

## Photoelectron Spectrum of $(\text{D}_2\text{O})_6^-$ Cluster Anions

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We recorded the photoelectron spectrum of  $(\text{D}_2\text{O})_6^-$  cluster anions and observed an abnormally enhanced intensity in the photoelectron transition of the low electron-binding-energy (EBE) isomer compared to the same transition in the  $(\text{H}_2\text{O})_6^-$  cluster anion. This isotope effect indicates that the low EBE isomer has an excess electron not bound near to the environment of the neutral water hexamer (the so-called surface state) but bound inside the neutral water hexamer (the so-called internal state).

Water cluster anions (or gas-phase-hydrated electrons) have been an interesting subject because of the electron binding nature of the excess electron [1–7]. Theory suggested that the excess electron in  $(\text{H}_2\text{O})_n^-$  with  $n < 32$  was in a surface state whereas that in  $(\text{H}_2\text{O})_n^-$  with  $n \geq 64$  was in an internal state [6]. A photoelectron spectroscopic study found that the excess electron in  $(\text{H}_2\text{O})_2^-$  was in a dipole bound state, that in  $(\text{H}_2\text{O})_{n=6,7}^-$  was in both surface and internal states, and that in  $(\text{H}_2\text{O})_n^-$  with  $n \geq 11$  was an internal state, which was essentially the counterpart of bulk hydrated electrons [7].

In the photoelectron spectra of  $(\text{H}_2\text{O})_{n=6,7}^-$  cluster anions, two electron-binding isomers (*i.e.*, the surface-state and the internal-state anions) were found. By using a plot of the vertical detachment energy (VDE) *vs*  $n^{-1/3}$ , the low electron-binding-energy (EBE) isomer was assigned as an internal-state anion whereas the high EBE isomer was assigned as a surface-state anion [7]. This assignment was based on a theoretical work by Landman et al, who suggested that the plot should not be a straight line for surface-state anions, but should be for internal-state anions [6]. In that plot, we observed that the VDE of the low EBE isomer was fitted to the straight line whereas the VDE of the high EBE isomer was not, from which the above assignment was obtained. Here, we present other evidence which supports the above assignment by recording the photoelectron spectrum of  $(\text{D}_2\text{O})_6^-$  cluster anions.

The negative-ion photoelectron spectrometer used in this study has been described in detail previously [8];

thus, 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 the water vapor in the gas mixture, and the small cluster anions discussed here were generated by expanding 4–6 atmospheres of a 1.0 %  $\text{H}_2\text{O}/\text{Ar}$  mixture through an 18- $\mu\text{m}$  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. The photoelectron spectra were recorded by using the 514.5 nm (= 2.409 eV) line of an argon-ion laser with an intra cavity power of 160 circulating watts. The resolution of the hemispherical electron energy analyzer was 27 meV.

Figures 1(a) and (b) present the photoelectron spectra of  $(\text{D}_2\text{O})_6^-$  and  $(\text{H}_2\text{O})_6^-$  cluster anions, respectively. Each spectrum consists of three peaks labelled as a, b, and c on the top of each peak, respectively. The electron binding energy obtained from the peak center is the VDE. The VDEs were obtained from a least-squares fit of the peaks and are provided in Table 1.

A summary of the assignment of peaks a, b, and c in a previous work [7] is as follows: The electronic transition does not much depend on the isotope whereas both the vibrational and the rotational transitions do. The positions of peaks a and b in the  $(\text{D}_2\text{O})_6^-$  cluster anion are the same as those in  $(\text{H}_2\text{O})_6^-$  cluster anion, respectively, within the experimental error limit, as can be seen in their VDEs in Table 1. Thus, the peaks a and b correspond to photoelectron transitions between two different electronic isomer anions and corresponding

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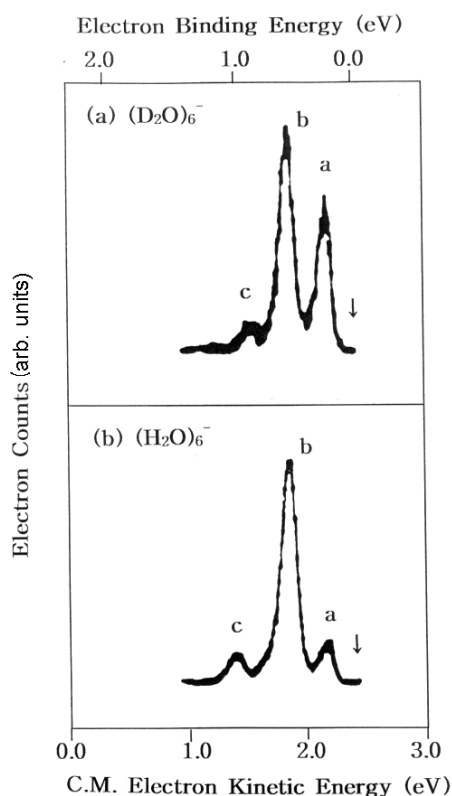


Fig. 1. (a) The photoelectron spectrum of  $(\text{D}_2\text{O})_6^-$  and (b) the photoelectron spectrum of  $(\text{H}_2\text{O})_6^-$ . The arrow indicates the detachment photon energy, which is 2.409 eV. C.M. denotes the center of mass.

neutrals. From the plot of the VDEs *vs*  $n^{-1/3}$  as mentioned above, peak a (or the low EBE isomer peak) was assigned as a photoelectron transition between the vibrational ground state of an internal-state anion and the vibrational ground state of the corresponding neutral. Peak b (or the high EBE isomer peak) was assigned as a photoelectron transition between the vibrational ground state of a surface-state anion and the vibrational ground state of the corresponding neutral. Peak c is separated from peak b by 2621 and 3646  $\text{cm}^{-1}$  for the  $(\text{D}_2\text{O})_6^-$  and the  $(\text{H}_2\text{O})_6^-$  cluster anions, respectively, which roughly correspond to the deuterated-water and the light-water stretches, respectively, and thus was assigned as a photoelectron transition between the vibrational ground state of the same surface-state anion as peak b and a vibrationally excited state by one quantum in the stretching-mode vibration of the corresponding neutral.

For the surface state, the excess electron is bound diffusively in a wide area near to the environment of the neutral-water cluster. Thus, the isotope effect (mostly by vibrations in this case) on electron binding is negligible. For the internal state, however, the excess electron is confined in a small area (the so-called cavity in the case of bulk water) formed by water molecules; thus, a close distance between the excess electron and the water

Table 1. Vertical detachment energies (VDEs) in meV.

	Peak a	Peak b	Peak c
$(\text{D}_2\text{O})_6^-$	172 $\pm$ 5	484 $\pm$ 5	809 $\pm$ 10
$(\text{H}_2\text{O})_6^-$	179 $\pm$ 5	489 $\pm$ 5	941 $\pm$ 5

molecules will result in a considerable isotope effect on electron binding. This will result in a spectral difference between the photoelectron transition of the internal state  $(\text{D}_2\text{O})_6^-$  and that of the internal state  $(\text{H}_2\text{O})_6^-$ . That is, in the case of internal-state anions, it is expected that water vibrations will affect the excess electron binding. Note that the zero-point energy (ZPE) of the  $(\text{D}_2\text{O})_6^-$  is lower than that of  $(\text{H}_2\text{O})_6^-$ . Thus, some population difference between the internal state  $(\text{D}_2\text{O})_6^-$  and the internal state  $(\text{H}_2\text{O})_6^-$  is expected. Since  $(\text{D}_2\text{O})_6$  has a lower ZPE than  $(\text{H}_2\text{O})_6$ , the internal state of  $(\text{D}_2\text{O})_6^-$  is more likely to be populated than that of  $(\text{H}_2\text{O})_6^-$ . Thus, the photoelectron transition of  $(\text{D}_2\text{O})_6^-$  should be stronger than that of  $(\text{H}_2\text{O})_6^-$ . As Figs. 1(a) and (b) show, peak a of  $(\text{D}_2\text{O})_6^-$  is stronger than that of  $(\text{H}_2\text{O})_6^-$ . Thus, peak a isomer should be related to an internal-state anion. However, the intensity of peak b did not show any isotope effect; thus, peak b isomer should be related to a surface-state anion, which is consistent with the previous assignment obtained by using the VDEs *vs*  $n^{-1/3}$  plot. Recently, a theory suggested that two electron-binding isomers exist in water hexamer anions [9]. Also, two additional experiments on  $(\text{H}_2\text{O})_6^-$  cluster anions by another group also confirmed two isomers and provided an identical assignment as this work [10,11].

Finally, the beam temperature ( $T$ ) of the water hexamer anions was empirically judged to be lower than 298 K. By using the intensity ratio in peak a of  $(\text{H}_2\text{O})_6^-$  to that of  $(\text{D}_2\text{O})_6^-$ , *i.e.*,  $I_{\text{H}}/I_{\text{D}} (\cong 1/3)$  and by using a Boltzmann distribution relation, *i.e.*,  $1/3 = \text{EXP}(-\Delta E/kT)$ , in which  $\Delta E$  is the ZPE difference between  $(\text{H}_2\text{O})_6^-$  and  $(\text{D}_2\text{O})_6^-$ , we estimated  $\Delta E$  to be 207  $\text{cm}^{-1}$  with  $T = 298$  K. Since  $T$  is expected to be lower than 298 K,  $\Delta E$  should be much smaller than 207  $\text{cm}^{-1}$ . This amount of energy is only related to the isotope effect resulting from intermolecular vibrations, which implies that the binding of the internal state-excess electron is likely affected by intermolecular vibrations.

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