Interstellar Hydrogen Bonding

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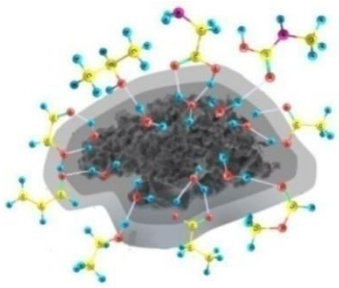
Introduction: Gas phase chemical reactions and reactions that occur on the surfaces of interstellar dust grains are the dominant processes by which molecules can be synthesized from the precursor atoms and ions. Of these two processes, reactions that occur on the surfaces of interstellar dust grains have been invoked for the formation of molecular hydrogen; as well as for the synthesis of larger interstellar molecules. Water molecules constitute about 70% of the interstellar dust grains (interstellar ice). These water molecules serve as the platform for hydrogen bonding.[1]



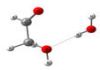
Methodology: The Gaussian 09 suite of programs[2] is employed for all the quantum chemical calculations reported here. Thee binding energies between the isomers and the water molecule on the surface of the interstellar dust grains are calculated at the MP2 level the with the 6-311++G** and aug-cc-pVDZ basis sets..[3,4] The reported binding energies have been corrected for the basis set superposition error (BSSE) using the counterpoise method developed by Boys and Bernardi.[5]

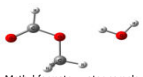
Results: From the results, there is a direct correlation between the binding energies of these complexes and the abundances of the interstellar molecules. As the binding energy of the complex increases, the abundance of the interstellar molecule decreases. This accounts for the observed deviations from the **E**nergy, **S**tability and **A**bundance (**ESA**) relationship.[6]

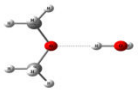
The most stable not being the most abundant

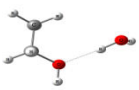
Complex	B. E (kcal/mol) (K equivalent) MP2(full)/6-311++G**	MP2(full)/aug-cc-pVDZ	ΔH^0_f(kcal/mol)
$C_2H_4O_2$ isomer complexes with water			
Acetic acid-H_2O	-6.9 (3,472.3)	-9.5(4,780.6)	-103.7
Glycolaldehyde-H_2O	-5.5 (2,767.8)	-5.9 (2,969.0)	-70.5
Methyl formate-H_2O	-3.3 (1,660.6)	-5.5 (2,767.7)	-89.4
C_2H_6O isomer complexes with water			
Ethanol-H_2O	-5.1 (2,566.5)	-5.5 (2,767.7)	-56.7
Dimethyl ether-H_2O	-5.0 (2,516.1)	-5.4 (2,717.4)	-49.0


Acetic acid...water complex


Glycolaldehyde...water complex


Methyl formate...water complex


Ethanol...water complex

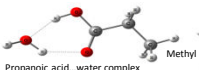

Dimethyl ether...water complex

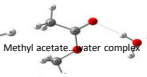
ESA RELATIONSHIP

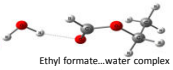
According to the relationship, interstellar abundances of related species are directly proportional to their stabilities in the absence of the effect of interstellar hydrogen bonding. This influences the astronomical observations of some related molecular species at the expense of others.

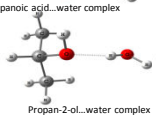
Delayed observation of the most stable isomers

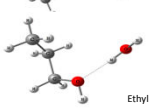
Complex	B. E (kcal/mol) (K equivalent) MP2(full)/6-311++G**	MP2(full)/aug-cc-pVDZ	ΔH^0_f(kcal/mol)	Astronomical status
$C_2H_4O_2$ isomer complexes with water				
Propanoic acid - H_2O	-8.4 (4,227.1)	-9.5 (4,780.7)	*-109.4*	Not observed
Methyl acetate-H_2O	-4.8 (2,415.5)	-5.0 (2,516.1)	-95.1	Observed
Ethyl formate - H_2O	-4.5 (2,264.5)	-5.0 (2,516.1)	-97.5	Observed
C_3H_8O isomer complexes with water				
Propan-2-ol-H_2O	-5.4 (2,717.4)	-5.9 (2,969.0)	-65.6	Not observed
Propanol-H_2O	-5.2 (2,616.8)	-5.7 (2,868.4)	-61.9	Not observed
Ethyl methyl ether-H_2O	-5.0 (2,516.1)	-5.4 (2,717.3)	*-57.4*	Observed

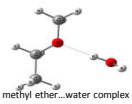

Propanoic acid...water complex


Methyl acetate...water complex


Ethyl formate...water complex

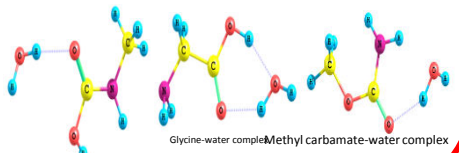

Propan-2-ol...water complex


Propanol...water complex

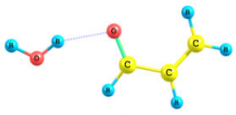

Ethyl methyl ether...water complex

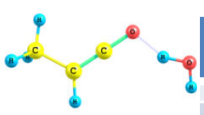
Unsuccessful observations: Amino acids

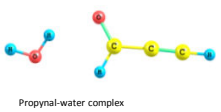
Complex	B. E (kcal/mol) (K equivalent) MP2(full)/6-311++G**	MP2(full)/aug-cc-pVDZ	Astronomical status
$C_2H_5NO_2$ isomer complexes with water			
Methyl carbamic acid-H_2O	-8.3 (4,176.8)	-9.4 (4,730.3)	Not observed
Glycine-H_2OO	-4.8 (2,415.5)	-5.1 (2,566.5)	Not observed
Methyl carbamate-H_2O	-3.1 (1,560.0)	-3.4 (1,711.0)	Tentative observation

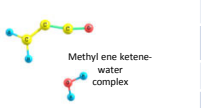

Methyl carbamic acid-water complex Glycine-water complex Methyl carbamate-water complex

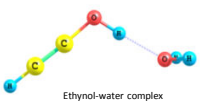
What could be searched for? Ketenes!!!

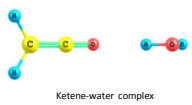

Propenal-water complex


Methyl ketene-water complex


Propynal-water complex


Methyl ene ketene-water complex


Ethynol-water complex


Ketene-water complex

Complex	B. E (kcal/mol) (K equivalent) MP2(full)/6-311++G**	MP2(full)/aug-cc-pVDZ	ΔH^0_f(kcal/mol)	Astronomical status
$C_3H_4O_2$ isomer complexes with water				
Propenal-H_2O	-4.6 (2,314.8)	-5.2 (2,617.1)	15.8	Observed
Methyl ketene-H_2O	-2.1 (1,056.9)	-2.8 (1,409.0)	-18.1	Not observed
C_3H_2O isomer complexes with water				
Propynal-H_2O	-4.2 (2,113.8)	-4.8 (2,415.8)	32.1	Observed
Methylene ketene-H_2O	-2.6 (1,308.5)	-3.0 (1,509.9)	24.8	Not observed
C_2H_2O isomer complexes with water				
Ethynol-H_2O	-7.6 (3,825.0)	-8.41 (4,227.1)	23.2	Not observed
Ketene-H_2O	-1.8 (905.8)	-2.0 (1,006.6)	-15.6	observed

Ketenes whose less stable isomers that are more strongly bonded to the surface of the interstellar dust grains have been observed are proposed as suitable candidates for astronomical observations. In line with this prediction, Ketenyl radical (HCCO) has just been astronomically detected.

Weakly Bound Complexes in Interstellar Medium (ISM): The conditions in the terrestrial laboratories where weakly bound complexes are observed are similar to the conditions in ISM[8]. The high binding energies of the complexes reported here imply that these complexes are present and detectable in ISM.

Conclusions: The present study reports the first extensive study of the existence and effects of interstellar hydrogen bonding. The binding energies of the hydrogen bonded complexes of interstellar molecules with water obtained from high level quantum chemical calculations show a direct relationship between the binding energies and the interstellar abundances of the molecules. Available interstellar observations data confirms the observed trend. Interstellar hydrogen bonding accounts for the deviations from thermodynamically controlled processes, the delay in detecting the most stable isomers whose less stable counterparts have been detected, the difficulty in observing amino acids (e.g glycine). From this and our previous studies, we propose ketenes as potential candidates for astronomical observations.

References

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