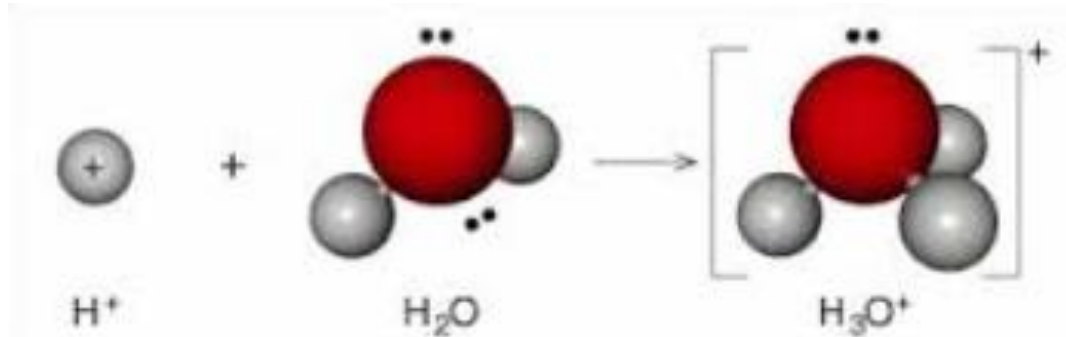


REACTIONS OF WATER AT THE MOLECULAR LEVEL: PROTONATED WATER CLUSTERS

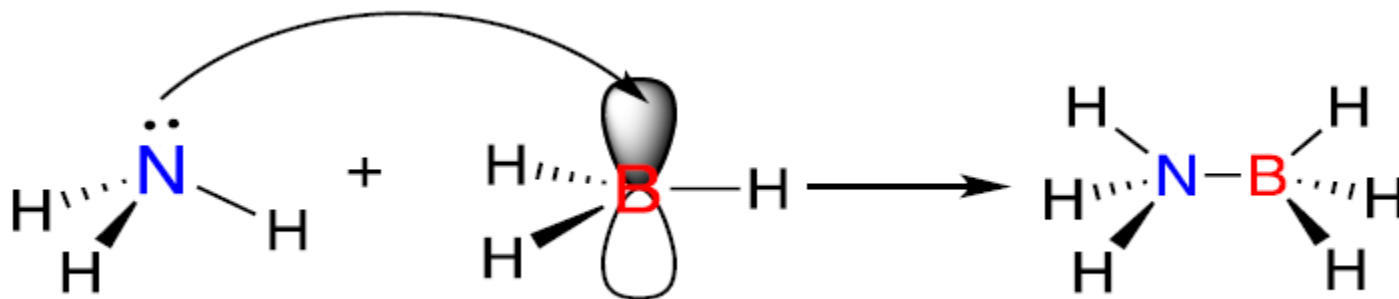
YUNUS KAYA
ULUDAG UNIVERSITY
BURSA, TURKEY

Formation of hydronium ion !!



- This is a mechanism with reaction of proton which lost its electron with water
- a bond formed is a coordinate covalent*
- This is a self-inducing reaction,
- The reaction entalpy is ca. -7.25 eV/molecule, theoretically.

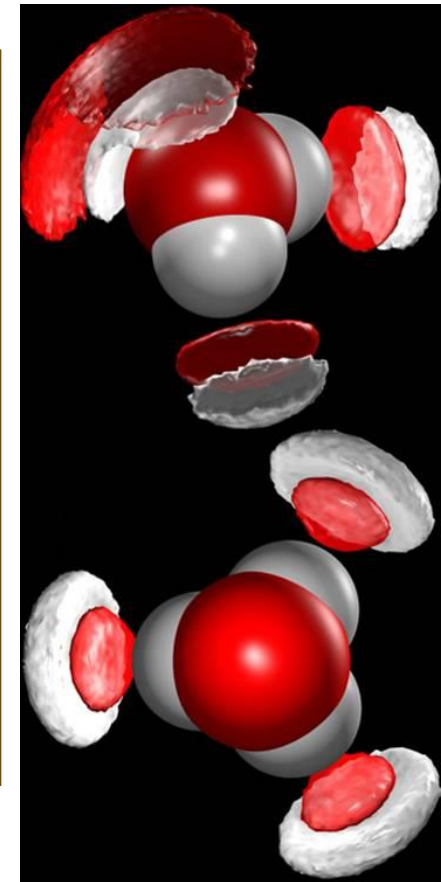
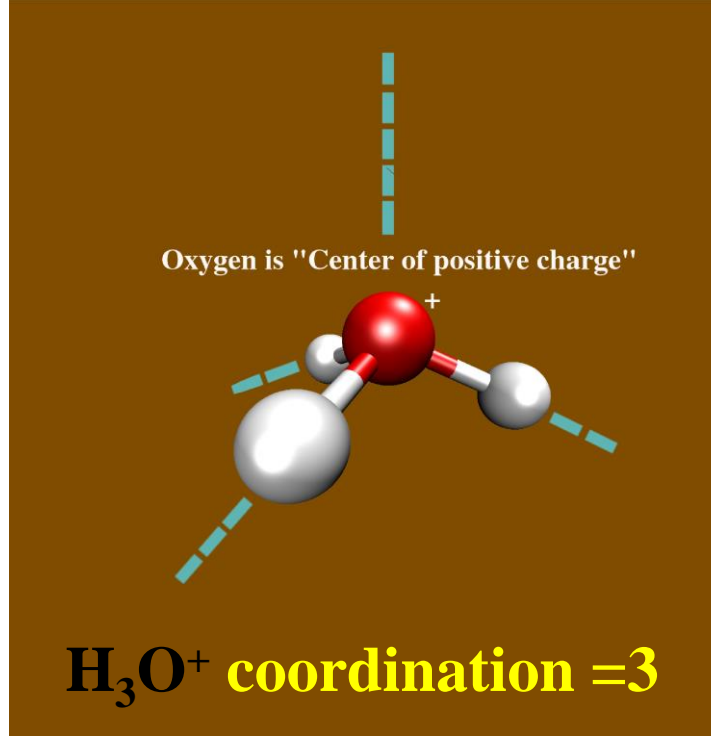
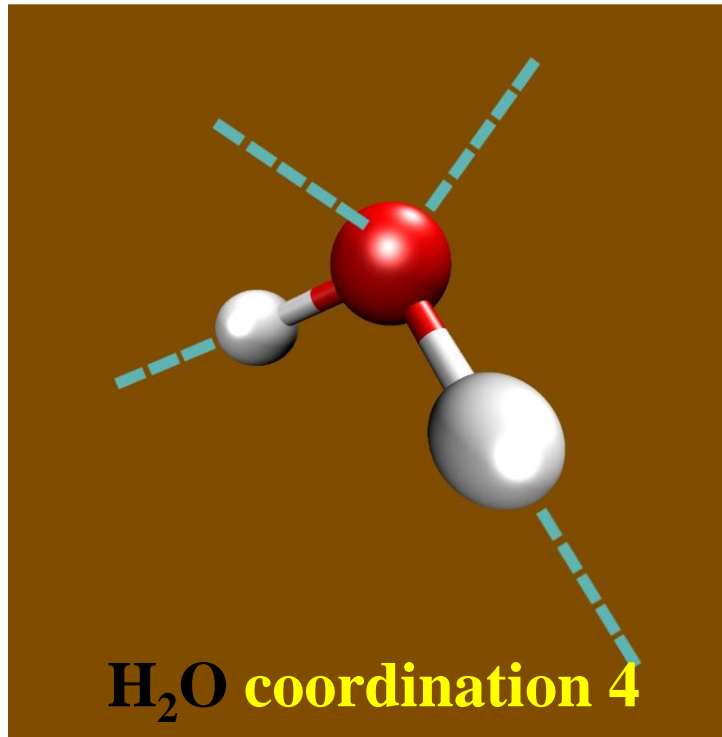
*Coordinate covalent bond



Ammonia-borane complexes contain a coordinate covalent bond

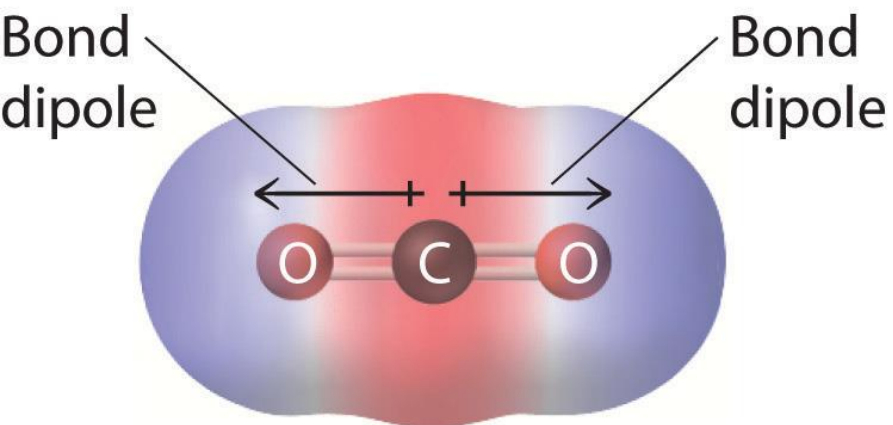
Water and hydronium ion !!

- Both molecules are polar
- These polar molecules make a strong hydrogen bond among them as shown below

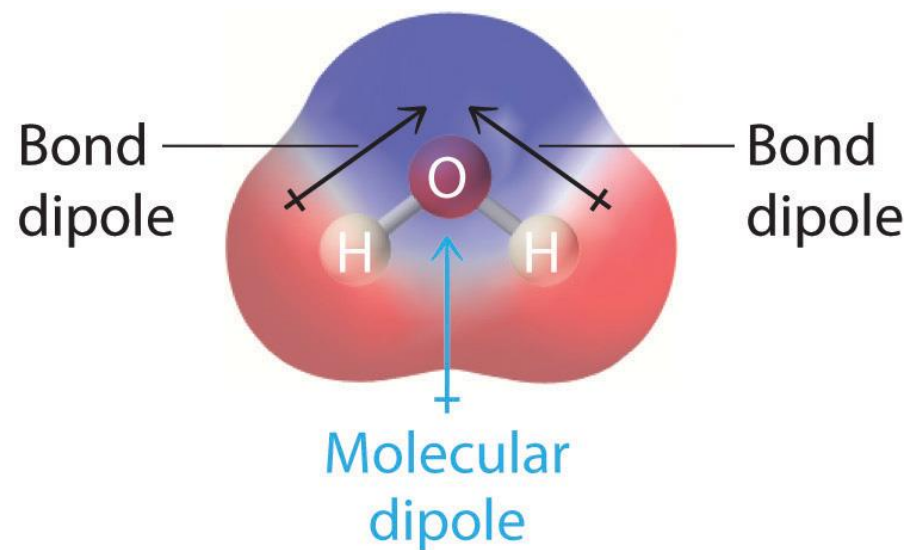


Comparison of dipole moment between water and carbon dioxide !!

- Net dipole moment of water molecule is 1.84 D



(a) No net dipole moment

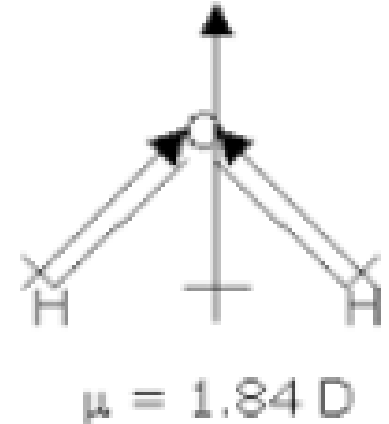
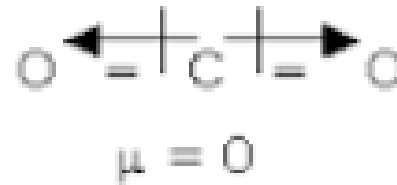


(b) Net dipole moment

Reaction reactivity of water and hydronium ion !!

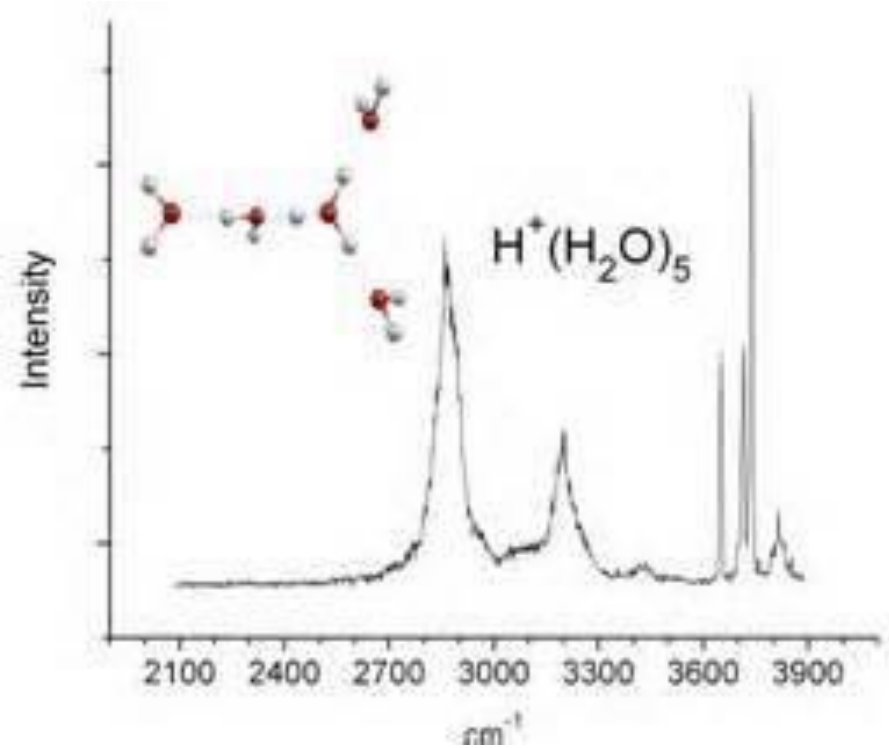
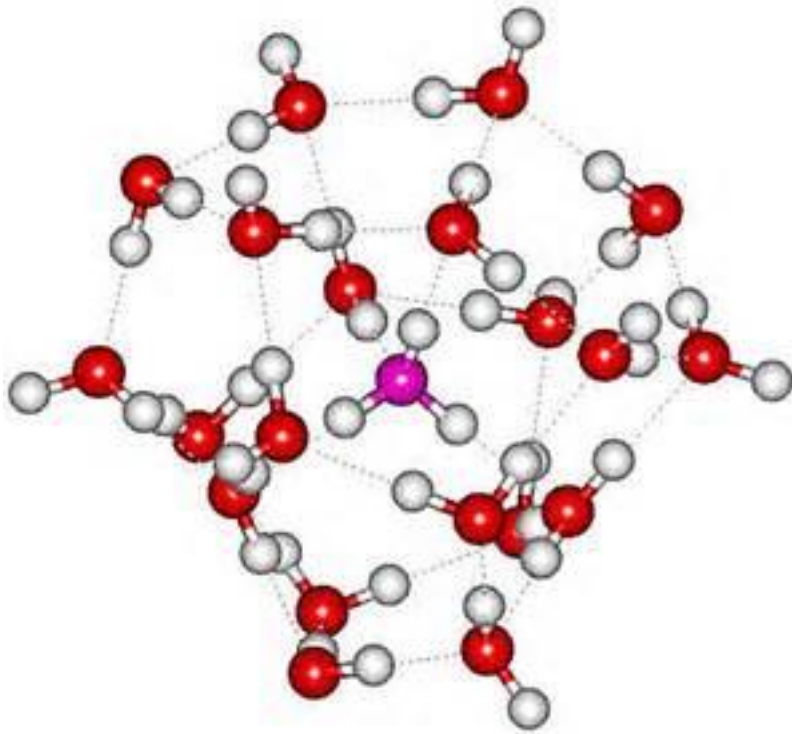
- These molecules are highly reactive according to the carbon dioxide.

- Because molecules are dipole, they are the polarized molecules (charge-induced dipole force), but carbondioxide is apolar, and it can have charge-induced dipole force.



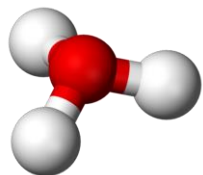
So, the presence of this molecule in TPC detectors causes many reactions !!

Ion clusters !!

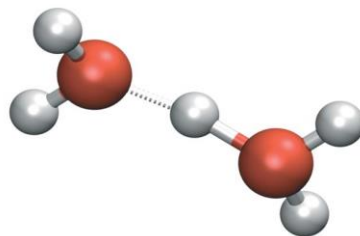


Magic number protonated water clusters

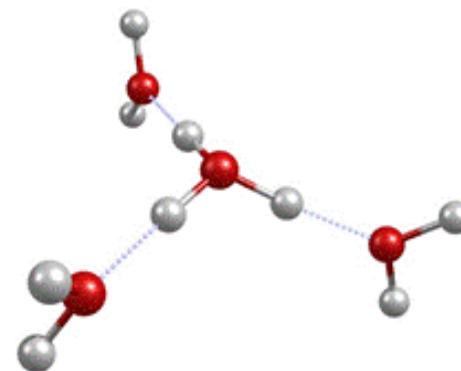
Sample form of hydronium ion suggested in literature !!



(a)



(b)



(c)

(a) Hydronium ion: H_3O^+

(b) Zundel cation: H_5O_2^+ (named for Georg Zundel)

(c) Eigen cation: H_9O_4^+ (named for Manfred Eigen)

✓ Why shapes and sizes of protonated water clusters are important?

Cluster size is related to directly ion mobility,

as the size of clusters higher, the mobility is slower,

✓ We need to know that

what is the cluster size in the operating conditions of detector

commonly in atmospheric pressure and 298 K

Literature studies!!

Wang and coauthors, 2003

TABLE 1: Determination of the Dissociation Energies (kcal mol^{-1}) of $\text{H}^+(\text{H}_2\text{O})_{4-10}$ and $\text{OH}^-(\text{H}_2\text{O})_{3-7}$ from Their Components at the Mean Trap Temperature T_m (K) and Comparison with Literature Values

clusters	T_m	this work				literature values ^c	
		E_n	$\langle E_{\text{vib}} \rangle^a$	$ak_B T_m^b$	E_{diss}	E_{diss}	
$\text{H}^+(\text{H}_2\text{O})_4$	325	10.2 ± 0.4	6.0 ± 0.4	0.97 ± 0.24	17.2 ± 0.7	17.3, 17.4	
$\text{H}^+(\text{H}_2\text{O})_5$	227	6.8 ± 0.1	4.6 ± 0.4	0.68 ± 0.17	12.1 ± 0.5	12.3, 11.1	
$\text{H}^+(\text{H}_2\text{O})_6$	203	4.9 ± 0.1	5.0 ± 0.5	0.61 ± 0.15	10.5 ± 0.6	11.2, 10.7	
$\text{H}^+(\text{H}_2\text{O})_7$	181	4.0 ± 0.1	4.9 ± 0.8	0.54 ± 0.13	9.4 ± 0.9	10.2, -	
$\text{H}^+(\text{H}_2\text{O})_8$	164	4.0 ± 0.1	5.0 ± 0.4	0.49 ± 0.12	9.5 ± 0.5	-	
$\text{H}^+(\text{H}_2\text{O})_9$	155	4.2 ± 0.1	u.d.	0.46 ± 0.11	-	-	
$\text{H}^+(\text{H}_2\text{O})_{10}$	150	4.0 ± 0.1	u.d.	0.45 ± 0.11	-	-	
$\text{OH}^-(\text{H}_2\text{O})_3$	323	10.3 ± 0.1	4.9 ± 0.4	0.96 ± 0.24	16.2 ± 0.5	-	
$\text{OH}^-(\text{H}_2\text{O})_4$	254	6.9 ± 0.1	4.3 ± 0.5	0.76 ± 0.19	12.0 ± 0.6	-	
$\text{OH}^-(\text{H}_2\text{O})_5$	216	6.0 ± 0.1	4.3 ± 0.6	0.64 ± 0.16	10.9 ± 0.7	-	
$\text{OH}^-(\text{H}_2\text{O})_6$	203	6.3 ± 0.1	4.6 ± 0.4	0.61 ± 0.15	11.5 ± 0.5	-	
$\text{OH}^-(\text{H}_2\text{O})_7$	192	6.9 ± 0.1	u.d.	0.57 ± 0.14	-	9.6	

P = ~100 Torr

Y.S. Wang, C.H. Tsai, Y.T. Lee, H.C. Chang, J.C. Jiang, O. Asvany, S. Schlemmer, D. Gerlich, *J. Phys. Chem. A*

Good and coauthors, 1970

TABLE I. Rate constants for ion-molecule reactions in pure nitrogen and nitrogen with traces of water at 300°K in the pressure range 0.5-3.5 torr.

Reaction	Rate constant for forward reaction	"Activation energy" for forward reaction	Rate constant for reverse reaction	ΔH forward reaction (kcal/mole)
(1) $N_2^+ + 2N_2 \rightarrow N_4^+ + N_2$	$k_1 = 8 \times 10^{-29}$ a	-2		$\sim -16^d$
(2) $N^+ + 2N_2 \rightarrow N_3^+ + N_2$	$k_2 = 5 \times 10^{-29}$ a	-1		$\sim -75^d$
$N^+ + N_2 \rightarrow N_3^+$	$k_2 = 1.3 \times 10^{-22}$ b	0		
(3) $N_4^+ + H_2O \rightarrow H_3O^+ + 2N_2$	$k_3 = 1.9 \times 10^{-9}$ b	0	0	
(4) $H_2O^+ + H_2O \rightarrow H_3O^+ + OH$	$k_4 = 1.8 \times 10^{-9}$ b	0	0	
(5) $H_3O^+ + H_2O + N_2 \rightleftharpoons H^+(H_2O)_2 + N_2$	$k_5 = 3.4 \times 10^{-27}$ a	c	$k_{-5} = 7 \times 10^{-26}$ b	-36 ^e
(6) $H^+(H_2O)_2 + H_2O + N_2 \rightleftharpoons H^+(H_2O)_3 + N_2$	$k_6 = 2.3 \times 10^{-27}$ a	c	$k_{-6} = 7 \times 10^{-26}$ b	-22.3 ^e
(7) $H^+(H_2O)_3 + H_2O + N_2 \rightleftharpoons H^+(H_2O)_4 + N_2$	$k_7 = 2.4 \times 10^{-27}$ a	c	$k_{-7} = 4 \times 10^{-26}$ b	-17 ^e

^a Units: cc² molecule⁻²·sec⁻¹.

^b Units: cc molecule⁻¹·sec⁻¹.

^c Probably negative and 1-2 kcal.

^d Reference 19.

^e Reference 18.

T = 300 K

P = 0.3-3.5 Torr

A. Good, D.A. Durden, P. Kebarle, J.Chem.Physc. 52, 1970, 212.

Zamith and coauthors, 2012

They experiments at 25 K, and $n = 30$

Mark and coauthors, 2012, Castleman and coauthor, 1986 and Viggiano and coauthors, 1988; They measured cluster size, $n = 22$ at 120 K and atmospheric pressure

S. Zamith, P. Labastie, J. L'Hermite, Journal of Chemical Physics, 136, 2012, 214-301.

Mark, T. D.; Castleman, A. W., Jr. Ado. Atom. Mol. Phys. 20, 1984, 65.

Castleman, A. W., Jr.; Keesee, R. G. Chem. Rev. 86, 1986, 589.

Viggiano, A. A.; Dale, F.; Paulson, J. F. J. Chem. Phys. 88, 1988, 2469.

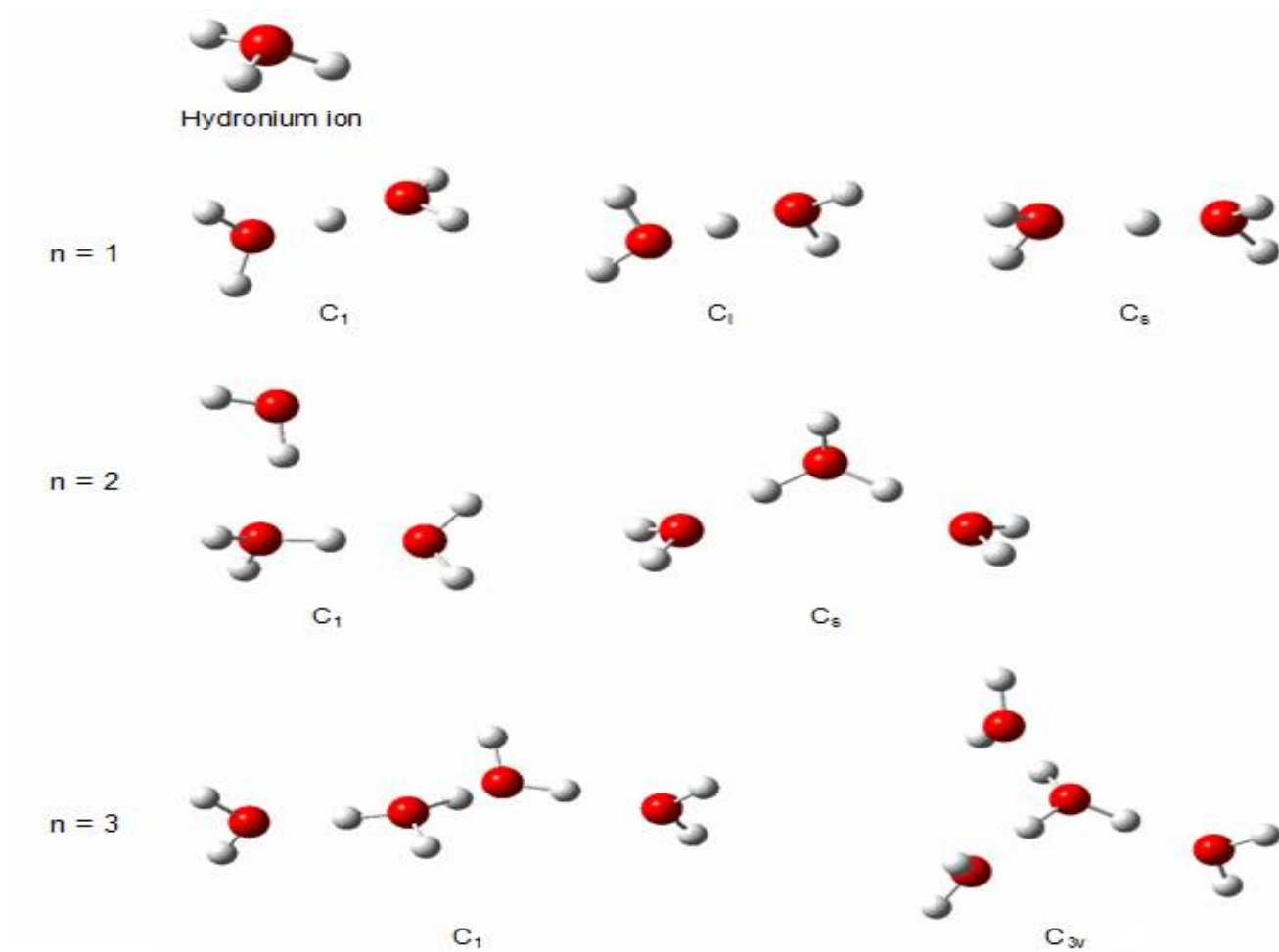
Theoretical studies!!

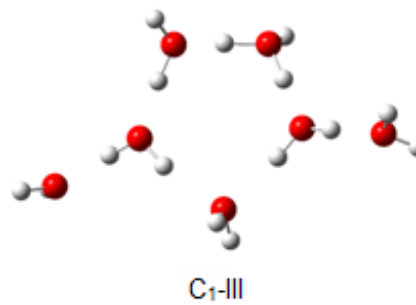
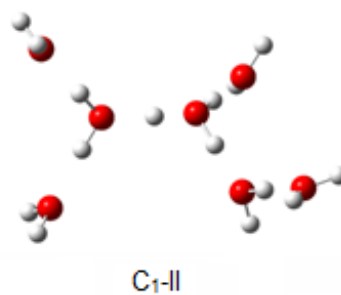
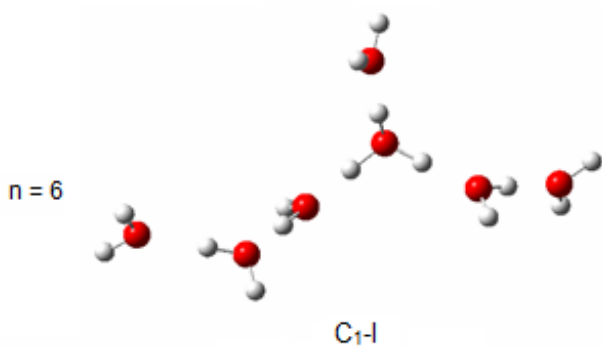
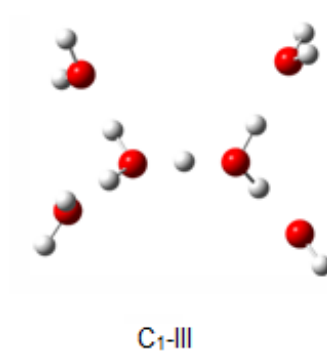
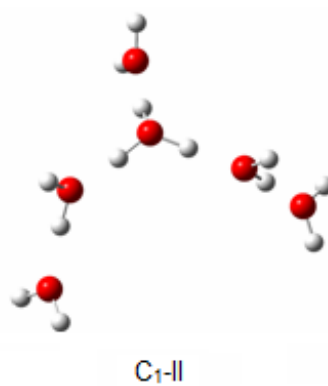
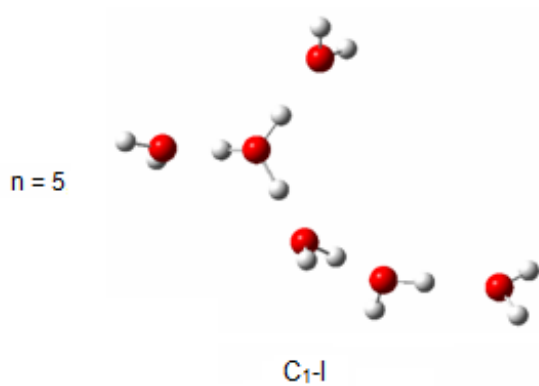
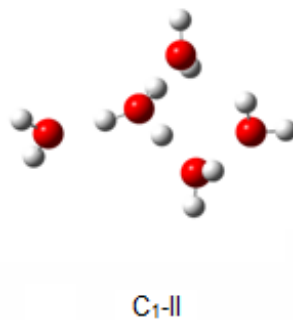
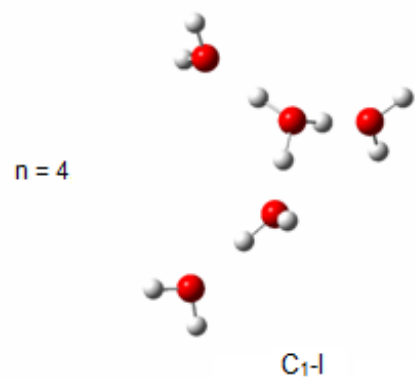
- ✓ We study on shapes and sizes of protonated water cluster!!
- ✓ We make model of $\text{H}^+(\text{H}_2\text{O})_n$ clusters ($n = 1-10$) with Gaussian 09 programme.
- ✓ We use Density Functional Theory* (DFT) and 6-311++G(d,p) basis set.
- ✓ We suggest different isomers for each cluster and so enthalpies, entropies and Gibbs free energies can be calculated.
- ✓ Our suggested isomers of $\text{H}^+(\text{H}_2\text{O})_n$ clusters are given in the next slide.

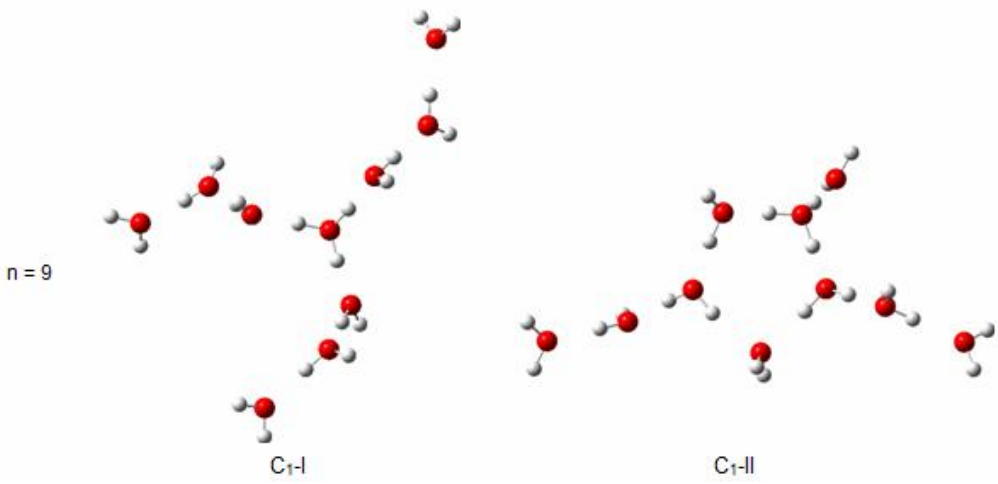
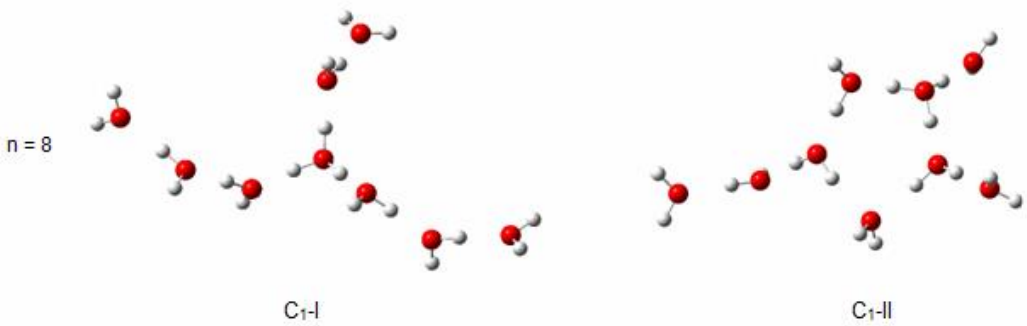
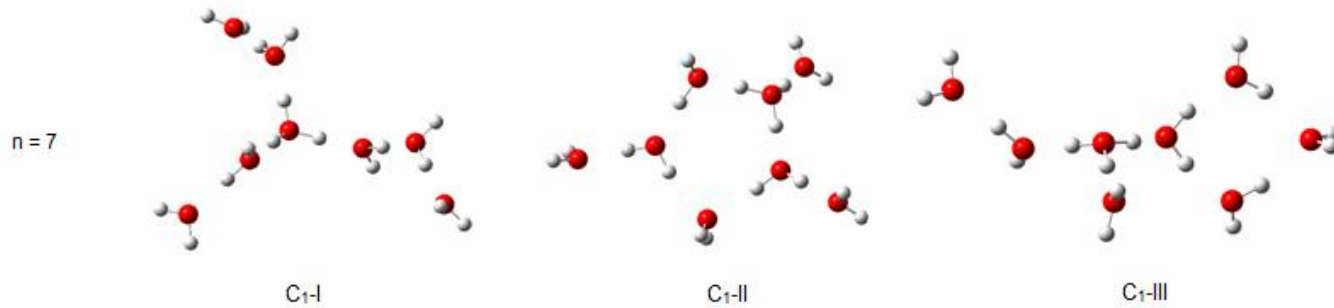
*Density Functional Theory (DFT)



✓ There are some forms of our suggested isomers







✓ Depending on the first calculations: we can say that if $n = 2$ the cluster may be showed $H^+(H_2O)_2$, but when $n = 3-10$, clusters may be displayed $H_3O^+(H_2O)_{2-9}$

✓ What is the cluster size in atmospheric pressure and at 298 K?

As literature and theoretical studies, the cluster size can be $\text{H}_3\text{O}^+(\text{H}_2\text{O})_4$ or $_5$ in atmospheric pressure and 298 K.

The causing of the formation of these large clusters are feature of the dipole of water molecule.

And so the cluster size of water is greater than the cluster size of CO_2 .

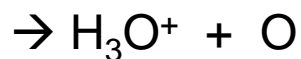
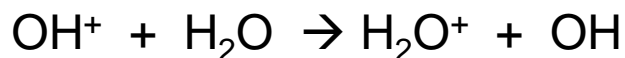
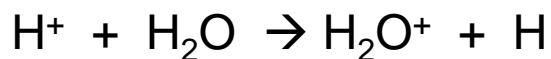
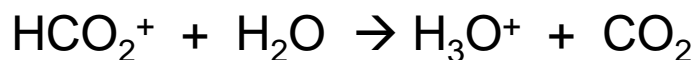
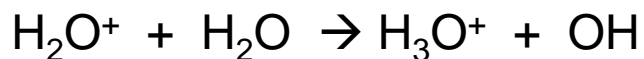
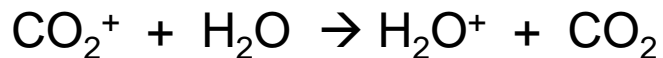
In this case ion mobility is reduced

And so in the presence of water the mobility in the detector will be reduced.

Now, we wonder that:

- Is there any other reactions of water? (Out of the hydronium ion)
- Of course, Yes
- Gases in the detector can be Ar, Ne, CO₂, CH₄, H₂O ..
- And also, so many reactions may be occurred in detectors.

For example, which reactions !!



As a result, we can mention that a lot of reactions in the presence of water.

And for protonated water cluster, size of the cluster may be $n = 4$ or 5 in atmospheric pressure and at 298 K .

**THANKS FOR YOUR
ATTANTION!!**