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Radiation Physics and Chemistry 68 (2003) 313–318

Radiation Physics and Chemistry

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Dissociation energies of protonated water clusters

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Abstract

Relative abundances of positively ionized water clusters formed in a low-pressure electrical discharge as function of reduced electric field were obtained by using drift cell and quadrupole mass spectrometer. It was noticed that some clusters say with $n = 4$ were more abundant than others, at comparable drift conditions. Dissociation energies have been derived from equilibrium conditions for relative clusters abundances. The Hartree–Fock method in 6-311G** molecular-basis set has been applied to calculations of binding energies for different structural "families" of clusters. © 2003 Elsevier Science Ltd. All rights reserved.

Keywords: Water; Clusters; Dissociation

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1. Introduction

Hydrated ions and ionic water clusters are the subjects of increasing interest, both experimental (Castleman and Keesee, 1988; Yang and Castleman, 1989; Honma et al., 1993; König and Fales, 1998) and theoretical (Cheng, 1998; Jiang et al., 2000; Hodges and Wales 2000). Protonated water clusters constitute the most abundant ionic species in the low stratosphere (Hauck and Arnold, 1984); water ions are important in atmospheric nucleation and chemical reactions. Hydronium ions are present in interstellar gas (Millar and Williams, 1993) and molecular cloud, near the Galactic centre (Goicoechea and Cernicharo, 2001). Recently, H_3O^+ ions have found large applications in a new-generation, high-sensitivity mass spectrometers using a "soft" ionization i.e. the proton transfer for studies of complex molecules, mainly of biological interest (Hansel et al., 1997).

In spite of numerous researches the very existence of certain protonated water oligomers in the atmospheric conditions and in particular their dissociation energies are uncertain. Moreover mass spectra of clusters obtained in different experiments are considerably dissimilar and analyses of their formation or dissociation paths are made sporadically (Zhong et al., 1999). In this work we present analysis of possible formation and dissociation reactions for our and other experimental methods of productions of water clusters.

2. Experimental method

We note two conceptually opposite practical approaches for generating water clusters: from a macroscopic liquid phase by dispersion, for example in electrospray method (Hulthe et al., 1997) or secondary ion mass spectrometry technique (SIMS) (Lancaster et al., 1979) and by aggregation, for example in supersonic beams (Hermann et al., 1982). In the present work we show a different approach, allowing to select "smoothly" protonated water clusters $H^+(H_2O)_n$ with $n = 1-7$. These clusters were created in electrical discharge (direct or alternate current) in pure water vapour under pressure of fractions of Torr. Apparatus was a combination of drift chamber (see Fig. 1) and quadrupole mass spectrometer with measured mass range up to 150 amu.

In the region of thermalization of ions between the negative discharge electrode and the first drift chamber

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0969-806X/03/$ - see front matter
doi:10.1016/S0969-806X(03)00307-4

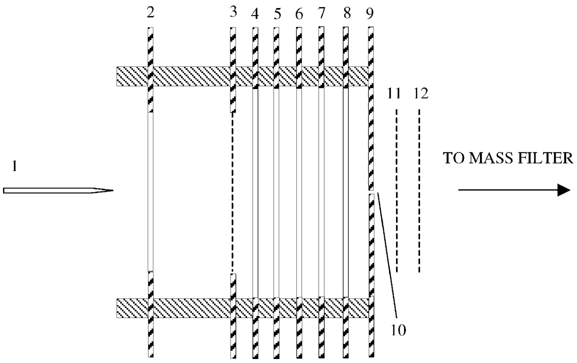

Fig. 1. Diagram of ion source and drift cell: 1 and 2, ion source; 3, tungsten grid; 4–9, guard electrodes; 3–9, drift region; 10, pinhole; 11 and 12, grids.

electrode, from 10^3 to 10^4 collisions of ions occur depending on clusters' sizes and working pressure. The vapour pressure was controlled by a membrane manometer Barocel, manufactured by Edwards. The two regions: of the discharge and the mass spectrometer were pumped out differentially. The minimal background pressure was 6×10^{-7} Torr.

In the drift region ions are accelerated by a homogenous electric field and then undergo collisions mainly with molecules of neutral water. These collisions determine an equilibrium of particular population of ions $H^+(H_2O)_n$ for a set value of the reduced electric field. Beyond the drift region there is an ion optics focusing clusters on the inlet of mass spectrometer. The ions, after leaving the source and drift region, are accelerated by the voltage from 10 to 170 V in order to achieve better focusing conditions.

Mass spectra of $H^+(H_2O)_n$ ions with $n = 1-7$ from the present experiment for two different pressures and drift voltages at HF discharge (in the case of DC discharge mass spectra are similar but all ions signal was lower) are shown in Fig. 2. We can note that for a constant drift voltage we have more clusters with larger n with the increase of pressure. On the other hand at the same pressure it is different—a higher drift voltage increases the number of smaller clusters.

As stated above, the presence of particular clusters in the spectra depend on particular experimental conditions, as discharge type, the distances between electrodes and first of all, the settings of ion focusing optics at the quadrupole entrance. However, if we optimize the focusing conditions and keep all other settings constants, apart from pressure and voltage in the drift cell, we note that clusters relative populations depend only on the ratio E/N, In Fig. 3 we show such relative populations obtained with constant focusing conditions. As seen from this figure, the relative populations reach their maxima at different values of E/N, for example 210 Td for $n = 4$.

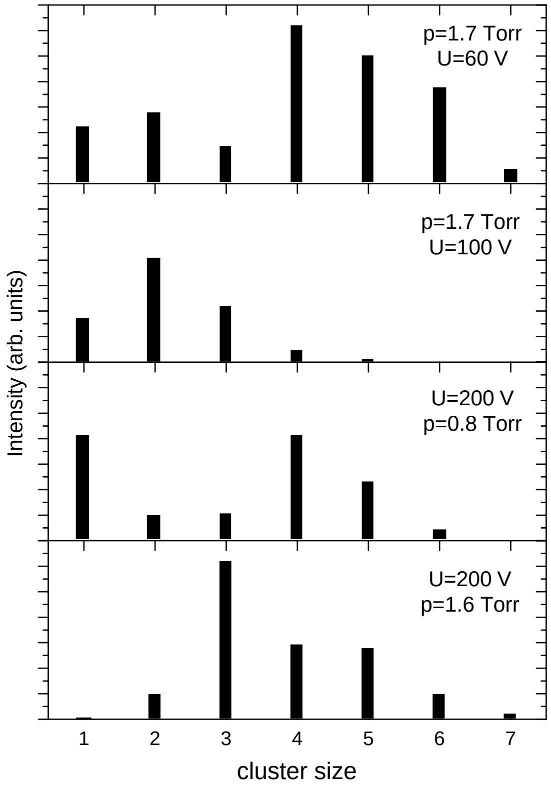

Fig. 2. Present mass spectra obtained for different experimental conditions.

Resuming: in the drift region water clusters undergo multiple collisions with neutral water molecules and clusters with different n reach at a given pressure and field intensity a statistical equilibrium. The kinetic energy gain from the field, the cross-section for interaction between ionized clusters and neutral water molecules and dissociation energies of clusters determine this dynamical equilibrium conditions. Dissociation energies are only one of the input data of such equilibrium and obtaining these values is not so straightforward. We will discuss it in detail below.

From the conceptual point of view the present experiment resembles those of Kebarle and co-workers (Kebarle et al., 1967; Cunningham et al., 1972) and their followers (Field and Beggs, 1971); Meot-Ner and Field, 1977). In those experiments clusters of different masses were observed at the same time and their relative populations were varied by changing gas pressure, see Fig. 3. However, as shown for example by Cunningham et al. (1972), the equilibrium constants evaluated from relative populations.

$$K_{n-1,n} = [H^+(H_2O)_n]/[H^+(H_2O)_{n-1}][H_2O]$$

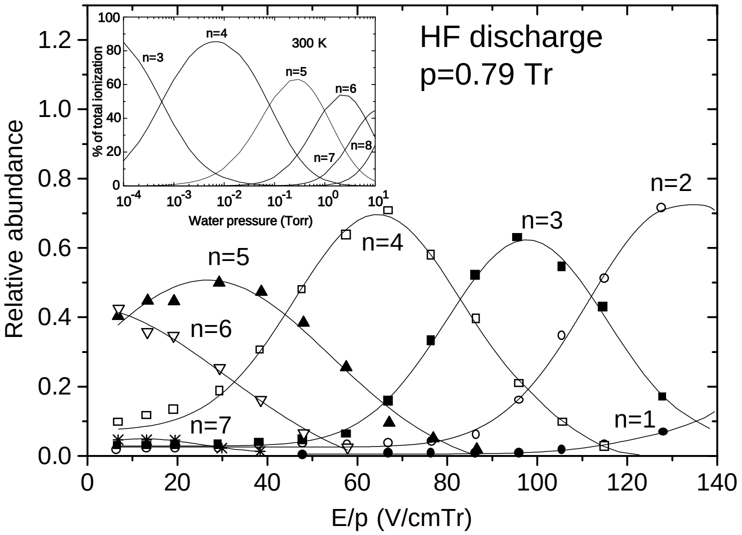

Fig. 3. Dependence of cluster population for alternate current HF discharge at variable ratio of electric field to pressure at constant pressure in the drift chamber. On insert thermodynamical results of Kebarle et al. (1967) are shown.

are independent from pressure but vary with temperature. Plotting equilibrium constant vs. inverse of temperature, dissociation enthalpies can be obtained.

In our experiment the clusters gain the energy necessary for the dissociation from the external electric field. Such a way of supplying the kinetic energy to the clusters was used, for example, by Honma et al. (1993) and by Magnera et al. (1989, 1991). However, they studied disintegration of only one type of clusters $H^+(H_2O)_n$ at a time and without any third bodies and therefore were able to determine the dissociation energies from the thresholds for comparison of $H^+(H_2O)_{n-1}$ clusters. The drawback of those experiments is that the solid phase (Magnera et al., 1991) or reaction with a third gas (CH_3CN) (Honma et al., 1993) must be used for the formation of the clusters. Therefore, the values obtained show a big span (from 35.97 to 45.66 kcal/mol for $n = 2$ (Honma et al., 1993) and 16–18 kcal/mol from $n = 4$ (Magnera et al., 1991). Additionally, such experiments cannot model processes in Earth atmosphere, where clusters are formed in reactions of only water molecules, and possibly in presence of electric fields (quite strong in the region of upwards movements).

The present experiment simulates, somewhat better, the conditions in a lower stratosphere—an intermediate pressure and the absence of third, chemically reactive gases. However, in our experiment the contemporary formation and disintegration of clusters takes place by adding or subtracting one water molecule. The attachment reactions can undergo via two-body "sticking" collisions.

$$H^+(H_2O)_{n-1} + H_2O \leftrightarrow H^+(H_2O)_n. \qquad (1)$$

It was observed experimentally (Hermann et al., 1982; Magnera et al., 1991) that clustering reactions are exothermic; however, we show by our calculations (see later) that some potential barriers are to overcome to form $H^+(H_2O)_n$ clusters, therefore the reactions (1) do not have exactly zero-energy thresholds. The detachment reaction requires collisions with third bodies, in our experiment with neutral water molecules.

$$H^+(H_2O)_n + H_2O + E_k \leftrightarrow (H_2O)_{n-1} + H_2O + H_2O. \qquad (2)$$

As shown later by our calculations, the formation of neutral water dimmers,

$$H^+(H_2O)_n + H_2O + E_k \leftrightarrow H^+(H_2O)_{n-1} + (H_2O)_2 \qquad (3)$$

rather than the direct single-molecule detachment Eq. (1) is energetically favourable. Additionally, other reactions are possible, like detachment of more than one water molecule or fully "explosive" dissociation, e.g.

$$H^+(H_2O)_n + H_2O + E_k \rightarrow n(H_2O) + H_3O^+.$$

Note that in all reactions the surplus of the kinetic energy of reactants can be transferred to the vibration excitations of the clusters formed which on their turn, undergoing successive collisions, will not follow the same kinetics as ground-vibrational state clusters.

Presence of all these possible channels make the analysis of our experiment extremely complex. To reproduce theoretically population curves like in Fig. 3 a complete Boltzmann-equation modelling would be needed, for more than one cluster species present. For such a modelling not only dissociation energies and thresholds for different vibrational modes are needed but also cross-sections for long-range interaction between clusters and water molecules. All these data are

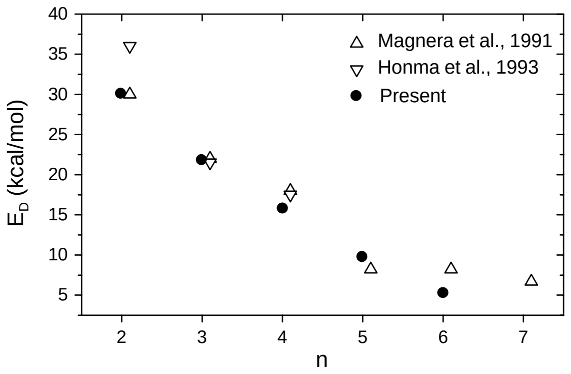

Fig. 4. Comparison between present experimental dissociation energies of protonated water clusters and other experimental values (Honma et al., 1993; Magnera et al., 1991).

not available experimentally and the theory of long interactions is at the preliminary stage also. Therefore, the determination of dissociation energies can only be qualitative, rather than strictly quantitative.

As a "first-order" approximation we determine these energies from the values of the electric field at the intersection points between n and $n-1$ clusters populations. At these values of the electric field, in the dynamic equilibrium conditions, the same number of n clusters disintegrate collisionally forming $(n-1)$ ones as the number of $(n-1)$ clusters "stick" with near-to zero kinetic energy to water molecules, re-forming the n clusters. Values of E_D obtained in this way are shown in Fig. 4.

Present experimental energies of dissociation are in very good agreement with those of Magnera et al. (1991) for $n=2$ and 3 (differences are below 10%). For $n=4,5$ disagreement increase to 30%. Results of Honma et al. (1993) are 25%, 2% and 13% higher than our for $n=2$, 3 and 4, respectively. For $n=6$ and 7 our dissociation experimental energies start to deviate from other results. One reason for this can be experimental conditions: the voltages applied to the drift cell are very low (few volts) and presence of contact potentials and/or electrical fields penetrating from the discharge region can lead to destruction of clusters, even in applied zero-field conditions.

3. Calculations

Theoretical studies of water clusters use ab initio (Wei and Salahub, 1994), semiempirical (Hodges and Wales, 2000) and density functional (Jiang et al., 2000) methods. However, in contrast to neutral clusters, little is known about the structure of protonated water clusters. Very often calculations of building energies were performed in extended molecular orbital basis sets but for few clusters or for more clusters but in low sets. Often the interest of research is limited only to calculations of geometrical parameters of the clusters (Suh et al., 2000) and no dissociation energies are given.

In the present work, the geometrical optimizations were performed by the Restricted Hatree–Fock ab initio method with using 6-31G** and 6-311G** split-valence basis sets. Details of the method were described previously (Wróblewski et al., 2001), where calculations were performed also for smaller basis sets (3-21G and 4-31G). All calculated structures are shown in Fig. 5. For $H^+(H_2O)_3$ the only stable structure is a linear one—the closed protonated clusters tends to open. This is different than for the neutral trimmer (Wróblewski et al., 2001), which is closed in the lowest-energy configuration. For higher clusters we calculated four "families": open linear and star-shaped, and closed configurations based on cyclic tetramer and pentamer. For $H^+(H_2O)_4$ ion the lowest calculated energy is for the star-shaped configuration (Fig. 5, structure V) and is lower than for closed (Fig. 5, structure VI) and linear (Fig. 5, structure IV) by 4.9 and 5.0 kcal/mol, respectively. Similarly for $H^+(H_2O)_{5-7}$ clusters—linear configurations are less stable by 5.87, 7.51 and 8.47 kcal/mol than structures IX ($n=5$), XIV ($n=6$) and XVIII ($n=7$), respectively (in 6-311G** basis).

4. Comparison of dissociation energies

Theoretical dissociation energies of protonated water clusters have been made from equation:

$$E_D = E_n - (E_{n-1} + E_{H_2O}),$$

where E_n is the total energy of $H^+(H_2O)_n$ cluster, E_{n-1} the total energy of $H^+(H_2O)_{n-1}$ clusters and E_{H_2O} the total energy of water molecule.

Dissociation energies are reported only for "allowed" transitions, i.e. these which involve only detachment of one water group and do not require regrouping of other molecules in the clusters. Such a requirement reflects our experimental conditions: in a mutual equilibrium condition $n \leftrightarrow (n-1)$ it is improbable that more complex than one-molecule detachment ↔ attachment reactions take place.

The comparison of present results with other theories is too complex to be included in a single figure—it must be divided into possible allowed-dissociation pathways. In Fig. 6 we show, compare, our theoretical data with calculations of Jiang et al. (2000). One notes, generally, a good agreement between the present and Jiang et al.'s data, apart from structure VIII (see Fig. 5) for which (Jiang et al., 2000) energy is higher by 1.5 kcal/mol.

In Fig. 6 we show the dependence of the dissociation energy on the cluster dimension for different

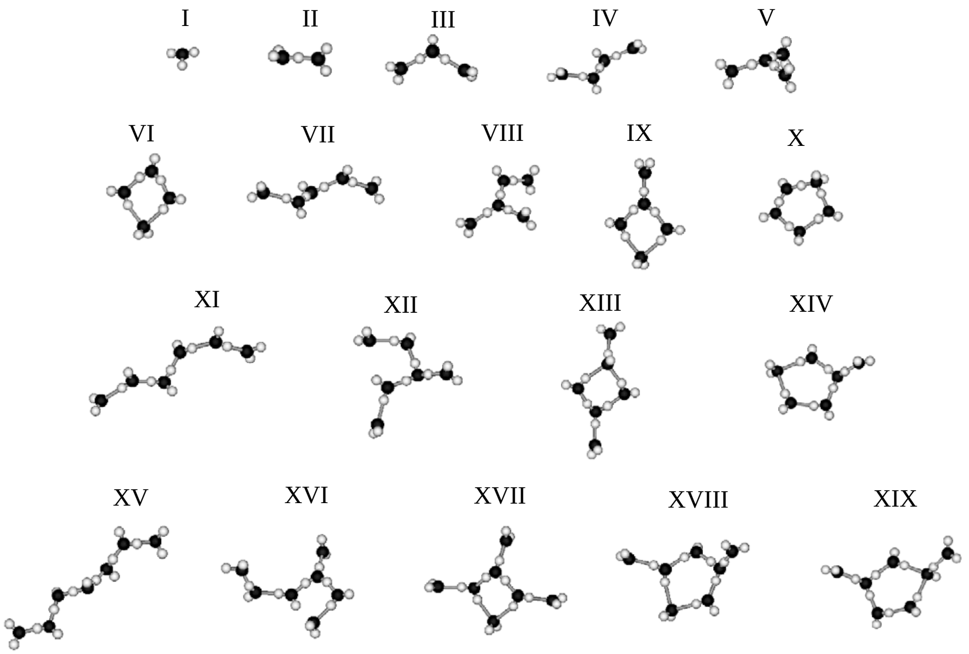

Fig. 5. Geometrical configurations of calculated protonated water clusters.

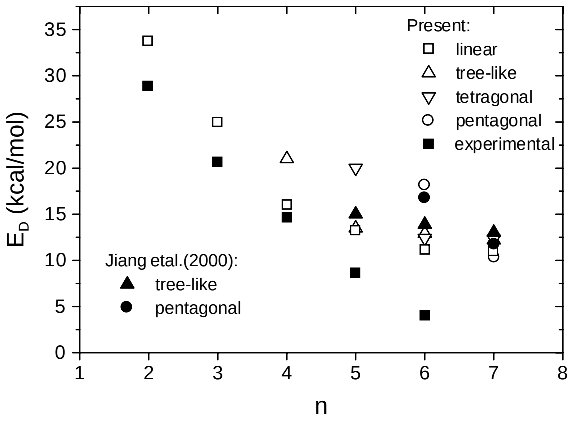

Fig. 6. Theoretical dissociation energies for different "families" of clusters compared to density functional calculations of Jiang et al. (2000).

allowed-dissociation "families": for all of them the dissociation energy lowers with increasing *n*. Our calculation shows, for example, that dissociation energy of $H^+(H_2O)_4$ cluster is higher than extrapolated tendency of heavier clusters. It can testify that for positively ionized water clusters $n = 4$ is a "magic" number, what we observe in some of our mass spectra, see Fig. 2.

In order to evaluate the feasibility of reaction Eq. (3) we have calculated the total energy of a neutral dimmer, which is −95446.12 kcal/mol. This lowers the threshold for dissociation of *n* clusters in two-body collisions by 6.4 kcal/mol. Thresholds for dissociation of clusters (extrapolation of curves as in Fig. 4) lie on average 3 kcal/mol below the values derived from "equilibrium" conditions—the agreement is reasonably good.

Finally, a preliminary evaluation of potential barriers in dissociation ↔ association transitions gives values of a few kcal/mol. For example, dissociation of the XIX heptamer into a tree-like hexamer passes through a local-minimum state lying 3.0 kcal/mol above the ground state.

5. Conclusion

We have developed a method of experimental studies of water cluster, simulating to a great extent atmospheric conditions, where these clusters are effectively observed. The method can be defined as a "swarm" one—clusters drifting in electrical field undergo mutual collisions. Determination of dissociation energies of clusters is intrinsically difficult in this method. However, the values derived from our simplified reasoning, are in good agreement with other determinations (Honma et al., 1993; Kebarle et al., 1967; Magnera et al., 1991).

The theoretical analysis shows that total energies of different conformers of the same size clusters can differ much, say by almost 6 kcal/mol for $n = 5$ and 7.5 kcal/mol for $n = 6$. The analysis shows that the dissociation energies can also vary, depending on a chosen "dissociation path". Our experimental data are close to the theoretical energies for a tree-like family clusters. These clusters are not the lowest-energy configurations, but lie close to them (1.3 kcal/mol above for $n = 7$).

Theoretical calculations show also that the internal (vibrational) energies of clusters at our experimental conditions are comparable to the dissociation energies. For example, the total energy of different vibrational modes populated at 300 K amounts to 5.4 kcal/mol for $n = 8$ and 4.5 kcal/mol for $n = 7$. The populating of different vibrational modes makes bigger the uncertainty on experimental determination of the dissociation energies for heavier clusters.

Future, "exact" experiments would possibly require selections of the conformers and their vibrational states.

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