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Reactivity and Thermochemical Properties of the Water Dimer Radical Cation in the Gas Phase[†]

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The reactivity of the water dimer radical cation toward a series of substrates has been studied in the gas phase using a Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometer. The water dimer radical cation, $H_4O_2^{\bullet+}$, has been prepared at low pressure in the FT-ICR cell through an exchange reaction of the xenon dimer radical cation with water. Under the applied low pressure conditions the water dimer radical cation is shown to react as an electron acceptor, a proton donor, and a reagent which can exchange an OH• moiety. Independent bracketing of both electron transfer and proton transfer processes leads to an energy difference of 1029—1037 kJ mol^{-1} between the water dimer radical cation and two nonassociated water molecules. This corresponds to an adiabatic ionization energy of 10.81—10.90 eV for the water dimer, $(H_2O)_2$, significantly lower than the 11.21 and 11.1 eV values, obtained from photoionization and photoelectron spectroscopy studies, respectively. The presently obtained results, however, seem to be consistent with results of ab initio calculations.

Introduction

Gaseous water dimers can be generated by association of water molecules in water vapor under relatively high pressure conditions.[1,2] The association between the water molecules is relatively strong as follows from the experimentally determined bond dissociation energy,[1,2] ΔH_{BDE}, of 15.0 kJ mol^{-1}. The water dimer has been the subject of a large number of theoretical studies. These studies have shown that the water dimer is stabilized by a relatively strong hydrogen bond between the water molecules.[3−13] The optimized structure (**1**) obtained by a recent ab initio study on the MP2/6-311+G** level[3] is shown in Figure 1. Several ab initio studies[4−12] have shown a bond dissociation energy ranging from 18 to 22 kJ mol^{-1}. A recent study on the 6-31G** level[13] predicts a somewhat lower value of 14.6 kJ mol^{-1}, which is very close to the experimental value.

Further, it has been shown that also the water dimer radical cation can be a stable long—lived species in the gas phase.[14−19] The water dimer radical cation can be generated by either photoionization of the water dimers in a supersonic jet of water vapor[14−16] or a consecutive exchange of xenon atoms by water molecules in the xenon dimer radical cation at a relatively low pressure.[17−19]

The ionization energy of the water dimer has been determined in both photoionization[14] and photoelectron[15] spectroscopy studies to be 11.21 and 11.1 eV, respectively. However, the photoelectron spectroscopy study indicates that upon ionization the water dimer undergoes a large geometric relaxation, which implies that the above energies must be considered as the upper limits of the adiabatic ionization energy of the water dimer. From the photoionization study[14] it follows that the appearance energy corresponding with the formation of H_3O^+ from the water dimer is 11.73 eV. This value is reproduced by a more recent photoelectron—photoion coincidence (PEPICO) study.[16] The above results reveal a lower limit between 0.5 and 0.6 eV, i.e. between 48 and 58 kJ mol^{-1} for the dissociation energy of the water dimer radical cation, to form H_3O^+ and OH•.

The most recent ab initio study on the 6-311G** level[20] predicts two stable structures for the water dimer radical cation. The most stable structure (**2**), shown in Figure 1, is described as a hydrogen bonded complex between H_3O^+ and OH•. Less stable by 37 kJ mol^{-1} is a dimer radical cation characterized by a two-center three-electron oxygen—oxygen bond (**3**) (hemibonded), shown in Figure 1. Interconversion from **2** to **3** is calculated to proceed via a barrier of 70 kJ mol^{-1}. Dissociation of structure **2** into H_3O^+ and OH• or into $H_2O^{\bullet+}$ and H_2O is endothermic by 92 or 195 kJ mol^{-1}, respectively. In agreement with these results, an earlier study on the 6-31G* level[21] predicted a dissociation energy corresponding to the formation of $H_2O^{\bullet+}$ and H_2O from the hemibonded structure **3** of 162 kJ mol^{-1}. It thus appears that the experimentally determined dissociation energy of 48 to 58 kJ mol^{-1}, corresponding with dissociation of the water dimer radical cation into H_3O^+ and OH•, deviates considerably from the theoretically predicted dissociation energy of 92 kJ mol^{-1}. This discrepancy may be caused by the experimentally determined ionization energy of the water dimer. If, as anticipated, the determined value of about 11.2 eV does not correspond with the adiabatic ionization energy, the stability of the radical cation of the water dimer will be underestimated as suggested by the results of the ab initio studies.

The present study is concerned with the experimental determination of the adiabatic ionization energy of the water dimer. The approach has been to bracket this ionization energy by studying the (non)occurrence of electron transfer in the reactions of thermalized water dimer radical cations with reference molecules under low pressure conditions.

Experimental Section

Experiments were performed with use of a Bruker CMS-47X Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometer equipped with a 4.7 T superconducting magnet and an external ion source. The instrument and the general operating procedures[19,22,23] have been described previously. The water dimer radical cation was generated at low pressure in the FT-ICR cell at room temperature, following a previously
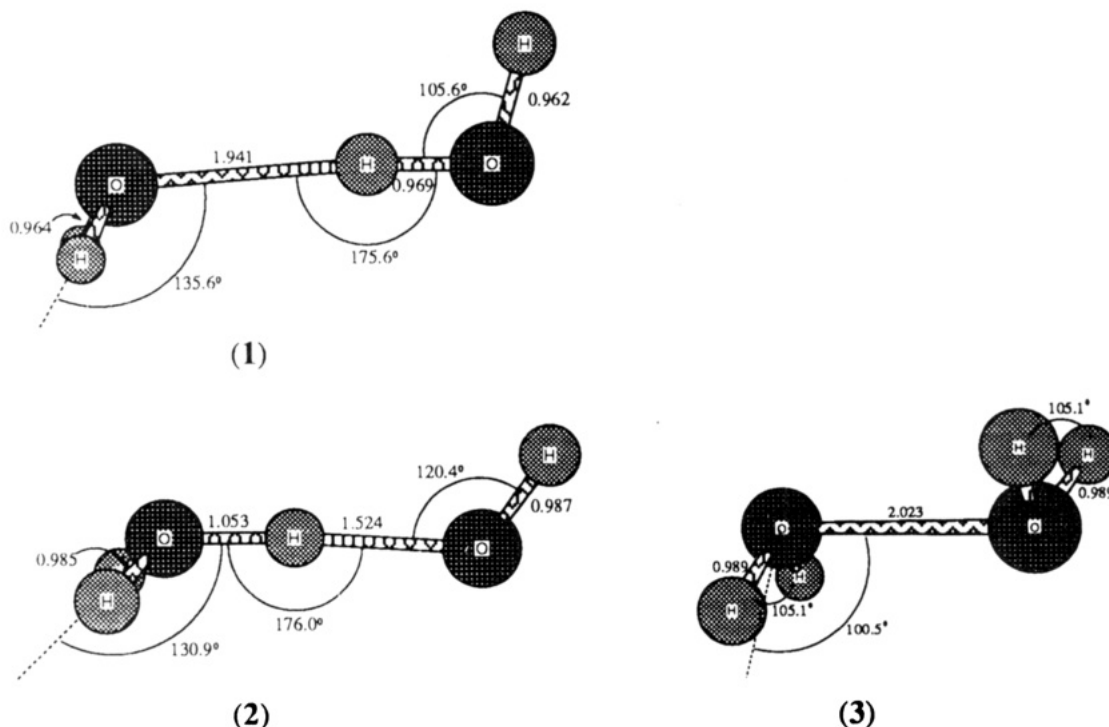
Figure 1. Stable structures for the water dimer (**1**) and the water dimer radical cation (**2**) and the structure (**3**) as obtained from ab initio calculations (see text).

described procedure.[19] Initially, the xenon dimer radical cations were generated under chemical ionization conditions in the external ion source using 40 eV electrons. The ions from the ion source were injected into the FT-ICR cell for 50 ms and subsequently trapped and thermalized with an 80 ms pulsed valve addition of argon up to a pressure of maximally 10^{-4} mbar. The thermalized $Xe_2^{\bullet+}$ ions were selected from the ion mixture and allowed to react with water at a partial pressure of about 5×10^{-9} mbar. Consecutive exchange of xenon by water molecules resulted in the formation of $(H_2O)_2^{\bullet+}$. After a reaction time of 2000 ms the product ions in the FT-ICR cell were thermalized with an 80 ms pulsed valve addition of argon up to a pressure of maximally 10^{-4} mbar. Thereafter, the thermalized $(H_2O)_2^{\bullet+}$ ions were selected from the product ion mixture, thereby carefully avoiding off resonance excitation of the selected ions.[23] Next, the reactions of the water dimer radical cations with reference compounds at partial pressures of up to 1×10^{-8} mbar were monitored as a function of the reaction time.

Materials. Propyne-d_3 was prepared according to a literature procedure.[24] All other chemicals employed were commercially available and used without further purification.
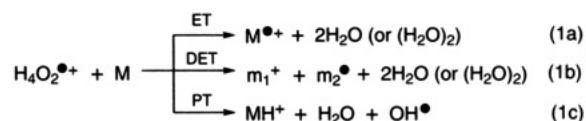
Results

The reactivity of the water dimer radical cation, $H_4O_2^{\bullet+}$, toward a series of substrate molecules, M, has been studied under low pressure conditions. It appears that the water dimer radical cation may react via three competing processes. Reaction may occur via electron transfer (ET) resulting in the formation of $M^{\bullet+}$. Unfortunately, since only product ions can be detected, it cannot be established if the reaction yields either nonassociated, $2H_2O$, or associated, $(H_2O)_2$, water molecules (see eq 1a). Alternatively, reaction may occur via dissociative electron transfer (DET) generating m_1^+ fragment ions (see eq 1b). Finally, reaction may occur via proton transfer (PT), yielding protonated substrate molecules, MH^+ (see eq 1c).

The observed occurrence (+) or nonoccurrence (−) of the above processes in the reactions of the water dimer radical cation

TABLE 1: Occurrence (+) and Nonoccurrence (−) of (Dissociative) Electron Transfer and Proton Transfer Processes in the Reaction between the Water Dimer Radical Cation and Substrate Molecules M

compound M	IE^a (eV)	$(D)ET^b$	PA^a (kJ mol^{-1})	PT^c
toluene	8.82	+	794	+
propyne-d_3	10.36^d	+	748	−
ethene	10.51	+	680	−
acetic acid	10.66	+	796	+
2-nitropropane	10.71	+^{e}		+
methoxyacetonitrile	10.75	−		+
methanol	10.85	−	761	−
nitroethane	10.88	−	773	−
propane	10.95	−	628	−
nitromethane	11.02	−	750	−$^+$
water	12.61	−	697	−

^{a} Ionization energies (IE) and proton affinities (PA) taken from refs 25 and 26. ^{b} Electron transfer (ET) and/or dissociative electron transfer (DET); see eqs 1a and 1b, respectively. ^{c} Proton transfer (PT); see eq 1c. ^{d} IE of unlabeled propyne. ^{e} Only DET observed.

$$H_4O_2^{\bullet+} + M \begin{cases} \xrightarrow{\text{ET}} M^{\bullet+} + 2H_2O \text{ (or } (H_2O)_2) & \text{(1a)} \\ \xrightarrow{\text{DET}} m_1^+ + m_2^\bullet + 2H_2O \text{ (or } (H_2O)_2) & \text{(1b)} \\ \xrightarrow{\text{PT}} MH^+ + H_2O + OH^\bullet & \text{(1c)} \end{cases}$$

with the series of substrate molecules, M, is listed in Table 1. Reaction with toluene shows the competing formation of $C_7H_8^{\bullet+}$, $C_7H_7^+$, and $C_7H_9^+$ ions, indicating that the ET, DET, and PT processes are all energetically accessible. Propyne−d_3 and ethene exclusively react via an ET process generating $C_3HD_3^{\bullet+}$ and $C_2H_4^{\bullet+}$ ions, respectively. For acetic acid competing formations of $C_2H_4O^{\bullet+}$ and $C_2H_5O^+$ indicate that both ET and PT processes are energetically accessible. 2-Nitropropane reacts both via a DET and PT process, resulting in the formations of $C_3H_7^+$ and $C_3H_8NO_2^+$, respectively. As expected, formation of long-lived i-$C_3H_7NO_2^{\bullet+}$ via an ET process is not observed since dissociation of these molecular ions into $NO_2^\bullet$ and i-$C_3H_7^+$ fragments can be estimated to be about 60 kJ mol^{-1} exothermic.[25,26] Methoxyacetonitrile reacts only via PT and not via

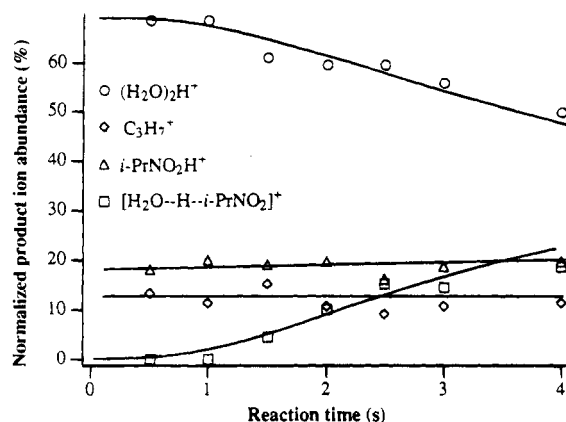**15446** *J. Phys. Chem., Vol. 99, No. 42, 1995*

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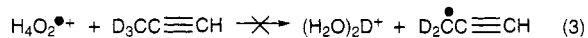**Figure 2.** Normalized product ion distribution associated with the reaction of the water dimer radical cation, $H_4O_2^{\bullet+}$, in a mixed atmosphere of water and 2-nitropropane, as a function of the reaction time. Partial pressures of water and 2-nitropropane were 3×10^{-9} and 6×10^{-9} mbar (ionization gauge manometer readings), respectively.
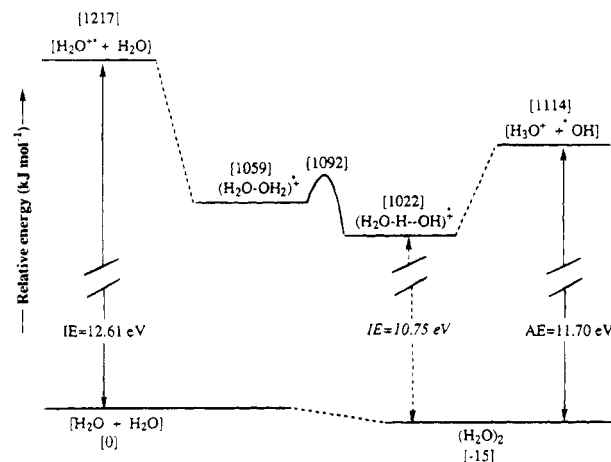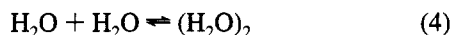

Figure 3. Schematic representation of a potential energy diagram involving the water dimer and its radical cations, based on available experimental and theoretical data (see text).

ET. Further, the water dimer radical cation is found to be unreactive toward methanol, nitroethane, propane, and nitromethane.

Interestingly, reaction with water is found to yield readily and exclusively the protonated water dimer $(H_2O)_2H^+$.

$$H_4O_2^{\bullet-} + H_2O \rightarrow (H_2O)_2H^+ + OH^\bullet \qquad (2)$$
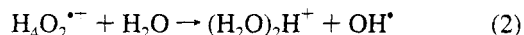
This reaction can be viewed as an exchange of an $OH^\bullet$ moiety for a water molecule, as represented in eq 2. It seems highly unlikely that the formation of $(H_2O)_2H^+$ in the reactions with M in the mixed atmosphere of M and water also is due to a hydrogen abstraction from M by the water dimer radical cation, since in the reaction with propyne-d_3, this would lead to the formation of unobserved $(H_2O)_2D^+$ ions (see eq 3).

$$H_4O_2^{\bullet+} + D_3CC{\equiv}CH \;\;{-\!\!\!\times\!\!\!-}\;\; (H_2O)_2D^+ + D_2\overset{\bullet}{C}C{\equiv}CH \qquad (3)$$

Reactions of the protonated water dimer, $(H_2O)_2H^+$, with toluene, acetic acid, 2-nitropropane, and methoxyacetonitrile, are found to proceed via proton transfer and water molecule exchange, leading to the competing formations of MH^+ and $[H_2O{\bullet\!\!\!-}H{-}M]^+$ ions, respectively. Reactions of the protonated water dimer, $(H_2O)_2H^+$, with methanol, nitroethane, and nitromethane, are found to yield exclusively $[H_2O{\bullet\!\!\!-}H{-}M]^+$ ions.

As an illustration, the product ion distribution associated with the reactions of the water dimer radical cation in a mixed atmosphere of water and 2-nitropropane is plotted in Figure 2. Figure 2 shows the formations of three primary product ions, i.e. $(H_2O)_2H^+$, $C_3H_7^+$, and $i\text{-PrNO}_2H^+$. Relative formation of the $C_3H_7^+$ and $i\text{-PrNO}_2H^+$ ions, which can be associated with a DET and PT reaction of $H_4O_2^{\bullet+}$ with 2-nitropropane, respectively, is relatively constant as the reaction progresses. The primarily formed $(H_2O)_2H^+$ ions in the reaction of the water dimer radical cation with water are clearly shown to undergo a reaction with 2-nitropropane, yielding the secondary $[H_2O{\bullet\!\!\!-}H{\bullet\!\!\!-}i\text{-}PrNO_2]^+$ ions.

Discussion

For convenience, a potential energy diagram is outlined in Figure 3, based on available experimental and theoretical data (see also the introductory section of this paper). From the experimental heats of formations[25,26] it follows that $[H_2O^{\bullet+} + H_2O]$ and $[H_3O^+ + OH^\bullet]$ are destabilized relative to $[H_2O + H_2O]$ by 1217 and 1114 kJ mol^{-1}, respectively. The experi-

mental heat of association[1,2] indicates that the water dimer, $(H_2O)_2$, is stabilized by 15 kJ mol^{-1}. These values are consistent with the ionization energy (IE) of H_2O of 12.61 eV and the appearance energy (AE) of 11.70 eV, corresponding with the formation of H_3O^+ from the water dimer as obtained from both photoionization[14] and PEPICO[16] studies. High level ab initio calculations[20] predict that the water dimer radical cation, $(H_2O{-}H{\bullet\!\!\!-}OH)^{\bullet+}$, characterized by an $O{-}H{-}O$ hydrogen bond as in structure (2) (Figure 1), is stabilized by 92 kJ mol^{-1} relative to $[H_3O^+ + OH^\bullet]$ and by 195 kJ mol^{-1} relative to $[H_2O^{\bullet+} + H_2O]$. Thus, the water dimer radical cation, $(H_2O{-}H{\bullet\!\!\!-}OH)^{\bullet+}$, is destabilized relative to $[H_2O + H_2O]$ by 1022 kJ mol^{-1}. Interconversion via a 70 kJ mol^{-1} barrier is predicted to lead to the 37 kJ mol^{-1} less stable water dimer radical cation, $(H_2O{-}OH_2)^{\bullet+}$, characterized by a two-center three-electron $O{-}O$ bond, as in structure 3 (Figure 1). This implies that the water dimer radical cation, $(H_2O{-}OH_2)^{\bullet+}$, is destabilized relative to $[H_2O + H_2O]$ by 1059 kJ mol^{-1}. Consequently, the dissociation of the water dimer radical cation, $(H_2O{-}OH_2)^{\bullet+}$, into $[H_2O^{\bullet+} + H_2O]$ is endothermic by 158 kJ mol^{-1}, which is close to the 162 kJ mol^{-1} predicted by independent ab initio calculations.[27]

The above consistent potential energy diagram anticipates an adiabatic ionization energy of about 10.75 eV for the water dimer, $(H_2O)_2$, which is considerably lower than the experimental upper limit of 11.21 and 11.1 eV, obtained from photoionization[14] and photoelectron spectroscopy[15] studies, respectively.

In order to gain insight, the present experimental results in Table 1 are rationalized in terms of thermodynamic properties of the water dimer radical cation. An upper and lower limit for the heat of formation of the water dimer radical cation can be estimated from the occurrence/nonoccurrence of electron transfer (ET) from the substrate molecules M to the water dimer radical cation (see eq 1a). It is assumed that under the applied experimental conditions (see Experimental Section) the water dimer radical cations have attained the most stable structure (2) in Figure 1. These results seem to be supported by the observations that in the reaction with water a very efficient exchange of an $OH^\bullet$ moiety for a water molecule occurs, while also the proton transfer reactions to M appear to be relatively efficient. This chemical behavior is compatible with structure 2 in which $OH^\bullet$ is bound to H_3O^+. Further, it is assumed that the ET processes described by eq 1a result in the formation of detectable $M^{\bullet+}$ and undetectable two neutral nonassociated water molecules, $[H_2O + H_2O]$, rather than a neutral water dimer, $(H_2O)_2$.[28,29] This is supported by the experimental entropy of

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association, ΔS_{assoc} of two water molecules.[1,2]

$$H_2O + H_2O \rightleftharpoons (H_2O)_2 \qquad (4)$$

$$\Delta G_{assoc} = \Delta H_{assoc} - T\Delta S_{assoc}$$

Even if in a thermoneutral electron transfer reaction the temperature of the products is around room temperature, $T = 300$ K, the initially formed water dimer is unstable with respect to dissociation into two water molecules (see eq 4) since it can be calculated from the experimental[1,2] $\Delta H_{assoc} = -15$ kJ mol^{-1} and the $\Delta S_{assoc} = -77.8$ J mol^{-1} K^{-1} that $\Delta G_{assoc} = +8$ kJ mol^{-1}. Therefore, under the applied conditions an entropy-driven dissociation of the water dimer can be expected.

In conclusion, it thus appears that the (non)occurrence of the studied ET processes (see Table 1) can be associated with the energy difference between $(H_2O-H\text{-}OH)^{\bullet+}$ and $[H_2O + H_2O]$. The results in Table 1 show that electron transfer to the water dimer radical cation occurs if the ionization energy (IE) of the substrate molecule M is lower than 10.66 eV and does not occur if the IE of M is higher than 10.75 (the observed DET process in the reaction with 2-nitropropane is disregarded due to the estimated exothermic DET, *vide supra*). Consequently, a lower and higher limit follows for the energy difference between $(H_2O-H\text{-}OH)^{\bullet+}$ and $[H_2O + H_2O]$ of 1029 and 1037 kJ mol^{-1}, respectively. This is only a few kilojoules per mole higher than the 1022 kJ mol^{-1} anticipated by the data in the energy diagram of Figure 3. Further, the obtained energy difference between $(H_2O-H\text{-}OH)^{\bullet+}$ and $[H_2O + H_2O]$ corresponds to an adiabatic ionization energy of 10.81–10.90 eV for the water dimer, $(H_2O)_2$, which is significantly lower than the 11.21 and 11.1 eV obtained from photoionization[14] and photoelectron spectroscopy[15] studies, respectively. Similarly, the energy difference between $(H_2O-H\text{-}OH)^{\bullet+}$ and $[H_2O + H_2O]$ can be estimated from the (non)occurrence of a proton transfer (PT) process (see eq 1c) in the reactions of the water dimer radical cations with substrate molecules M. From the results in Table 1 it appears that PT occurs if the proton affinity (PA) of M is higher than 794 kJ mol^{-1} and does not occur if the PA of M is lower than 773 kJ mol^{-1}. This bracketing based on PT shown in eq 1c implies that the energy difference between $(H_2O-H\text{-}OH)^{\bullet+}$ and $[H_2O + H_2O]$ can be estimated to be 1017–1038 kJ mol^{-1} and agrees with the energy difference of 1029–1037 kJ mol^{-1}, as obtained from the independent bracketing based on ET, shown in eq 1a.

From the determined energy difference it can be calculated[25,26] that the heat of formation of the most stable water dimer radical cation, $(H_2O-H\text{-}OH)^{\bullet+}$ is between 545 and 553 kJ mol^{-1}. Both experimental[30,31] and theoretical[32] results have shown that the dissociation energy of the protonated water dimer, $(H_2O)_2H^+$, to form H_3O^+ and H_2O is about 149 kJ mol^{-1}, which corresponds to a heat of formation of the protonated water dimer, $(H_2O)_2H^+$, of about 200 kJ mol^{-1}. This, together with the presently estimated heat of formation for the water dimer radical cation, implies that the observed reaction between the water dimer radical cation and water yielding the protonated water dimer via exchange of a OH$^\bullet$ moiety by a water molecule as shown in eq 2 is moderately exothermic. In spite of this, the exchange reaction with water is found to be highly efficient (see also Figure 2), which reveals that the reaction is not hindered by a considerable energy barrier. This conclusion seems compatible with an above made assumption that under the applied experimental conditions the studied water dimer radical cation has attained the most stable structure (**2**), shown

in Figure 1, resembling a hydrogen bonded complex between H_3O^+ and OH$^\bullet$.

Conclusions

Under the applied low pressure conditions the water dimer radical cation is shown to react as an electron acceptor, a proton donor, and a reagent which can exchange an OH$^\bullet$ moiety. Independent bracketing of both electron transfer and proton transfer processes leads to an energy difference of 1029 and 1037 kJ mol^{-1} between the water dimer radical cation and two nonassociated water molecules. This corresponds to an adiabatic ionization energy of 10.81–10.90 eV for the water dimer, which is significantly lower than the 11.21 and 11.1 eV obtained from photoionization[14] and photoelectron spectroscopy[15] studies, respectively. The presently obtained results however, seem to be consistent with results from ab initio calculations.

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