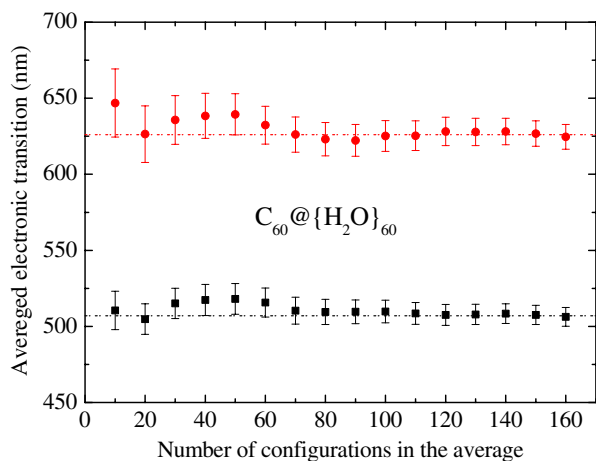
$C_{60}@\{H_2O\}_{60}$ predict weak absorptions in the visible region. Our calculated average values for these transitions were 507 ± 63 and 626 ± 91 nm, which sound with the experimental [8] ones located at 450 and 620 nm. In fact, analyzing the averaged transitions (Fig. 6) we observe a larger standard deviation of the mean values, as compared to the transitions in Fig. 5. This clearly shows that these transitions occurring in the hydrates depend strongly on the ordering of water molecules in each configuration. Also, the convergence is only attained increasing the size of the chain for L tending to 160 configurations.

4. Summary and conclusions

In this work important aspects of a C_{60} fullerene aqueous solution ($C_{60}FAS$) were investigated from MC simulation at room temperature and atmospheric pressure. The quantity of water molecules in the sphere-like layers around C_{60} and the shift in the UV–vis spectra due to hydration were determined. To perform the calculations, an efficient sequential MC/QM methodology [19,21–24] has been employed. The MC simulation was performed using standard procedure and the QM calculations were carried out on statistically uncorrelated structures with the INDO/CIS approximate method. From the spherical integration of RDF we have found the number of water molecules in the solvation shells of C_{60}. In these calculations, sphere-like clusters containing ca. 65 (corresponding to the first hydration shell) and 216 (up to the second hydration shell) water molecules around the fullerene surface were obtained. Our statistical analysis confirms the supposed existence in real solutions [4,8,9,11] of highly symmetric hydrated clusters containing supramolecular complexes of the $C_{60}@\{H_2O\}_n$ type. These are stabilized by dispersion interactions between C_{60} and water, and also by re-ordering of hydrogen bonded water around C_{60}. For the first hydration shell, the calculated classical interaction energy was -0.63 ± 0.27 kcal mol^{-1} and 1.3 hydrogen bonds per water molecules was estimated, using the SPC potential model. Considering the second solvation shell, whereas the C_{60}–water interactions are diminished the number of hydrogen-bonded water molecules in the layer is increased.

We have also successfully calculated the spectral properties of $C_{60}HyFn$ considering only the first hydration shell around C_{60}. In the total, 160 uncorrelated MC configurations containing $C_{60}@\{H_2O\}_{60}$ clusters were generated. Thus, the QM calculations were performed for all supramolecular aggregates. Each calculation starts with an appropriate anti-symmetric wave-function of 720 valence electrons. The self-consistent field was performed using the spectroscopic INDO level [26–28], with transition energies calculated via singly excited configuration interaction (CIS). In this way, we have obtained converged averages for the transition energies of the hydrated state of C_{60} at 268 ± 5 and 350 ± 9 nm. These are in very good agreement with previous experiments [8,11] and reinforce that the

Fig. 6. Convergence of the calculated transition energies in the visible region of the $C_{60}@\{H_2O\}_{60}$ aggregate absorption spectra.

water layers only cause a mild perturbation in the absorption spectra of fullerene. Moreover, the results show that including only the first hydration shell around C_{60} is enough to analyze the spectral properties of this hydrated fullerene. Also, in connection with the experiments, the calculated UV–vis absorption spectra of $C_{60}HyFn$ suggest the existence of single hydrated fullerene in aqueous solutions. In conclusion, we expect with this study contributing to elucidate both structure and electronic properties of hydrated fullerenes.

Acknowledgements

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