

# CLUSTERS WHICH OCCUR AT INTERFACES OF WATER AND ICE

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## 1 INTRODUCTION

Although water and ice are the most usual substances in the world they are in fact very mysterious. In our previous works<sup>1,2</sup> we have used the group-theoretical methods. They gave straightforward rules for example for Raman scattering of light or activity in infra-red radiation. However it appears that water not only in solid and liquid states has interesting properties. Important are intermediate phases – so called clusters. Water clusters have been the subject of many experimental and theoretical investigations because of their importance in understanding cloud and ice formation, solution chemistry and a large number of biochemical processes<sup>3,4</sup>. The water clusters may adsorb plenty of organic molecules (methanol, acetone, acetaldehyde, formic acid, benzene *etc.*)<sup>5,6,7,8,9</sup>. Adsorption of foreign molecules is also important from atmospheric and astrochemistry points of view especially for the mechanism of catalytic depletion of stratospheric ozone or heterogeneous reactions occurring on the surface of polar stratospheric clouds<sup>10,11,12,13</sup>.

## 2 METHOD AND RESULTS

We have studied neutral pure water clusters and neutral mixed water clusters which contain hydrogen chloride  $\text{HCl}-(\text{H}_2\text{O})_n$  and methanol  $\text{CH}_3\text{OH}-(\text{H}_2\text{O})_n$ ,  $n$  varying from 1 to 6. Configurations of clusters have been calculated by Hartree-Fock *ab-initio* method with  $6-311 G^{**}$  molecular basis set. The advantage of using this set is that calculations are relatively fast if compared to more extended basis sets (for example  $6-311++G^{**}$  set which includes diffuse functions), so numerous configurations can be easily optimized, but the precision of calculations, in terms of dissociation energies of clusters, is still high, see for example our previous work for protonated water clusters<sup>14</sup>. Using of the molecular basis sets with diffuse functions is essential in case of negative charged molecules. We have studied only neutral clusters.

Table 1 gives the total energies for CH<sub>3</sub>OH, HCl and H<sub>2</sub>O molecules. The data of this table are used to calculate the energy differences in Table 2 and 3.

**Table 1** Total energy for methanol, hydrogen chloride and water

	kcal/mol		
	methanol	hydrogen chloride	water
E <sub>tot</sub>	-72192,91	-288713,96	-47720,28
ZPE	34,38	4,47	14,37
E <sub>tot</sub> <sup>*</sup>	-72158,53	-288709,49	-47705,91

\* - with the zero point energy correction

Results are given in Tables 2 and 3 where E<sub>tot</sub> is the total energy of the structure, E<sub>D</sub> – the dissociation energy (the energy difference between the total energy of the cluster and the energies of the separate parts), SE – the stabilization energy (the energy difference between the total energy of the cluster and the energies of the individual molecules) and ZPE – the zero point energy of vibrations. The stabilization energies vary from 4,47 to 36,82 kcal/mol for clusters containing hydrogen chloride and from 22,25 to 58,24 kcal/mol for those with methanol, depending of the number of water molecules. Dissociation energies for the pure water clusters given in Figure 1 are in good agreement with experimental results for the protonated water clusters<sup>14</sup>.

**Table 2** Dissociation and stabilization energies for CH<sub>3</sub>OH-(H<sub>2</sub>O)<sub>n</sub> clusters

	n=					
	1	2	3	4	5	6
E <sub>tot</sub>	-119937,17	-167668,44	-215400,57	-263129,74	-310859,08	-358588,35
E <sub>D</sub>	-23,98	-10,99	-11,85	-8,89	-9,06	-8,99
SE	-23,98	-34,97	-46,82	-55,71	-64,77	-73,76
ZPE	50,48	68,18	85,52	101,99	118,9	136,12
E <sub>tot</sub> <sup>*</sup>	-119886,69	-167600,26	-215315,05	-263027,75	-310740,18	-358452,23
E <sub>D</sub> <sup>*</sup>	-22,25	-7,66	-8,88	-6,79	-6,52	-6,14
SE <sup>*</sup>	-22,25	-29,91	-38,79	-45,58	-52,1	-58,24

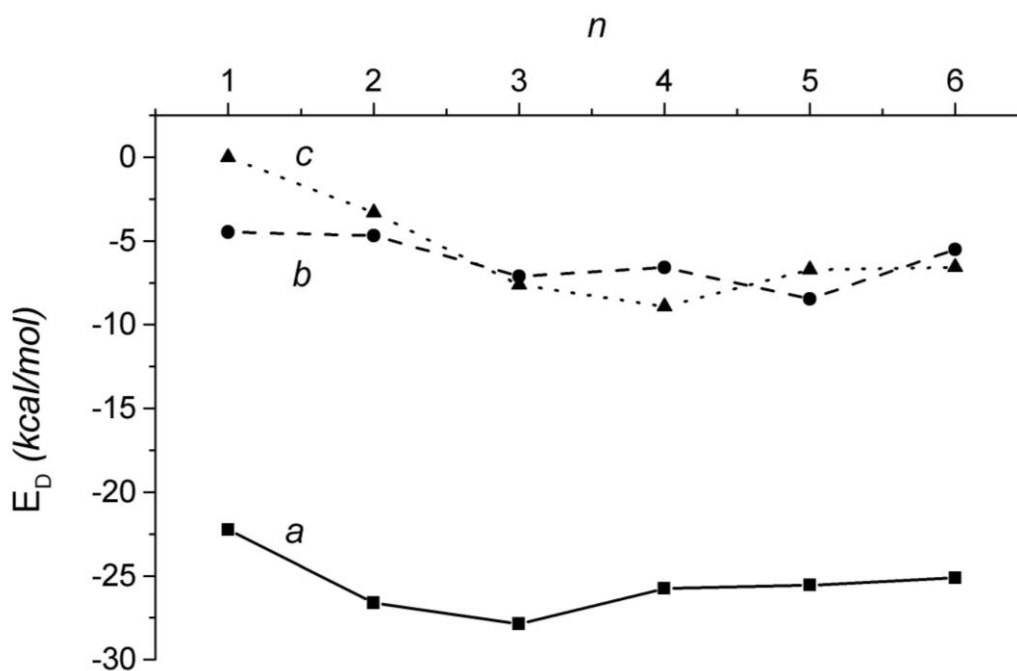
\* - with the zero point energy correction

**Table 3** Dissociation and stabilization energies for HCl-(H<sub>2</sub>O)<sub>n</sub> clusters

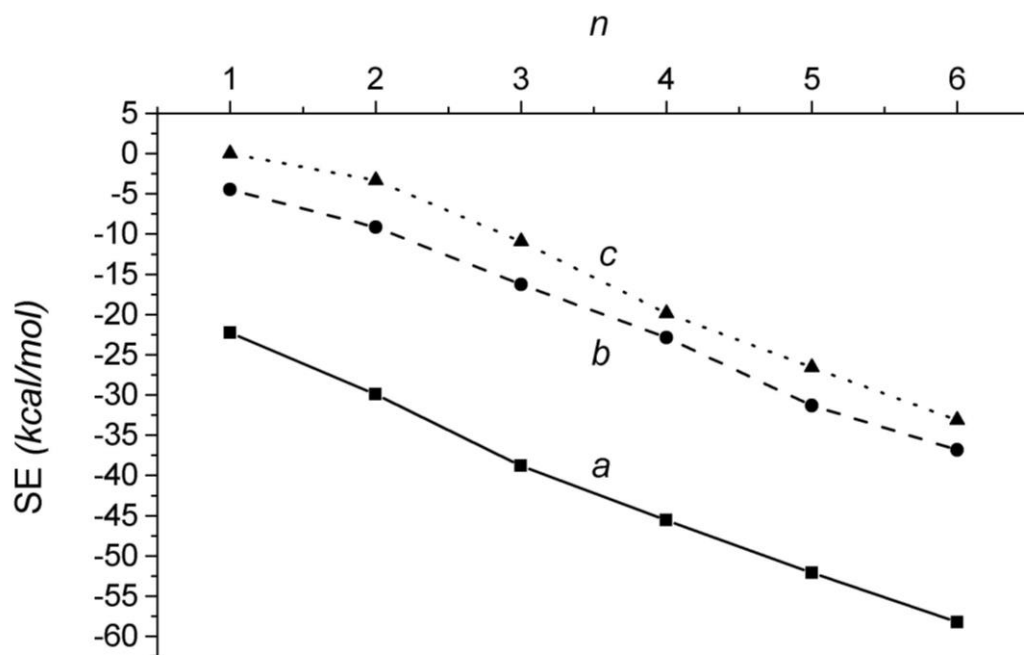
	n=					
	1	2	3	4	5	6
E <sub>tot</sub>	-336440,39	-384168,3	-431898,41	-479627,61	-527359,54	-575088,05
E <sub>D</sub>	-6,15	-7,63	-9,83	-8,92	-11,65	-8,23
SE	-6,15	-13,78	-23,61	-32,53	-44,18	-52,41
ZPE	20,52	37,84	54,93	71,63	89,19	106,28
E <sub>tot</sub> <sup>*</sup>	-336419,87	-384130,46	-431843,48	-479555,98	-527270,35	-574981,77
E <sub>D</sub> <sup>*</sup>	-4,47	-4,68	-7,11	-6,59	-8,46	-5,51
SE <sup>*</sup>	-4,47	-9,15	-16,26	-22,85	-31,31	-36,82

\* - with the zero point energy correction

Figures 1 and 2 show the dissociation and stabilization energies for the mixed water clusters calculated in Tables 2 and 3. We can see that the most stable clusters with methanol and hydrogen chloride are the clusters containing 3 and 5  $\text{H}_2\text{O}$  molecules. The dissociation and stabilization energies are the lowest for the water clusters contained the methanol molecules. These energies for the pure water clusters and for the mixed clusters with hydrogen chloride are almost the same although there is a problem of H-bonds formation. This is the topic for the future study.

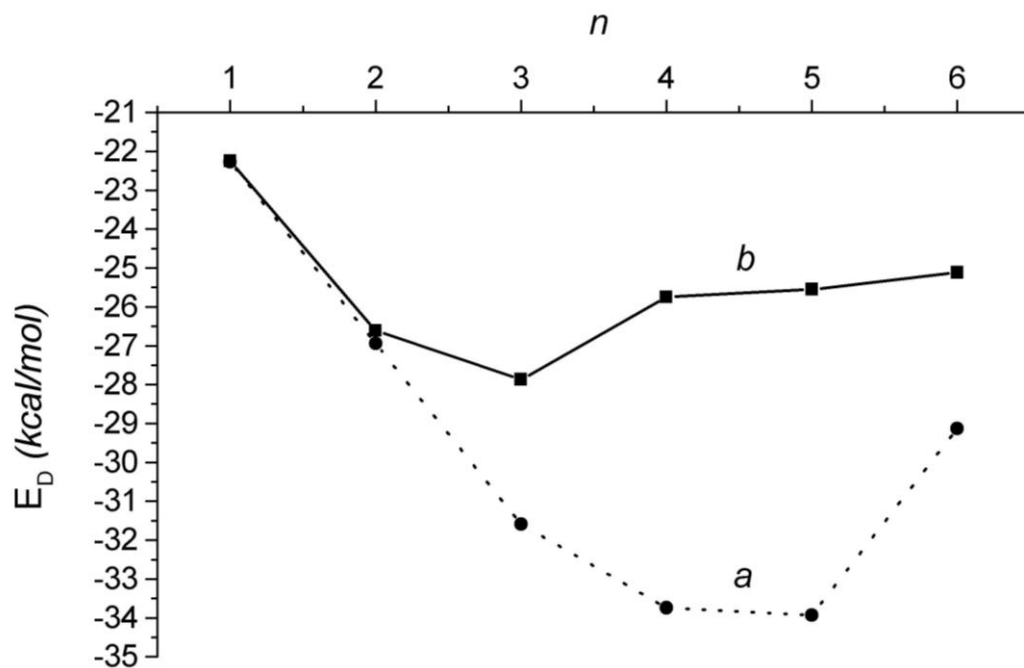


**Figure 1** Dissociation energy of the guest molecule in  $\text{CH}_3\text{OH}-(\text{H}_2\text{O})_n$  (a),  $\text{HCl}-(\text{H}_2\text{O})_n$  (b) and  $\text{H}_2\text{O}-(\text{H}_2\text{O})_n$  (c) clusters as a function of the number  $n$  of  $\text{H}_2\text{O}$  molecules.

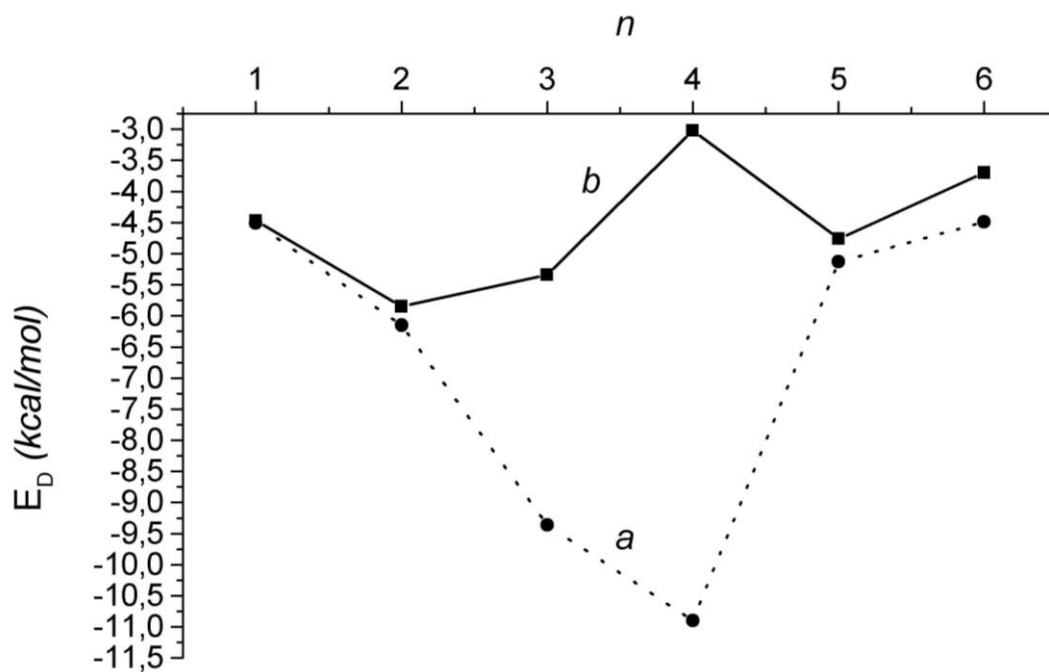


**Figure 2** Stabilization energy for  $CH_3OH-(H_2O)_n$  (a),  $HCl-(H_2O)_n$  (b) and  $H_2O-(H_2O)_n$  (c) clusters as a function of the number  $n$  of  $H_2O$  molecules.

Using information from Table 1 we can calculate the dissociation energies, as reported in Tables 2 and 3, in case of separation from the mixed water clusters of the methanol molecule (Figure 3) and for the hydrogen chloride molecule (Figure 4). This is done also for the adiabatic separation. In this separation configurations of remaining  $(H_2O)_n$  structure are the same that in mixed clusters and differ from pure optimized water clusters.

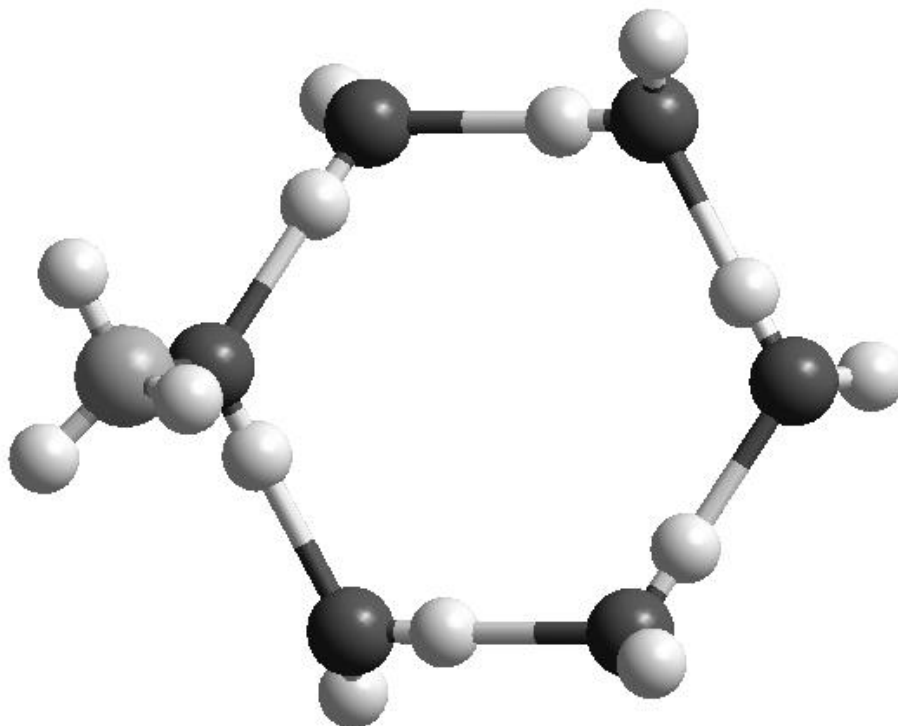


**Figure 3** Dissociation energy in case of separation of the methanol molecule from  $\text{CH}_3\text{OH}-(\text{H}_2\text{O})_n$  clusters, a - adiabatic separation, b - after relaxation of the remaining structure  $(\text{H}_2\text{O})_n$ .



**Figure 4** Dissociation energy in case of separation of the methanol molecule from  $\text{HCl}-(\text{H}_2\text{O})_n$  clusters, a - adiabatic separation, b - after relaxation of the remaining structure  $(\text{H}_2\text{O})_n$ .

From Figure 3 we see that for  $\text{CH}_3\text{OH}-(\text{H}_2\text{O})_n$  not only the water clusters with three and five water molecules are the most stable but also with four ones. But for  $\text{HCl}-(\text{H}_2\text{O})_n$  situation is different (Figure 4). Remaining  $(\text{H}_2\text{O})_n$  structure for  $n=4$  changes its configuration very significant. This is result of the strong H bonds.



**Figure 5** *The water cluster contained the methanol molecule ( $\text{CH}_3\text{OH}$  – left) and five water molecules.*

### 3 CONCLUSION

Exploiting quantum mechanical methods we can obtain interesting results concerning not only values of energies of different water clusters but also their behaviour in interaction with other molecules. For example similar energies of pure water clusters and mixed clusters with hydrogen chloride are important in understanding of photodissociation processes in stratosphere<sup>15</sup>. We can use our considerations to the water clusters containing other molecules<sup>16</sup>. We should also consider protonated and negatively charged clusters. This is important in investigation of the charge transfer for example in storm clouds. And last remark. From Figure 5 we see how essential are laws of symmetry – how is built-in the methanol molecule in the water cluster. The physical system is so built that its energy is the lowest. In quantum chemistry we can say that the symmetry results from the cooperativity of the H bonds. Recently<sup>17-23</sup> we see that there exist stable mixed methanol and hydrogen chloride clusters containing up to 4-5 molecules of water. Similar calculation has been applied also to geometrical optimizations of simple organic compounds<sup>24</sup>.

## References

- 1 L. Ziemczonek and M. Suffczyński, *Il Nuovo Cimento*, 1991, **13**, 55.
- 2 L. Ziemczonek, in *Proceedings of the International School on Symmetry and Structural Properties of Condensed Matter, 6-12 Sept. 1990, Zajaczkowo near Poznań, Poland*, ed. by W. Florek, T. Lulek and M. Mucha, World Scientific, 1991, p. 403.
- 3 S. Maheshwary, N. Patel, N. Sathyamurthy, A.D. Kulkarni and S.R. Gadre, *J. Phys. Chem. A*, 2001, **105**, 10525.
- 4 Ch.J. Burnham, J. Li, S.S. Xantheas and M. Leslie, *J. Chem. Phys.*, 1999, **110**, 4566.
- 5 M. Ahmed, C.J. Apps, C. Huges, N.E. Watt and J.C. Whitehead, *J. Phys. Chem. A*, 1997, **101**, 1250.
- 6 M. Compoin, C. Toubin, S. Picaud, P.N.M. Hoang and C. Girardet, *Chem. Phys. Lett.*, 2002, **365**, 1.
- 7 L. Ziemczonek, T. Wróblewski and G. P. Karwasz, *Book of Abstracts, LEEMI IV – NEGATIVE IONS: Experiment and Theory, 6-9 Oct. 2005, Castle Smolenice, Slovakia*, Alexander von Humboldt Stiftung, European Science Foundation, 2005, p. 46.
- 8 D.J. Safarik, R.J. Meyer and C.B. Mullins, *J. Vac. Sci. Technol. A*, 2001, **19**, 1537.
- 9 S. Bobev and K.T. Tait, *American Mineralogist*, 2004, **89**, 1208.
- 10 R.G. Hynes, J.C. Mössinger and R.A. Cox, *Geophys. Research Lett.*, 2001, **28**, 2827.
- 11 C. Toubin, P.N.M. Hoang, S. Picaud and C. Girardet, *Chem. Phys. Lett.*, 2000, **329**, 331.
- 12 C. Toubin, S. Picaud, P.N.M. Hoang, C. Girardet, R.M. Lynden-Bell and J.T. Hynes, *J. Chem. Phys.*, 2003, **118**, 9814.
- 13 S. Haq, J. Harnett and A. Hodgson, *J. Phys. Chem. B*, 2002, **106**, 3950.
- 14 T. Wróblewski, L. Ziemczonek, E. Gazda and G.P. Karwasz, *Radiation Physics and Chemistry*, 2003, **68**, 313.
- 15 Q. Li and J. R. Huber, *Chem. Phys. Lett.*, 2002, **354**, 120; 2001, **345**, 415.
- 16 B. Fluckiger and M.J. Rossi, *J. Phys. Chem. A*, 2003, **107**, 4103.
- 17 L. Turi, *J. Chem. Phys.*, 1999, **110**, 10364.
- 18 I. Bakó, P. Jedlovsky and G. Pálinkás, *J. Mol. Liquids*, 2000, **87**, 243.
- 19 M. Tsuchiya, Y. Shida, K. Kobayashi, O. Taniguchi and S. Okouchi, *I. J. Mass Spectrom*, 2004, **235**, 229
- 20 S.V. Shevkunov, *Colloid Journal*, 2004, 66, 495.
- 21 E.G. Goken and A. W. Castelman Jr., *J. Geophys. Res.*, 2010, **115**, D16203.
- 22 F.M. Balci and N. Uras-Aytemiz, *J. Phys. Chem. A*, 2011, **115**, 5943.
- 23 F.M. Balci, N. Uras-Aytemiz, R. Escribano and P.C. Gómez, *Comput. Th. Chem.*, 2014, **1038**, 71.
- 24 T. Wróblewski, L. Ziemczonek, K. Szerement and G.P. Karwasz, *Czech. J. Phys*, 2006, **56**, B1110.