The solvation of iodine anions in water clusters: PES studies

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Abstract: We have measured the photoelectron-spectra of I^- $(H_2O)_n$ clusters in the size range n=1-60. We have found that the first six water molecules form a solvation layer with an average 0.35 eV electrostatic stabilization of the anion. At larger cluster sizes the electrostatic stabilization of water does not fit a continuous dielectric solvent. The most stable structures of the clusters consist of internally solvated anions. In the size range n=34-40 we have found evidence for existence of cluster structures with surface solvated anions.

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1. Introduction

The details of ion-water cluster interactions are of great importance for the understanding of the solvation phenomena in bulk solutions and in confined systems. Alkali metal cations and halogen anions solvated in clusters have served as model systems for both experimental [1] and theoretical [2] studies of this problem. The solvation shells model is well accepted in describing solvation phenomena in the bulk solution [3]. According to this model, a first shell of solvent molecules rearrange around the ion. Subsequent solvent layers are hardly perturbed in structure by the central ion. It is not obvious though, that by building the solvated ion cluster, one solvent molecule at a time, the bulk solvation layer structure is reproduced. Perera and Berkowitz [2b] have suggested in a recent publication that Cl^- is practically external to a cluster of $(H_2O)_{20}$.

photoelectron-Spectroscopy (PES) of anions solvated in clusters is a suitable technique for the investigation of ion-solvation in clusters. Since it measures directly the binding energy of the solvated anion it is very sensitive to the structure in the polar cluster. PES can be applied successfully to clusters containing up to hundreds of ligands.

The vertical photodetachment process can be easily simulated in theoretical calculations of ion solvation in clusters by a sudden switching off the interactions related to the electron on the anion. As a result, PES binding energies can be directly compared with molecular dynamics and ab initio calculations.

Recently we have reported about PES solvation studies of iodide anion in up to 15 water molecules [4]. In this report we present the extension of these studies to 60 water molecules.

2. Experimental

The anion-clusters are produced by a pulsed electron-beam in the early stages of a pulsed supersonic expansion. The expanding gas consists of 1-2 bar of Ar, 10 mbar of H_2O, and about 1 mbar of benzile-iodide. The newly formed charged clusters are cooled by further flow in the expansion, and mass-separated by a reflecting time-of-flight mass-spectrometer. This cluster source follows the design of Alexander et al [5]. The mass-selected ions are impulse decelerated to ~20 eV kinetic energy, to reduce Doppler-broadening.

All the PES are taken with 7.1 eV (the H_2 7th AS of the 3rd harmonic of a Nd:Yag laser). The kinetic energy of the electrons is analyzed with a 250 cm magnetic TOF photoelectron spectrometer [6] which follows the design principles of Kruit and Read [7]. The resolution is ~50 meV at 1.5 eV of electron kinetic energy. The spectrometer is calibrated with PES of the halogen anions (Cl^-, Br^-, I^-) [8] taken with several laser photon-energies. A detailed description of the experimental apparatus is given elsewhere [4,9].

3. Results and discussion

Fig. 1 displays representative photoelectron spectra of iodine anion bound to n water molecules where n = 1-60. The typical spin-orbit split peaks of the bare iodine anion

shift to higher binding energies with the increase of cluster size. We assign the lowest binding-energy peak of each spectrum to the vertical photodetachment energy of the solvated iodide. The difference between this photodetachment energy and the electron affinity of the bare ion, E_{stab}, is essentially the electrostatic stabilization of the solvated ion in its equilibrium configuration.
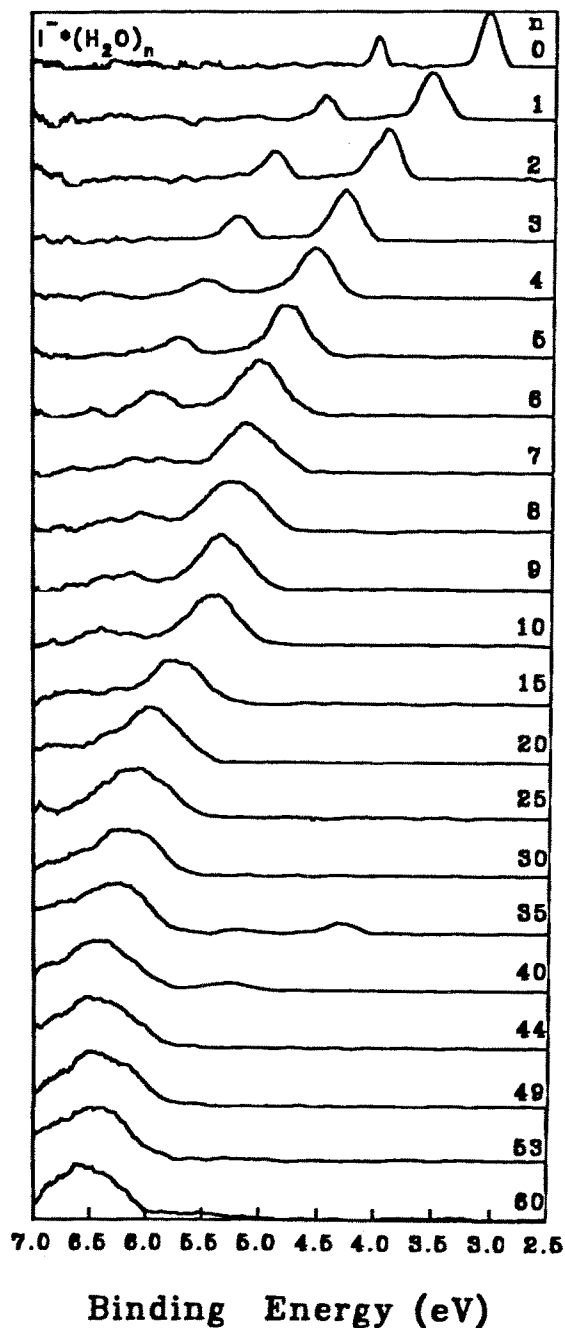
Fig. 2 presents E_{stab} as a function of cluster size. In the size range of n=1-6 E_{stab} increases in steps of 0.45 to 0.18 eV, averaging on 0.35 eV for the first six water molecules. In larger clusters the increase of E_{stab} with n becomes moderate (<0.07 eV). The fact that the six first water molecules stabilize the anion with an average energy so close to E_{stab} of a single ligand indicates that six water molecules form the first solvation layer of I⁻. Subsequent solvent-molecules, in higher solvation layers, provide smaller interactions with the ion.

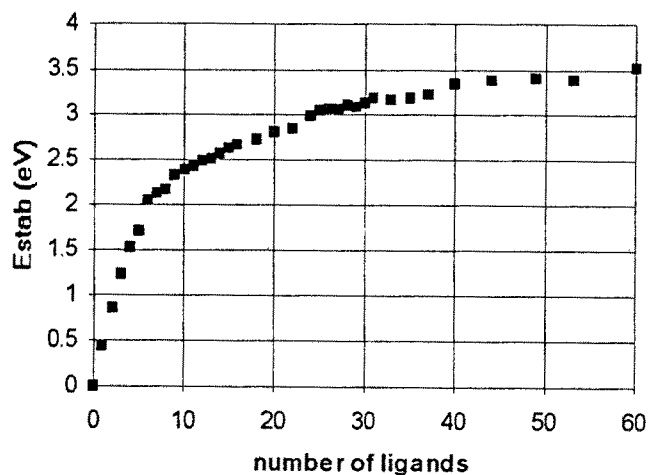Fig. 1. The PES of I⁻ solvated in water clusters. Detachment laser energy is 7.1 eV.

Fig. 2. The stabilization energies of I⁻ solvated in water clusters

We were concerned by the possibility that energy losses, caused by the scattering of the photoelectron by the water molecules, will reduce the apparent electron-affinity. Using cross-sections of electron scattering by water [10] we have deconvoluted the "genuine" PES. This analysis shows that even in our largest clusters E_{stab} changes by marginally small values of (up to 0.14 eV for n~60).

It should be stressed that the values of E_{stab} through the whole size-range of our clusters is consistent with a structure in which I⁻ is solvated inside the water clusters. Although such a structure is optimal for reducing the electrostatic interaction with the anion, it does not necessarily result in the lowest energy of the cluster. The calculations of Berkowitz [2b] and coworkers indicate that for large Cl⁻ $(H_2O)_n$ clusters the anion resides on the surface. In I⁻ $(H_2O)_n$ clusters the experimental values of E_{stab} are inconsistent with such a picture. Low intensity spectral features which can be attributed to surface solvated iodine anion will be discussed later in this report.

Next we were trying to analyze the nature of water cluster interaction in clusters containing more then six water molecules. In the case of classical dielectric solvent, the electrostatic stabilization should converge to the bulk value proportionally to R^{-1}, where R is the radius of the cluster. In our analysis we have assumed that the clusters

consist of anion (of finite volume) solvated in the center of the water sphere (having liquid water density). The results of this analysis with the uncorrected E_{stab} are displayed in Fig. 3 together with the bulk value for the vertical E_{stab} measured by Delahay and coworkers [11]. After correcting the values of E_{stab} for electron scattering the quality of the fit to R^{-1} improves. The analysis of E_{stab} as a function of the cluster radius shows however that for n>6 the solvation cluster cannot be considered plainly as a continuous dielectric medium (The Born model) since the slope from the analysis does not fit the bulk dielectric constants of water [9].
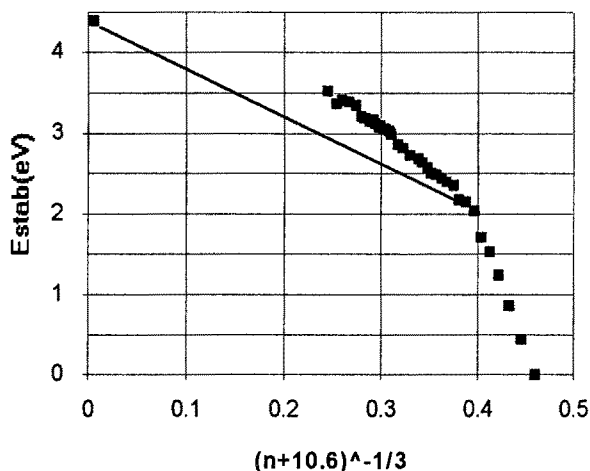
As the cluster grows, water molecules are rearranged in subsequent layers characterized by a smaller electrostatic stabilization to the electron on the ion. The solvation effect of these additional water ligands cannot be described in terms of classical polarizability of a dielectric water solvent.

Fig. 3. The dependence of the cluster stabilization energies as a function of the cluster radius. The numerical factors of 10.6 relates to the self volume of I⁻ togethter with the first solvation layer. The straight line represents the classical dielectric solvation extrapolation from bulk solution.

In the size range of *n*= 34-40 small peaks, with typical spin orbit coupling of iodine, appear in the spectra at lower binding energies than the regular PES pattern (i.e. *n*=35 in Fig 1). The appearance of these peaks could be invoked only by special extreme, warm cluster generation conditions. We attribute these peaks to **surface** iodine ions. These surface anions are less stabilized by the water clusters, than the regular internal iodine anions. Since surface solvated ions are difficult to generate, we believe that these clusters are the energetically unstable forms of water solvated anions.

4. Conclusions

We have studied the solvation of iodide in water clusters by using PES. We have identified the formation of the first solvation layer consisting of six water molecules.

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