

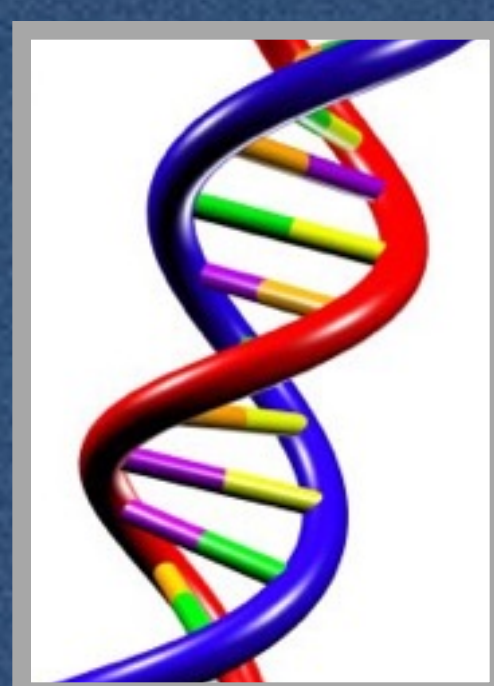
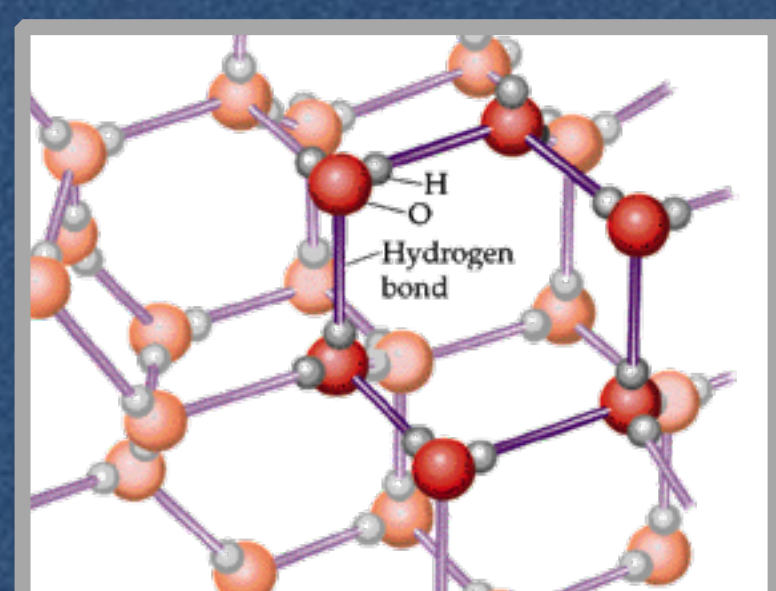


Quantum-Chemical Study of Hydrogen-Bonded Complexes: Understanding Solvent Shifts in the IR Spectra of Alcohols

Margaret D Phillips and Dr. J.A. Phillips (mentor) ❖ Department of Chemistry, UWEC

Context: Hydrogen Bonding

Hydrogen Bonding is an “interaction between the hydrogen atom in a polar bond and an electronegative O, N, or F atom.” Hydrogen bonding is important in a wide variety of natural phenomena, including the unique physical properties of ice (*below left*) and the interactions between base pairs in the double helix of DNA (*below right*).



Methods

Chemical Computations: Computer simulations of the electron distributions give insight into structure, bonding, and energetic properties of molecules and their interactions.

All computations were performed using:

- Software: Gaussian 09 version D.01
- Methods: M06, B3LYP, W-B97X-D, B3PW91, MP2, CCSD, CCSD(T)
- Basis sets: aug-cc-pVTZ, 6-311+G(2df,2pd)
- Equilibrium geometries: opt=tight
- Frequencies: Scaled M06
- Charges: Natural Population Analysis

For a given hydrogen-bonded system: A-H - - B

- ΔE : The interaction energy:

$$\Delta E = E(A-H \cdots B) - [E(A-H) + E(B)]$$

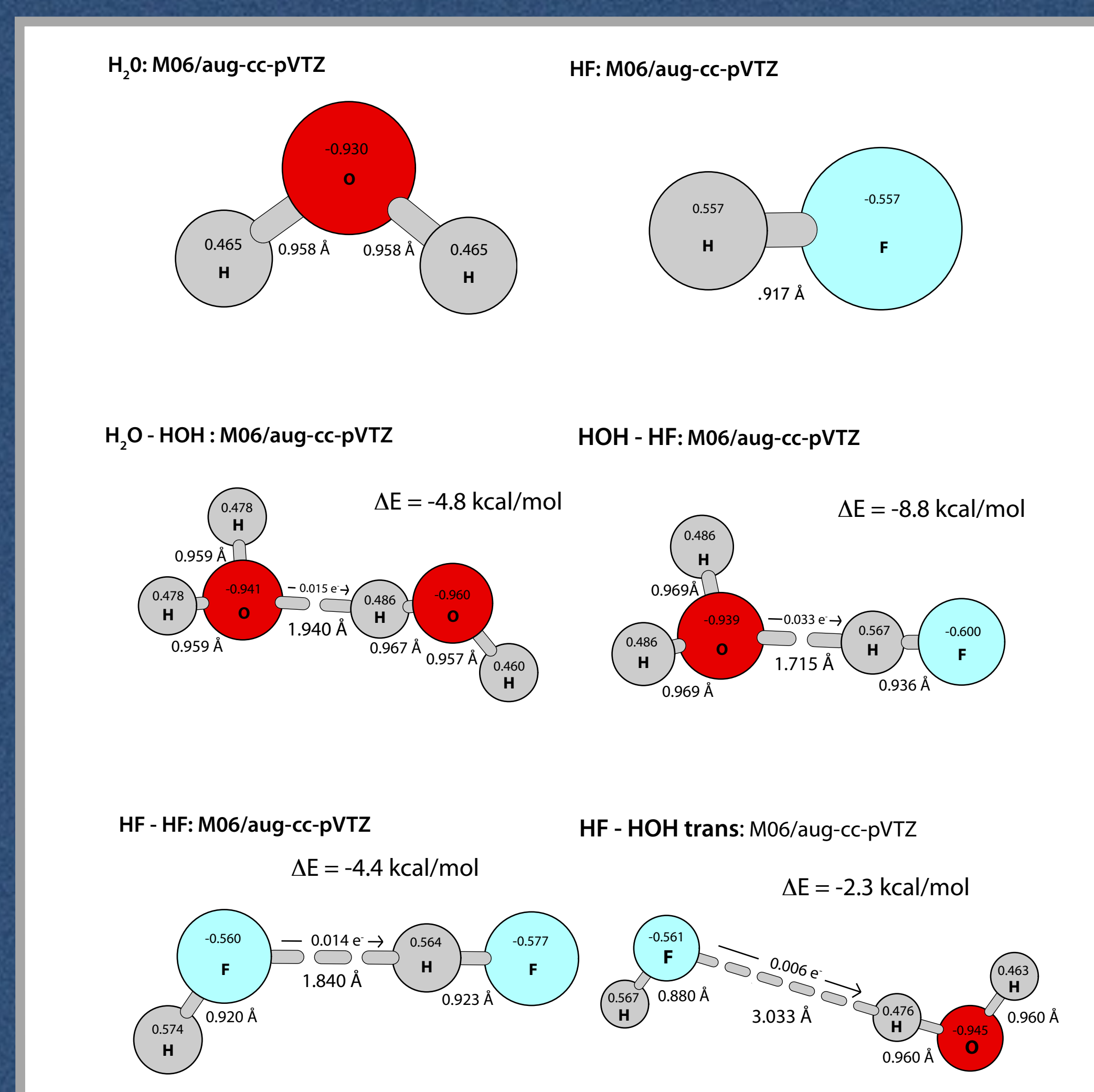
- ΔR_{HA} : The bond length of the “donor” molecule (HA) lengthens as a result of the interaction
- Charge transfer: Calculated atomic charges convey the extent of bona fide chemical bonding - electron transfer from B to HA.
- $\Delta \nu_{OH}$: Frequency shift - The “pitch” of the H-A Bond lowers as a result of H-Bonding.

HF & H₂O Complexes

Initially, we were interested in whether the hydrogen bonding in HF (*l*) or in H₂O (*l*) is stronger.

Therefore, we examined a series of binary complexes involving HF & H₂O: (H₂O)₂, (HF)₂, and three isomers of H₂O-HF.

We calculated the interaction energy (ΔE), elongation of the donor bond (ΔR_{HA}), and the extent of electron transfer between the components of the complex.



We observed the following trends in the results:

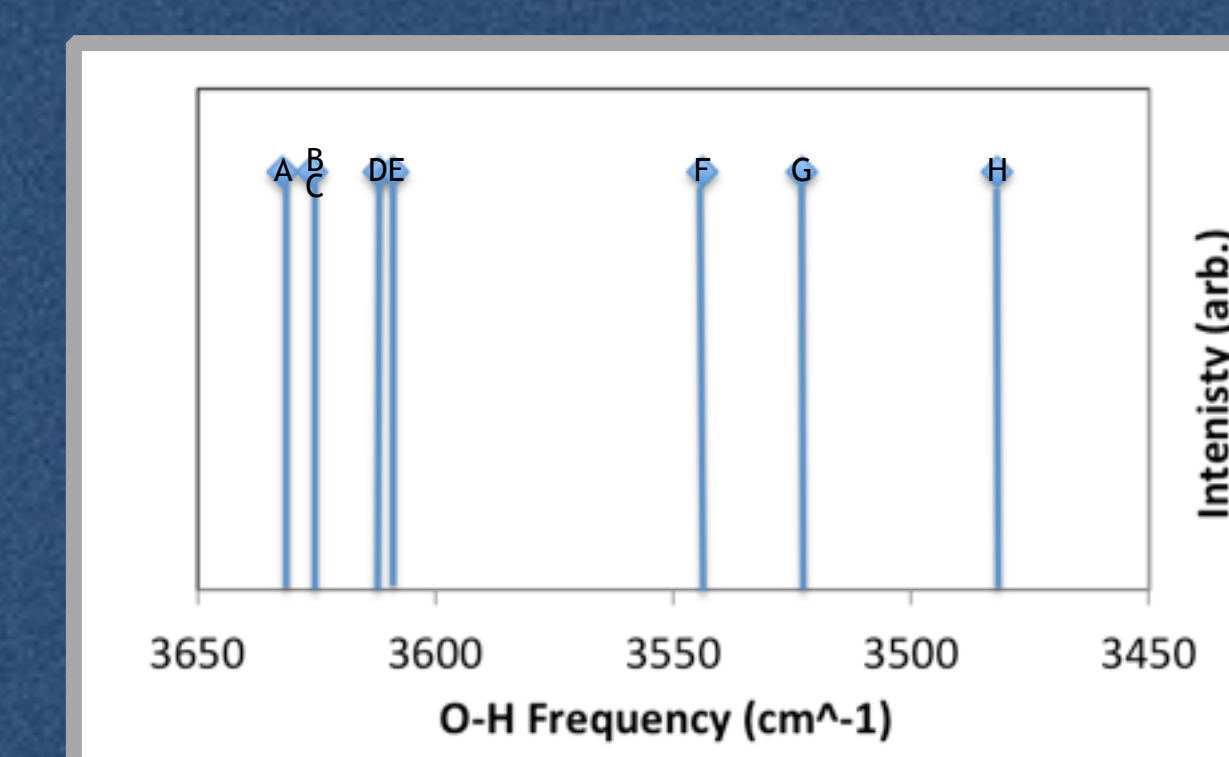
- ΔE : HOH-HF > (H₂O)₂ ≥ (HF)₂ > HF-HOH
- ΔR_{HA} : Lengthens 0.01 Å to 0.02 Å and the elongation parallels the interaction energy.
- Charge transfer: NPA analysis indicates 0.001 electrons are transferred to the H-Bond donor molecule (HA), and this also parallels the interaction energy.

Acknowledgments

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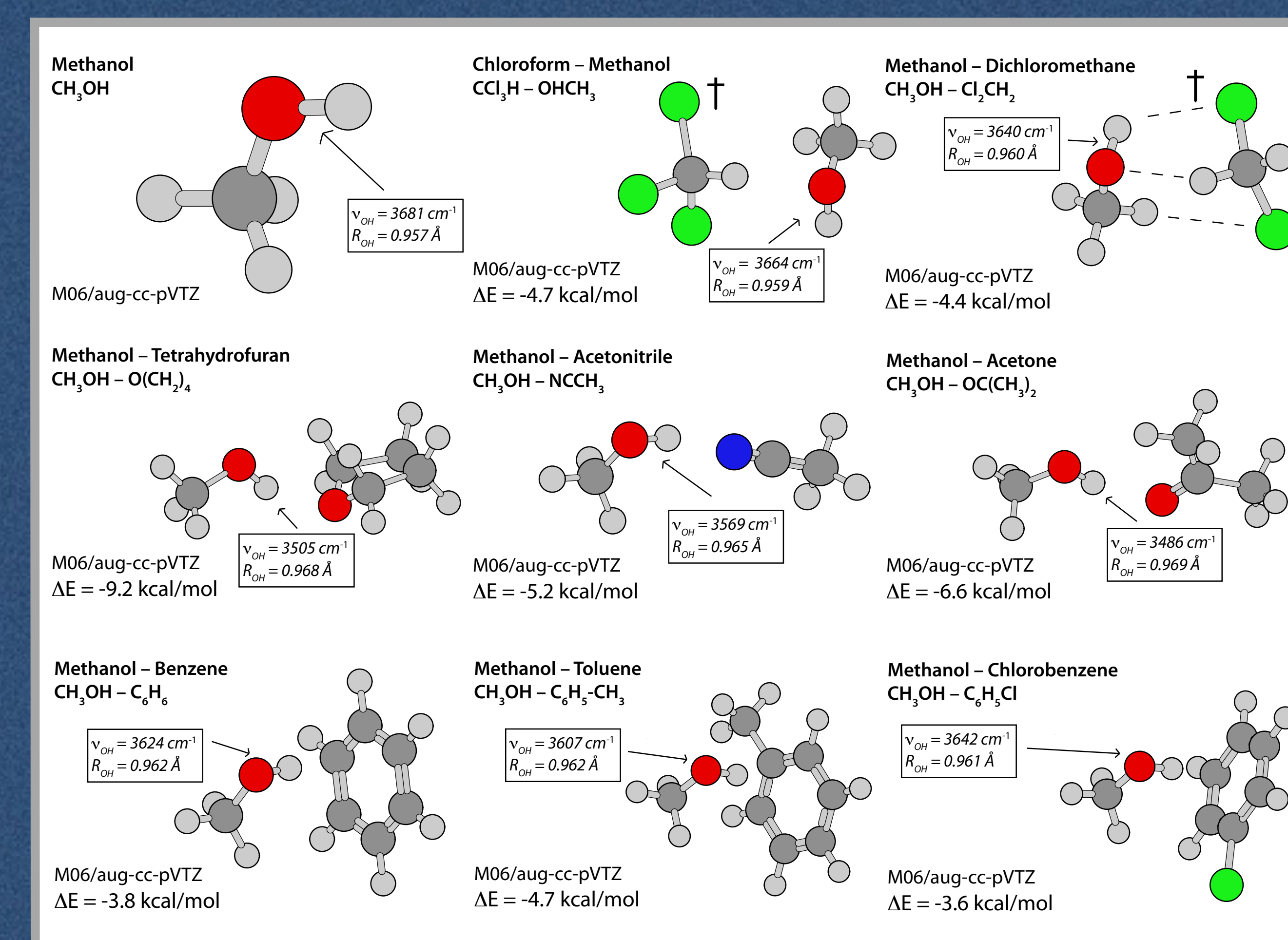
Methanol Complexes

Last spring, students in CHEM 438 collected infrared spectra of alcohols in a series of solvents and observed the following trend in the O-H stretching frequencies (ν_{OH}) of methanol:



Solvents:
 A: Chloroform
 B: Dichloromethane
 C: Chlorobenzene
 D: Benzene
 E: Toluene
 F: Acetonitrile
 G: Acetone
 H: Tetrahydrofuran

Computational Results:



Overall trend in shifts largely parallels calculations:

- ΔR_{OH} : Trend intact, except two strongest systems are reversed (*G and H from above*).
- $\Delta \nu_{OH}$: Same as ΔR_{OH} with B and C also reversed.
- ΔE : The trend is intact, with two notable exceptions: Dichloromethane (B) & Chloroform (A), which are stronger than expected.

*** Note: In these structures above (†), the hydrogen-bonding interaction is reversed. Methanol is the acceptor rather than the donor! ***

Works Cited:

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