Is Dihydrogen Bonding Analogous to Hydrogen Bonding?

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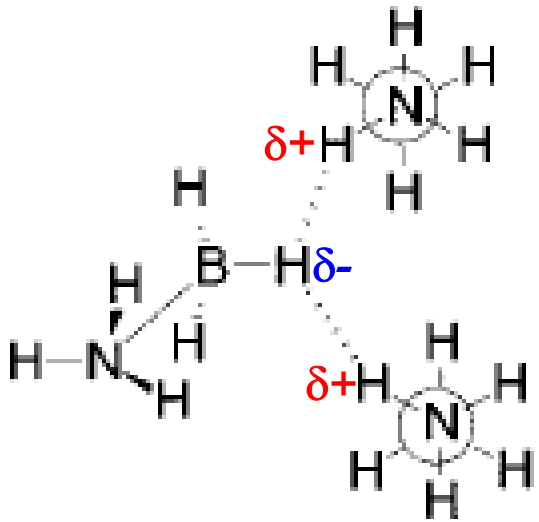
Dihydrogen Bonding

X = O, N, F, Cl, C

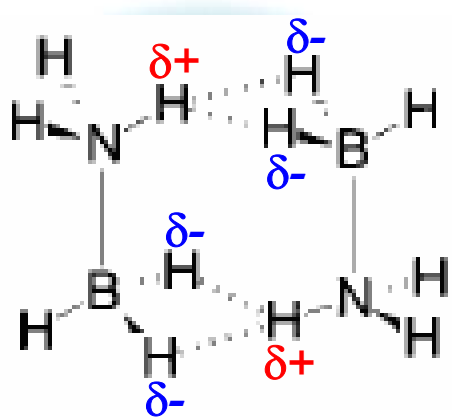
E = M, B

Interaction analogous to Hydrogen Bonding;
Between two oppositely charged hydrogen atoms

Dihydrogen Bonding (N—H•••H—B)



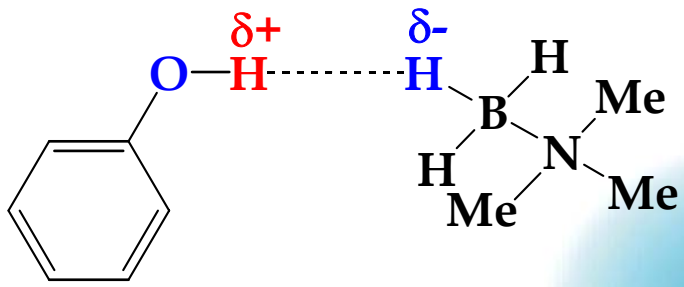
Network of dihydrogen bonds in solid BH_3-NH_3



Simulated structure of the BH_3-NH_3 dimer

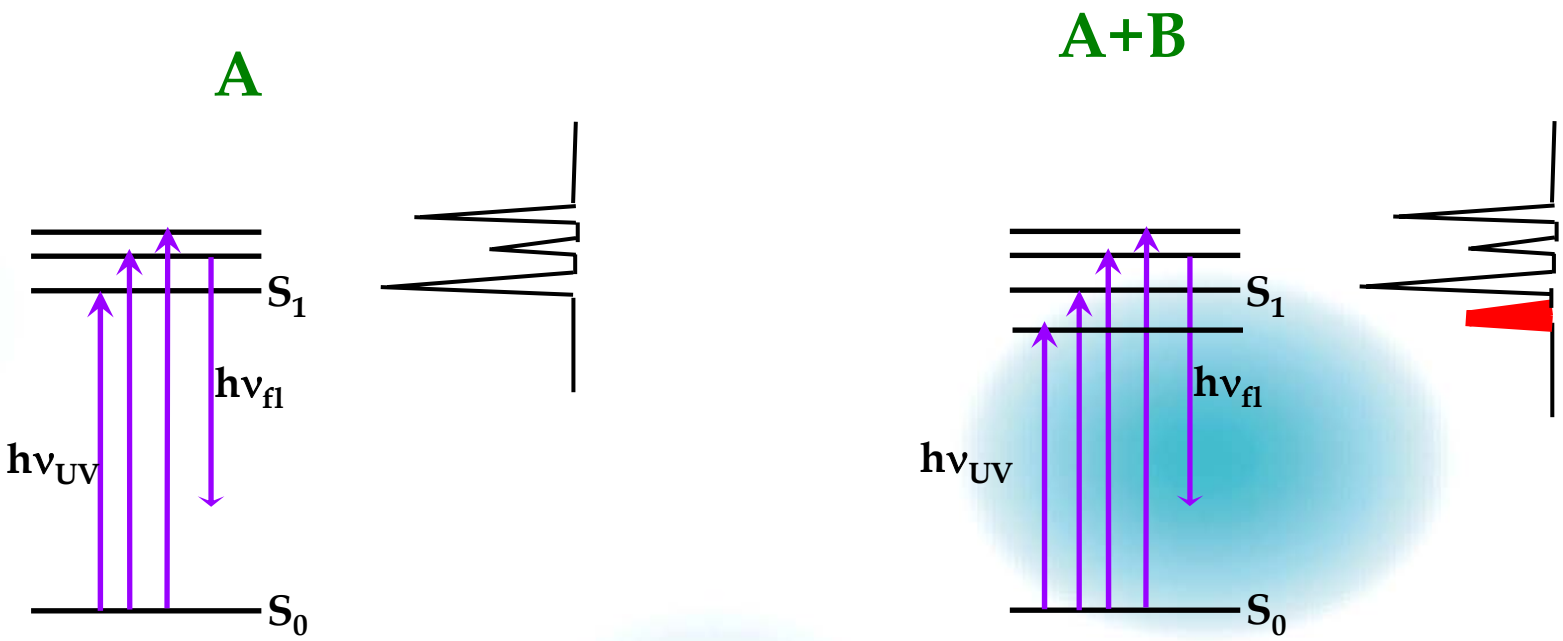
$\Delta E \sim 50$ kJ mol^{-1}

Dihydrogen Bonding in the Gas Phase



Hetero dimer of Phenol with Borane-trimethylamine

Fluorescence Detection

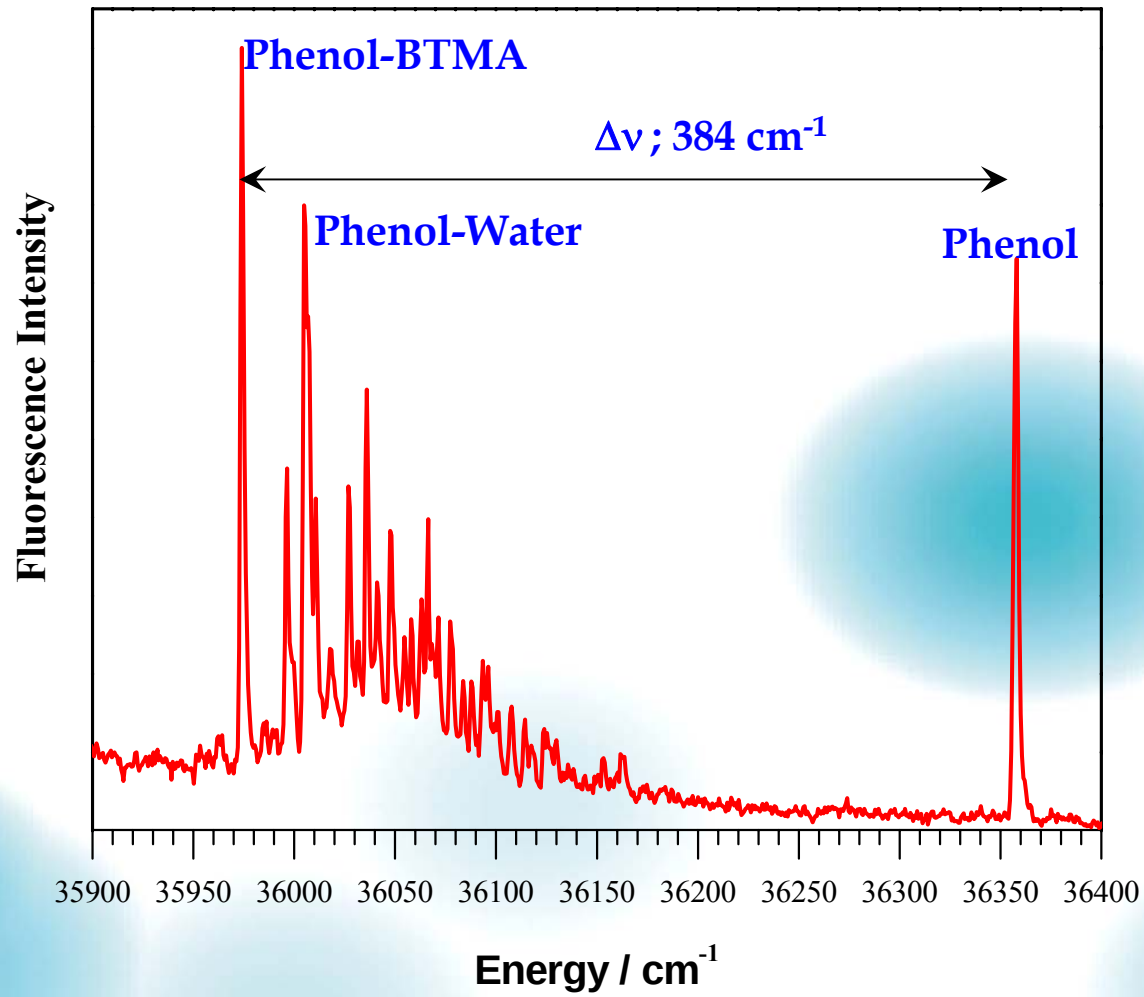


Laser Induced Fluorescence spectrum

Laser Induced Fluorescence Spectrum

The formation of complexes can be inferred

Fluorescence Spectrum



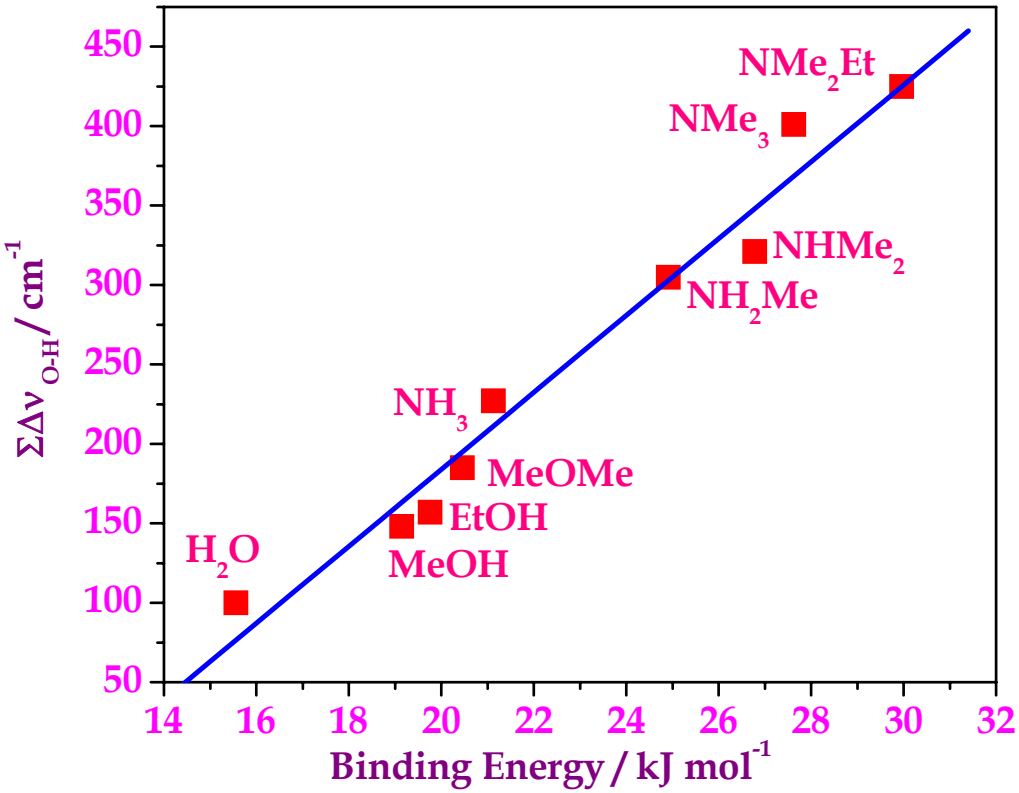
Hydrogen Bonding; IR Spectroscopy

Because of the sensitivity of the vibrational spectrum (ν_s in particular) to the hydrogen bond formation; IR spectroscopy provides

- **a definitive criterion for the detection of hydrogen bonds**
- **direct evidence of the role of the proton in the association**
- **a quantitative index for properties of hydrogen bonded systems**
- **a convenient tool in a wide variety of hydrogen bond studies**

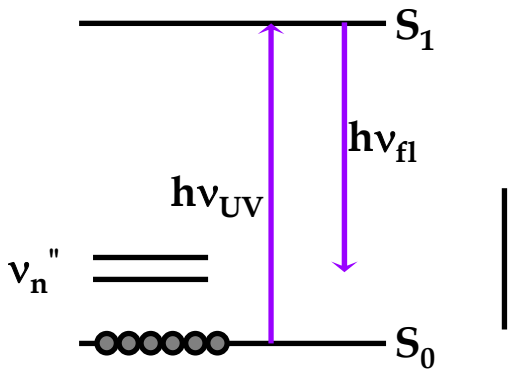
G. C. Pimentel & A. L. McCleallan in *"The Hydrogen Bond"*

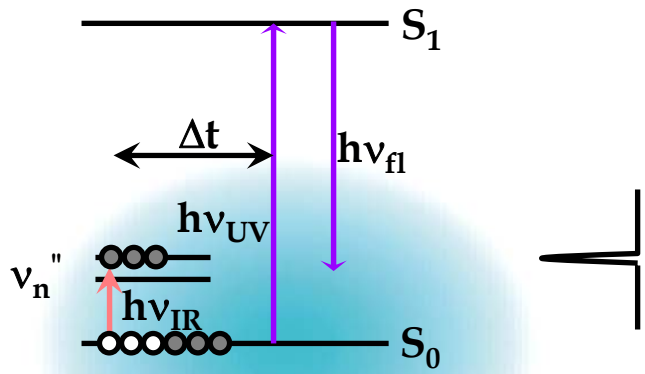
ΔE vs. Δν Correlation



ΔE vs. Δν plot for hydrogen bonded complexes of Water Calculated at MP2/6-311++G(d,p) Level

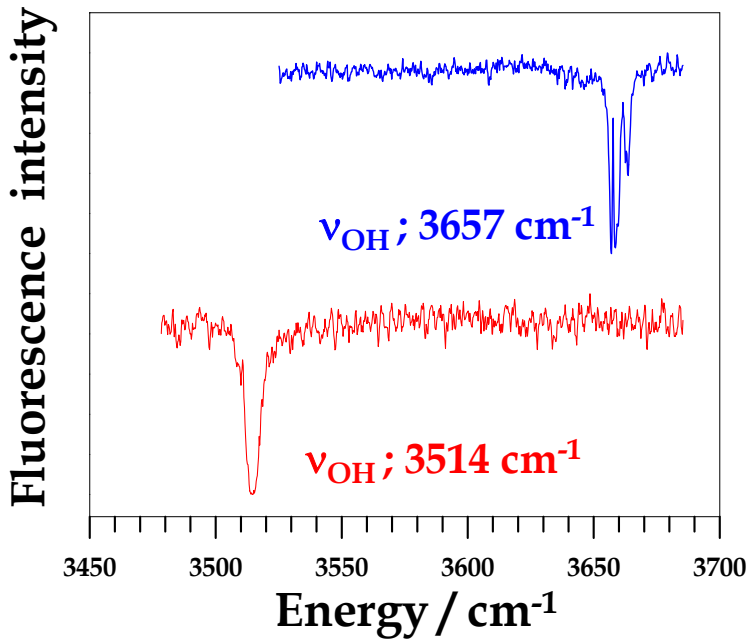
Fluorescence Detected Infrared Spectroscopy





In this technique the selectivity comes form the $S_1 \leftarrow S_0$ electronic transition, and is sensitivity because few percent change in the population of ground state can be detected.

IR-UV Double Resonance Spectroscopy

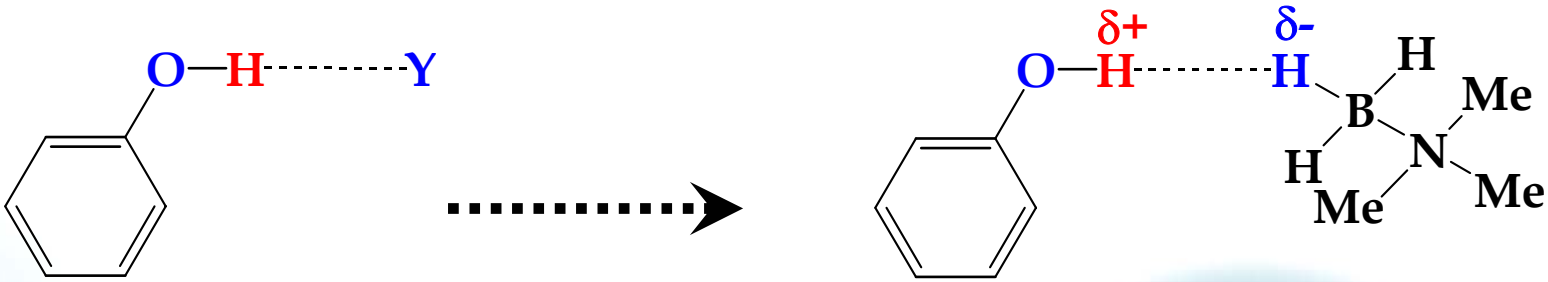


IR spectrum of phenol in the OH stretching region.

IR spectrum of phenol-BTMA in the OH stretching region.

$\Delta\nu_{OH} = 143$ cm^{-1}

Dihydrogen Bonding of Phenol



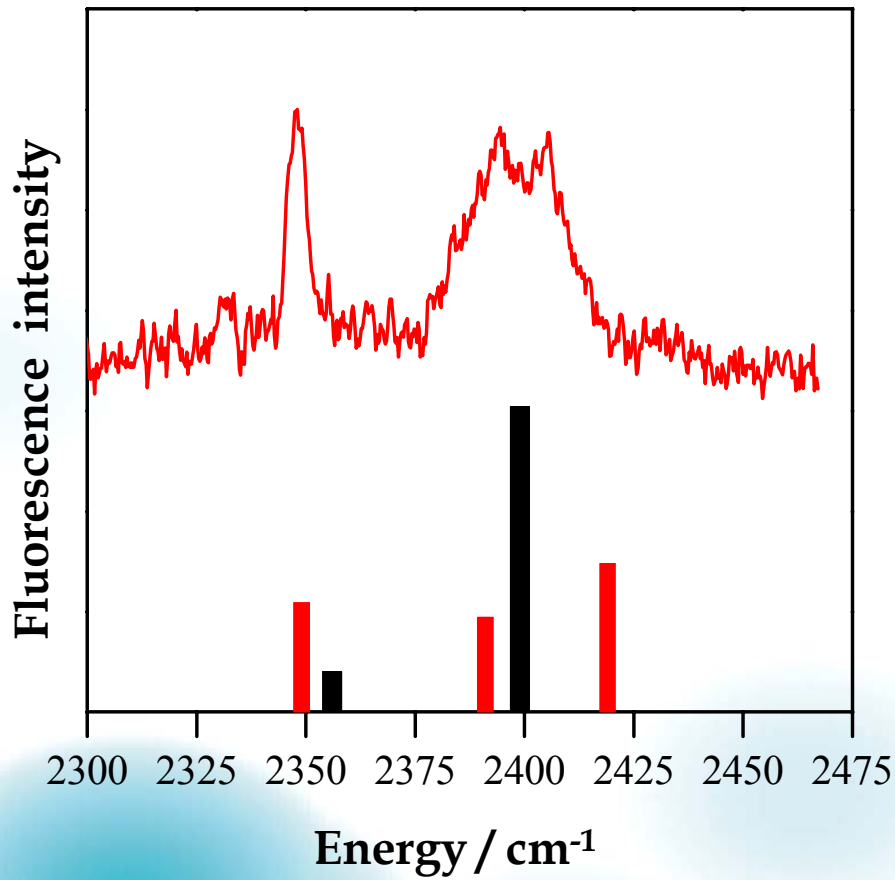
Y = $H_3B{\leftarrow}NMe_3$

phenol-water ($\Delta\nu_{OH}$ = 133 cm^{-1})

phenol –borane-trimethylamne ($\Delta\nu_{OH}$ = 143 cm^{-1})

phenol-methanol ($\Delta\nu_{OH}$ = 210 cm^{-1})

IR-UV Double Resonance Spectroscopy



BH_3 Group
→ C_3 Symmetry
→ Two Bands

Dihydrogen Bonding
→ Loss of Symmetry
→ Three Bands

IR spectrum of phenol-BTMA in the BH stretching region.

Summary

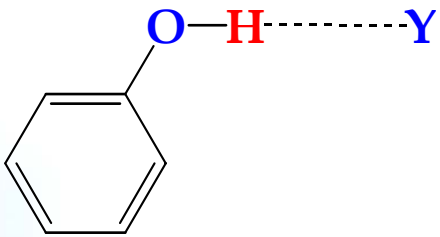
The 384 cm^{-1} red shift in the phenolic chromophore suggest BTMA hydrogen bonds with phenol

The shift in the 143 cm^{-1} shift in the OH stretching vibration of phenol also suggest that the BTMA is hydrogen bonded to phenol

The appearance of three bands in the BH stretching region indicates the BH_3 group of BTMA is interacting with the phenolic OH group

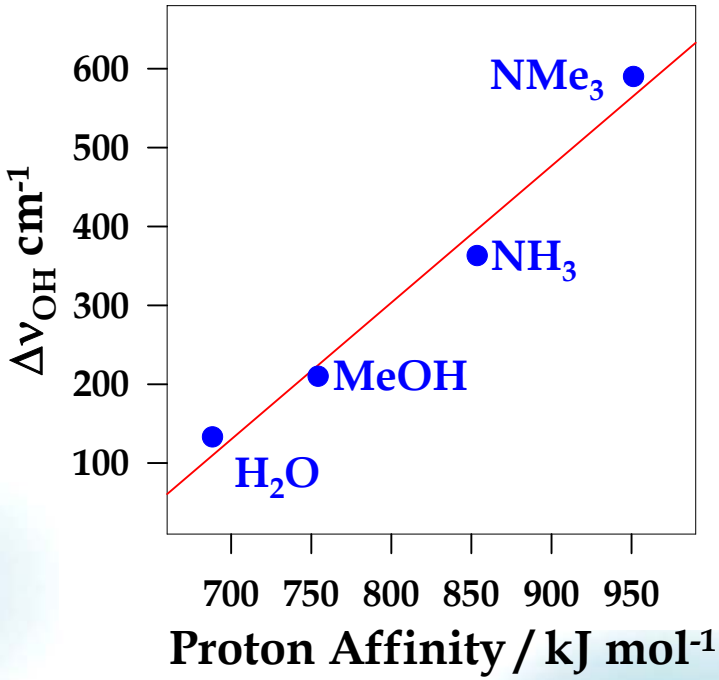
The above results unequivocally characterize the foramtion of the O-H…H-B dihydrogen bonded complex between phenol and borane-trimethylamine.

Hydrogen Bonding of Phenol

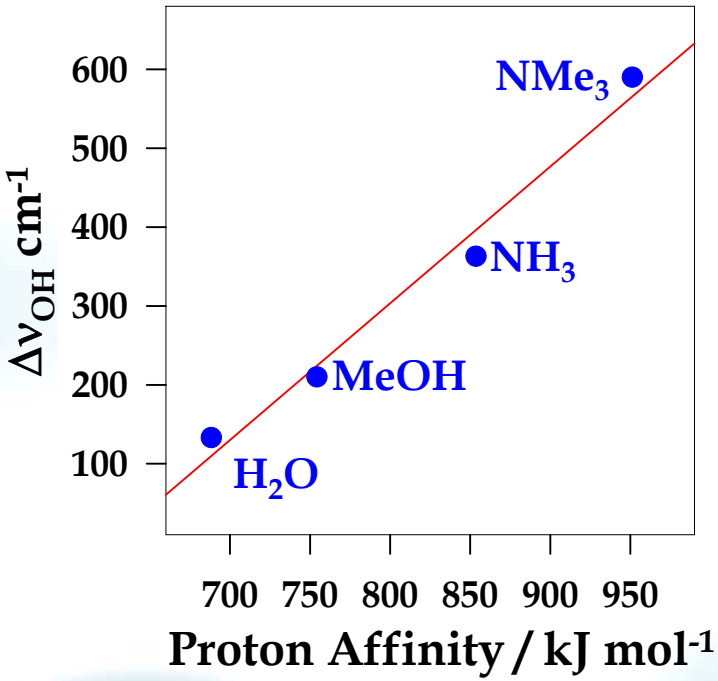


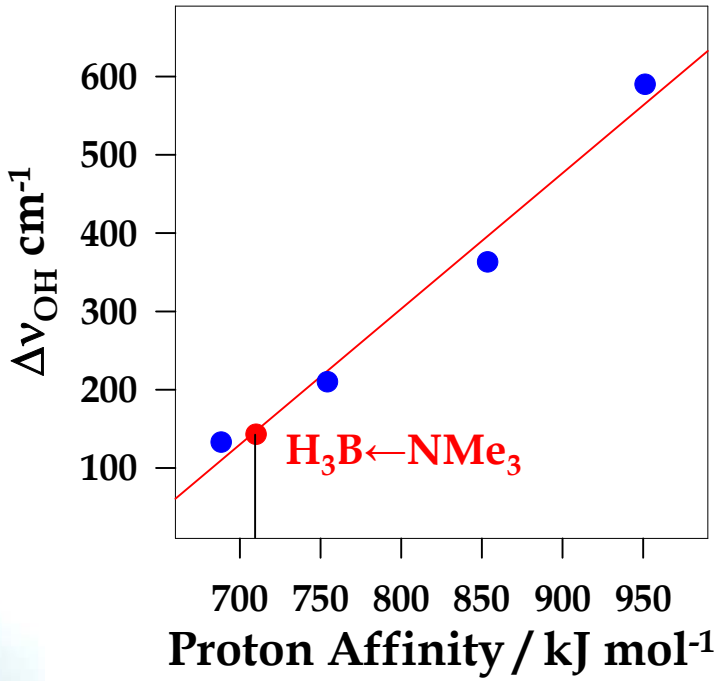
Y = H_2O, MeOH, NH_3, NMe_3

$$\Delta E_{HB} \propto \Delta \nu_{OH} \propto PA_Y$$



Proton Affinity of $H_3B{\leftarrow}NMe_3$





Proton Affinity of $H_3B{\leftarrow}NMe_3$: 710 ± 10 kJ mol^{-1}

Proton Affinity of $H_3B{\leftarrow}NMe_3$

Proton Affinity of $H_3B{\leftarrow}NMe_3$: 710 kJ mol^{-1}

→ Dihydrogen Bonding follows the same correlation as Hydrogen Bonding

Is there an Independent way to Verify?

Proton Affinities

Compilation of Gas-Phase Proton Affinities

E. P. L. Hunter and S. G. Lias, J. Phys. Chem. Ref. Data (1998).

"It has been shown that standard *ab initio* molecular orbital calculations at the G2 level of theory consistently yield values of proton affinities within 10 kJ mol^{-1} of experimental values, which is usually within error limits of the later."

G2 IS THE WAY

Proton Affinity of $H_3B{\leftarrow}NMe_3$

Estimated PA of $H_3B{\leftarrow}NMe_3$: 708 kJ mol^{-1}

Calculated G2-PA of $H_3B{\leftarrow}NMe_3$: 826 kJ mol^{-1}

$\Delta PA = 116$ kJ mol^{-1}

What Went Wrong?

Proton Affinity of $H_3B{\leftarrow}NMe_3$

Either Experimental Estimation is Wrong

OR

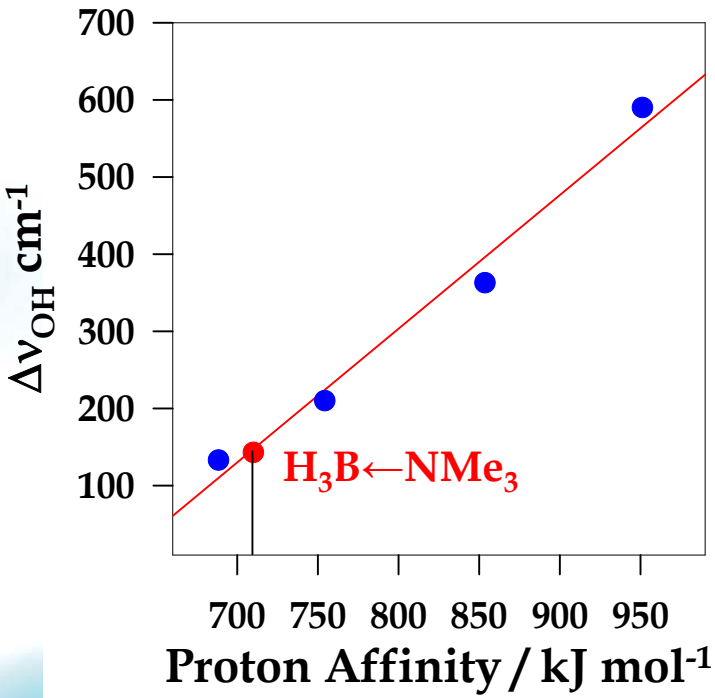
The Performance of G2 Theory PA is not up to the Mark

Diborane as Test Case

Experimental PA : 615 kJ mol^{-1}
Calculated G2PA : 619 kJ mol^{-1}

Experimental Estimation is Wrong

Proton Affinity of $H_3B{\leftarrow}NMe_3$



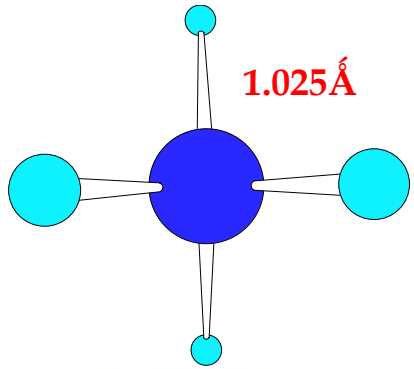
Correlation does not hold for Dihydrogen Bonding

↓

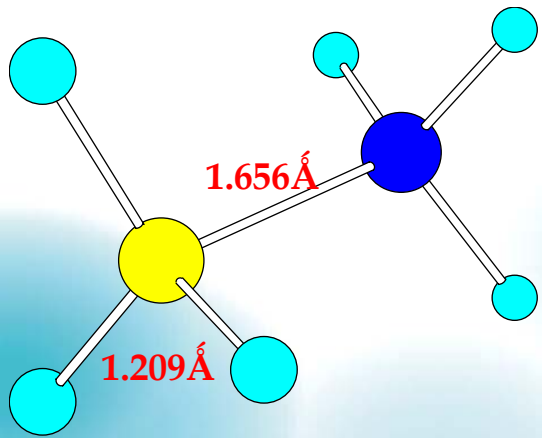
Why?

Protonated Structures

MP2/6-311++G(d,p)

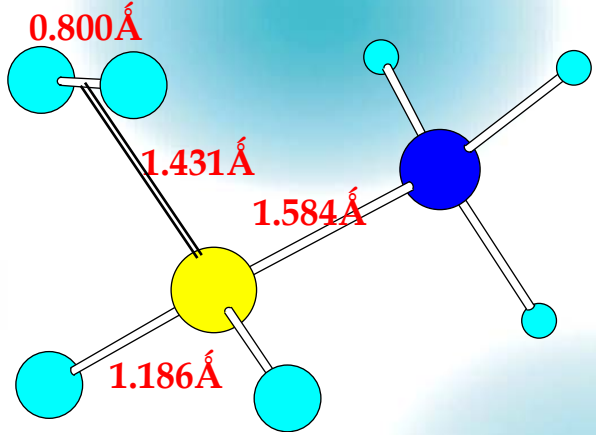


Structure of H_3NH^+



Structure of $H_3B{\leftarrow}NH_3$

H^+



Structure of $(H_3B{\leftarrow}NH_3)H^+$

Protonated Structures

Borane-Amine	G2-PA (kJ mol^{-1})	B–N (Å)	B–H_a (Å)	B–H_c (Å)	H_c–H_d (Å)
H_3B–NH_3	801.3	1.584	1.186	1.431	**0.800**
H_3B–NH_2Me	817.1	1.573	1.187	1.442	**0.798**
H_3B–$NHMe_2$	828.3	1.567	1.188	1.448	**0.796**
H_3B–NMe_3	836.8	1.566	1.189	1.452	**0.796**

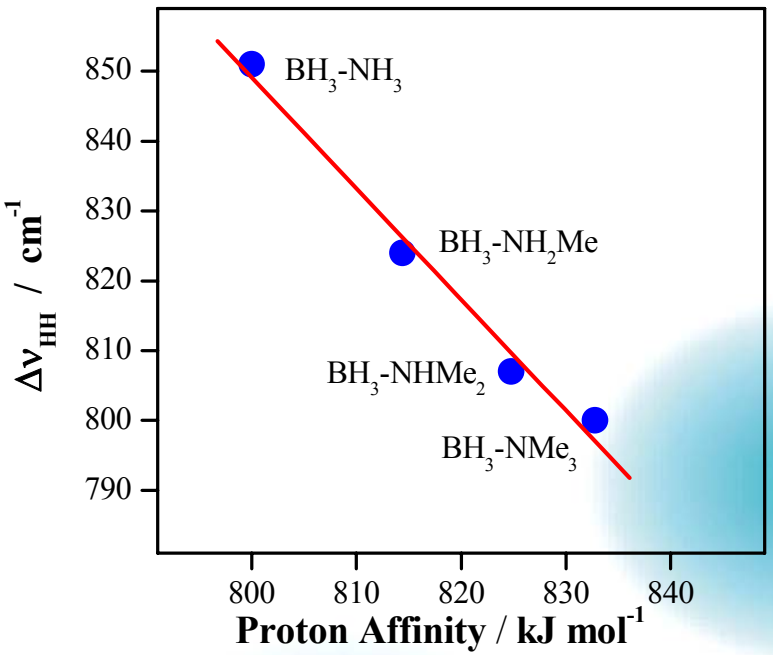
The Proton Affinity of Borane-Amines is related to the ease of formation of H_2

Protonated Structures; Binding Energies

Complex	G2 (kJ mol^{-1})	MP2/6-31++G(d,p) (kJ mol^{-1})	MP2/Aug-cc-pvdz (kJ mol^{-1})
H_2 – $[BH_2{-}NH_3]^+$	–9.87	–8.65	–13.45
H_2 – $[BH_2{-}NH_2Me]^+$	–8.73	–7.63	–12.10
H_2 – $[BH_2{-}NHMe_2]^+$	–7.25	–6.95	–10.07
H_2 – $[BH_2{-}NMe_3]^+$	–6.48	–6.18	–8.63

The Proton Affinity of Borane-Amines is related to the ease of formation of H_2

Protonated Structures; The H-H Stretching



The Proton Affinity of Borane-Amines is related to the ease of formation of H_2

Comparison

$$AH + B \rightarrow AH \cdots B \rightarrow A^- + HB^+$$

Hydrogen Bonding is a Precursor to Proton Transfer Reactions

$$AH + HB \rightarrow AH \cdots HB \rightarrow A^- + H_2 \cdots B^+ \rightarrow A^- + H_2 + B^+$$

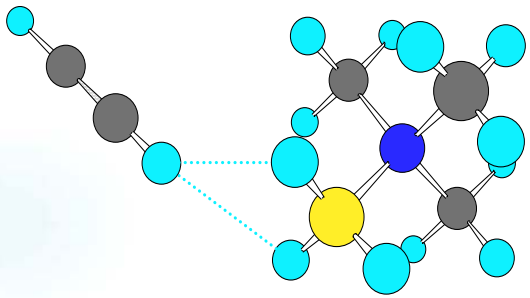
Dihydrogen Bonding is a Precursor to Dehydrogenation Reactions

Comparison of Hydrogen & Dihydrogen Bonding

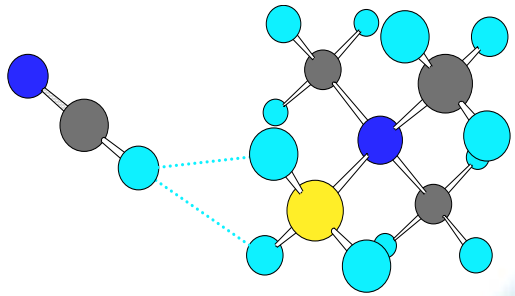
Donors	Acceptors
C_2H_2	H_2O
HF	MeOH
HCN	EtOH
H_2O	MeOMe
MeCOOOH	NH_3
$MeCONH_2$	NH_2Me
	$NHMe_2$
	NMe_3
	NMe_2Et
	BH_3NMe_3

60 Calculations at
MP2/6-311++G(d,p) Level

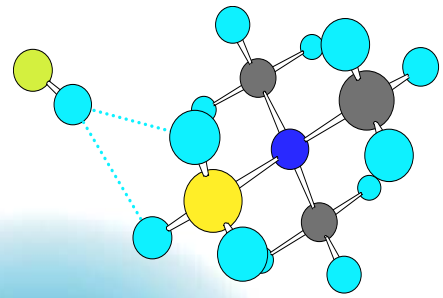
Structures of BTMA Complexes



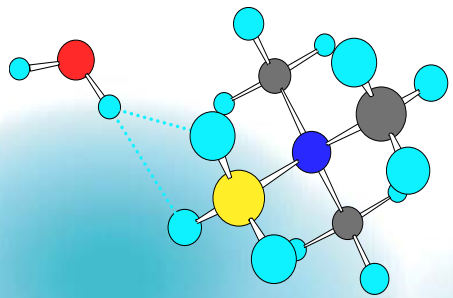
C_2H_2 – BH_3NMe_3



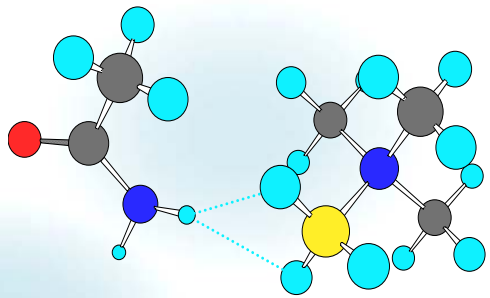
HCN – BH_3NMe_3



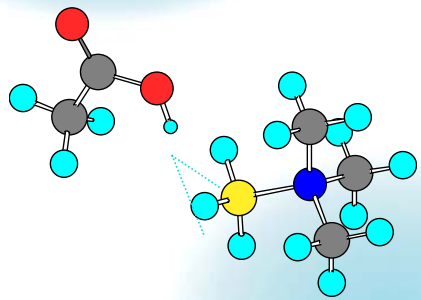
HF – BH_3NMe_3



H_2O – BH_3NMe_3

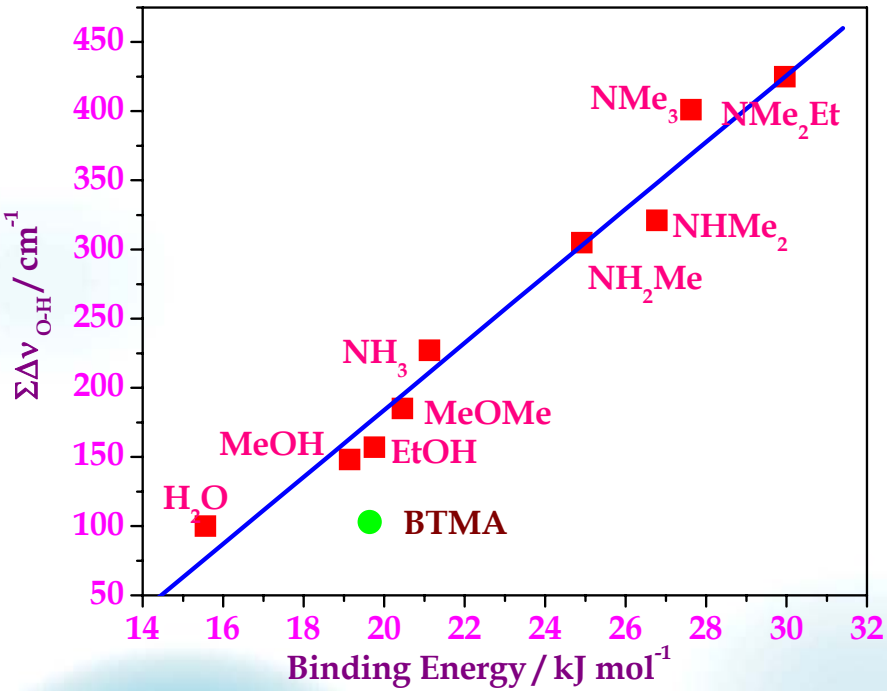


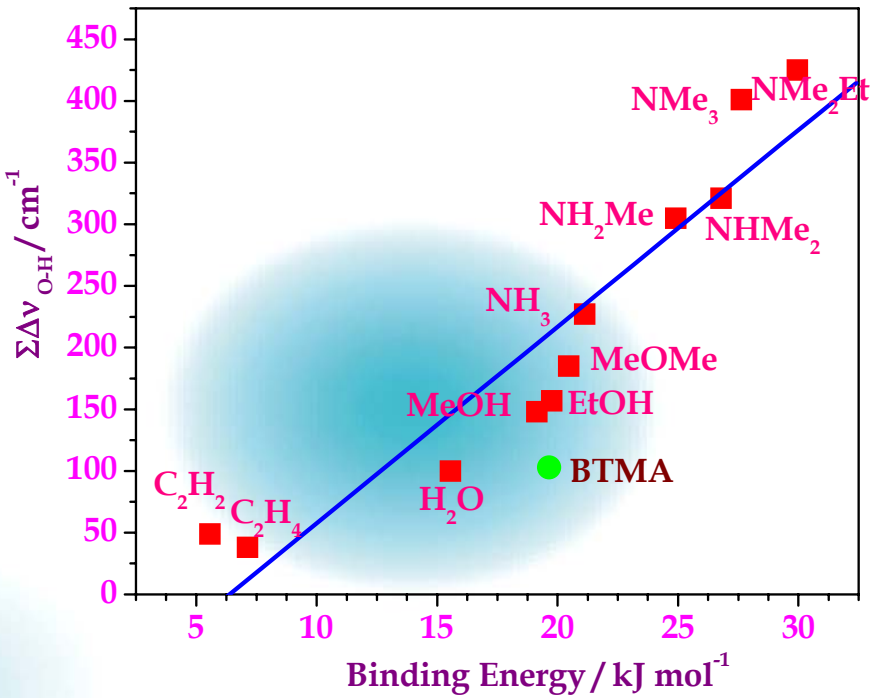
$MeCONH_2$ – BH_3NMe_3



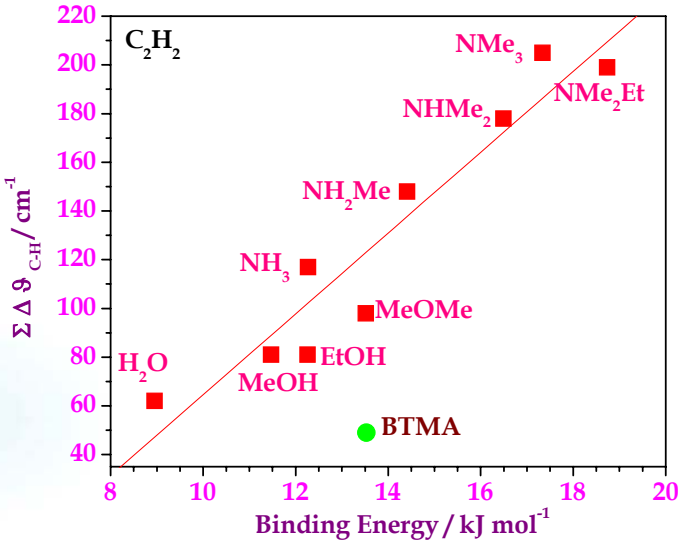
MeCOOH – BH_3NMe_3

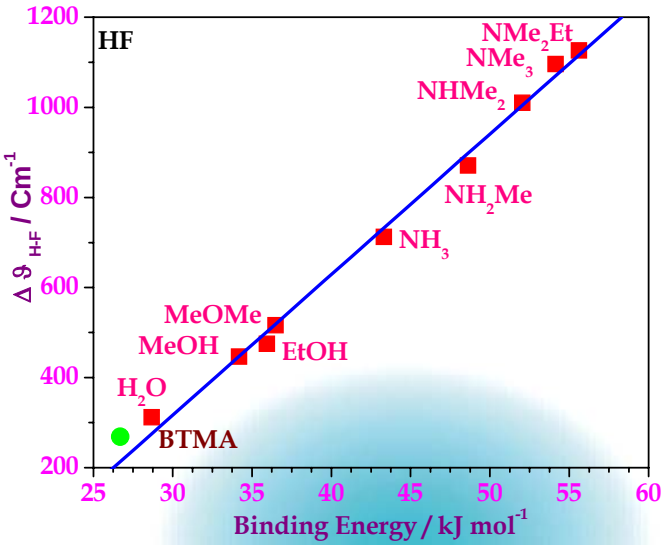
ΔE vs. Δν Correlation

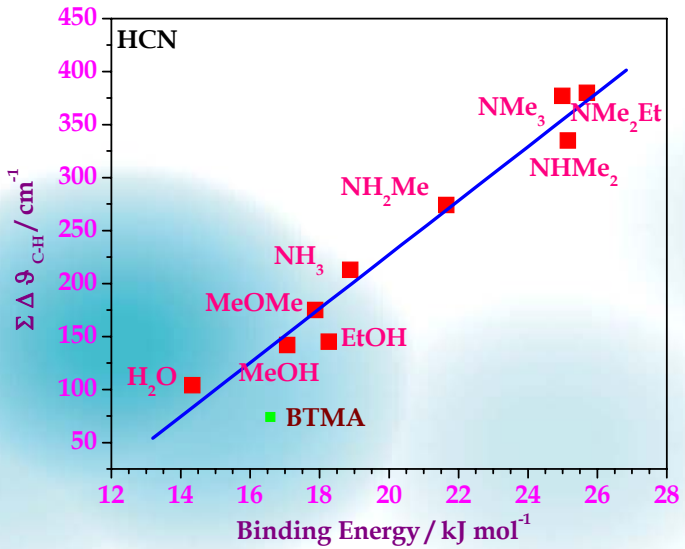


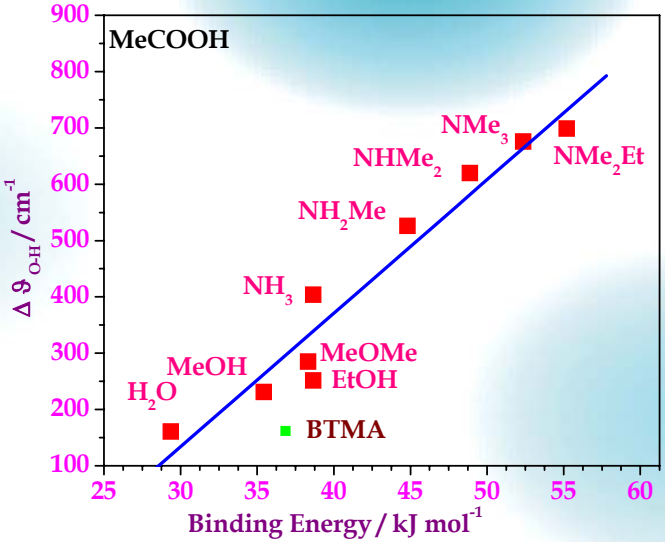


ΔE vs. Δν Correlation

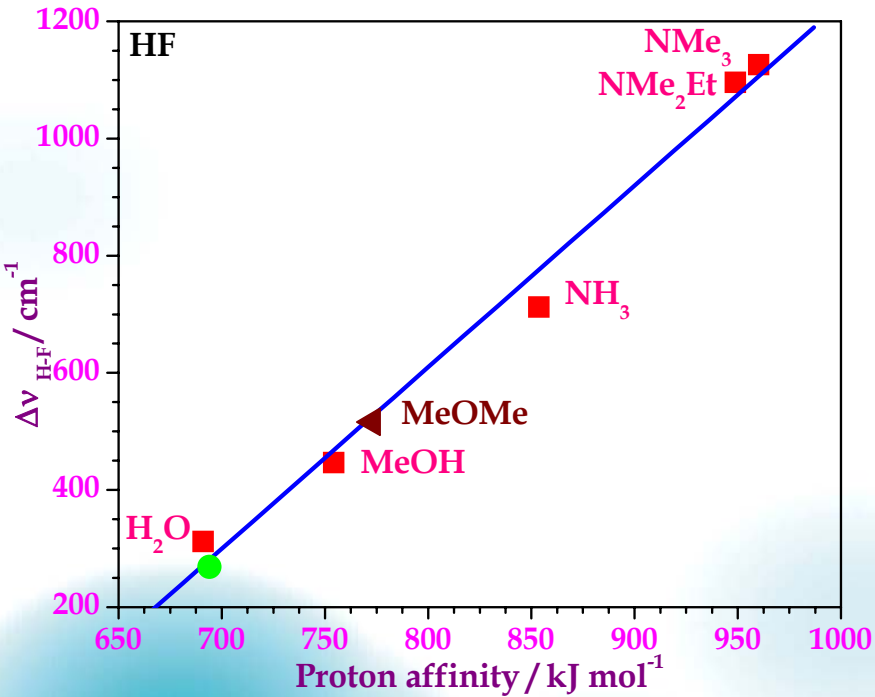


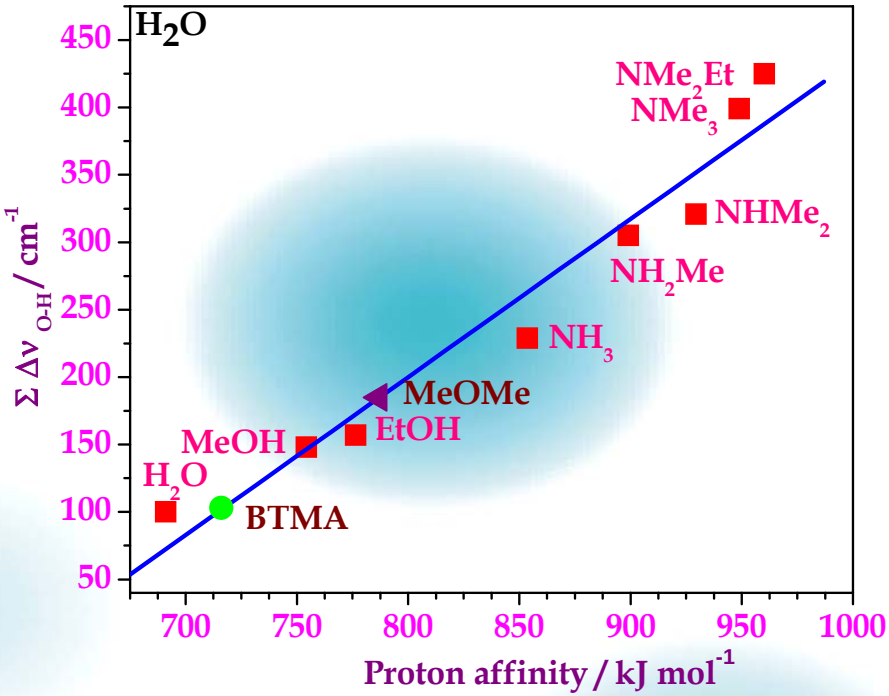




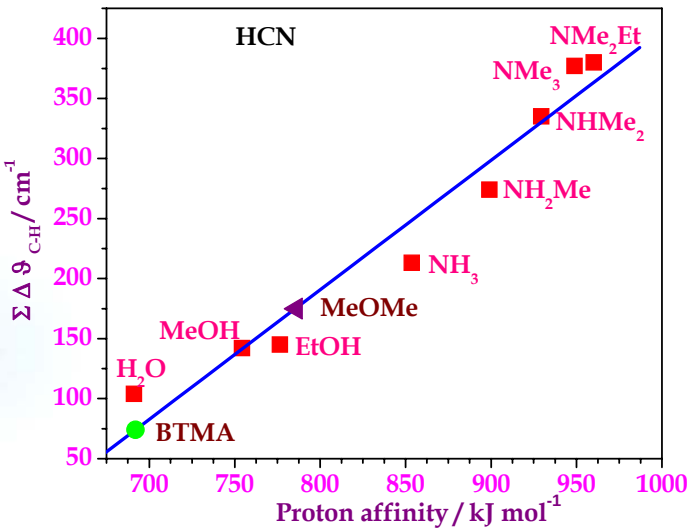


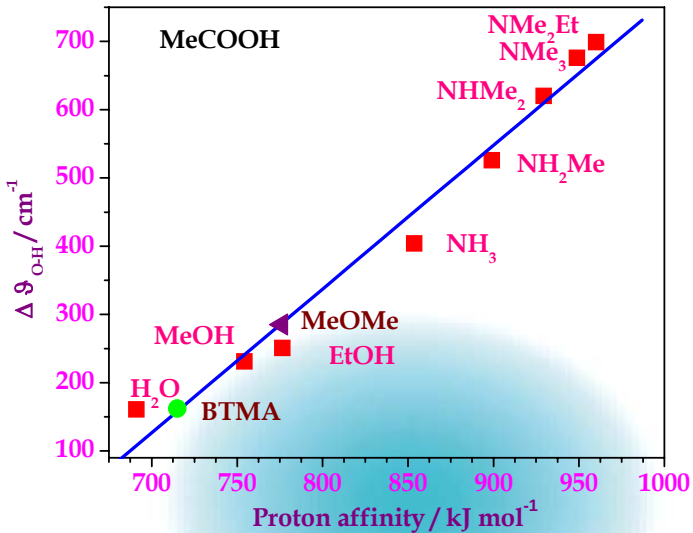
The Proton Affinity vs. Δν Correlations

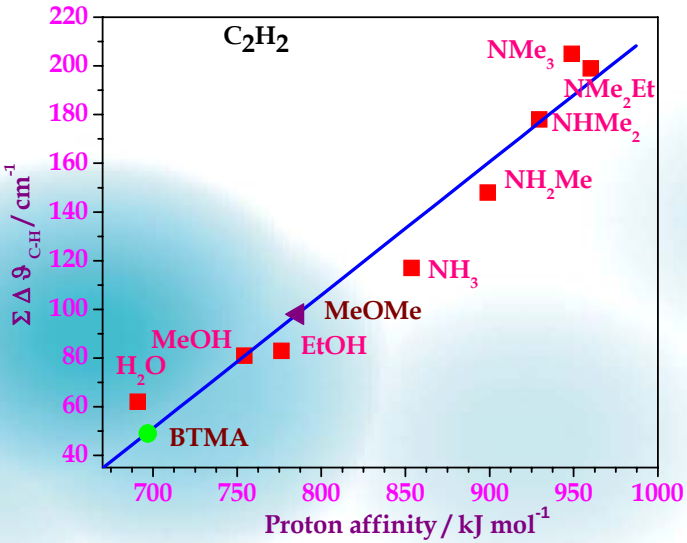


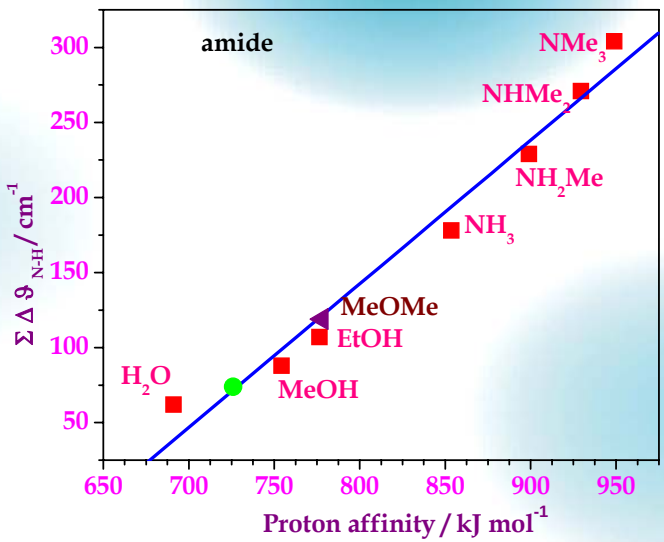


The Proton Affinity vs. Δν Correlations







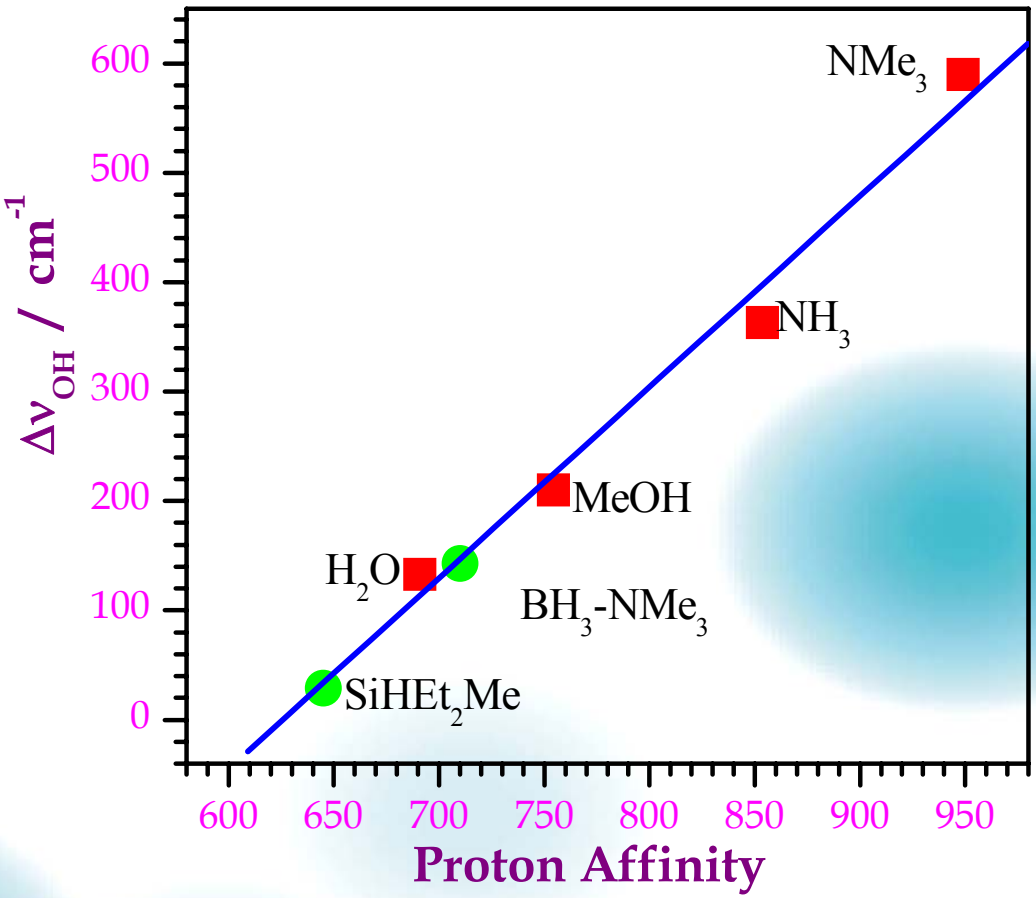


The Scaling law

	C_2H_2	HF	HCN	H_2O	MeCOOH	$MeCONH_2$	EST. PA	EXP. PA	RATIO
MeOMe	786	773	786	787	776	778	781±6	792	0.99
BTMA	697	694	692	716	715	726	707±14	837	0.84

The hydrogen bond correlation under estimates the proton affinity of a dihydrogen bond acceptor by a factor of 0.84

The Proton Affinity Correlation



The proton affinities of BTMA and $SiHEt_2Me$ can be estimated as 708 and 645 kJ mol^{-1}, respectively

The Scaling law: Verified

The Estimated Proton Affinity of BTMA:		**708 kJ mol^{-1}**
True Proton Affinity of BTMA	**:**	**(708 / 0.84)** **843 kJ mol^{-1}**
Calculated G2 Proton Affinity of BTMA	**:**	**837 kJ mol^{-1}**

The Estimated Proton Affinity of $SiHEt_2Me$:		**645 kJ mol^{-1}**
True Proton Affinity of $SiHEt_2Me$	**:**	**(645 / 0.84)** **768 kJ mol^{-1}**
Calculated G2 Proton Affinity of $SiHEt_2Me$	**:**	**768 kJ mol^{-1}**

Conclusions

Dihydrogen Bonding is an interaction analogous to Hydrogen Bonding;

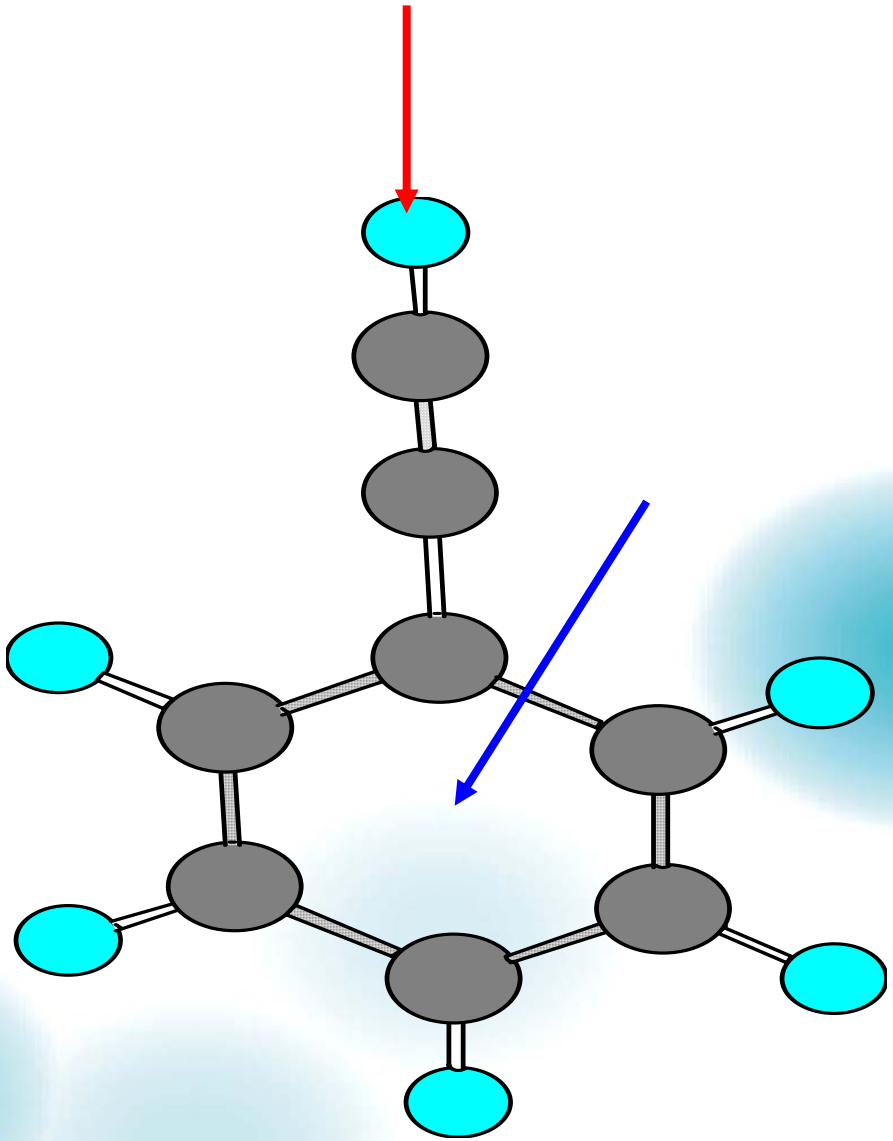
However, is on the average 16% weaker than normal Hydrogen Bond

Hydrogen Bonding; Generic Definition

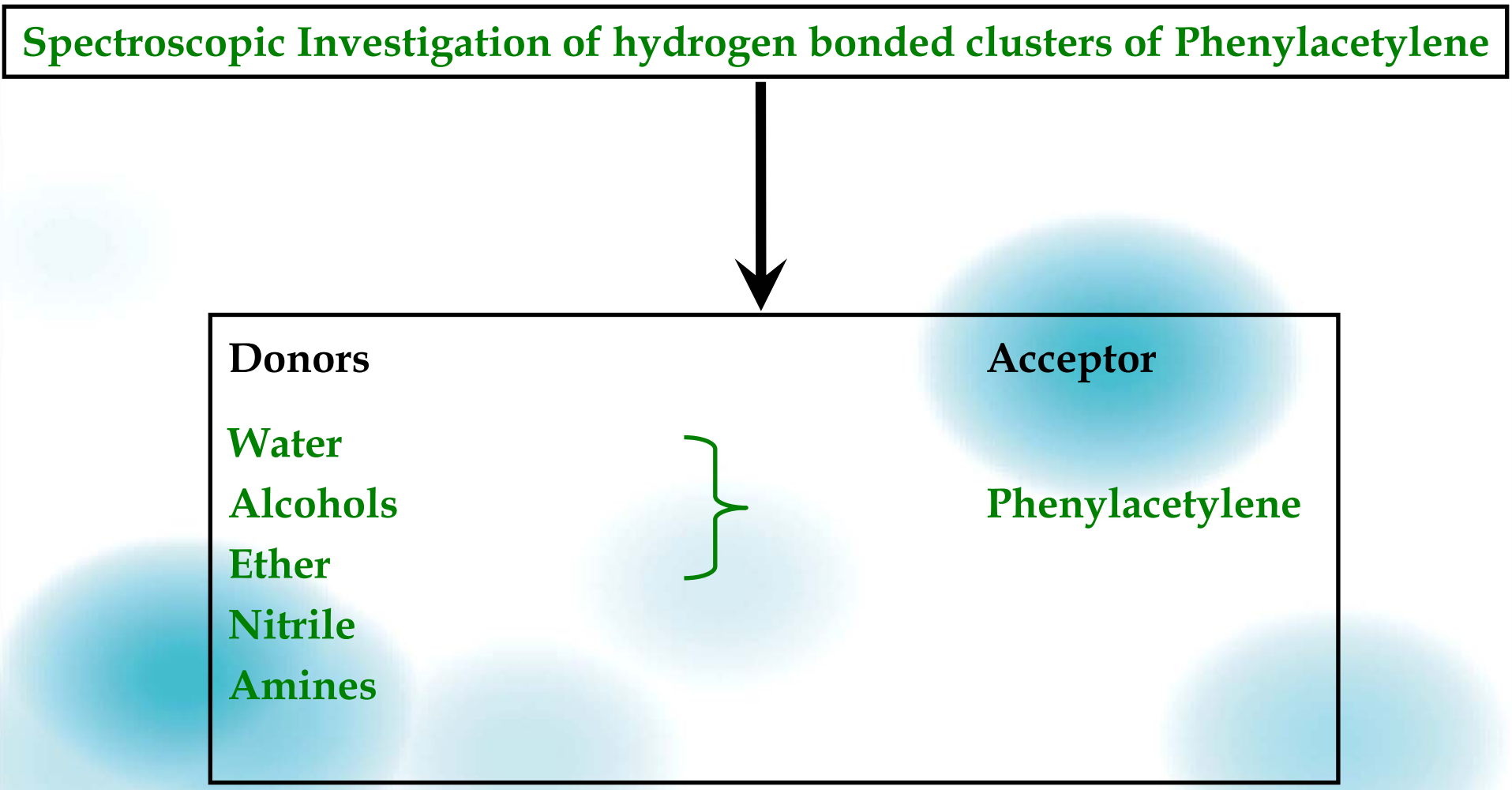
Hydrogen bonding is the interaction of positively charged hydrogen with electronically saturated but coordinatively unsaturated molecules, with excess electron density

Spectrometer

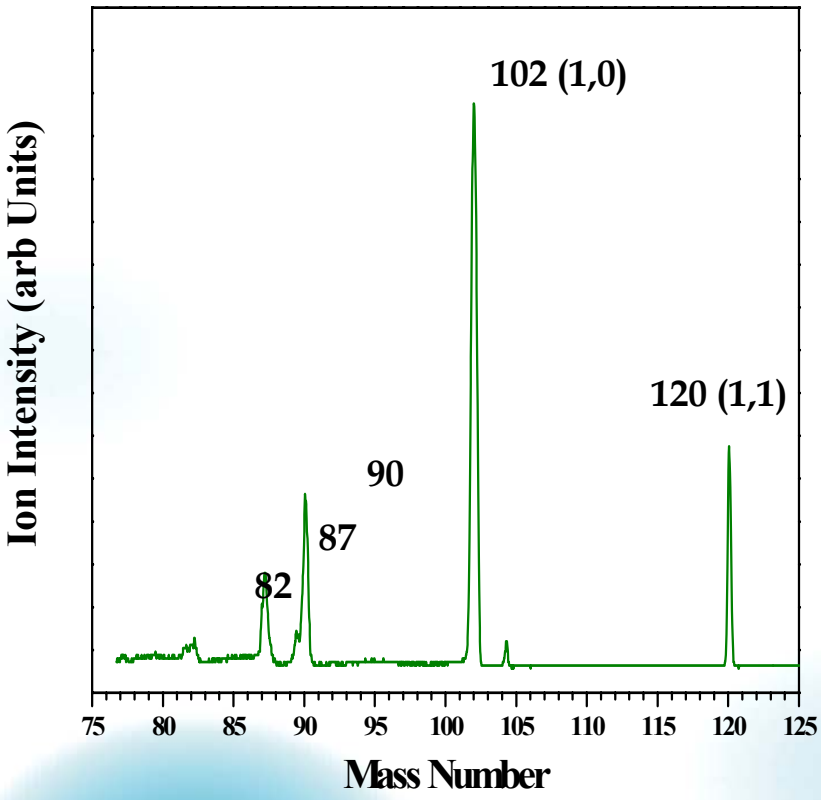
Hydrogen bonding with Phenylacetyelene



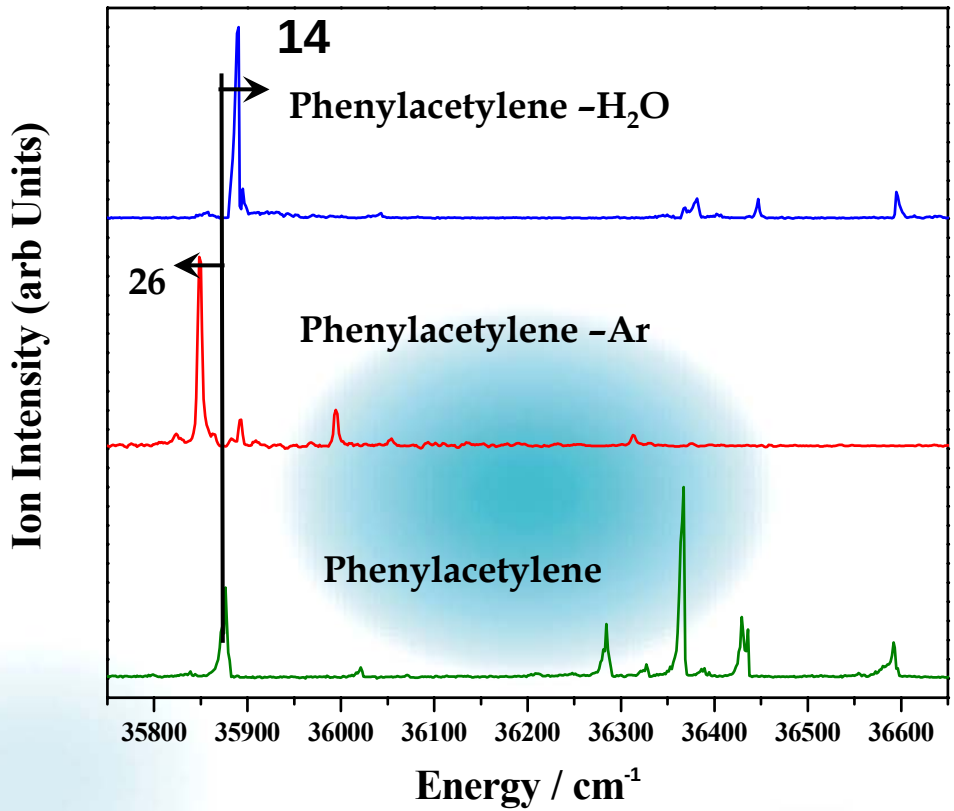
Hydrogen bonding with Phenylacetyelene



The R2PI Mass and Excitation Spectra

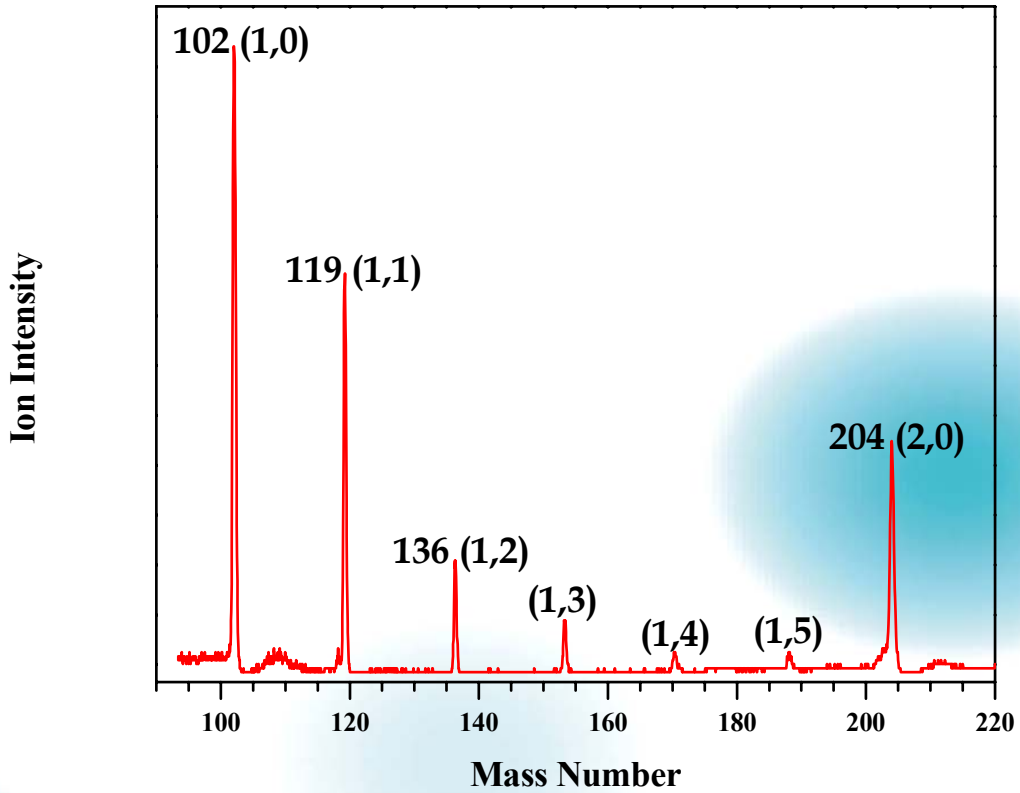


The mass spectrum of phenylacetylene-H_2O system



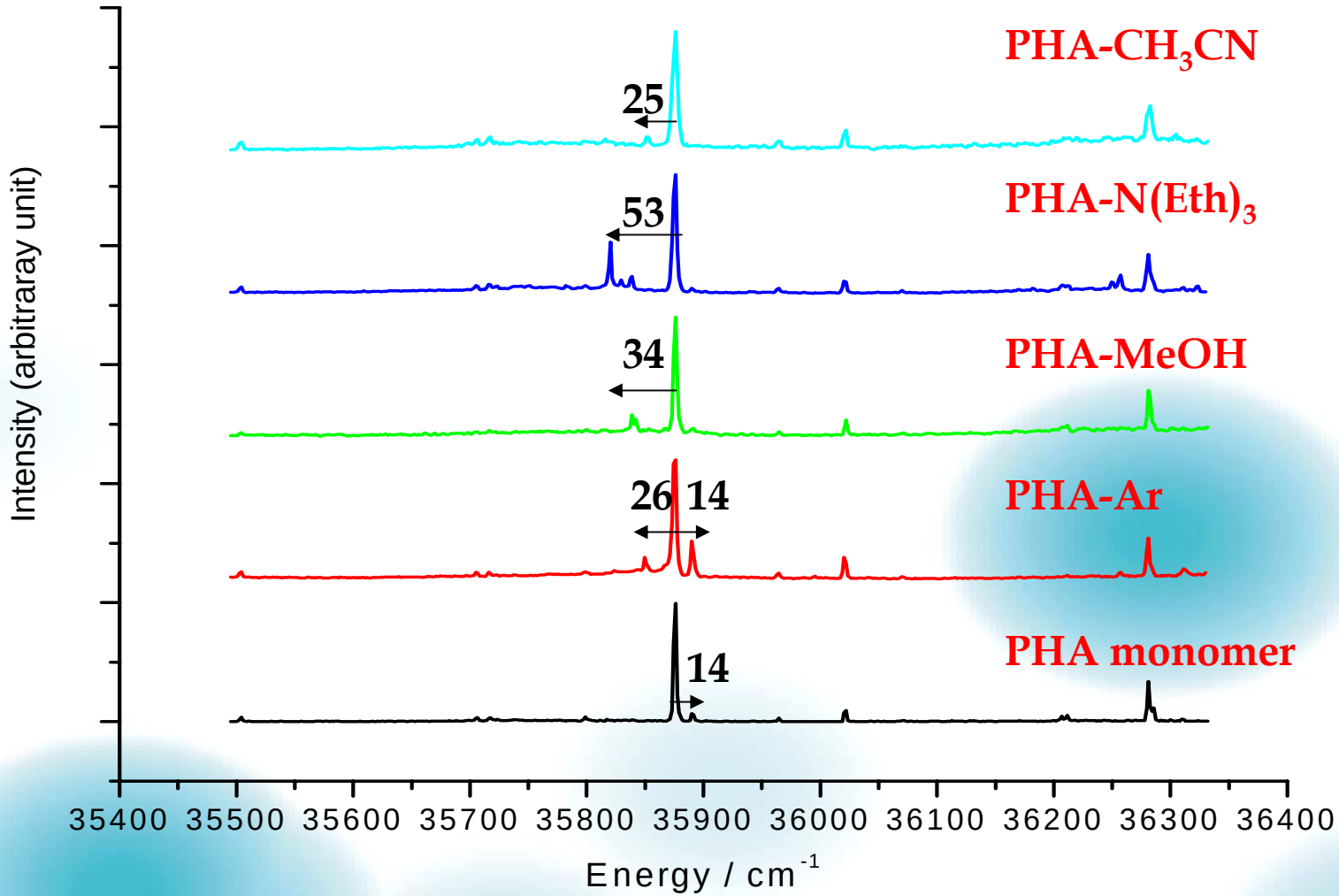
The band origin of Ar complex shifts to the red by 26 cm^{-1} and that of H_2O cluster shifts to the blue by 14 cm^{-1}

The R2PI Mass Spectra



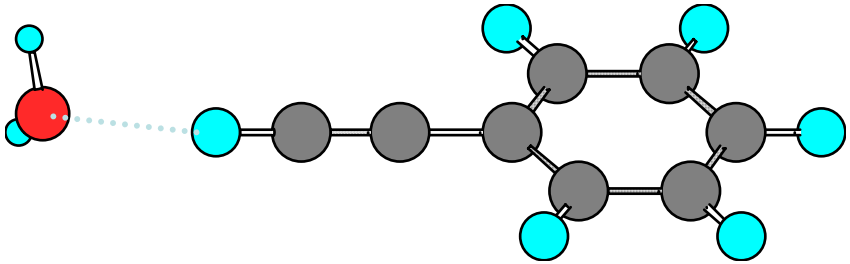
The mass spectrum of phenylacetylene-NH_3 system

LIF Excitation Spectra

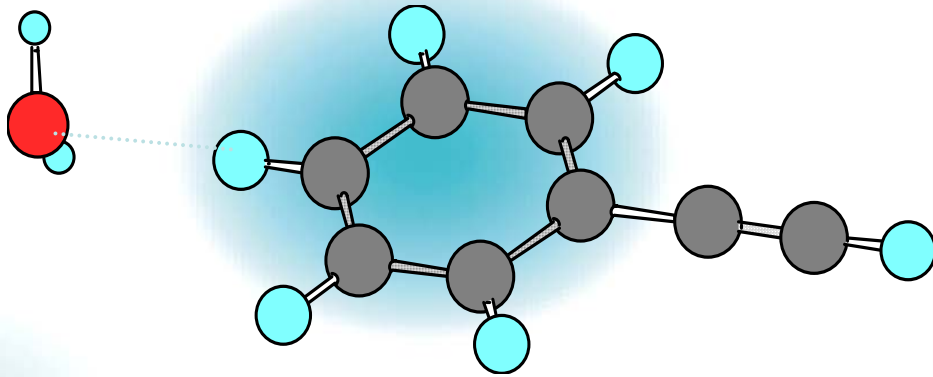


Switching from π to σ hydrogen bonding

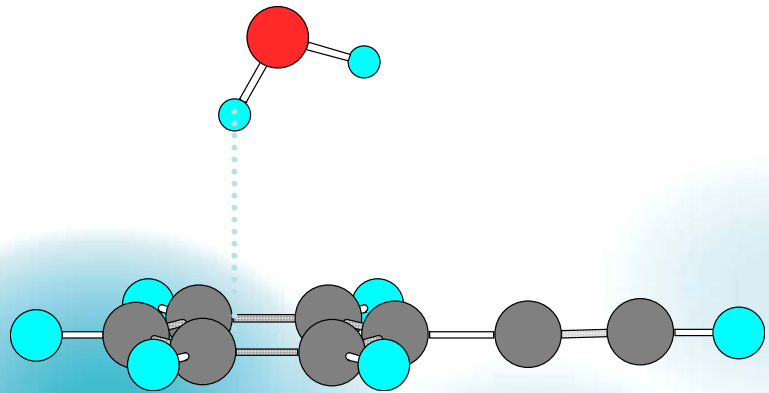
Theoretical calculation



13.0 kJ mol^{-1}

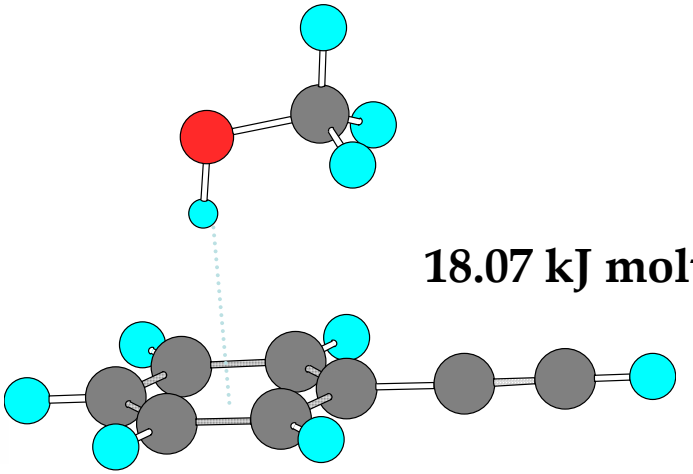


8.3 kJ mol^{-1}

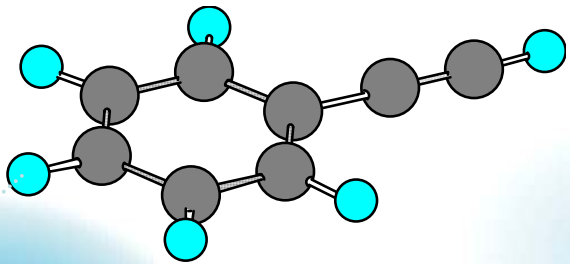


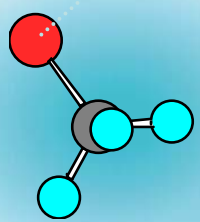
12.9 kJ mol^{-1}

Theoretical calculation

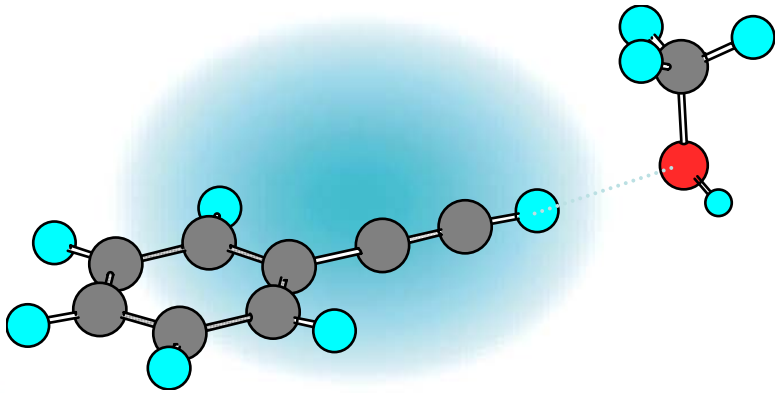


18.07 kJ mol^{-1}





10.73 kJmol^{-1}



15.44kJ mol^{-1}

Acknowledgements

Prof. Naohiko Mikami; Tohoku University

Mr. Prashant Chandra Singh; IIT Bombay

Mr. Biswajit Bandhopadhyay, IIT Bombay

IIT Bombay; CSIR; BRNS; DST