Chem 391: Goals for the Semester

Goals for the semester:

1. Tools to **measure** structure (spectroscopy)
   note that biophysics explains tools, I will simply tell what they measure

2. Organizing principles to **describe** structure
   Just like words for different colors can help organize visual world

3. Tools to **measure** function
   Binding can be measured by K_{eq}, catalysis measured by k_{cat}

4. Organizing principles to link function to structure: **thermodynamics**
   I desperately want all to think about contributions of ΔH and ΔS to spontaneity.

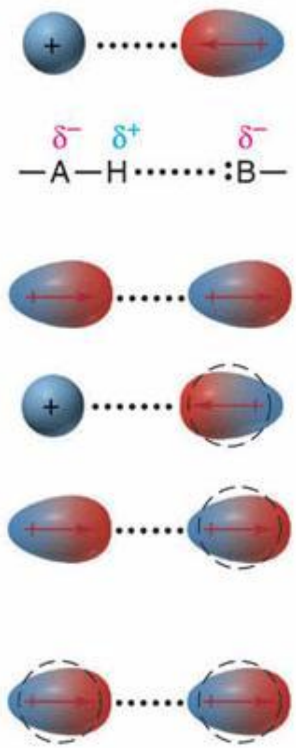
Covalent Bonding

C-C	83 kcal/mol	1.54 Å
C=C	147 kcal/mol	1.34 Å
C-O	86 kcal/mol	1.43 Å
C=O	127 kcal/mol	1.20 Å
C-H	99 kcal/mol	1.09 Å
O-H	111 kcal/mol	0.96 Å
N≡N	227 kcal/mol	1.10 Å

Some Intermolecular Contacts

Molecular dimer	**$\Delta H_{interaction}$ ($^{kcal}/_{mol}$)**	**distance (Å)**
$CH_4 \cdot CH_4$	0.3	3.5
$SiH_4 \cdot SiH_4$	0.6	4.2
$H_2O \cdot CH_4$	0.9	3.5
$HCl \cdot HCl$	1.2	3.8
$HF \cdot HF$	2.9	2.7
$H_2O \cdot H_2O$	3.2	2.8

Gallery of IMFs



Nonbonding (Intermolecular)		E (kcal/mol)	
Ion-dipole	Ion charge–dipole charge	10-150	Na^+····OH_2
H bond	Polar bond to H–dipole charge (high EN of N, O, F)	2-10	:Ö—H····:Ö—H (each O also bonded to H)
Dipole-dipole	Dipole charges	1-5	I—Cl····I—Cl
Ion–induced dipole	Ion charge–polarizable e^- cloud	1-3	Fe^{2+}····O_2
Dipole–induced dipole	Dipole charge–polarizable e^- cloud	0.5-2.4	H—Cl····Cl—Cl
Dispersion (London)	Polarizable e^- clouds	0.01-10	F—F····F—F

http://itl.chem.ufl.edu/2045/lectures/lec_g.html

Does an H-bond Matter in Water?

TABLE I

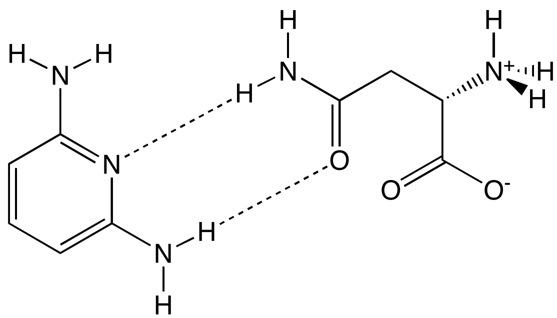
THERMODYNAMICS OF INTERAMIDE HYDROGEN BOND FORMATION BY N-METHYLACETAMIDE AT 25°

Solvent	Association constant for dimerization, k_2	$\Delta F°$, kcal. mole^{-1}	$\Delta H°$, kcal. mole^{-1}	$\Delta S°$, gibbs mole^{-1}
Carbon tetrachloride	4.7 (5.8)	−0.92	−4.2	−11
Dioxane	0.52 (0.58)	0.39	−0.8	− 4
Water	0.005 (0.005)	3.1	0.0	−10

Klotz & Franten (1962) *JACS* **84**, 3461-3466

Which of these H-bonding Schemes is Satisfactory?

A.



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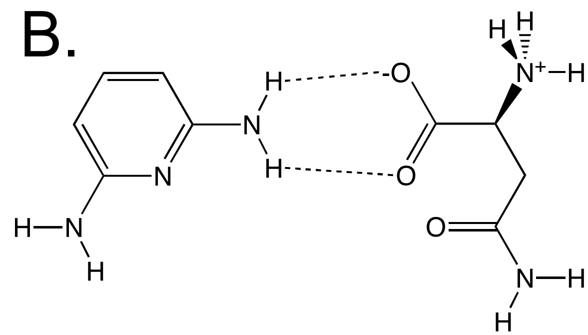

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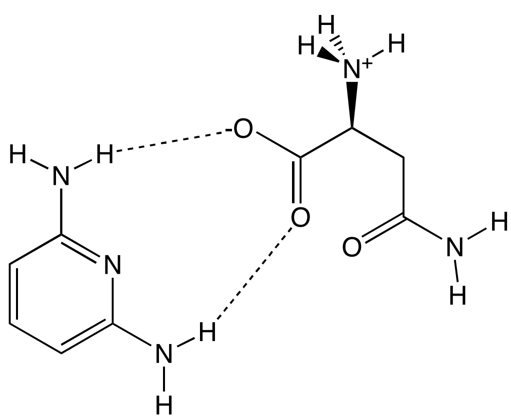
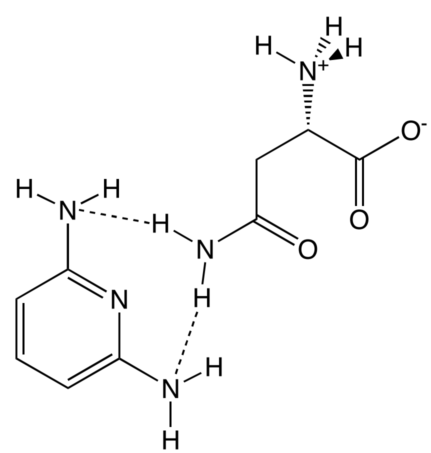


D.

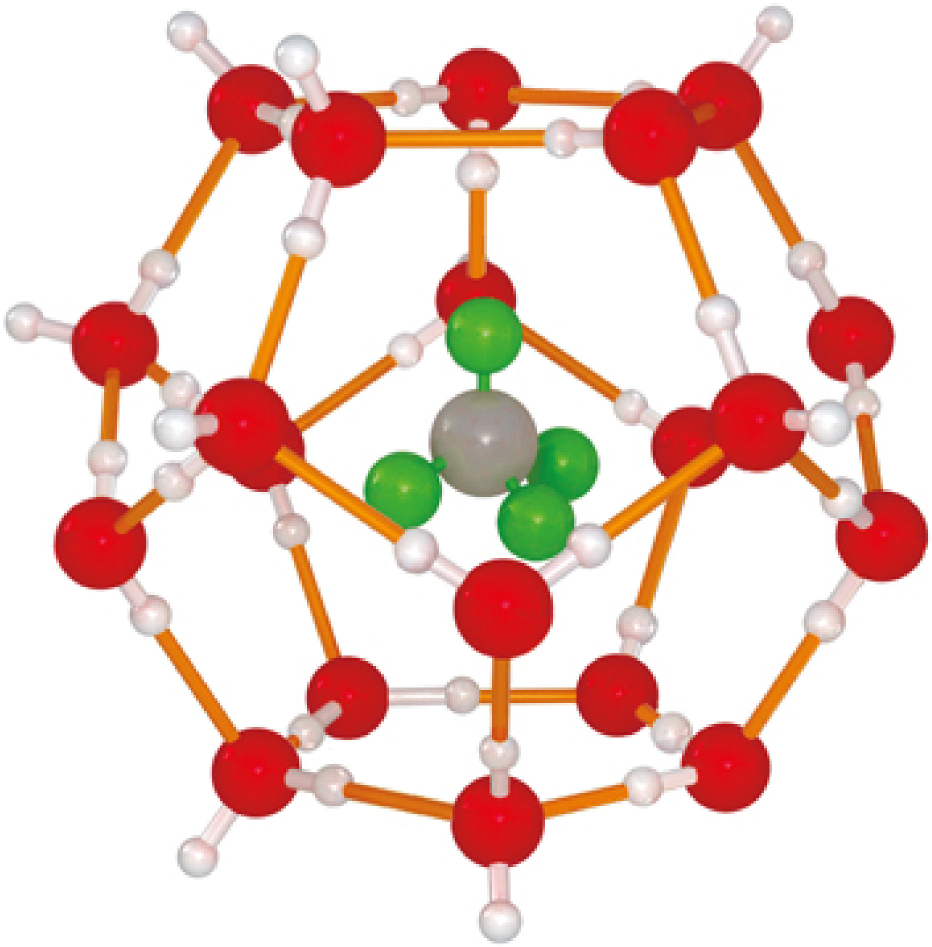


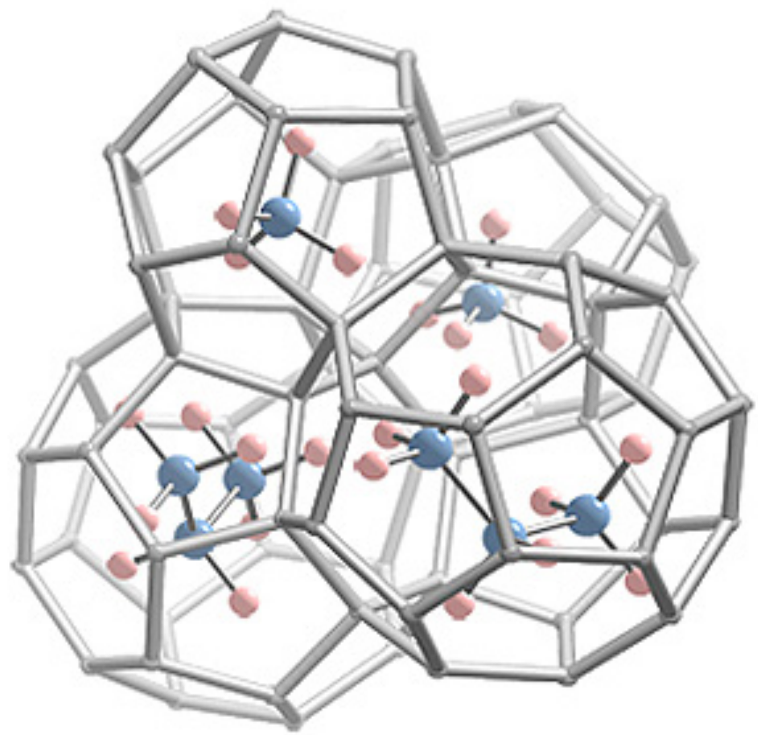
E. All of the above

Transfer of Methane from CCl_4 to H_2O

Transfer	**ΔG°** **($^{kcal}/_{mol}$)**	**ΔH°** **($^{kcal}/_{mol}$)**	**ΔS°** **($^{cal}/_{mol•K}$)**
$CH_{4(g)} \rightarrow CH_{4(H2O)}$	+6.3	-3.2	-32
$CH_{4(g)} \rightarrow CH_{4(CCl4)}$	+3.5	-0.5	-14
$CH_{4(CCl4)} \rightarrow CH_{4(H2O)}$	+2.8	-2.7	-18

Clathrates





Methane Clathrate