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28 April 2000

**CHEMICAL
PHYSICS
LETTERS**

Chemical Physics Letters 321 (2000) 333–337

www.elsevier.nl/locate/cplett

Electronic properties of dipole-bound $(\text{H}_2\text{O})_2^-$, $(\text{D}_2\text{O})_2^-$, $(\text{H}_2\text{O})_2^- \text{Ar}_{n=1,2,3}$, and $(\text{D}_2\text{O})_2^- \text{Ar}_{n=1,2,3}$ using negative ion photoelectron spectroscopy

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Received 7 June 1999; in final form 14 March 2000

Abstract

We present the mass spectral and the photoelectron spectroscopic studies of dipole bound $(\text{H}_2\text{O})_2^-$, $(\text{D}_2\text{O})_2^-$, $(\text{H}_2\text{O})_2^- \text{Ar}_{n=1,2,3}$, and $(\text{D}_2\text{O})_2^- \text{Ar}_{n=1,2,3}$. We measured vertical detachment energies (VDEs) of these dipole bound cluster anions and also estimated their adiabatic electron affinities (EA_{as}) to be close to their VDEs, respectively. The photoelectron spectra of $(\text{H}_2\text{O})_2^- \text{Ar}_{n=1,2,3}$ and $(\text{D}_2\text{O})_2^- \text{Ar}_{n=1,2,3}$ closely resemble those of $(\text{H}_2\text{O})_2^-$ and $(\text{D}_2\text{O})_2^-$, respectively except for a slight successive spectral shift by ~ 5 meV to a higher electron binding energy with additional argon atoms, which indicates that the argon atoms hardly perturb the water dimer anion geometry. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

The dipole bound anion species have been an interesting issue because of their electron binding nature [1,3–22]. Theories had predicted a critical dipole moment of a molecule for binding an excess electron through its dipole field to be 2.5 D [1]. Thus H_2O itself which has a closed shell electronic structure and 1.85 D cannot bind an electron whereas $(\text{H}_2\text{O})_2$ which has 2.6 D [2] can bind an electron.

The highlighting issues regarding dipole bound cluster anions are (i) the electronic nature of the excess electron, (ii) the cluster anion stability with

respect to the neutral, and (iii) the cluster anion equilibrium geometry with respect to that of the neutral. The present experimental work addresses these issues, respectively, such that (i) the excess electron is dipole bound, (ii) the cluster anion is more stable than the neutral, and (iii) the cluster anion geometry is somewhat different from the neutral cluster equilibrium geometry.

Here, we present the photoelectron spectroscopic study of $(\text{H}_2\text{O})_2^-$, $(\text{D}_2\text{O})_2^-$, $(\text{H}_2\text{O})_2^- \text{Ar}_{n=1,2,3}$, and $(\text{D}_2\text{O})_2^- \text{Ar}_{n=1,2,3}$ using a technique of negative ion photoelectron spectroscopy. These anions represent a typical dipole bound state photoelectron spectrum. We measured electron binding energies, and discussed the three important issues mentioned in the previous paragraph.

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2. Experimental

The negative ion photoelectron spectrometer has been described previously [23], and only details pertinent to the present study are described here. A supersonic expansion source was used to generate the water cluster anions. The formation of various water cluster anions was particularly sensitive to the partial pressure of water vapor in the gas mixture, and the small cluster anions discussed here were generated by expanding 4–6 atm of a 0.3% H₂O / Ar mixture through an 18 μ m diameter nozzle hole at 20 °C. Typical source conditions were as follows: the thoriated filament bias voltage was –20 to –40 V, its emission current was 1 to 4 mA, and the extraction voltage was 300 V. As shown in Fig. 1, the water dimer anion and its argon clusters were the predominant species with only small amounts of the hexamer and heptamer water anions also being produced. It is important to note that if a small amount of OH[–](H₂O) were present in the ion beam unresolved from (H₂O)₂[–], it could not contribute to the photoelectron spectrum of the dimer anion since OH[–](H₂O) does not photodetach at visible wave-

lengths. The photoelectron spectra were recorded using the 488.0 nm with an intra cavity power of 120 circulating watts and 514.5 nm with an intra cavity power of 160 circulating watts of the argon ion laser. The resolution of the hemispherical electron energy analyzer was 27 meV.

3. Results and discussion

3.1. Photoelectron spectra

The photoelectron spectra of (H₂O)₂[–] and (D₂O)₂[–] are presented in Fig. 2. Each spectrum consists of a large narrow feature at low electron binding energy (EBE) and additional weak spectral features at higher EBE. The most intense peak corresponds to the vertical photodetachment transition between the ground states of the anion and the corresponding neutral. The EBE of the peak maximum is the vertical detachment energy. The VDEs for these transitions are provided in Table 1. The weak peaks in the photoelectron spectrum are assigned as vibrational features, representing photodetachment transitions from the ground state of the dimer anion to vibrationally excited states of the neutral dimer. These vibrational features are separated from the origin peak by 0.207 eV and 0.462 eV for (H₂O)₂[–], and 0.152 eV and 0.339 eV for (D₂O)₂[–] (see Table 1), which roughly correspond to light and deuterated water bending and stretching, respectively. The photoelectron spectra of (H₂O)₂[–]Ar_{n=1,2,3} and (D₂O)₂[–]Ar_{n=1,2,3} are presented in Fig. 3. These spectra closely resemble that of the water dimer anion except for being shifted to a slightly higher EBE with an increasing number of Ar atoms. This indicates that the additional Ar atoms hardly perturb the water dimer anion core geometry. The VDEs for both hydrated and deuterated systems are presented in Table 1. In the (H₂O)₂[–]Ar_{n=1,2,3} spectra, the weak vibrational features essentially correspond to the same modes observed in the uncomplexed dimer anion spectra. While the photoelectron spectrum of (D₂O)₂[–]Ar is analogous to that of (D₂O)₂[–], the spectra of (D₂O)₂[–]Ar_{n=2,3} contain additional features which are attributed to photodetachment transitions from cluster anions of equal mass, i.e. (D₂O)₆[–] and

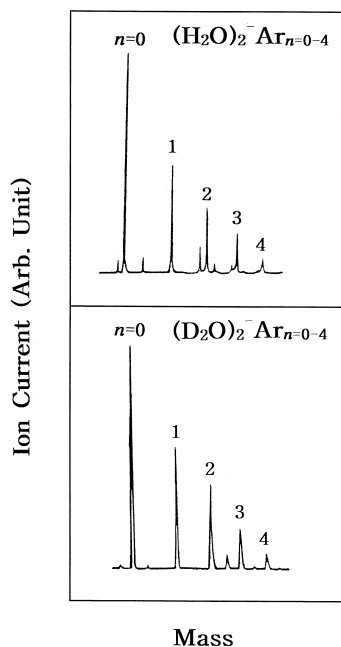


Fig. 1. Mass spectra of (H₂O)₂[–]Ar_{n=0–4} and (D₂O)₂[–]Ar_{n=0–4}.

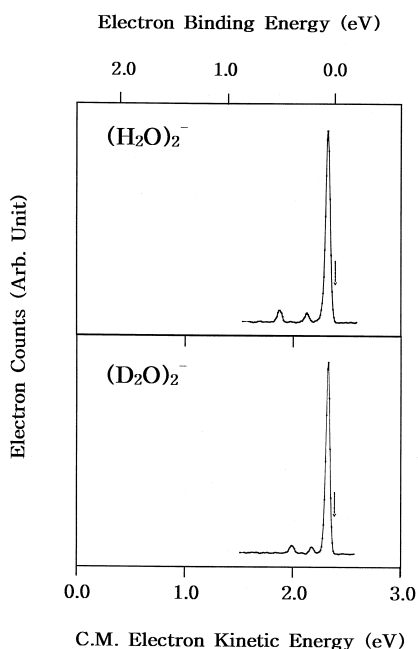


Fig. 2. The Photoelectron spectra of $(\text{H}_2\text{O})_2^-$ and $(\text{D}_2\text{O})_2^-$. The arrow indicates detachment photon energy which is 2.409 eV.

$(\text{D}_2\text{O})_6^- \text{Ar}$, respectively because these cluster anions were also produced in small quantities.

3.2. Vertical detachment energy (VDE) and adiabatic electron affinity (EA_a)

The electron binding energy obtained from the peak center is the vertical detachment energy (VDE). The VDEs are obtained from the least squares fit of the peaks and are provided in Table 1. In general, $\text{VDE} \geq \text{EA}_a$, and only when the anion and the neutral have identical equi-

Table 1

Vertical detachment energies (VDEs) in eV

Cluster anion	Origin peak	Bending	Stretching
$(\text{H}_2\text{O})_2^-$	0.045 ± 0.005	0.252 ± 0.006	0.507 ± 0.006
$(\text{H}_2\text{O})_2^- \text{Ar}$	0.049 ± 0.006	–	–
$(\text{H}_2\text{O})_2^- \text{Ar}_2$	0.056 ± 0.006	–	–
$(\text{H}_2\text{O})_2^- \text{Ar}_3$	0.059 ± 0.006	–	–
$(\text{D}_2\text{O})_2^-$	0.042 ± 0.005	0.194 ± 0.006	0.381 ± 0.006
$(\text{D}_2\text{O})_2^- \text{Ar}$	0.049 ± 0.006	–	–
$(\text{D}_2\text{O})_2^- \text{Ar}_2$	0.051 ± 0.008	–	–
$(\text{D}_2\text{O})_2^- \text{Ar}_3$	0.058 ± 0.008	–	–

librium configurations, $\text{VDE} = \text{EA}_a$. Since $\text{VDE} \geq \text{EA}_a$, the VDE represents an upper limit to the cluster EA_a . On the other hand, photoelectron transitions of water dimer anions with a full width at half maximum (FWHM) of 47 ± 5 meV are surprisingly narrow, such as those of molecular anions. This narrowness indicates that the structural distortion is minimal and the origin is accessed during photodetachment. Thus, a lower limit to the cluster EA_a , of 12 meV was obtained from the threshold of the photoelectron transition. Within these limits, the EA_a of $(\text{H}_2\text{O})_2$ is between 12–45 meV. This range agrees with the previous rough experimental estimates of EA_a of $(\text{H}_2\text{O})_2$ from field detachment experiments, which is 9 to 17 meV [3,4].

3.3. Cluster anion geometry

The Franck–Condon feature of the photoelectron spectrum of $(\text{H}_2\text{O})_2^-$ indicates that the equilibrium geometry of $(\text{H}_2\text{O})_2^-$ is only slightly different from

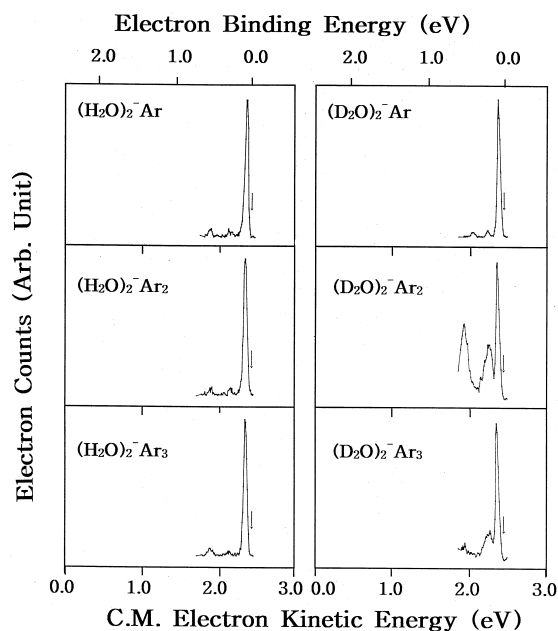


Fig. 3. The Photoelectron spectra of $(\text{H}_2\text{O})_2^- \text{Ar}_{n=1-3}$ and $(\text{D}_2\text{O})_2^- \text{Ar}_{n=1-3}$. The arrow indicates detachment photon energy which is 2.409 eV. The spectra of $(\text{D}_2\text{O})_2^- \text{Ar}_{n=2,3}$ contain additional features which are attributed to photodetachment transitions from cluster anions of equal mass, i.e. $(\text{D}_2\text{O})_6^-$ and $(\text{D}_2\text{O})_6^- \text{Ar}$, respectively because these cluster anions were also produced in small quantities.

that of $(\text{H}_2\text{O})_2^-$. A question arises, regarding whether the slight geometry change is an intra-molecular geometry change, or an inter-molecular geometry change, or both. The vibrational frequencies observed in the spectrum are similar to the neutral water dimer frequencies [24–26]. They are also similar to the dimer anion frequencies that were obtained from a vibrationally induced photodetachment study [22]. These correspondences do not support the intra-molecular geometry being changed. Thus, this leaves Franck–Condon overlaps as being due to an inter-molecular geometry change.

On the other hand, Johnson and coworkers suggested different mechanisms to explain weak vibrational features observed in the photoelectron spectrum of the dipole bound molecular anion, CH_3CN^- [12]. They argued that vibrational features are still observable at zero Franck–Condon overlaps even though the clusters can easily modify the weak inter-molecular geometry to accommodate the excess electron, which will provide substantial Franck–Condon factors. However, Bouteiller et al. proposed that the electron could modify the weak bond angle to a higher dipole configuration in order to more strongly bind the excess electron [11]. In their calculation, they varied the in-plane weak bond angle from the neutral equilibrium geometry (i.e., the trans-linear hydrogen bonded form) to the cis-linear hydrogen bonded form and found a potential minimum near to the cis-linear hydrogen bonded form, which supports our interpretation.

3.4. Solvation by argon atoms

Recall that the spectra of the water dimer / argon cluster anions closely resemble that of the water dimer anion except for being shifted to slightly higher EBE with an increasing degree of complexation. This indicates that the attached argon atoms do not perturb the water dimer anions much. Thus, the excess electron is only slightly influenced by argon atoms, which is likely due to the strongly short range repulsive but weak long range attractions between the excess electron and argon atoms [27].

Although the increasing binding energy could be considered a solvent stabilization energy, similar to the stabilization energy which has been observed for more conventional ion-molecule complexes, it is clear

that the water dimer / argon cluster anions are not conventional ion-molecule complexes. Because the excess electron in the water dimer anion has an estimated spatial distribution of 10–100 Å, it may be more appropriate to think of these clusters as $[(\text{H}_2\text{O})_2\text{Ar}_n]^-$ rather than as $(\text{H}_2\text{O})_2^-\text{Ar}_n$. As a consequence, the stabilization energies associated with clustering additional argon atoms onto the dimer anion are much smaller than they are for other ion-molecule systems containing a weakly bound sub-ion solvated by rare gas atoms. For example, the initial stabilization energies for NO^-Ar_n were 50–60 meV [28], which are an order of magnitude larger than 5 meV observed for the water dimer / argon cluster anions.

4. Conclusion

In this work we have presented both the mass spectra and the negative ion photoelectron spectra of $(\text{H}_2\text{O})_2^-$, $(\text{D}_2\text{O})_2^-$, $(\text{H}_2\text{O})_2^-\text{Ar}_{n=1,2,3}$, and $(\text{D}_2\text{O})_2^-\text{Ar}_{n=1,2,3}$. In these cluster anions, the excess electron is dipole bound. The vibrational feature at a higher EBE indicates that there is a slight geometry distortion between the anion and the neutral, which is expected to be an inter-molecular weak bond distortion towards a higher dipole configuration. The photoelectron spectra of water dimer / argon cluster anions resemble those of $(\text{H}_2\text{O})_2^-$ and $(\text{D}_2\text{O})_2^-$, respectively except for being a spectral shift to a higher EBE with increasing complexation by argon atoms. This implies that the additional argon atoms do not much perturb the water dimer anion geometry. The spectra of the water dimer / argon cluster anions demonstrate the diffuse nature of the excess electron from the small EBE increase with additional argon atoms, which is much smaller than the EBE increase of conventional ion-molecule complexes.

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