Protonated Water Clusters in TPC Detector

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Proposal protonated water clusters (n = 1-9)

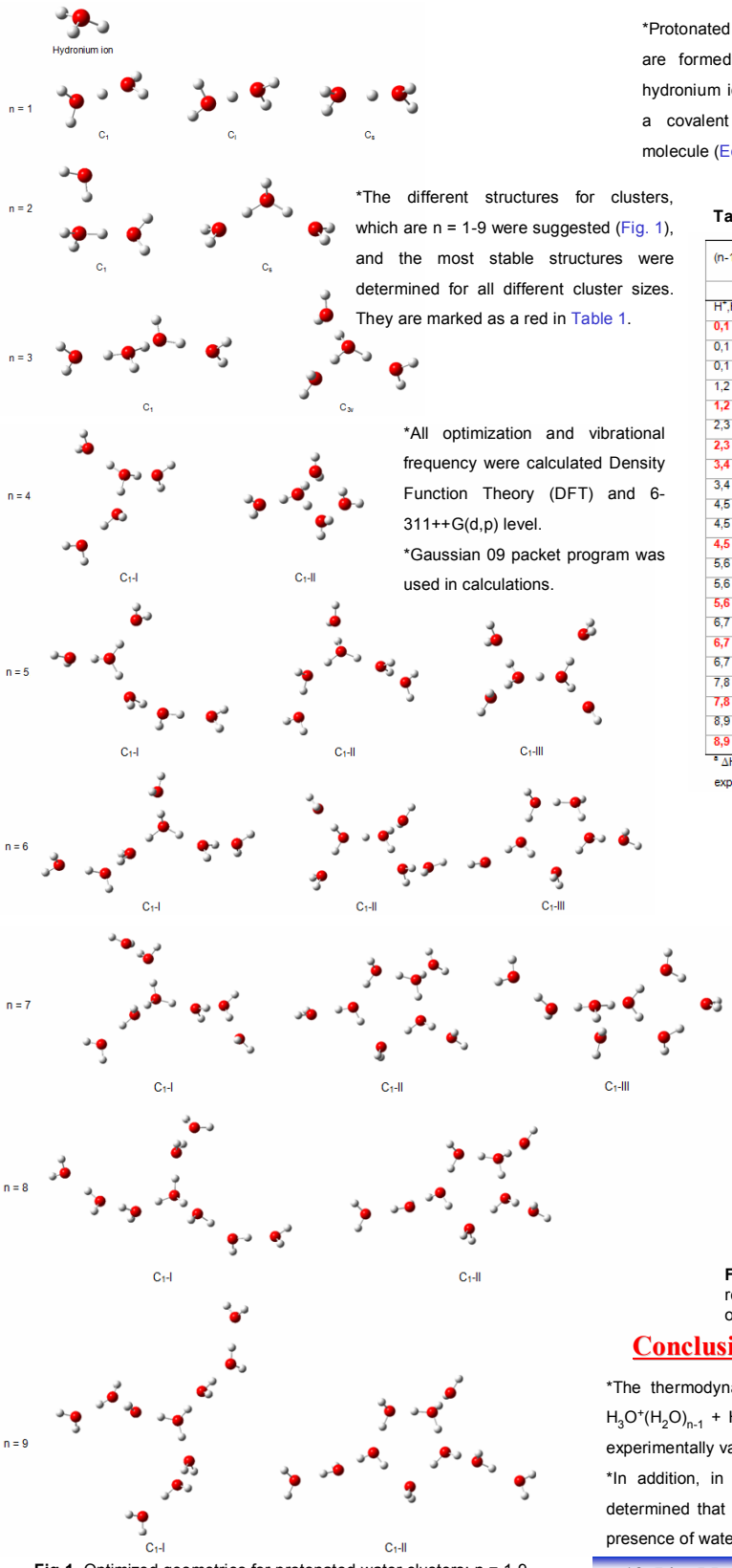

Fig.1. Optimized geometries for protonated water clusters: n = 1-9

*The different structures for clusters, which are n = 1-9 were suggested (Fig. 1), and the most stable structures were determined for all different cluster sizes. They are marked as a red in Table 1.

*All optimization and vibrational frequency were calculated Density Function Theory (DFT) and 6-311++G(d,p) level.

*Gaussian 09 packet program was used in calculations.

Formation of protonated water clusters

*Protonated water clusters with n≥1 are formed around a very stable hydronium ion in which proton forms a covalent bond with the water molecule (Eq. 1 and 2).

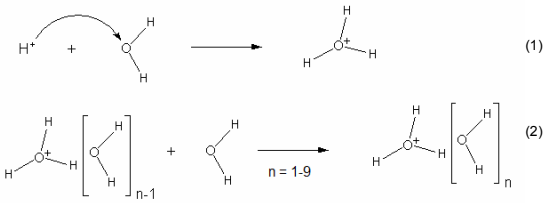

Table 1 Data for the Equilibria: $H_3O^+(H_2O)_{n-1} + H_2O = H_3O^+(H_2O)_n$[a]

(n-1,n)	Symmetry point	-ΔH°n-1,n					-ΔS°n-1,n					-ΔG°n-1,n			-pK
		DFT	b	c	d	e	DFT	b	c	d	e	DFT	d	e	
H+,H2O+	C2v	687.8		689.7		690.3	84.7					662.6			
0,1	C1	154.7	133.7	146.3	132.2	150.6	75.4	105.0	126.2	101.7	139.3	132.2	101.7	104.6	23.2
0,1	Cs	145.8					62.4					127.2			
0,1	Cs	143.5					74.5					121.3			
1,2	C1	73.9					115.8					39.4			
1,2	Cs	93.1	89.9	84.4	81.6	93.3	128.8	104.7	98.6	90.8	121.3	54.8	54.4	56.9	9.6
2,3	C1	70.3					81.3					46.1			
2,3	C2v	76.9	76.6	74.8		71.1	84.9	120.7	118.7		118.4	51.6	39.7	35.6	9.0
3,4	C1-I	56.0	59.6	53.1		64.0	90.9	122.7	97.8		136.3	28.9	23.4	23.0	5.1
3,4	C1-II	44.8					47.5					30.6			
4,5	C1-I	50.8					91.8					23.4			
4,5	C1-II	39.6					76.2					16.8			
4,5	C1-III	48.0	53.2	48.5		54.4	74.9	123.1	104.5		126.8	25.7	17.2	16.3	4.5
5,6	C1-I	42.3					118.5					7.0			
5,6	C1-II	47.2					111.8					13.9			
5,6	C1-III	48.8	68.2	44.7		49.0	112.5	198.3	109.1		123.8	15.3	12.6	11.7	2.7
6,7	C1-I	38.6					90.5					9.5			
6,7	C1-II	40.5				43.1	82.3				113.0	16.0			2.8
6,7	C1-III	38.9					87.5					12.9			
7,8	C1-I	34.7					89.2					8.3			
7,8	C1-II	37.3					90.5					10.3			1.8
8,9	C1-I	31.1					89.2					7.5			
8,9	C1-II	33.2					93.4					5.3			0.9

[a] ΔH° and ΔG° in kJ/mol, ΔS° in J/mol. Standart state 1 atm. DFT are our calculated values in present work, b, c, d, e and f are experimental values in literature. [b]Likholyot [19], [c]Hiraoka [20], [d]Cunningham [6], [e]Kebarle [5].

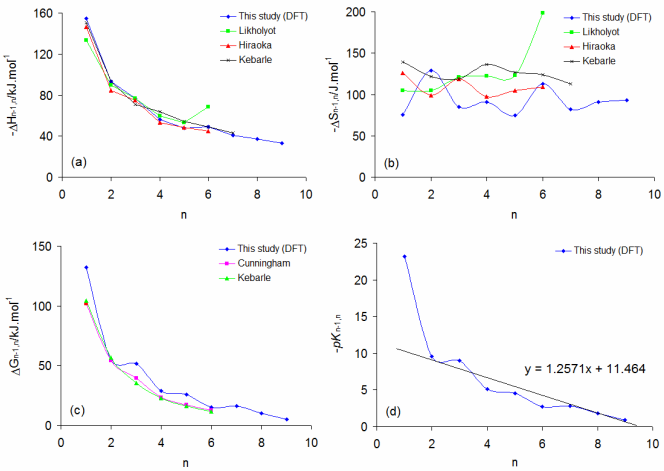

Fig.2. Comparison of enthalpy, entropy and Gibbs free energy changes for proton hydration reactions obtained in this work with previous data by Kebarle, Likholyot, Hiraoka, Cunninghans and our DFT calculations.

Conclusion

*The thermodynamic parameters are $\Delta H^\circ_{n-1,n}$, $\Delta G^\circ_{n-1,n}$, $\Delta S^\circ_{n-1,n}$ and equilibrium constants $K_{n-1,n}$ for reactions $H_3O^+(H_2O)_{n-1} + H_2O = H_3O^+(H_2O)_n$ were calculated at same basis set, and calculated results are fairly close to experimentally values from literature (Fig. 2).

*In addition, in conclusion of all theoretical calculations, the cluster size of protonated water cluster were determined that n may be between 6 and 9 in atmospheric pressure and at room temperature. Therefore, the presence of water in TPC detectors, the mobility of ions is reduced.