Proton transfer reactions for ionized water clusters

T. Wròblewski, L. Ziemczonek, G. P. Karwasz

Institute of Physics, Pomeranian Pedagogical Academy, Arciszewskiego 22, 76-200 Slupsk, Poland

Received 29 April 2004

Calculations of formation energies of the ionized water clusters and energies of reactions between small (including less than eight water molecules) neutral and positively ionized water clusters are presented. Moreover, we discuss some reaction paths between neutral and positively charged dimers, trimers and tetramers and proton transfer reactions (PTR) between cyclic clusters and H_3O^+ ions which can appear in beam experiments on formation and ionization of water clusters. Calculations were made using ab initio Hartree–Fock method for 4–31G and 6–311G** atomic orbitals basis sets.

PACS: 36.40.Wa
Key words: water clusters, proton affinity

1 Introduction

Knowledge of ionic reactions is the fundamental problem in modeling low-temperature plasmas; dynamics of proton transfer is, in particular, important for ionization processes in electrospray mass spectroscopy and in proton–transfer mass spectroscopy. Hydronium ion (H_3O^+) is frequently used as the ionizing factors in this latter type of spectrometry [1]. However, as well known, in low pressure discharges also heavier ionized water clusters are formed [2]. In this work we calculate proton affinity energies for numerous configuration of ionized water cluster and mixed water–methanol clusters.

Atomic or molecular clusters – intermediate structures between gas and condensed phase are interesting in many fields of science. Studies of physical properties of clusters like geometrical structures, dissociation energies and their interaction with atoms, molecules and surfaces of solid play great role in contemporary physics, chemistry, ecology, geophysics, biology and physiology. In particular, neutral and ionized water clusters have been studied for many years, both experimentally [2]–[7] and theoretically [8]–[14]. Studies of condensation processes can be helpful in understanding of anomalous properties of water, for example their temperature–density behaviour at about 4 °C.

We can distinguish two conceptually opposite practical approaches to generation of water clusters. The first starts with a macroscopic solution to be dispersed into small droplets reduced by evaporation, for example in electrospray method [7]. In the second method, single atoms, molecules or ions aggregate with water molecules or other ligands around it. Example of this second method are supersonic beam techniques [5] or electrical HF and DC discharges in pure water vapour [2]. Mass spectra in different types of experiments are quite complex, i.e. relative abundances of $H^+(H_2O)_{21}$ ion for bigger clusters [4], [7] and $H^+(H_2O)_4$ ion for smaller clusters

[2], [3] are higher. In the present work we discuss some aspects of positively ionized water clusters formation in three cases: (i) proton affinity of neutral cyclic water clusters and formation by proton transfer from ion of hydronium, (ii) reaction between small neutral and ionized water clusters and (iii) a clusters growth by gradual association of water molecules.

2 Method

Ab initio calculations for neutral and protonated clusters were carried out at the Restricted Hartree Fock (RHF) method. Several molecular orbitals basis–sets at the split-valence level: 3–21G, 4–31G (only s and p, without d–orbitals) and 6–31G** and 6–311G** (with d–orbitals) were tested [15]–[17], not all of them for the same configurations. At the split–valence level, primitive exponents are shared between s and p functions for the valence shells [15]. Usually, for optimising the computational time, first the same configurations were calculated in lower basis, and only after obtaining the "almost–final" geometrical configuration, the highest molecular orbitals basis sets were applied. Final calculations have been performed in 6–311G** base with two polarization functions and split valence orbitals to compute the total energies of clusters and in 4–31G base to compute zero point vibrational energies.

3 Results and discussion

Geometrical optimization of neutral and protonated water clusters were made for 15 different structures. All the optimized structures are shown in Fig. 1. In the case of neutral clusters we calculated total energies for open water dimer (I), cyclic water trimer to pentamer (II–IV), case heksamer (V) and prism heptamer and octamer (VI, VII). Calculations for protonated water clusters were performed for tree–like monomer to tetramer (VIII–XI) and closed pentamer to octamer (XII–XV). Both neutral and ionized clusters are reported as global minimum energy [12], [13].

Neutral water clusters, produced for example in supersonic beam, must be ionized to detect them in mass spectrometers. In this case protonated water clusters are detected and their formation is explained by reactions between products of ionization and neutral components of beam. However, to the authors knowledge there are no calculations of these reaction energies.

The first process which may lead to formation of ionized water clusters are proton transfer reactions. Proton transfer in water clusters has been studied theoretically using molecular dynamic [18], ab initio Hartree–Fock method [19] and density functional theory [20], but only sporadically in the calculations of formation energy of protonated water clusters [10]. In this paper we calculated proton affinity (PA) of global minimum [13] neutral water clusters (structures II–VII), defines as $PA = E(\mathrm{H}^+(Y)) - E(Y)$ and corrected with zero–poin vibrational energies, where E is the total energy and $Y = (\mathrm{H_2O})_n$.

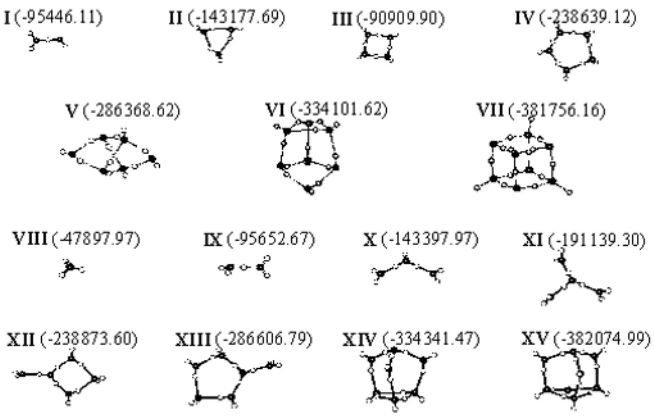

Fig. 1. Geometrical configurations and total energies (in kcal/mol) of neutral (structures I–VII) and protonated (structures VIII–XV) water clusters.

PA calculated energies vs. cluster size are presented in Fig. 2 and compared to the results of Cheng [10] and Kawai *et al.* [21]. We note that these energies increase with n but the increase between $(H_2O)_7$ and $(H_2O)_8$ is bigger than in other cases. This result agrees with the studies on fragmentation of water clusters [22], where it can be noted that the ion intensity of $H^+(H_2O)_7$ is relatively smaller than of $(H_2O)_8$ in mass spectra of clusters.

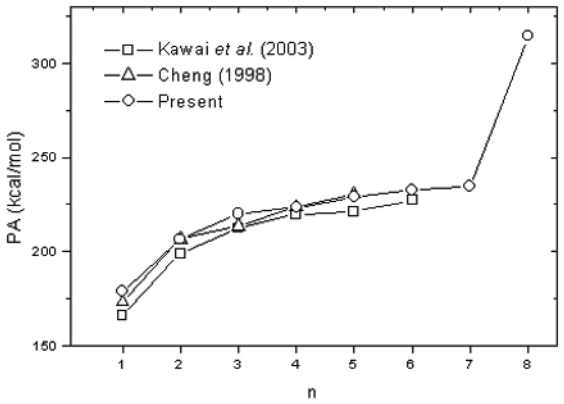

Fig. 2. Proton affinities of water clusters compared to values of Cheng [10] and Kawai et al. [21].

Reactions between neutral and protonated water clusters can be the second possible mechanism of cluster growth. We calculated the reaction energies between water monomer, linear dimer, cyclic trimer and tetramer and protonated water

tetramer (the latter structure essentially completes the first solvation layer, as already concluded by Eigen [23]), according to the scheme (energy values are given in brackets):

$$H_2O + H^+(H_2O)_4 = H^+(H_2O)_5\ (14.02\,\text{kcal/mol})\,, \tag{1}$$

$$(H_2O)_2 + H^+(H_2O)_4 = H^+(H_2O)_6\ (21.37\,\text{kcal/mol})\,, \tag{2}$$

$$(H_2O)_3 + H^+(H_2O)_4 = H^+(H_2O)_7\ (24.48\,\text{kcal/mol})\,, \tag{3}$$

$$(H_2O)_4 + H^+(H_2O)_4 = H^+(H_2O)_8\ (25.78\,\text{kcal/mol})\,, \tag{4}$$

There can be noted that energies of reactions [2]–[4] monotonically rise and only energy of reaction [1] is lower. It is caused by the fact that the energy of dimerisation of water, which in our calculation is 5.56 kcal/mol, has not been taken into account.

In different type of experiments protonated water clusters are produced during ionization of pure water vapour by electron, proton and α particle impact [3] or in electric discharges [2]. In this case clusters are growing probably by gradual association of water molecules:

$$H^+(H_2O)_{n-1} + H_2O = H^+(H_2O)_n \tag{5}$$

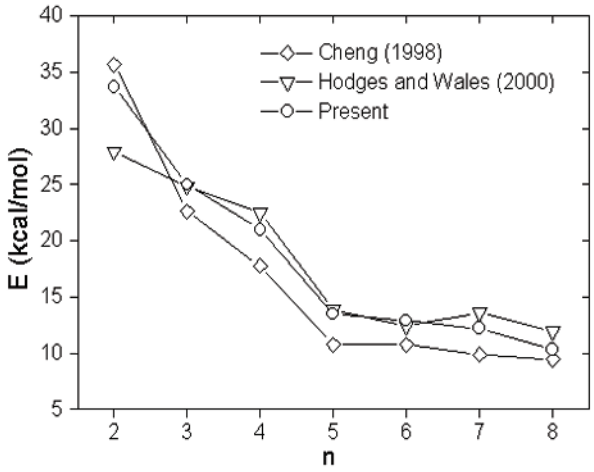

Fig. 3. The formation energies of $H^+(H_2O)_n$ clusters calculated in 6–311G** RHF level compared with molecular dynamic calculations of Cheng [10] and KJ model potential calculations of Hodges and Wales [12].

In Fig. 3 we show calculated energies of protonated water clusters formation compared to values of others authors. Generally, the formation energies decrease with number of clusters. The present data agree well with those of Cheng [10] for $n = 2$ and 3 clusters, but for $n = 4 \ldots 8$ they are a bit higher (note that Cheng

calculated different geometrical conformers). Our values agree also well with data of Hodges and Wales [12] except of $n = 2$ clusters for which present value is higher by 5.8 kcal/mol.

4 Conclusions

The present calculations show that the energies of proton transfer and reaction between neutral and ionized water clusters increase with clusters number in contrast to their growth by association of water molecules. We suggest that these energies should be taken into consideration in the analysis of mass spectra in different experiments.

References

[1] A. Hansel, N. Oberhofer, W. Lindinger, V. A. Zenevich, G. B. Billing: Int. J. Mass Spectr. **185/186/187** (1999) 559.

[2] T. Wróblewski, E. Gazda, G. Karwasz and J. Mechlińska–Drewko: Int. J. Mass Spectr. **207** (2001) 97.

[3] P. Kebarle, S. K. Searles, A. Zolla, J. Scarborough and M. Arshadi: J. Am. Chem. Soc. **89** (1967) 6393.

[4] X. Yang and A. W. Castleman Jr.: J. Am. Chem. Soc. **111** (1989) 6845.

[5] K. Honma, L. S. Sunderlin and A. W. Castelman Jr: J. Chem. Phys. **99** (1993) 1623.

[6] T. F. Magnera, D. E. David, and J. Michl: Chem. Phys. Lett. **182** (1991) 363.

[7] G. Hulthe, G. Stenhagen, O. Wennerström and C. H. Ottosson: J. Chromatogr. **777** (1997) 155.

[8] M. D. Newton: J. Chem. Phys. **67** (1977) 5535.

[9] C. A. Deakyne, M. Meot–Ner (Mautner), C. L. Campbell, M. G. Hughes and S. P. Murphy: J. Chem. Phys. **84** (1986) 4958.

[10] H. P. Cheng: J. Phys. Chem. A **102** (1998) 6201.

[11] J. Ch. Jiang, Y. Sh. Wang, H. Ch. Chang, Sh. H. Lin, Y. T. Lee, G. Niedner-Schatteburg and H. Ch. Chang: J. Am. Chem. Soc. **122** (2000) 1398.

[12] M. P. Hodges and D. J. Wales: Chem. Phys. Lett. **324** (2000) 279.

[13] D. J. Wales and M. P. Hodges: Chem. Phys. Lett. **286** (1998) 65.

[14] T. Wróblewski, G. P. Karwasz and L. Ziemczonek: Słupskie Prace Matematyczno-Fizyczne **1** (2001) 277.

[15] J. S. Binkley, J. A. Pople, W. J. Hehre: J. Am. Chem. Soc. **102** (1980) 939.

[16] R. Krishnan, J. S. Kinkley, R. Seeger, J. A. Pople: J. Chem. Phys. **72** (1980) 650.

[17] A. D. McLean, G. S. Chandler: J. Chem. Phys. **72** (1980) 5639.

[18] H. P. Cheng and J. L. Krause: J. Chem. Phys. **107** (1997) 8461.

[19] A. Lami and G. Villani: Chem. Phys. Lett. **238** (1995) 137.

[20] P. L. Geissler, T. Van Voorhis and Ch. Dellago: Chem. Phys. Lett. **324** (2000) 149.

[21] Y. Kawai, S. Yamaguchi, Y. Okada, K. Takeuchi, Y. Yamauchi, Sh. Ozawa, H. Nakai: Chem. Phys. Lett. **377** (2003) 69.

[22] T. Schindler, Ch. Berg, G. Nieder–Schatteburg and V. E. Bondybey: Chem. Phys. Lett. **250** (1996) 301.

[23] M. Eigen: Angew. Chem. **75** (1963) 489.