Problem Set 7

On commutators, constants of the motion, the uncertainty principle

The precise statement of the uncertainty principle is:

$$\sigma_S\, \sigma_R \geq \tfrac{1}{2} \langle\, [\, \mathbf{S}\, ,\, \mathbf{R}\,]\, /i\, \rangle$$

where $\sigma_S^{\ 2} \equiv \int \Psi^* (\mathbf{S} - \langle S \rangle)^2\, \Psi\, d\tau$, where the operators for observables S and R are **S** and **R** and the brackets have their standard meanings. Use no other form for a statement of the uncertainty principle in this class.

1. Consider a hydrogen-like atom (ion) of charge Z when the atom (ion) is in its ground state:

$$\Psi_{1s} = \{1/\sqrt{\pi}\}\, \{Z/a_0\}^{3/2} \exp[-Zr/a_0]$$

where a_0 is the Bohr radius, $a_0 = \hbar^2/me^2 = 0.529 \times 10^{-8}$ cm.

(a) Calculate the average distance of the electron from the nucleus for this state. You may leave your answer in terms of the Bohr radius.

(b) Calculate the most probable distance of the electron from the nucleus for this state. You may leave your answer in terms of the Bohr radius.

(c) What are the expected outcomes of the measurement of the z component of the electron's orbital angular momentum for the atom in this state, given that the operator for this component is

$$L_z = (\hbar/i)\partial/\partial\varphi \text{ ?}$$

(d) Calculate the average z component of the electron's orbital angular momentum for this ground state.

(e) Does L_z commute with the hamiltonian for a hydrogen-like atom ? Show whether the z component of the electron's orbital angular momentum in this hydrogen-like atom is a constant of the motion. Given that for this system,

$$\mathbf{H} = -(\hbar^2/2m)\nabla^2 - Ze^2/r$$

where $\nabla^2 = \partial^2/\partial r^2 + (2/r)\, \partial/\partial r + \{r^2 \sin\theta)^{-1} \partial/\partial\theta(\sin\theta\, \partial/\partial\theta) + \{r^2 \sin^2\theta)^{-1}(\partial^2/\partial\phi^2)$

Explain each application of the uncertainty principle in problems 2,3,4. The reasoning is more important here, not just the answers.

2. (a) If the diameter of an atomic nucleus is taken to be 10^{-12} cm, compute approximately the least kinetic energy that a proton within the nucleus can have.

(b) Calculate in a similar manner the least kinetic energy of an electron in an atom 10^{-8} cm in diameter. Compare with the ground state energy of the hydrogen atom.

(c) When an electron in an atom is excited into a level above the ground state, it remains in the excited state for a length of time on the order of 10^{-8} seconds. Use the uncertainty principle to compute the minimum width of the spectral line (λ = 5000 Å) emitted when the electron returns to the ground state. This minimum line width is called the natural line width of a spectral line. Give your answer in Angstroms.

3. One of the long-standing problems of stereochemistry is that of determining barriers to pyramidal inversion of nitrogen in amines. While failures to separate enantiomorphs had indicated at an early stage that the barriers must be low, no quantitative estimates were reported prior to the discovery that the barriers in aziridines are large enough for study by the dynamic NMR method, lying in the range 15-20 kcal/mole. Using only the <u>uncertainty principle</u> we can get an <u>estimate</u> of the barrier. Let us do this for a specific example.

In dibenzylmethylamine there are (among others) two kinds of protons H_A and H_B in a CH_2 group, which are separated by a chemical shift of 30.5 Hz. Rapid inversion of the nitrogen pyramid makes the two hydrogens rapidly interchange environments.

(a) Based on the uncertainty principle, what is the (lower, upper, which one?) limit on the lifetime of each pyramidal configuration if the peaks in the NMR spectrum due to the two hydrogens in the CH_2 group collapse at -135°C?

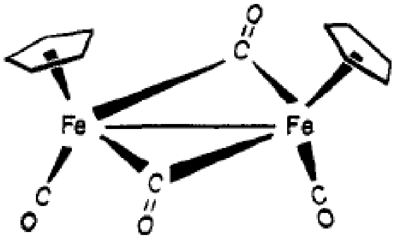
(b) From this (upper or lower?) limit of lifetime in seconds, estimate the (upper or lower?) limit for the rate constant of inversion, k, in s^{-1} at -135°C.

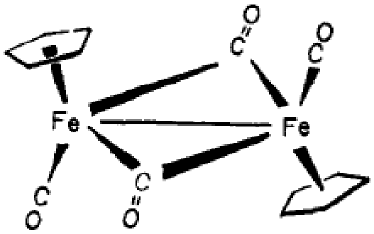
(c) Using Eyring's absolute rate theory:

$k = (k_B T/h) \exp[-\Delta G\ddagger/k_B T]$ where k = rate constant, s^{-1}
k_B = Boltzmann's constant = 1.987 cal mol^{-1} deg^{-1}
h = Planck's constant = 6.62618×10^{-27} erg s

find an approximate value for $\Delta G\ddagger$, the free energy barrier to inversion, in Kcal mol^{-1}.

4. The two C_5H_5 groups in $Fe_2(CO)_4(C_5H_5)_2$ have chemically equivalent environments in any of the three possible structures proposed by A. R. Manning [J. Chem. Soc. A 1319 (1968); 1498 (1969)]





cis bridged

trans bridged

non-bridged
(you can draw this one)

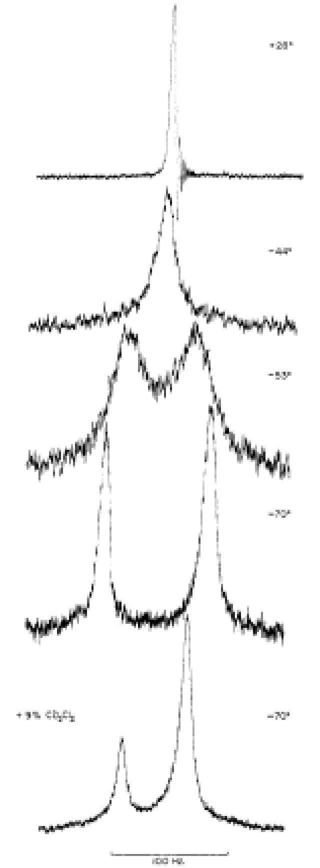


Figure 1. Pmr spectra (100 MHz) for $(C_5H_5)_2Fe_2(CO)_4$ at various temperatures. Upper four traces made using $C_6D_5CD_3$–CS_2 (1/3, v/v). Lower trace made using same solvent to which ~9% volume of CD_2Cl_2 was added.

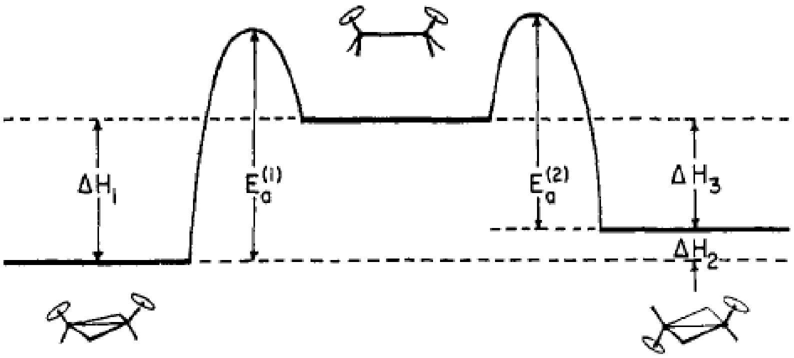
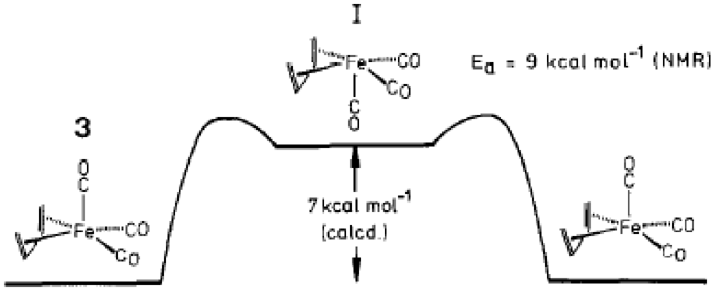
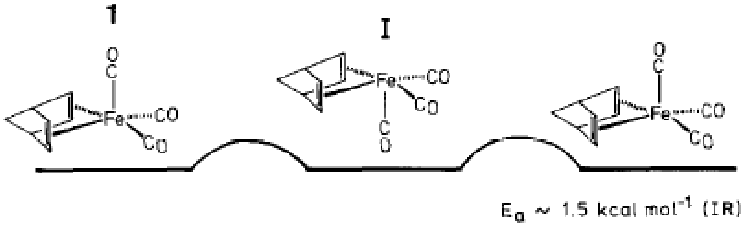


Figure 2. Schematic diagram of reaction coordinate for interconversion of *cis*-bridged, *trans*-bridged, and nonbridged structures of $(C_5H_5)_2Fe_2(CO)_4$.

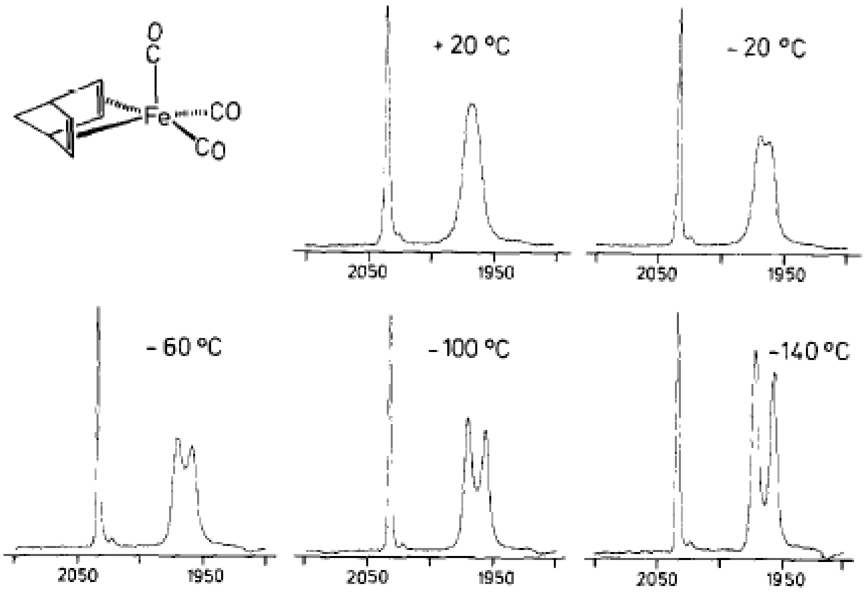
The proton NMR spectrum at -70 °C [J. Am. Chem. Soc. 92, 2156 (1970)] shows two peaks , i. e., two kinds of C_5H_5 groups. At -44 °C the spectrum shows only one broad peak which upon warming to room temperature (+28 °C) showed considerable narrowing. The two peaks at -70 °C are separated by 9.2 Hz. Using the uncertainty principle, get a rough estimate of the lifetime at -44° C of either of the two structures corresponding to the two peaks.

5. As you have seen above, coalescence of NMR signals is typically associated with rate constants in the order of 10^4 s^{-1}. Similar coalescence of vibrational bands in the infrared spectra would imply that the underlying processes take their course in the picosecond time domain (proton transfer reactions and conformational rearrangements, for example). In J. Mol. Struct. 174, 107-112 (1988) it was reported that η^4-norbornadiene)Fe(CO)$_3$ and related complexes reveal a coalescence phenomenon involving the CO stretching vibrational bands. This is interpreted in terms of fast CO site exchange. A cartoon for this exchange is given in the paper for two cases with rather different barriers, depending on the nature of diene ligand, one barrier obtainable from NMR the other from IR:





The IR spectra show coalescence at 20°C of the two peaks that at low enough temperature (exchange rate extemely slow) are separated by 15 cm^{-1} (the 1971 and 1956 cm^{-1} peaks).



(a) Based on the <u>uncertainty principle</u> what is the (lower, upper, which one?) limit on the lifetime of each configuration <u>at 20°C</u> when the peaks just coalesce?

(b) From this (upper or lower?) limit of lifetime in seconds, calculate the (upper or lower?) limit for the rate constant for CO site exchange at 20°C, k, s^{-1}.

(c) Using Eyring's absolute rate theory:

$k = (k_BT/h) \exp[-\Delta G‡/k_BT]$ where k = rate constant, s^{-1}
k_B = Boltzmann's constant = 1.987 cal mol^{-1} deg^{-1}
h = Planck's constant = 6.62618x10^{-27} erg s

find an approximate value for ΔG‡, the barrier height, in Kcal mol^{-1}.