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Citation: The Journal of Chemical Physics **95**, 9416 (1991); doi: 10.1063/1.461172 View online: http://dx.doi.org/10.1063/1.461172 View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/95/12?ver=pdfcov Published by the AIP Publishing

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Photoelectron spectroscopy of iodine anion solvated in water clusters

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(Received 19 August 1991; accepted 7 October 1991)

The microscopic details of ion-cluster interactions are of great importance for the understanding of solvation phenomena. In the pursuit of this purpose, alkali metal cations and halogen anions solvated in clusters have served as model systems in experimental^{1,2} and theoretical³ studies.

Kebarle and his co-workers have pioneered the experimental thermodynamic studies of ion solvation in clusters.¹ By utilizing high pressure mass-spectrometric techniques they have determined numerous thermodynamic quantities of both positively and negatively charged ions by stepwise addition of solvent molecules to form a cluster. Since then, a large number of studies have addressed the phenomena of stepwise solvation of ions. Several recent reviews describe the activity in this field.²

The traditional experimental techniques of high pressure mass spectrometry and flow tubes are limited in their ability to study ions solvated in large clusters (n > 8). The information drawn from these studies is thermodynamic and includes both intrasolvent and solvent-solvent interactions.

Photoelectron spectroscopy (PES) of negatively charged ions solvated in clusters can supplement the massspectrometric results in many respects: (i) The PES experiments can be extended to clusters containing hundreds of ligand molecules, as demonstrated in the photoelectron studies of electrons solvated in water clusters by K. Bowen and co-workers.⁴ (ii) The photoelectron ejection is fast on the time scale of the relaxation rates of the solvent molecules. The experimental information extracted in PES experiments pertains mainly to vertical transition, where no rearrangement of the solvent occurs. Consequently, the energetics of PES is insensitive to solvent–solvent interactions which are almost identical in the initial and final states. Only second order solvent–solvent interactions, caused by solvent polarization by the ions, are relevant.

Recently, we have reported on preliminary studies of solvation, obtained by applying the PES technique.⁵ In this paper, we present for the first time the systematic studies of iodine anions solvated in water clusters $-I - (H_2O)_n$ where n = 1-15. This study enables us to conclude on the formation of the first solvation layer around the ion and to analyze its energetics.

The experimental system (Fig. 1) is described briefly. The negatively charged clusters are produced in the early stages of a supersonic expansion from a pulsed nozzle. The supersonic expansion consists of 1–2 bars argon, 10 mbar H_2O , and about 1 mbar of I_2 or benzyl-iodide. A 1000 eV electron beam intersects the supersonic beam a few mm downstream the nozzle, producing iodine atoms and ions by fragmentation. Secondary, low energy electrons initiate

the creation of the negatively charged clusters.⁶

The newly formed charged clusters are cooled by further flow in the supersonic expansion, and mass separated by a time-of-flight mass spectrometer (TOFMS). The reflecting TOFMS (resolution of $t/\Delta t = 1000$) is a modification of the original linear reflectron.⁷ A pulsed mass gate selects single-mass species so that only the desired clusters will enter the photoelectron spectrometer. The selected ions are decelerated 2 cm before the photodetachment zone by a voltage impulse down to low kinetic energies (~10 eV). This step is crucial to the reduction of Doppler-energy broadening of the photoelectron spectra.

The kinetic energy of the laser-photodetached electrons is analyzed with a magnetic time-of-flight photoelectron spectrometer.⁸ The time-of-flight spectrum of the photodetached electrons is recorded on a transient recorder, and further analyzed by a microcomputer to generate the binding energy spectra of the detached photoelectrons. 6.07 eV photons (the H_2 5th Raman AS of 3rd harmonic of a Nd:Yag laser) are used to photodetach the electrons.

The photoelectron spectrometer⁸ follows the design principles of Kruit and Read.⁹ The spectrometer combines a pulsed high magnetic field (~ 1000 gauss) at the photo-



FIG. 1. The PES experimental setup includes a reflecting time-of-flight mass spectrometer and a magnetic time-of-flight photoelectron spectrometer. The charged clusters are generated in supersonic expansion by a pulsed electron gun.

9416 J. Chem. Phys. 95 (12), 15 December 1991 0021-9606/91/129416-04\$003.00 © 1991 American Institute of Physics

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detachment zone and low magnetic field (~ 10 gauss) along the 250 cm time-of-flight tube. This spectrometer is characterized by its high collection efficiency of the electrons(>98%), excellent rejection of surface electrons generated by the scattered light, and parallel detection of all kinetic energies. To minimize stray signal from background molecules, the spectrometer is positioned in a cryopumped ultrahigh vacuum chamber.

The resolution of the spectrometer is 50 meV at 1.5 eV electron kinetic energy. It is a substantial improvement over previous spectrometers of the same design.⁸ This was achieved by using a voltage impulse to decelerate the ions prior to the photodetachment, resulting in constant velocity reduction. This approach is superior to the constant energy-deceleration technique previously used. The impulse deceleration allows the reduction of the average kinetic energy of the ions to about 30 eV with only minor ion-signal reduction. The spectrometer is calibrated with photodetachment spectra of the negative halogen ions [Cl⁻, Br⁻, I⁻ (Ref. 10)].

Figure 2 displays the photoelectron spectra of the iodine anion bound to n water molecules where n = 1-15. The values of the first peak of the binding energies of the detached electrons are summarized in Table I. We assume, that for all the clusters the peak indicates the vertical detachment energy in the geometry of the solvated ions.

We believe that for the $I^- \cdot H_2O$ dimer, the ground state of $I^- \cdot H_2O$ can be optically accessed, and that the onset of the PES spectrum is the adiabatic binding energy. Thus the thermodynamic solvation energy of the dimer can be expressed as the energy difference between the PES onsets of I^- and $I^- \cdot H_2O$, respectively. Indeed, this energy difference in $I^- \cdot H_2O$ is in good agreement (within 0.01 eV) with the results of Kebarle and co-workers.¹

The analysis of data concerning larger solvation clusters is substantially more complex: The solvation energy of an ion in clusters ΔH_s^i is defined as the energy required to bring the ion from infinity and solvate it in a cluster B_n . The relation between the solvation energy in the cluster and the photoelectron experiment is illustrated in Fig. 3 and expressed in Eq. (1).

$$\Delta H_s^i(n) = -BE_V(n) + \Delta H_s^n(n) + \Delta H_R(n) + \text{EA}, \quad (1)$$

where $\Delta H_R(n)$ is the rearrangement energy of the ligands in the solvated ion geometry to the equilibrium geometry of the cluster containing the neutral atom, $\Delta H_s^n(n)$ is the solvation energy of the bare atom in the cluster and is usually considered very close to 0, and EA is the electron affinity of the bare atom.

The mass spectrometric results are related to the solvation energy by Eq. (2) (see Fig. 3),

$$\Delta H_s^i(n) = \Delta H_{O,n} + \Delta H_V(n), \qquad (2)$$

where $\Delta H_{0,n}$ is the sum of the measured stepwise solvation enthalpies to form an ion solvated in *n* ligand molecules, while $\Delta H_{vap}(n)$ is the enthalpy of evaporating clusters of *n* ligands.



FIG. 2. Photoelectron spectra of I^- bound to *n* water molecules, where n = 1-15. The spectra were obtained with 6.07 eV photons. Resolution is better than 130 meV.

The difference between the vertical photodetachment energy and the electron affinity of the bare ion, E_{stab} is defined in Eq. (3).

$$E_{\text{stab}} = BE_V(n) - EA = -\Delta H_s^i(n) + \Delta H_s^n(n) + \Delta H_R(n).$$
(3)

TABLE I. PES results for $I^ (H_2O)_n$ and related experimental and theoretical thermodynamic data. All values are in eV, estimated errors range from 0.02 to 0.05 eV for small to large clusters.

| n | $\frac{BE_{V}(n)}{3.06}$ | $BE_{\nu}(n) - EA$ | $\Delta H_{O,n}$ Thermodynamic data | | $\Delta H_{O,n}$ Simulation results | | |
|----|--------------------------|--------------------|--|------|--|----------------------|--|
| 0 | | | a | b | ¢ | | |
| 1 | 3.51 | 0.45 | 0.44 | 0.48 | 0.43 | | |
| 2 | 3.92 | 0.86 | 0.86 | 0.91 | 0.81 | 0.88 | |
| 3 | 4.29 | 1.23 | 1.27 | 1.31 | 1.18 | 1.37 | |
| 4 | 4.59 | 1.53 | | | Symmetric/pyramidal | | |
| 5 | 4.77 | 1.71 | | | | | |
| 6 | 5.11 | 2.05 | | | | | |
| 7 | 5.20 | 2.14 | | | | | |
| 8 | 5.28 | 2.22 | | | | 2. ¹⁴ - 1 | |
| 9 | 5.40 | 2.34 | | | | | |
| 10 | 5.46 | 2.40 | | | | | |
| 11 | 5.49 | 2.43 | | 2 | | | |
| 12 | 5.55 | 2.49 | | | | | |
| 13 | 5.63 | 2.57 | | | | | |
| 14 | 5.64 | 2.58 | | | | | |
| 15 | 5.69 | 2.63 | | | | | |

^aP. Kebarle, Annu. Rev. Phys. Chem. 28, 445 (1977) (Ref. 1).

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It provides to a good approximation the electrostatic stabilization of the solvated ion in its equilibrium configuration. This is true since the interaction between the bare atom and the cluster in the equilibrium configuration of the solvated ion is small. Solvent-solvent interactions are almost identical in the initial and final states of the photodetachment process, and hardly influence E_{stab} ; Solventsolvent interactions due to ion-induced polarization, which disappear once the photoelectron is detached, are of the order of a few hundredths of eV only.¹¹

Figure 4 presents E_{stab} as a function of cluster size. Note that the increase in E_{stab} in clusters containing more than six water molecules levels off. This is a strong indication that six water molecules form the first solvation layer around the iodine anion. The addition of subsequent solvent molecules to the second solvation layer involves smaller interactions with the ion, due to the larger dis-







FIG. 4. The dependence of $E\Delta_{\text{stab}} = BE_{\nu}(n) - EA$ on the cluster size. Note, that above $n = 6 E_{\text{stab}}$ levels off. This plot indicates that the first solvation layer around I⁻ consists of six water molecules.

tance. This observation is inconsistent with the finite temperature simulations of Lin and Jordan,¹² which predict only three water molecules in the first solvation layer around I^- . The results of Lin and Jordan do indicate, however, that at lower temperatures the clusters tend to rearrange in geometries containing a larger number of water molecules in the first solvation layer.

A useful test for the concept of the first solvation layer is the comparison between our PES results and the water solution results of Delahay and his co-workers.¹³ The vertical photodetachment energy of iodine solvated in water is 7.43 eV. We assume that water beyond the first solvation layer is well approximated by a continuous dielectric medium. Thus, we can apply the Born model to evaluate the ion-solvent interactions beyond the first solvation layer.

The vertical binding energy in the PES of I^- solvated in a cluster of the first solvation layer can be obtained by subtracting from 7.43 eV the Born contributions beyond the first solvation layer (1.44 eV¹⁴), the outer-sphere reorganization energy (0.80 eV¹⁴), and the surface potential of the bulk water (0.08 eV). This calculated value of 5.11 eV is practically identical to our experimental value for the vertical binding energy in I^- (H₂O)₆ (5.1 eV). This is a strong support to our interpretation that six water molecules constitute the first solvation layer of I^- solvated in water clusters.

The formation of a second solvation layer is not the only explanation for the leveling of the stabilization energies in clusters containing more than six water molecules. It is possible that in large clusters, the iodine ion is floating on the solvent surface. Indication for such behavior in large Cl⁻-water clusters, has been predicted in recent simulations done by Berkowitz and co-workers,¹⁵ and observed experimentally in SF₄-Ar_n clusters by Scoles and co-workers.¹⁶

In conclusion, we have demonstrated the usefulness of PES of solvated ions in the investigation of the solvation process and in the identification of the first solvation layer. Extension of these experiments to higher cluster sizes, higher photon energies, and other anions is now in progress.

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