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Dissociation pathways 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.

Keywords: Water, Clusters, Dissociation

1. Introduction

Hydrated ions and ionic water clusters are the subjects of increasing interest, both experimental [1,2] and theoretical [3,4]. Protonated water clusters constitute the most abundant ionic species in the low stratosphere; water ions are important in atmospheric nucleation and chemical reactions. Hydronium ions are present in interstellar gas [5] and molecular cloud, near the Galactic centre [6]. Recently, H_3O^+ ions have found large applications in a new-generation, high-sensitivity mass spectrometers using a "soft" ionisation i.e. the proton transfer for studies of complex molecules, mainly of biological interest [7].

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 or secondary ion mass spectrometry technique (SIMS) and by aggregation, for example in supersonic beams. 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 and quadrupole mass spectrometer with measured mass range up to 150 amu.

Mass spectra of $H^+(H_2O)_n$ ions with n=1-7 from the present experiment for two different pressures and drift voltages are shown in fig. 1. 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, for example 210 Td for n=4.

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 an equilibrium and obtaining these values is not so straightforward.

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. [1] and by Magnera et al. [8]. However, they studied disintegration of only one type of clusters $H^+(H_2O)_n$ at a time and without any third

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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 [8] or reaction with a third gas (CH_3CN) [1] 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 [1] and 16 to 18 kcal/mol from n=4 [8]. Additionally, such experiments can not 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).

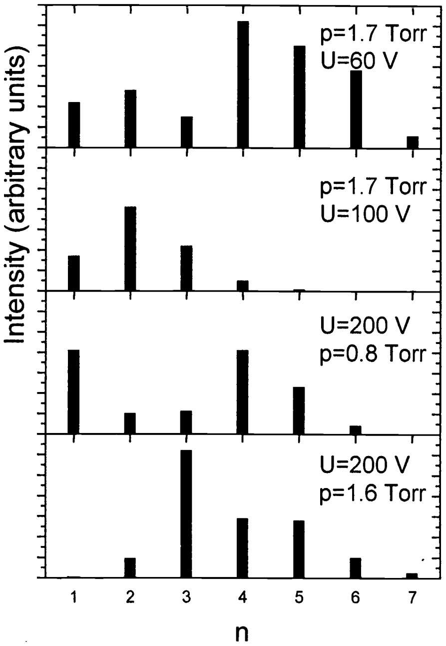

Fig. 1. Mass spectra of protonated water clusters at different experimental conditions.

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 of subtracting one water molecule.

Our experimental energies of dissociation are shown in fig. 2. They are in very good agreement with these of Magnera et al. [8] for n=2 and 3 (differences are below 10%). For n=4,5 disagreement increase to 30%. Results of Honma et al. [1] 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 the conditions of zero-field applied.

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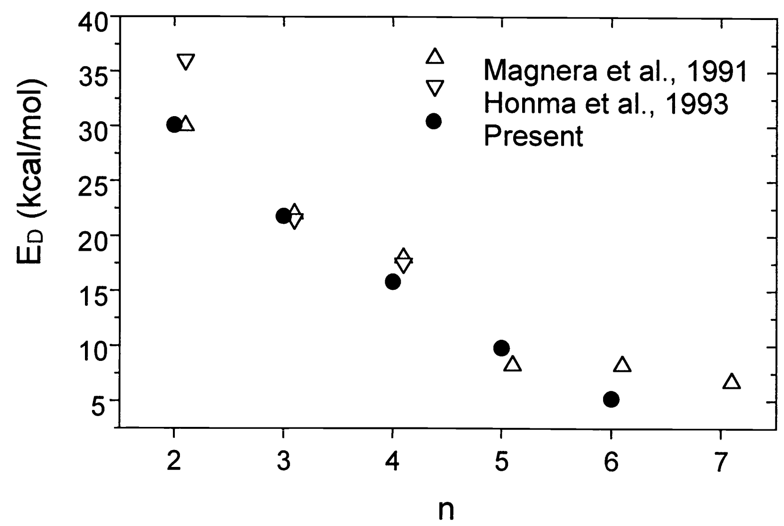

Fig.2. Experimental dissociation energies of water clusters.

3. Calculations

Our theoretical studies of water clusters use *ab initio* method. However, in the 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 [9]. Often the interest of researches is limited only to calculations of geometrical parameters of the clusters [10] and no dissociation energies are given.

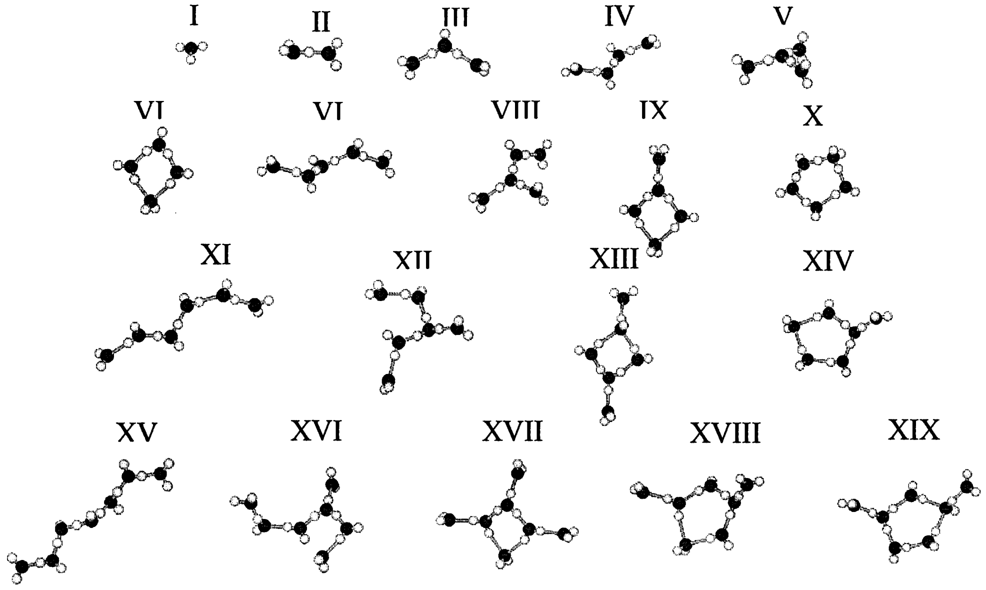

Fig. 3. Geometrical structures of water clusters.

In present work the geometrical optimisations were performed by the Restricted Hatree-Fock *ab initio* method with using 6-31G** and 6-311G** split-valence basis sets. Details of method were described previously [11], where calculations were performed also for smaller basis sets (3-21G and 4-31G). All calculated structures are shown below on the figure 3. 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 [11] 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 (structure V) and is lower

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than for closed (structure VI) and linear (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.

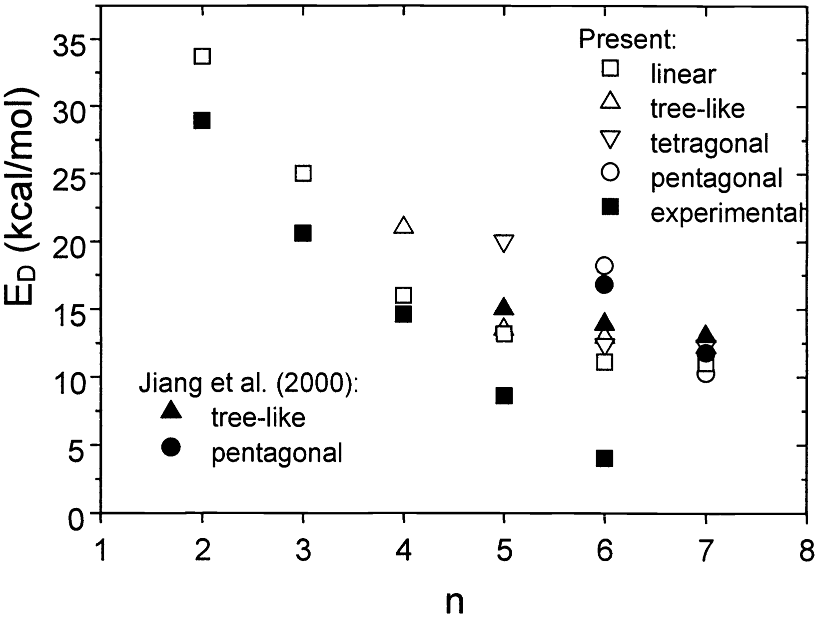

Fig. 4. Theoretical dissociation energies for different configurations of clusters compare to experimental values.

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. 4 we show comparison our theoretical data with calculations of Jiang et al. [3]. One notes generally a good agreement between present and Jiang et al.'s data, apart from structure VIII for which Jiang et al. [3] energy is higher by 1.5 kcal/mol.

In fig. 4 we show the dependence of the dissociation energy on the cluster dimension for different 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 ionised water clusters *n*=4 is a "magic" number, what we observe in some our mass spectra, see fig. 1.

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