

# Cluster size dependence of the H/D exchange reaction rate constant for protonated water clusters $\text{H}^+(\text{H}_2\text{O})_n$ ( $n = 2-11$ )

Satoru Yamaguchi<sup>a,b,\*</sup>, Satoshi Kudoh<sup>b</sup>, Yoshiki Okada<sup>b</sup>, Takaaki Orii<sup>b</sup>, Kazuo Takeuchi<sup>a,b</sup>

<sup>a</sup> Graduate School of Science and Engineering, Saitama University, 255, Shimoohkubo, Saitama-shi, Saitama 338-8570, Japan

<sup>b</sup> RIKEN (The Institute of Physical and Chemical Research), 2-1 Hirosawa, Wako-shi, Saitama 351-0198, Japan

Received 16 February 2002; in final form 22 April 2002

## Abstract

The collisions of size- and energy-selected  $\text{H}^+(\text{H}_2\text{O})_n$  ( $n = 2-11$ ) with  $\text{D}_2\text{O}$  have been investigated using guided-ion beam mass spectrometry. The H/D exchange reaction was observed by incorporation of  $\text{D}_2\text{O}$  into  $\text{H}^+(\text{H}_2\text{O})_n$ . The measured rate constants of this reaction are found to depend strongly on the cluster size; the rate constants drastically decrease up to  $n = 6$ , and then level off for  $6 \leq n \leq 11$ . This size dependence is discussed in terms of the structure of protonated water clusters: the core  $\text{H}_3\text{O}^+$  and  $\text{H}_5\text{O}_2^+$  ions, so-called Eigen and Zundel cations respectively, are completely surrounded by the first water layer and cause the rate constants for  $6 \leq n \leq 11$  essentially insensitive to  $n$ . © 2002 Elsevier Science B.V. All rights reserved.

## 1. Introduction

Protonated water clusters,  $\text{H}^+(\text{H}_2\text{O})_n$ , are important in ion chemistry in the stratosphere and lower ionosphere [1]. In addition,  $\text{H}^+(\text{H}_2\text{O})_n$  in the troposphere plays an important role as a generation source of aerosol particles [2]. Reactions of  $\text{H}^+(\text{H}_2\text{O})_n$  with various molecules have been investigated with particular attention to their size-dependent reactivity [3]. For instance, in the

reactions of  $\text{H}^+(\text{H}_2\text{O})_n$  with deuterated ammonia, both proton transfer and ligand exchange reactions were observed for  $n = 2-4$ , whereas only the former reaction dominated for  $n = 1$  [4]. Similar size-specific reactions between  $\text{H}^+(\text{H}_2\text{O})_n$  ( $n = 1-4$ ) and acetonitrile have been reported [5].  $\text{H}^+(\text{H}_2\text{O})_n$  for  $n < 9$  dissolved no HCl molecule, one for  $9 \leq n \leq 13$  did one HCl molecule at most, whereas one for  $n \geq 13$  dissolved at most two HCl molecules [3]. The reactions of  $\text{H}^+(\text{H}_2\text{O})_n$  with  $\text{D}_2\text{O}$  are of particular interest because they involve the H/D exchange reaction, which reflects the fundamental features of protonated van der Waals water clusters. It is also worthwhile to study the H/D exchange reaction rate in the clusters as a

\* Corresponding author. Fax: +81-48-462-4702.

E-mail address: s-yama@postman.riken.go.jp (S. Yamaguchi).

function of cluster size, since the size dependence of chemical and physical properties is one of the interesting the key issues in cluster science.

The product ion distributions for the bimolecular reactions of  $\text{H}^+(\text{H}_2\text{O})_n$  ( $n = 2-4$ ) with  $\text{D}_2\text{O}$  were studied using a selected ion flow tube apparatus. It was found that thorough randomization of the H and D atoms occurred prior to unimolecular dissociation in the ion–molecule transient complex [6]. However, no energy selection or single-collision conditions were achieved in this experiment.

In the present Letter, we have investigated the collision of size- and energy-selected protonated water clusters  $\text{H}^+(\text{H}_2\text{O})_n$  ( $n = 2-11$ ) under single-collision conditions with  $\text{D}_2\text{O}$  using guided-ion beam mass spectrometry to clarify the size-specific H/D randomization of  $\text{H}^+(\text{H}_2\text{O})_n$ .

## 2. Experimental

The experiments were performed with a tandem mass spectrometer equipped with an octopole ion beam guide. A detailed description of the apparatus and experimental procedures has been reported elsewhere [7]. The nitrogen gas bubbled through a water reservoir at 25 °C was introduced to a corona discharge cluster ion source. Protonated water clusters  $\text{H}^+(\text{H}_2\text{O})_n$  ( $n = 2-11$ ) were produced in a free jet through a nozzle of 100  $\mu\text{m}$  in diameter. The translational energy distributions of the mass-selected cluster ions were narrowed to about 0.03 eV in the center-of-mass frame using a Bessel box energy analyzer. The background pressure in the collision cell was less than  $2 \times 10^{-7}$  Torr. The collision cell was filled with  $\text{D}_2\text{O}$  gas at  $5 \times 10^{-6}$  to  $6 \times 10^{-6}$  Torr, where  $\text{H}^+(\text{H}_2\text{O})_n$  was allowed to collide only once with a  $\text{D}_2\text{O}$  molecule. The experiments were performed at 25 °C and at the collision energy  $E_{\text{coll}}$  of 0.05 eV in the center-of-mass frame.

## 3. Results

Figs. 1a,b show typical mass spectra of the cluster ions produced from  $\text{H}^+(\text{H}_2\text{O})_5$  when the target gas,  $\text{D}_2\text{O}$ , was present and absent in the

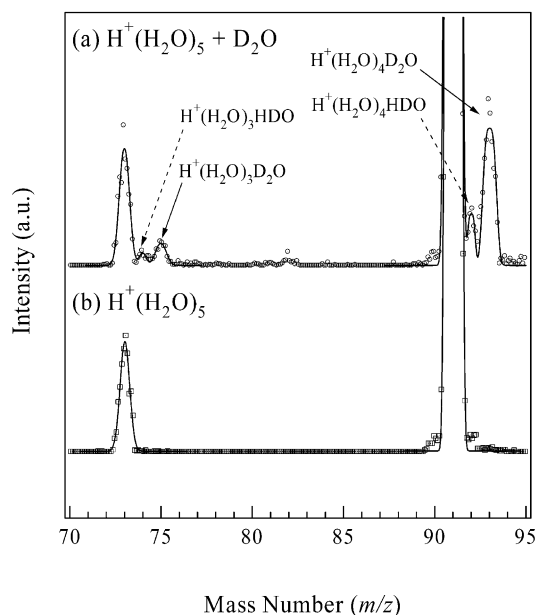


Fig. 1. Typical mass spectra of the cluster ions produced from  $\text{H}^+(\text{H}_2\text{O})_5$  with and without the  $\text{D}_2\text{O}$  target gas in the collision cell.

collision cell, respectively. The cluster ions observed were the parent ion,  $\text{H}^+(\text{H}_2\text{O})_5$ , at 91  $m/z$  and the daughter ion,  $\text{H}^+(\text{H}_2\text{O})_4$ , at 73  $m/z$  without the target gas. With the  $\text{D}_2\text{O}$  gas in the cell, the ions observed were  $\text{H}^+(\text{H}_2\text{O})_4(\text{D}_2\text{O})$  at 93,  $\text{H}^+(\text{H}_2\text{O})_4(\text{HDO})$  at 92,  $\text{H}^+(\text{H}_2\text{O})_5$  at 91,  $\text{H}^+(\text{H}_2\text{O})_3(\text{D}_2\text{O})$  at 75,  $\text{H}^+(\text{H}_2\text{O})_3(\text{HDO})$  at 74, and  $\text{H}^+(\text{H}_2\text{O})_4$  at 73  $m/z$ . We observed the ions produced by the H/D exchange reaction at 92 and 74  $m/z$  in the collision of  $\text{H}^+(\text{H}_2\text{O})_5$  with  $\text{D}_2\text{O}$ . The ions produced by the H/D exchange reaction were also observed in collision with other sizes of the protonated water clusters,  $\text{H}^+(\text{H}_2\text{O})_n$  ( $n = 2-11$ ). The overlapping peaks in Fig. 1 were deconvoluted by fitting them with modified Gaussian functions, and all intensities were calculated from the integrated area of the modified Gaussians curves.

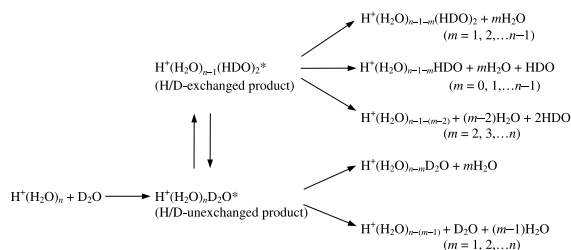
As shown in Fig. 1b, a product cluster ion,  $\text{H}^+(\text{H}_2\text{O})_4$ , resulting from the unimolecular dissociation of the parent cluster ion without the target  $\text{D}_2\text{O}$  gas was observed, and the same peak was also observed with  $\text{D}_2\text{O}$ , as shown in Fig. 1a. The intensities of these peaks were very close. We

found that the incorporation of  $D_2O$  into  $H^+(H_2O)_n$  ( $n = 2-11$ ) dominantly took place and that hardly any dissociation was induced directly by the collision at 0.05 eV.

## 4. Discussion

### 4.1. H/D exchange reaction rate constant

Two types of incorporation-product cluster ions, namely the ions containing a  $D_2O$  molecule and those containing HDO molecules, were observed in the collision of  $H^+(H_2O)_n$  ( $n = 2-11$ ) with a  $D_2O$  molecule, as shown in Fig. 1. The reaction mechanism is considered to be as follows: the  $D_2O$  molecule is first captured by the parent cluster ion to form a hot cluster ion,  $H^+(H_2O)_n D_2O^*$ . Then, the H/D-exchanged product,  $H^+(H_2O)_{n-1}(HDO)_2^*$ , is generated by randomization of H and D atoms. Subsequently, several  $H_2O$  and HDO molecules and one  $D_2O$  molecule are released from either of the hot ions. All possible reaction pathways can be described as follows:



An ab initio calculation suggests that  $H^+(H_2O)_n$  can overcome negligibly small energy barriers among possible geometric isomers [8]. So we assume that vibrationally excited water cluster ions are interconverted freely to all the geometric isomers, and  $H_2O$ ,  $D_2O$ , and HDO molecules are released from them with equal probability. Under this assumption, the intensity,  $I_{n+1}^{\text{ex}}$ , of the H/D-exchanged product  $H^+(H_2O)_{n-1}(HDO)_2^*$  is estimated [7] using the following equation from the intensities of the observed daughter ions of  $H^+(H_2O)_{n-1}(HDO)_2^*$ :

$$I_{n+1}^{\text{ex}} = \sum_{m=0}^{n-1} \frac{1}{2} \frac{2n+3}{2n+1} \frac{C_{2m+2}}{C_{2m+1}} I_{n-1-m}^{\text{ex}}, \quad (1)$$

where  $I_{n-1-m}^{\text{ex}}$  is the measured intensity of the daughter ions produced by the loss of one molecule of HDO and  $m$  ( $m = 0, 1, 2, \dots, n-1$ ) molecules of  $H_2O$  from  $H^+(H_2O)_{n-1}(HDO)_2^*$ .

The intensity,  $I_{n+1}^{\text{uex}}$ , of the H/D-unexchanged product  $H^+(H_2O)_n(D_2O)^*$  is given by

$$\begin{aligned}
 I_{n+1}^{\text{uex}} = & \sum_{m=1}^{n-1} \frac{2n+3}{2n+1} \frac{C_{2m}}{C_{2m}} \left( I_{n-m}^{\text{uex}} - \frac{1}{2} \frac{2n+1}{2n+1} \frac{C_{2m}}{C_{2m-1}} I_{n-m}^{\text{ex}} \right) \\
 & + \frac{2n+3}{2n+1} \frac{C_{2m}}{C_{2m}} I_0^{\text{uex}}, \quad (2)
 \end{aligned}$$

where  $I_{n-m}^{\text{uex}}$  is the measured intensity of the daughter ions produced by the loss of  $m$  ( $m = 1, 2, 3, \dots, n$ ) molecules of  $H_2O$  from  $H^+(H_2O)_n(D_2O)^*$ . The branching fraction for the H/D-exchanged product,  $R_{n+1}^{\text{ex}}$ , and that for the H/D-unexchanged product,  $R_{n+1}^{\text{uex}}$ , are then given by the following two equations:

$$R_{n+1}^{\text{ex}} = \frac{I_{n+1}^{\text{ex}}}{I_{n+1}^{\text{ex}} + I_{n+1}^{\text{uex}}} \quad (3)$$

and

$$R_{n+1}^{\text{uex}} = \frac{I_{n+1}^{\text{uex}}}{I_{n+1}^{\text{ex}} + I_{n+1}^{\text{uex}}}. \quad (4)$$

Fig. 2 shows the cluster-size dependence of  $R_{n+1}^{\text{ex}}$  thus obtained from our experimental data;  $R_{n+1}^{\text{ex}}$  increases with the cluster size. We find that  $R_{n+1}^{\text{ex}}$  depends strongly on the cluster size.

The daughter ions  $H^+(H_2O)_n$  ( $n < 5$ ) are observed even without the target gas, as shown in Fig. 1b. These ions are produced by the unimolecular dissociation of  $H^+(H_2O)_5$ . The fraction  $S_n$  of the parent cluster ions, which survives through unimolecular dissociation at the detector, is given by

$$S_n = \exp(-k_n t_n) = \frac{I_p}{I_p + I_u}, \quad (5)$$

where  $k_n$  is the rate constant for unimolecular dissociation of  $H^+(H_2O)_n$ ,  $t_n$  is the flight time of the cluster ion, and  $I_p$  is the intensity of the parent cluster ion arriving at the detector, and  $I_u$  is that of the ions produced in the unimolecular dissociation.

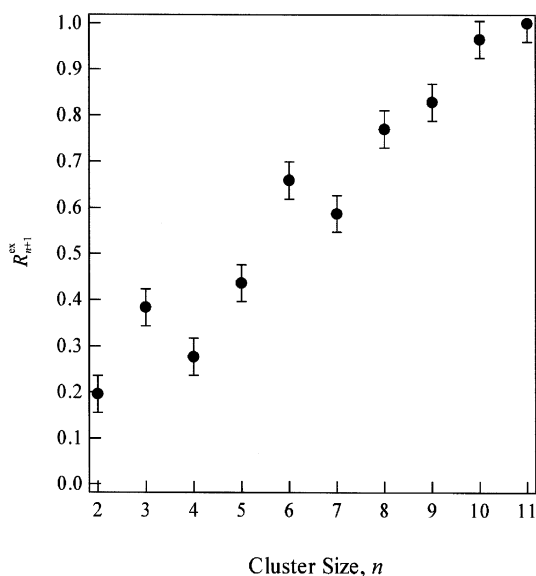


Fig. 2. Cluster-size dependence of the branching fraction,  $R_{n+1}^{ex}$ , for H/D-exchanged product.

tion. The rate constant  $k_n$  for the unimolecular dissociation of  $H^+(H_2O)_n$  is related to the internal energy of the parent ion,  $E_n$ , using

$$k_n = A \left( \frac{E_n - V_n}{E_n} \right)^{L_n - 1}, \quad (6)$$

where  $A$  is the frequency of the internal mode with regard to the  $H^+(H_2O)_{n-1}-H_2O$  bond dissociation,  $V_n$  is the dissociation energy of the  $H^+(H_2O)_{n-1}-H_2O$  bond, and  $L_n$  is the number of intermolecular vibrational modes. The frequency  $A$  is estimated from [9] to be  $4.3 \times 10^{14}$  Hz. The values of  $V_n$  are adopted from the data obtained using the anisotropic site potential model [10] which, for  $n = 2-11$ , are 1.22, 1.02, 0.87, 0.61, 0.59, 0.62, 0.62, 0.58, 0.55, and 0.57 eV. The internal energy  $E_n$  of the parent cluster ion is evaluated using Eqs. (5) and (6) from the experimental values of  $S_n$  and  $t_n$  and from the theoretical values of  $A$ ,  $V_n$ , and  $L_n$ ; this estimation follows that reported in [11]. The  $E_n$  values obtained for  $H^+(H_2O)_n$  ( $n = 2-11$ ) are 1.23, 1.07, 1.03, 0.82, 0.90, 1.06, 1.19, 1.24, 1.28, and 1.45 eV. For  $n = 6$ , for instance, we adopted the  $V_n$  values of 0.57 and 0.60 eV for typical  $H^+$ -centered and  $H_3O^+$ -centered isomers from the results of ab initio calculation performed at B3LYP/

6-31+G\* level [8]. The  $E_n$  values for their isomers evaluated from these  $V_n$  values were 0.88 and 0.92 eV, respectively. The values of  $V_n$  and  $E_n$  derived from the results in [8,10] were found to agree well at  $n = 6$ .

The internal energy of the vibrationally excited water cluster ions,  $E_{n+1}$ , produced by the collision is evaluated from  $E_n$  as

$$E_{n+1} = E_n + V_{n+1} + E_{coll}, \quad (7)$$

where  $V_{n+1}$  is the dissociation energy of the  $H^+(H_2O)_n-H_2O$  bond. The  $E_{n+1}$  values for  $n = 2-11$  are found to be 2.29, 1.99, 1.69, 1.46, 1.56, 1.74, 1.83, 1.84, 1.90, and 2.03 eV. The mean lifetime for unimolecular dissociation of the vibrationally excited water cluster ions,  $t_{n+1}$ , is evaluated from the  $E_{n+1}$  value using

$$k_{n+1} = \frac{1}{t_{n+1}} = A \left( \frac{E_{n+1} - V_{n+1}}{E_{n+1}} \right)^{L_{n+1} - 1}, \quad (8)$$

where  $k_{n+1}$  is the unimolecular dissociation rate constant of the vibrationally excited water cluster ions, and  $L_{n+1}$  is the number of intermolecular vibrational modes. As shown in Table 1, we find that the mean lifetime significantly increases with the cluster size.

It has been reported [6,12,13] that thorough randomization of H and D generates cluster ions with stable structures in thermal equilibrium. The total number of isomers of a vibrationally excited water cluster ion,  $H^+(H_2O)_n D_2 O^*$  or  $H^+(H_2O)_{n-1} (HDO)_2^*$ , possessing two D atoms at different positions is given by  ${}_{2n+3}C_2$ , because the number of the positions that can be occupied by a D atom is

Table 1  
Lifetimes  $t_{n+1}$  for unimolecular dissociation of vibrationally excited water cluster ions

$n$	$t_{n+1}$ (s)
2	$1.48 \times 10^{-12}$
3	$4.20 \times 10^{-11}$
4	$6.98 \times 10^{-11}$
5	$6.70 \times 10^{-9}$
6	$1.03 \times 10^{-7}$
7	$1.81 \times 10^{-7}$
8	$1.69 \times 10^{-7}$
9	$3.49 \times 10^{-7}$
10	$3.46 \times 10^{-6}$
11	$1.14 \times 10^{-6}$

$2n + 3$ . In this context, the number of isomers which can contain a  $D_2O$  molecule is  $(n + 1)$ ; therefore, the number of isomers containing two HDO molecules is  $\{_{2n+3}C_2 - (n + 1)\}$ . The ratio of the concentration of  $H^+(H_2O)_{n-1}(HDO)_2^*$  to that of  $H^+(H_2O)_n(D_2O)^*$  in equilibrium is given by  $\{_{2n+3}C_2 - (n + 1)\}/(n + 1)$ . Therefore, the branching fractions for the H/D-exchanged product and H/D-unexchanged product,  $R_{n+1}^{ex\infty}$  and  $R_{n+1}^{uex\infty}$ , in equilibrium are represented by  $\{_{2n+3}C_2 - (n + 1)\}/_{2n+3}C_2$  and  $(n + 1)/_{2n+3}C_2$ , respectively. Then, the following equation gives the time-dependent change in the branching fraction  $R_{n+1}^{ex}(t)$  in the H/D exchange reaction where  $H^+(H_2O)_{n-1}(HDO)_2^*$  is formed from  $H^+(H_2O)_n(D_2O)^*$ :

$$R_{n+1}^{ex}(t) = R_{n+1}^{ex\infty}(1 - e^{-k_{n+1}^{ex}t_{n+1}}). \quad (9)$$

Here  $k_{n+1}^{ex}$  is the H/D exchange reaction rate constant for protonated water cluster  $H^+(H_2O)_n(D_2O)^*$ . We calculated  $k_{n+1}^{ex}$  using Eq. (9) from the values of  $R_{n+1}^{ex\infty}$  and  $R_{n+1}^{ex}$  (Fig. 2), and the lifetime,  $t_{n+1}$ , for unimolecular dissociation of vibrationally excited water cluster ions (Table 1). Fig. 3 shows the cluster-size dependence of the H/D exchange reaction rate constant,  $k_{n+1}^{ex}$ . We find that the rate

constant decreases drastically from about  $10^{11} s^{-1}$  to about  $10^7 s^{-1}$  as the cluster size increases from  $n = 2-6$  but that the rate constant stays around  $1 \times 10^7 s^{-1}$  in the range of  $n = 6-11$ .

#### 4.2. Origin of the size dependence of H/D exchange reaction rate constant

The observed size dependences are such that  $R_{n+1}^{ex}$  (Fig. 2) and  $t_{n+1}$  (Table 1) increase with  $n$ , but that  $k_{n+1}^{ex}$  (Fig. 3) decreases with  $n$ . The reverse dependence for  $R_{n+1}^{ex}$  and  $k_{n+1}^{ex}$  can be ascribed to the size dependence of the mean lifetime  $t_{n+1}$  of the vibrationally excited water cluster ions, as discussed below.

The H/D exchange reaction is considered to occur either by proton transfer or by direct exchange of hydrogen atoms between  $H_2O$  and  $D_2O$  [14]. If this reaction is mainly dominated by the direct exchange of hydrogen atoms between  $H_2O$  and  $D_2O$ , then the rate constant is expected to increase with the cluster size. The strongly negative size dependence of  $k_{n+1}^{ex}$  observed here suggests that this reaction is not dominated by the direct exchange of hydrogen atoms between  $H_2O$  and  $D_2O$  but by the proton transfer. The proton is known to be quite mobile in molecular clusters as well as in solutions, due to its own quantum nature [15,16]. Two candidates for the ion core in  $H^+(H_2O)_n$ , which may contribute to proton mobility, are the  $H_3O^+$  and  $H_5O_2^+$  cations, sometimes known as the Eigen [17] and Zundel [18] cations, respectively. It is reported that the cores of the Eigen and Zundel cations are completely surrounded by the first water shell for  $n = 4$  and 6, respectively [19,20], whereas these cations are exposed to the exterior and are reactive for  $n \leq 3$  and 5, respectively. Measurements of vibrational predissociation spectroscopy and ab initio calculations [8,21] suggest that  $H^+(H_2O)_n$  for  $2 \leq n \leq 5$ , but not for  $n \geq 6$ , have active ion cores to which  $D_2O$  can directly stick and that these cores consequently promote proton transfer. Therefore, it is understandable that direct proton transfer between  $D_2O$  and the active ion core in clusters with  $2 \leq n \leq 5$  enhances  $k_{n+1}^{ex}$ , as shown in Fig. 3. In addition, the ratio of the number of isomers which possess the active ion cores to the total number of isomers of

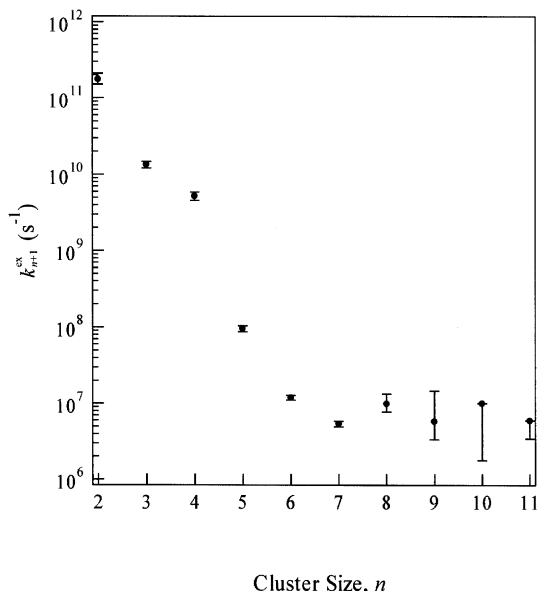


Fig. 3. Cluster-size dependence of the rate constant,  $k_{n+1}^{ex}$ , for H/D exchange reaction.

$\text{H}^+(\text{H}_2\text{O})_n$  increases with decreasing cluster size. Both of these factors are expected to contribute to the observed remarkable increase in  $k_{n+1}^{\text{ex}}$  at smaller cluster sizes shown in Fig. 3. On the other hand, the observed insensitivity of  $k_{n+1}^{\text{ex}}$  for  $n \geq 6$  to the size can be ascribed to the presence of the water shell outside the ion core in  $\text{H}^+(\text{H}_2\text{O})_n$  that hampers direct proton transfer between the core and  $\text{D}_2\text{O}$ . Thus we can account for the size dependence of  $k_{n+1}^{\text{ex}}$  by the structures of  $\text{H}^+(\text{H}_2\text{O})_n$ .

We note in addition that  $k_{n+1}^{\text{ex}}$  depends on the internal energy,  $E_{n+1}$ , of vibrationally excited water cluster ions generated by the collision of  $\text{H}^+(\text{H}_2\text{O})_n$  with  $\text{D}_2\text{O}$ . The  $E_{n+1}$  values for  $2 \leq n \leq 11$  estimated in the present study are all nearly equal, being in the range of 1.46–2.29 eV. The  $E_{n+1}$  values for  $n = 3$  and 11 are 1.99 and 2.03 eV, respectively, whereas the  $k_{n+1}^{\text{ex}}$  values differ by as much as three orders of magnitude,  $10^{10}$  and  $10^7 \text{ s}^{-1}$ , as shown in Fig. 3. Therefore, we conclude that the size dependence of  $k_{n+1}^{\text{ex}}$  originate mainly from that of the structure of the cluster ions and only slightly, if ever, from  $E_{n+1}$ .

As for the observed trend of similarity in the  $k_{n+1}^{\text{ex}}$  values for  $n \geq 6$ , an important question arises: ‘Do these  $k_{n+1}^{\text{ex}}$  values approach that for bulk liquid water?’ To our best knowledge, however, no reliable experimental value has yet been determined for this rate constant in bulk liquid water. The equilibrium constant for the H/D exchange reaction [22,23] and the diffusion constant for HDO [24] and  $\text{D}_2\text{O}$  [25] in the bulk phase have been reported by many authors since the discovery of  $\text{D}_2\text{O}$  in 1931. It was only recently, however, that the H/D exchange reactions on ice surfaces [26] and liquid water surfaces [14] gave qualitative explanations of the H/D exchange reaction rate. We hope that the  $k_{n+1}^{\text{ex}}$  values for  $n \geq 6$  reported in the present paper be extended to larger  $n$  values to link the rate constants for water clusters to that for bulk water.

### Acknowledgements

We are grateful to Drs. R. Nakane, M. Shimizu, G. Vasaru, and T. Suzuki and Mr. S. Isomura for

their advice on the rate constant of H/D exchange reaction for the bulk phase.

### References

- [1] A.A. Viggiano, *Mass Spectrom. Rev.* 12 (1993) 115.
- [2] R.P. Turco, J.-X. Zhao, F. Yu, *Geophys. Res. Lett.* 25 (1998) 635.
- [3] G. Niedner-Schatteburg, V.E. Bondybej, *Chem. Rev.* 100 (2000) 4059.
- [4] K. Honma, L.S. Sunderlin, P.B. Armentrout, *Int. J. Mass Spectrom. Ion Processes* 117 (1992) 237.
- [5] K. Honma, L.S. Sunderlin, P.B. Armentrout, *J. Chem. Phys.* 99 (1993) 1623.
- [6] D. Smith, N.G. Adams, M.J. Henchman, *J. Chem. Phys.* 72 (1980) 4951.
- [7] T. Orii, Y. Okada, K. Takeuchi, M. Ichihashi, T. Kondow, *J. Chem. Phys.* 113 (2000) 8026.
- [8] J.-C. Jiang, Y.-S. Wang, H.-C. Chang, S.H. Lin, Y.T. Lee, G. Niedner-Schatteburg, H.-C. Chang, *J. Am. Chem. Soc.* 122 (2000) 1398.
- [9] C.E. Klots, *Z. Phys. D: At., Mol. Clusters* 20 (1991) 105.
- [10] M.P. Hodges, D.J. Wales, *Chem. Phys. Lett.* 324 (2000) 279.
- [11] M. Ichihashi, S. Nonose, T. Nagata, T. Kondow, *J. Chem. Phys.* 100 (1994) 6458.
- [12] S.T. Graul, M.D. Brickhouse, R.R. Squires, *J. Am. Chem. Soc.* 112 (1990) 631.
- [13] N.G. Adams, D. Smith, M.J. Henchman, *Int. J. Mass Spectrom. Ion Phys.* 42 (1982) 11.
- [14] Y.Q. Li, P. Davidovits, Q. Shi, J.T. Jayne, C.E. Kolb, D.R. Worsnop, *J. Phys. Chem.* 105 (2001) 10627.
- [15] M.E. Tuckerman, D. Marx, M.L. Klein, M. Parrinello, *Science* 275 (1997) 817.
- [16] D. Marx, M.E. Tuckerman, J. Hutter, M. Parrinello, *Nature* 397 (1999) 601.
- [17] M. Eigen, *Ang. Chem., Int. Ed. Eng.* 3 (1964) 1.
- [18] G. Zundel, in: P. Schuster, G. Zundel, C. Sandorfy (Eds.), *The Hydrogen Bond-Recent Developments in Theory and Experiments*, North-Holland, Amsterdam, 1976, p. 687.
- [19] N. Agmon, *Isr. J. Chem.* 39 (1999) 493.
- [20] H.-C. Cheng, *J. Phys. Chem.* 102 (1998) 6201.
- [21] C. Chaudhuri, Y.-S. Wang, J.C. Jiang, Y.T. Lee, H.-C. Chang, G. Niedner-Schatteburg, *Mol. Phys.* 99 (2001) 1161.
- [22] T. Jones, A. Sherman, *J. Chem. Phys.* 5 (1937) 375.
- [23] C.L. Chen, P. Bopp, M. Wolfsberg, *J. Chem. Phys.* 77 (1982) 579.
- [24] W.J.C. Orr, J.A.V. Butler, *J. Chem. Soc.* (1935) 1273.
- [25] L.G. Longworth, *J. Phys. Chem.* 64 (1960) 1914.
- [26] M.A. Everest, C.J. Pursell, *J. Chem. Phys.* 115 (2001) 9843.