REGULAR ARTICLE

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Analysis of main factors determining the prediction of stabilization energies of halide-water clusters

Abstract This work studies the main factors determining the stabilization energy [$E_{stab}(n)$] of a series of halide clusters, $[X(H_2O)_n]^-$ (X≡F, Br and I). This property measures the difference between the ionization process of the hydrated and isolated halide. In a previous paper [J. Chem. Phys., 121, 7269 (2004)], the $E_{stab}(n)$ was studied for a large number of clusters (up to $n = 60$) by using classical computer simulations based on first-principles polarizable potentials to describe the halide–water interactions. In this work we analyze what features of the MCDHO-type model are necessary for a proper reproduction of the experimental E_{stab}. The role of the charge redistribution (polarizability) of the water molecule and halide anion, the geometrical relaxation of water molecule (flexibility), as well as the replacement of water clusters by a dielectric continuum of different dielectric permittivities are presented and discussed. The parallel behavior of the E_{stab} magnitude with the dielectric permittivity of the continuum and with the number of water molecules forming the cluster supports that the electrostatic interactions are the main responsible for the changes induced on the electron structures determining the energetics of the photodetachement process. The photodetachment process does not only occur without nuclear relaxation but also with a small electron redistribution of water molecules.

1 Introduction

Experimental and theoretical studies on the structure and energetics of clusters are of great importance to help in understanding the microsolvation phenomena of ionic solutions. Photoelectron spectroscopy (PES) is well established in studying the electronic structure of negatively charged clusters [1–9] because it provides a direct information on the vertical ionization potentials and the stabilization energies [$E_{stab}(n)$]

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of the anions. $E_{stab}(n)$ is defined as the energy gap between the vertical photodetachment energy of the ion in the cluster (BE_v) and the electron affinity of the bare neutral atom (EA),

$$E_{stab}(n) = BE_v(n) - EA \quad (1)$$

n being the number of solvent molecules in the cluster.

Alternatively, $E_{stab}(n)$ can be envisaged as the ionization potential difference between the isolated and solvated anion,

$$A^- \rightarrow A + e^-$$
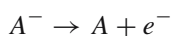
$$(AS_n)^- \rightarrow (AS_n) + e^- \quad (2)$$

where A and A^- are the isolated species and (AS_n) and (AS_n^-) the solvated ones, and it could be interpreted in terms of the net electrostatic stabilization of the charge on the anion due to the solvation effect. The quantum-mechanical computation of the stabilization energy for a cluster with n solvent molecules requires the determination of the energy difference associated to the electron ionization process for the isolated halide anion and the halide solvated by the n solvent molecules. When $n >> 1$, the ab initio computation of $E_{stab}(n)$ is unfeasible due to the size of the molecular system and the increasing number of stable conformations. For this reason, it was of interest to look for computational methods suitable for the estimation of $E_{stab}(n)$ alternative to the direct quantum mechanical computation. Thus, the photodetachment energy could be calculated by switching off the interactions related to the negative charge on the anion or removing an electron from the HOMO in quantum chemical calculations. We carried out a previous study [10] of the stabilization energies of halide ion (F$^-$, Br$^-$ and I$^-$)–(H$_2$O)$_n$ clusters using first-principles interaction potentials based on the MCDHO [11] (Mobile Charge Densities in Harmonic Oscillator) model. These halide–water interaction potentials were developed in our group and published elsewhere [12,13]. In our recent work [10] the $E_{stab}(n)$ was calculated as the average difference between the interaction energy of $[X(H_2O)_n]^-$ and $[X(H_2O)_n]$ clusters along a Monte Carlo (MC) trajectory. This strategy had already been applied by other authors [14–17] on halide–water clusters. Dang et al. [15] show,

through the use of both quantum and classical simulations, that classical ones could be used to estimate E_{stab} because the quantum effect is approximately the same for the anionic and neutral species. The novelty of our contribution was the use of the same interaction potential for the ionic and neutral clusters except for the fact that the halide charge of the MCDHO interaction potential was switched off in the case of the neutral aggregates. It is worth pointing out that these interaction potentials were developed from first principles, so that no parametrization term was included related to the property examined here. Theoretical results derived from this approach agreed fairly well with those experimentally obtained for the three halides. To compute the average E_{stab} (n) in $[X(H_2O)_n]^-$ clusters using the MCDHO ion–water interaction potentials two assumptions were made. First, the photodetachment process is vertical so that the geometry of the cluster does not change. Second, the induced polarization on the water molecules in $[X(H_2O)_n]^-$ aggregates remains unchanged in the neutral cluster. Therefore, it is assumed that neither nuclear nor electronic relaxation in the cluster take place during the photoionization process. These assumptions are, basically, the same as that in Koopmans' theorem. Nevertheless, Markovich et al. [6] interpret the width of the experimental peaks of the photoelectron spectra in terms of changes in the equilibrium geometries between the initial (ionic) and the final (neutral) states and the contribution of different isomers. Although the latter contribution was taken into account in our previous work through the MC trajectories, the contribution due to any relaxation of the neutral (final) cluster was not considered in any way.

The aim of this work is to get insight into the main features responsible for the satisfactory answers obtained under the previous assumptions. The analysis of which ingredients or features of the MCDHO model are needed for a proper reproduction of the experimental $E_{stab}(n)$ is performed. In this line, the effect of the electrostatic relaxation in the photoelectron process will be studied. Closely related to this analysis, the comparative behavior of a dielectric continuum as well as the "local" dielectric behavior of some clusters have been undertaken.

2 Computational methods

2.1 Restrictions imposed to the MCDHO model

The MCDHO-type model is a shell-model that includes intramolecular flexibility and polarizable character in the description of the species that form the system to simulate. The water molecule is described by three positive charges located in the experimental gas-phase geometry of the molecule, Z_O and Z_H being the value of the positive charges for the oxygen and hydrogen atoms, respectively. A negative mobile charge, $q_O = -Z_O - 2Z_H$, attached to the oxygen atom by an harmonic oscillator is used to model the polarizability (see Fig. 1). The intramolecular flexibility of water molecules is included by means of a Morse potential for the O–H
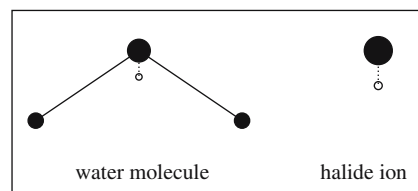
Fig. 1 Schematic representation of MCDHO model. Positive charges Z_O, Z_H and Z_{X^-} are placed at the nuclei positions (*bold sphere*), and the mobile charges q_O and q_{Br^-} are attached to the oxygen atom and the bromide atom by a harmonic oscillator potential (*white sphere*)

bonds and a fourth degree polynomial for the HOH angle, combined both with the electrostatic interaction among the charges, except for the Z_O–q_O interaction. In the case of the halide anions, the monoatomic ion is described by a positive charge, Z_{X^-}, and a negative mobile charge, q_{X^-}, with a total value, $q_{X^-} = -Z_{X^-} - 1$, attached to it (see Fig. 1).

In the original MCDHO paper where the potential for water was introduced [11] authors considered the case where the water molecules were restrained to be rigid. They found that the energy was less affected than the RDFs. In the present work, in order to get a better understanding of the main factors controlling the estimation of $E_{stab}(n)$, we have followed a similar strategy to that of the afore mentioned work [11] and imposed several restrictions to the MCDHO model, without further readjustment:

MCDHO-restriction_A: The polarizable character of the halide anion was eliminated by considering that the positive charge, Z_{X^-}, and its associated negative mobile charge, q_{X^-}, are located in the same position during the MC simulation.

MCDHO-restriction_B: The water molecules were forced to keep the equilibrium molecular geometry, that is to say, a rigid model of the water molecule at its experimental geometry. The polarizable character of the water molecule and the halide anion were maintained as in the original model.

MCDHO-restriction_C: The polarizable character of both the water molecule and the halide anion, as well as the flexibility of the water molecule were eliminated. Then, neither nuclear nor electronic polarization were considered during the MC simulation. These are the same kind of restrictions found in well known and widely employed rigid and non-polarizable interaction potentials, such as OPLS [18], MCY [19], SPC [20], and the like. Among them, and in order to study the influence of considering explicitly or implicitly many-body effects and the empirical or first-principles origin of the interaction potentials on the property under study, OPLS [18,21–23] model was also considered for the sake of comparison. It is worth pointing out that OPLS and MCDHO-restriction_C interaction potentials are similar in the sense that they do not have terms accounting for polarizability and flexibility of the species that form the system.

2.2 Monte Carlo Simulations and $E_{stab}(n)$ computation

MC simulations of $[X(H_2O)_n]^-$ clusters (X≡F, Br and I, and $n = 1 - 6$) considering the previous restrictions were

performed. 200M configurations (M $\equiv 10^6$) of MC simulations at 200 K were produced for each cluster. Configurations were saved every 10 M steps for further analysis. The choice of this temperature is based on previous works [10,14–17], which have shown that the effect of temperature in the prediction of the $E_{stab}(n)$ is not significant as long as it is high enough to avoid cluster trapping into local equilibrium configurations, that is, an appropriate sampling of the configurational space is guaranteed. The temperature of the clusters studied experimentally is thought to be around 70 K [6,7,24]. Although an appropriate estimation of the E_{stab} at 70 K using MC simulations is possible via parallel tempering methods, the non-dependence of the property on temperature caused the choice of 200 K as a simulation temperature.

$E_{stab}(n)$ was computed as:

$$E_{stab}(n) = < E_{int[X(H_2O)_n]} - E_{int[X(H_2O)_n]^-} >_{[X(H_2O)_n]^-} \quad (3)$$

where $E_{int[X(H_2O)_n]}$ and $E_{int[X(H_2O)_n]^-}$ are the interaction energy of the $[X(H_2O)_n]$ and $[X(H_2O)_n]^-$ clusters, respectively. The subscript $[X(H_2O)_n]^-$ denotes that the geometry for the neutral $[X(H_2O)_n]$ cluster is the same as that of the ionic cluster. For each saved configuration both energies where computed, the difference taken and a final average was performed.

2.3 Consideration of electronic relaxation during the photodetachment process to compute stabilization energies

In our previous work [10], $E_{stab}(n)$ was computed assuming that neither nuclear nor electronic relaxation in the cluster takes place during the photoionization process. This means that the nuclear geometry and the position of mobile charges of the water molecules are identical in the charged and neutral clusters. This assumption has been followed to compute $E_{stab}(n)$ from MC simulations of $[X(H_2O)_n]^-$ clusters ($X \equiv F$, Br and I and $n = 1 - 6$). However, if an electronic relaxation during the photodetachment process is considered, the reorganization of the position of the mobile charges of water molecules, q_O, must be permitted under the new resulting field. This charge redistribution must be taken into account when the interaction energy of the $[X(H_2O)_n]$ cluster is computed. In this case $[X(H_2O)_n]^-$ and $[X(H_2O)_n]$ clusters keep the same nuclear geometry but present different charge distribution of the water molecules. A comparison of these two situations in MCDHO MC trajectories without any restriction is presented and discussed in the next section.

2.4 Estimation of the stabilization energies of $[X(H_2O)_n]^-$ clusters using a continuum model

The continuum model [25–27] was used to compute $E_{stab}(n)$ on the basis of Koopmans' theorem. We have used the polarizable continuum model (PCM) of the Pisa group [28], in its integral equation formalism (IEF-PCM) version [29,30]. The radius of the bare ions were chosen following the Simple united atom topological model [31] (UA0). Each isolated halide ion immersed in a cavity surrounded by a dielectric continuum was considered. A set of increasing values for the dielectric permittivity, ϵ, (from 1 to 80) was applied in order to examine the behavior of the E_{stab} with the dielectric permittivity of the solvent. Provided the statistical behavior is accounted for and a cluster with an extremely large number of solvent molecules is considered the static dielectric permittivity of the solvent should be achieved. It is to be expected that halide clusters with small number of solvent molecules will present intermediate "effective" dielectric behavior, which could be represented by a dielectric permittivity lower than the corresponding to pure solvent. The change of ϵ can then be assimilated to clusters of different size.

In the case of the fluoride anion, the semi-continuum model was applied taking into account a cluster with six water molecules. The contribution of water molecules to the cavity was considered on the base of the UA0 model. All computations have been performed with the Gaussian03 package [32].

3 Results and discussion

Figure 2 shows the $E_{stab}(n)$ estimations as a function of the cluster size and the different restrictions imposed to the MCDHO-model. OPLS [18,21–23] results were also included in Fig. 2. For the sake of completeness, MCDHO estimations without any restriction were included [12,13]. In the case of the iodide and bromide anions, MCDHO estimations resemble experimental data [6,7]. The elimination of the ion polarizability (MCDHO-restriction_A) induces worse results. Likewise, the use of rigid water molecules (MCDHO-restriction_B) at the equilibrium geometry of the MCDHO model also worsen the results but in a lesser extent than the elimination of the ion polarizability. This result points out that the polarizability of the halide ion is a more important factor in determining the property than the deformation of the water molecules in the halide–water clusters. Van Gunsteren et al. [33] have supported the prevalence of the polarizability against the flexibility of solvent molecules in classical MD computations. The $E_{stab}(n)$ estimations obtained from OPLS and MCDHO-restriction_C interaction potentials are those that present the most important deviations. The former overestimates the experimental values whereas the latter underestimates them. These results indicate the need to implicitly include many-body effects when dealing with the hydration of halide anions in water clusters, as has already been pointed out in previous studies [12,14–17,34,35].

In the case of the fluoride anion, however, the more restrictions that the MCDHO model presents, the better are the results that are achieved. This fact could seem a nonsense, however, it must be considered that our previous work [10] showed that fluoride results presented an offset between calculated and experimental estimations of $E_{stab}(1)$, and once this offset is corrected, the rest of the results, $E_{stab}(n)$, fit in good agreement with the experimental data [24]. For this reason, an offset of -0.33 eV was applied to all the MCDHO-type

F⁻

Br⁻

I⁻
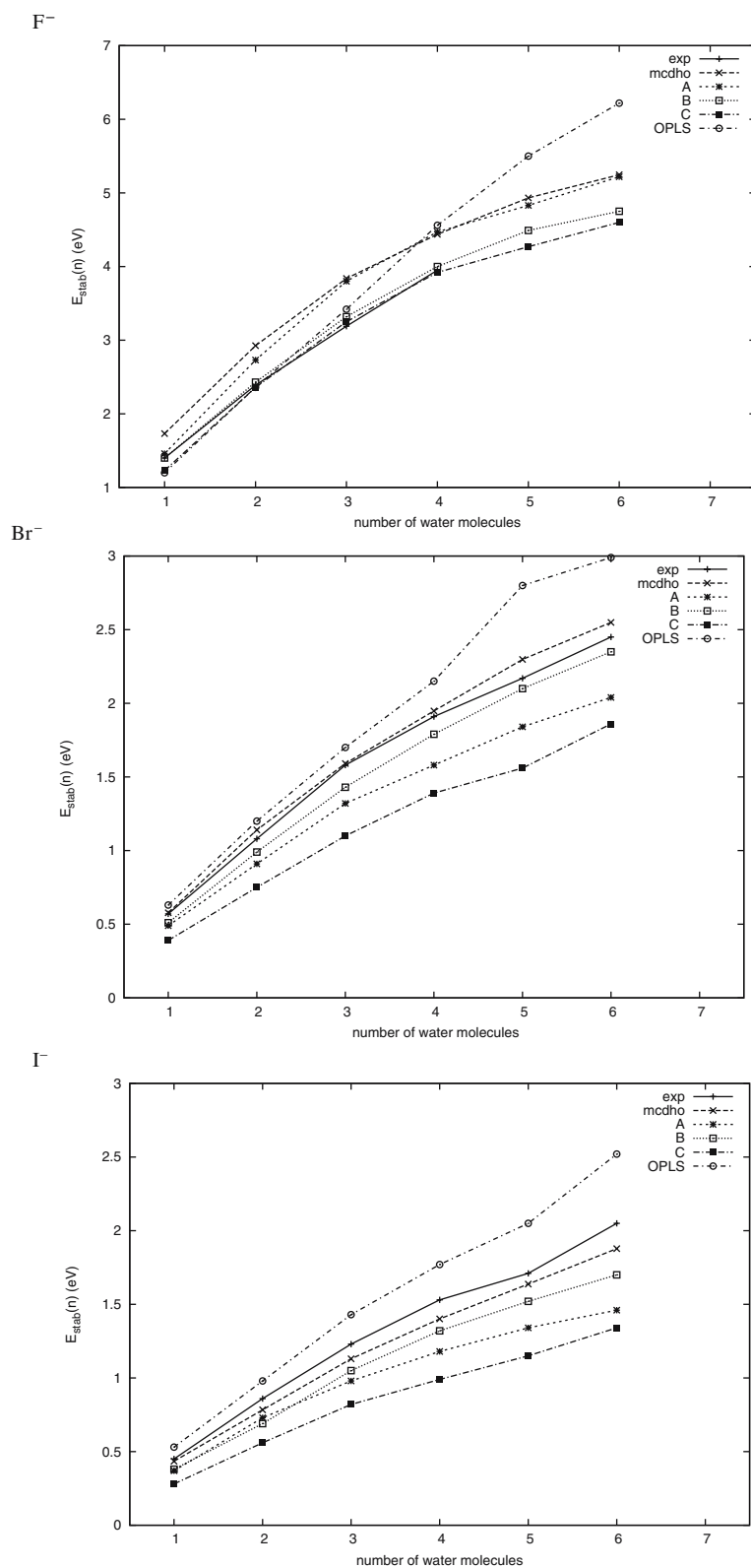
Fig. 2 Comparison of the experimental MCDHO, MCDHO-restriction_A, MCDHO-restriction_B, MCDHO-restriction_C and OPLS-predicted E_{stab} (n) (eV) for $[X(H_2O)_n]^-$ clusters (X≡F, Br and I for $n = 1$–6) at 200 K
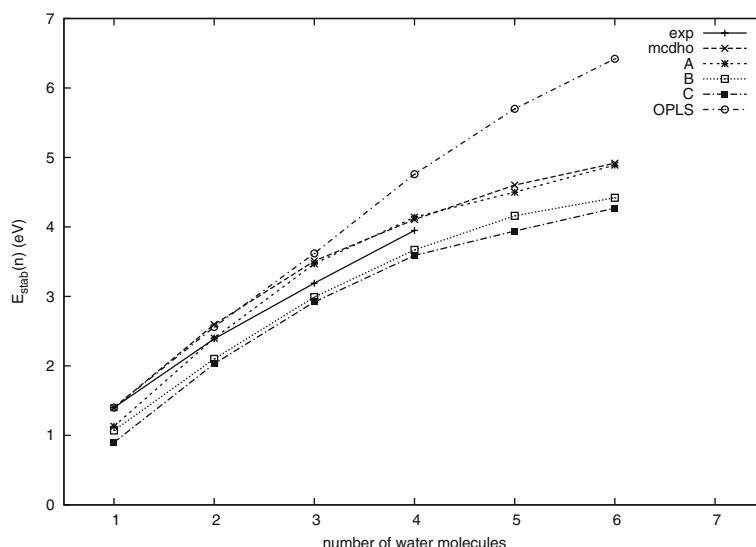
Fig. 3 Plot of experimental MCDHO, MCDHO-restriction_A, MCDHO-restriction_B, MCDHO-restriction_C and OPLS-predicted $E_{stab}(n)$ (eV) for $[F(H_2O)_n]^-$ clusters ($n = 1 - 6$) at 200 K with an offset of -0.33 eV in the MCDHO-type estimations and 0.20 in the OPLS ones

$E_{stab}(n)$ estimations. Similarly, an offset of $+0.20$ eV was applied in the case of the OPLS results by comparison between the calculated and experimental data. The corrected fluoride results are shown in Fig. 3, the similarity with respect to the experimental data acquires now a logical order. The MCDHO and MCDHO-restriction_A estimations resemble the experimental data while MCDHO-restriction_B and MCDHO-restriction_C, as well as OPLS estimations present more important deviations, specially in the case of the OPLS model when n increases. Contrary to the bromide and iodide results, the restriction in which a rigid water molecule is used is slightly worse than that in which the fluoride polarizability is not considered. This fact, as previously detailed, remarks the differences along the group. The polarizable character of the fluoride ion is smaller than the bromide and iodide ones, conversely, the polarizing character of the fluoride ion is much more important, what leads to significant asymmetric deformations in the geometry of the water molecules and explains the need for using a flexible model to properly estimate $E_{stab}(n)$ for the fluoride–water aggregates. The deformation energy of a MCDHO water molecule in the $F(H_2O)^-$ cluster is 3.2 kcal/mol whereas for the $Br(H_2O)^-$ and $I(H_2O)^-$ clusters the value is reduced to 0.7 and 0.5 kcal/mol, respectively.

For the three anions, OPLS deviations increase with the number of water molecules to a greater extent than in the MCDHO-restriction_C case. This fact remarks the different origins of these two sets of interaction potentials. The OPLS interaction potential is a pair-wise additive interaction potential in which many-body effects are included in an average way, via the fit to experimental results of macroscopic properties. MCDHO-restriction_C interaction potential was developed on the basis of a polarizable and flexible model that considers three-body terms on the basis of a microscopic size system and first-principles calculations. Even though it is restricted in a second step, main features of its development such as the quantum-chemical origin, are kept to a certain degree.

The experimental behavior of $E_{stab}(n)$ for large n values ($n \geq 50$) in the case of the iodide anion is asymptotic (see Fig. 4). Although there is no available experimental data for the bromide and fluoride anions, theoretical estimations [10] predict the same behavior at large n values. This trend is also found with all the interaction potentials used in this work, even in the case of the OPLS interaction potentials that show an increase in their estimations for small n values ($n \leq 6$). This overestimation persists for the bigger clusters but its behavior becomes asymptotic (see Fig. 4). It seems that the cluster sizes studied remain too small for the "macroscopic nature" of the OPLS potential. Therefore, it is understandable that its ability to deal with the $E_{stab}(n)$ property is limited. In any case we would like to emphasize that this should not be interpreted as a general shortcoming of this interaction potential, as far as is parametrization was done in a different framework of that analyzed here. It is not surprising that extrapolation of OPLS to describe the energetics of these microscopic aggregates gives moderate success.

An additional factor to be examined is the effect of allowing electronic relaxation of water molecules in the neutral cluster. That is, to allow a certain electronic relaxation of the final state (neutral cluster) during the photodetachment process. Figure 5 shows the comparison of the MCDHO estimations with and without electronic relaxation of the water molecules in the neutral clusters. (The same offset of Fig. 3 has been applied to fluoride results.) According to Eq. (3), allowing the electronic relaxation of the water molecules in the cluster without charge should produce a decrease in the estimation of $E_{stab}(n)$. The relaxation of water molecules in the neutral cluster leads to increase in its corresponding interaction energy (more negative value for $E_{int[X(H_2O)_n]}$), and then $E_{stab}(n)$ becomes less positive. On descending in
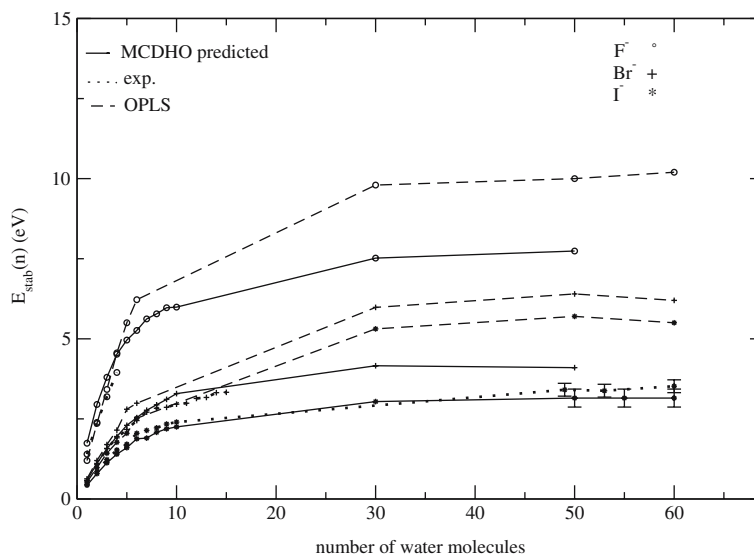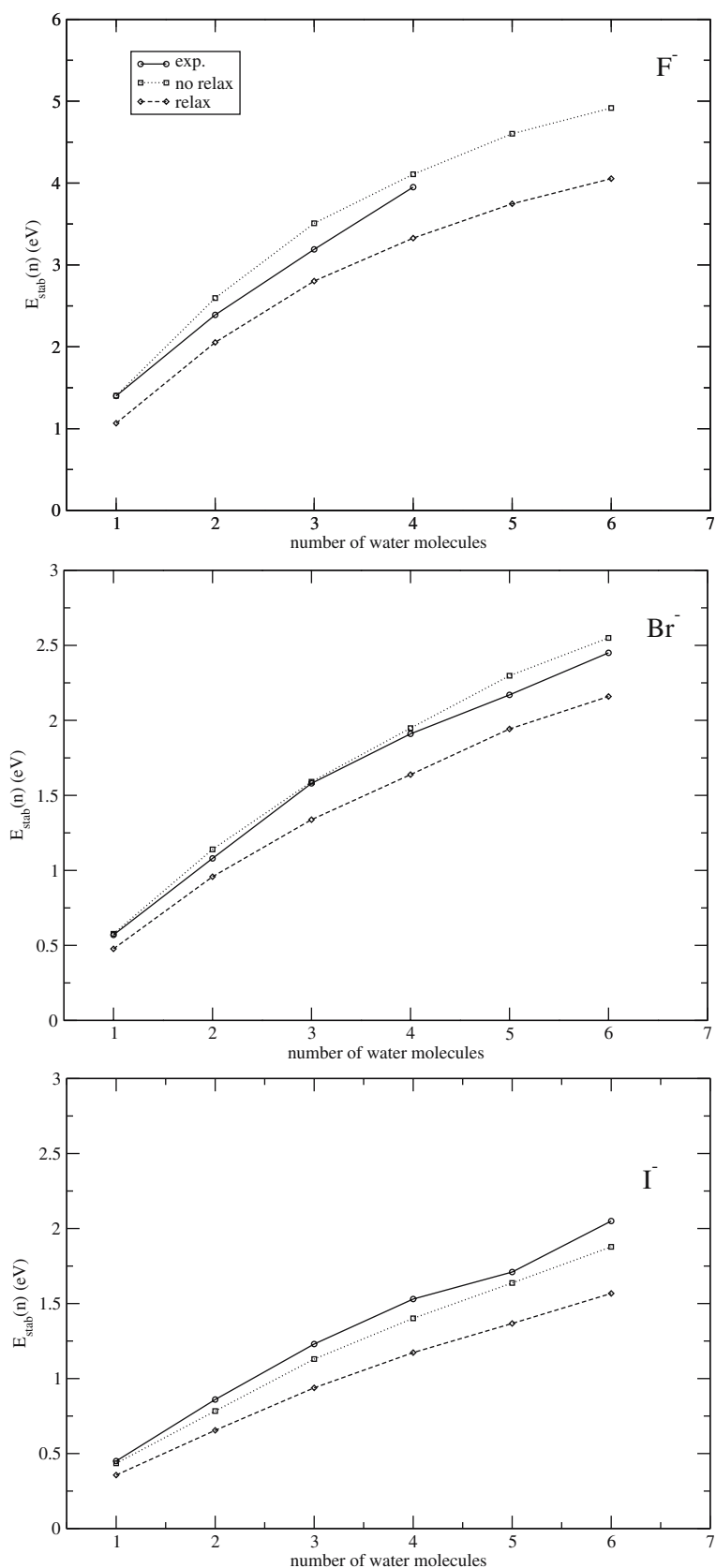
Fig. 4 Comparison of the MCDHO, OPLS and experimental $E_{stab}(n)$ (eV) for $[X(H_2O)_n]^-$ clusters (X≡F, Br and I for $n = 1$–60) at 200 K. The uncertainty for $[I(H_2O)_{(n \geq 50)}]^-$ has been included

the halide group, the difference between the estimations with and without electronic relaxation is smaller. This fact is in agreement with the smaller perturbation that water molecules suffer in the halide–water clusters from the fluoride to the iodide anions. Figure 5 shows that there is not an improvement of the $E_{stab}(n)$ estimations for the halide anions when the electronic relaxation of the water molecules is allowed in the neutral clusters. This seems to indicate that the vertical ionization process does not only occur without nuclear relaxation, but also without electron redistribution in the water molecules of the neutral cluster. This fact might be interpreted as a consequence of the essential local character of the photodetachment process, that is, it involves mainly the halide ion rather than the hydrated cluster as a whole.

Some studies [6,7,36] have applied the use of the continuum model to describe $E_{stab}(n)$ in terms of classical polarizability of a dielectric solvent. They conclude that the applicability of the simple continuum dielectric model for ion solvation in moderately small ($n \leq 125$) clusters is questionable because, qualitatively, results show the appropriate trend but not at quantitative level. A combination of the continuum and semi-continuum model applying the Koopmans' theorem to either X^- or $[X(H_2O)_n]^-$ systems, to estimate $E_{stab}(n)$ has been carried out in this work. An analysis of the changes in the HOMO nature of the halide anions when passing from gas phase to a continuum medium characterized by its dielectric permittivity has been performed. Several works have appeared in the literature dealing with the same kind of computations but applied to other properties. For example, the study of solvent effect on the frontier orbitals to predict the possible changes of chemical reactivity induced by solvation [37–39]. The results for the solvation of the halide ion within a cavity surrounded by a continuum dielectric of different ϵ values (in the range 1–80) are displayed in

Fig. 6. E_{stab} value increases with the dielectric permittivity asymptotically from what could be understood as an increase of this magnitude with the number of solvent molecules up to the value for infinite dilute solution. The experimental evidences are also encountered, namely, $E_{stab}(n)$ decreases from F^- to I^- clusters and there is more similarity between bromide and iodide results. The absolute values of $E_{stab}(n)$ are not similar to those derived from the cluster approach, since they account for different solvation models under different conditions. Nonetheless, the behaviors of the E_{stab} magnitude as a function of the dielectric permittivity and the number of water molecules are extremely similar. When the continuum model is applied, the electrostatic interactions are the main responsible for the changes induced on the halide orbital energies. When the statistical approach is applied, the elimination of the halide charge has been proved to properly represent the magnitude under study. This means that the change associated with the physical process in the halide cluster framework mainly lies on electrostatic changes inside the cluster. Therefore, both independent models show the same trend owing to the fact that electrostatic interactions are dominant in determining the value of the property.

An intermediate solvation model is the semi-continuum one, which accounts for the specific solute–solvent interactions by surrounding the anion with a small number of water molecules and the electrostatic solute–solvent interactions by including the whole aggregate inside a dielectric continuum [40,41]. This semi-continuum model has been applied to four different clusters chosen randomly from a MC simulation containing one fluoride anion and six water molecules. The semi-continuum model was not considered in the case of the bromide and iodide anions due to the high asymmetry found in their water clusters, which precludes the examination of a representative structure including the halide inside

Fig. 5 Comparison of the experimental E_{stab} (n) (eV) for $[X(H_2O)_n]^-$ clusters ($X\equiv F$, Br and I for $n = 1$–6) at 200 K with the MCDHO estimations with and without electronic relaxation of the water molecules in the cluster
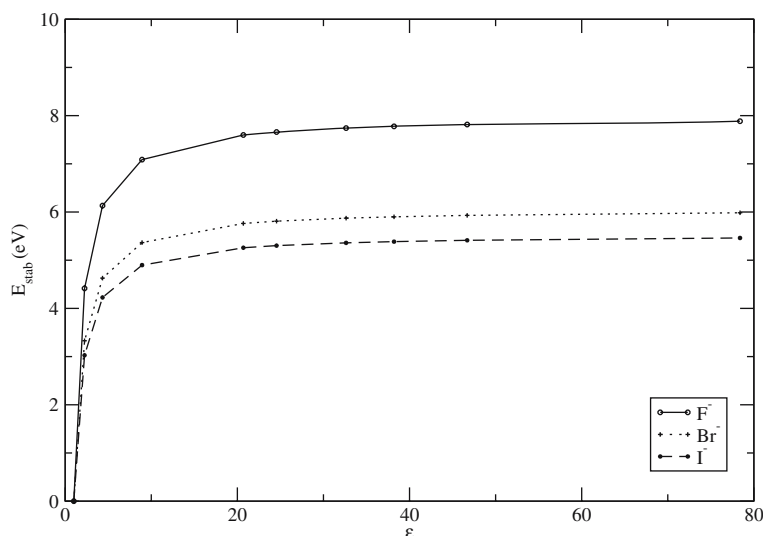
Fig. 6 Plot of E_{stab} (n) (eV) calculated from Koopmans' theorem using the continuum model versus dielectric constant for the fluoride, bromide and iodide anions
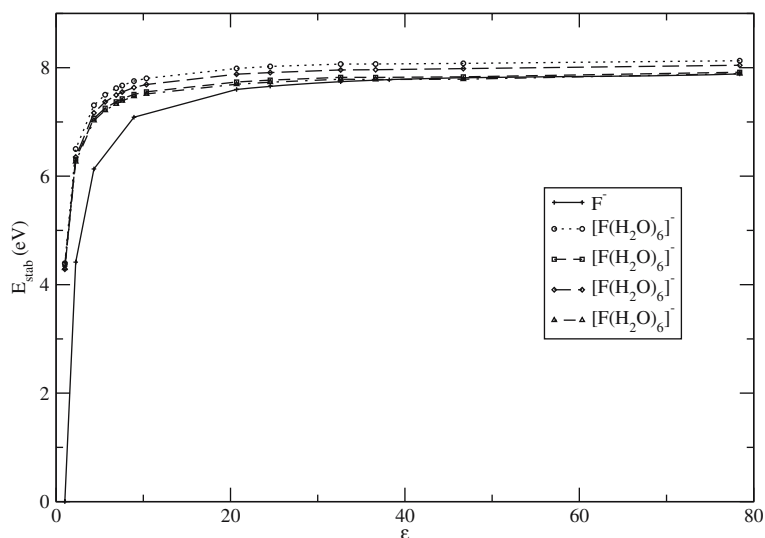
Fig. 7 Plot of E_{stab} (n) (eV) calculated from Koopmans' theorem using the semi-continuum model versus dielectric constant for four different $[F(H_2O)_6]^-$ clusters

the cluster. Results are shown in Fig. 7. It can be seen that the asymptotic value of the $E_{stab}(n)$ is reached at a lower value of the dielectric constant than in the case of the bare ion (for $\epsilon = 10$, E_{stab} for $[F(H_2O)_6]^-$ has already reached the asymptotic value found with' $\epsilon = 60$ for F$^-$). The consideration of a discrete solvation shell involves that a part of the dielectric effect of the medium, associated with short-range and specific interactions, is already satisfied by the macroscopic quantum-chemical representation. This contributes to the quick reaching of the dielectric behavior of the solvent. The discrepancies in $E_{stab}(n)$ among the different $[F(H_2O)_6]^-$ clusters reflect the fluctuations of the property as a function of the structure but the behavior with respect to a continuum dielectric is the same.

4 Concluding remarks

The comparison of the E_{stab} (n) estimations obtained by imposing different restrictions to the MCDHO model leads to the need for considering all the characteristics of the model to properly reproduce experimental data. We have found that it is more important to have a flexible water model than a polarizable ion model in the case of the fluoride ion. On the contrary, ion polarizability is more important than water flexibility in the case of the bromide and iodide ions.

Comparison among the results obtained from the different types of intermolecular potentials employed leads to two main conclusions:

- the importance of explicitly including many-body effects, and
- the advantage of first-principles interaction potentials to reproduce properties for which no specific parametrization term has been included in their development.

This study has been focused on relatively small clusters for which the MCDHO model supplies a better estimation of $E_{stab}(n)$ than OPLS. The OPLS results should not be interpreted as a failure of this model because it was developed to be used in systems mimicking aqueous solutions and not isolated and small aggregates.

The parallel behavior of $E_{stab}(n)$ computed with the classical simulations and the continuum model supports the fact that this magnitude is largely determined by electrostatic factors. Thus, the assumption of switching off the charge in the interaction potentials is a good approximation.

Electronic water relaxation during the photodetachment process does not lead to better results. This fact indicates that the photodetachment process does not only occur without nuclear relaxation but also with a small electron redistribution of water molecules from what might be interpreted as a consequence of the local character of the photodetachment process, which focuses on the halide anion.

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