

## Lecture Outline Ch 6: NMR - *Further Topics in One Dimensional NMR*

assigned problems: 2-4, 6, **7-8**, 9-10, **11**, 12, **14-20**.

(turn in bold problems for homework grade)

### I. Dynamic Effects in NMR

#### A. Exchangeable Groups

1. the NMR timescale
2. effects of fast exchange - decoupling and chemical shift averaging
3. proton exchange
  - a. alcohols
  - b. exchange of protons between unlike groups

#### B. Isomerization

1. keto-enol tautomerization - generally slow on NMR timescale
2. degenerate rearrangements - Cope rearrangement

#### C. Conformational Dynamics

1. VT-NMR, coalescence temperature ( $T_c$ ), and rate
2. example: N,N-dimethylacetamide
  - a.  $T_c = 80^\circ\text{C} = 353\text{K}$
  - b. rate equation:  $k_{(T_c)} = \pi/(2)^{1/2} \Delta\nu = 2.22 \Delta\nu$ ,  $T_{(353)} = 17.8 \text{ s}^{-1}$
  - c. Eyring equation:  $k_{(T_c)} = [k/h] T_c e^{-\Delta G^\ddagger/(RT_c)}$ ,  $\Delta G_{(353)} = 18.7 \text{ kcal/mol}$
3. example: cyclohexane ring inversion

### II. Protons on Nitrogen

- A. Exchange and Quadrupole Broadening
- B. Coupling to  $^{14}\text{N}$  ( $I=1$ ) - rare, but  $^1J_{\text{NH}} \sim 50 \text{ Hz}$ ,  $\text{CH}_3\text{NH}_3^+\text{Cl}^-$
- C. Amides NH Signals

### III. Solvent Effect on Chemical Shift

- A. Shifts Due to Diamagnetic Anisotropy of Solvent
- B. Chemical Shift Reagents: Eu(III) paramagnetic reagents
- C. Chiral Shift Reagents - resolution of enantiotopic signals (ee determination)

### IV. Decoupling (double resonance)

### V. NOE Difference Spectra - dissection of spatial relations of nuclei

- A. alkene stereochemistry
- B. ring stereochemistry