Analytical Chemistry Cumulative -- March 2006
by Yoshitaka Ishii

Answer the following 4 questions Q1-Q4. Total 110 points. The pass line is ~70 points. Points may be scaled by an adequate scaling function. Unless specified, answer each question concisely using no more than one paragraph and 5 equations.

Q1. NMR Transition Energy, Bulk Magnetic Moment, Sensitivity [40 points; A-D 10 each]

(A) When you place a spin ½ system in a static magnetic field B_0 along the z-axis, the Zeeman energy for the spin in the spin state m (m = ± ½) is given by

$$E_m = -\gamma B_0 I_Z = -\gamma B_0 \eta m, \qquad (1)$$

where γ is a gyromagnetic ratio, which depends of kinds of nuclei.

Obtain the transition energy AND frequency of the NMR signal. Show how you obtained them.

(B) Each nuclear spin *I* has a magnetic moment, the z-component of which is given by

$$\mu_Z = \gamma I_z = \gamma \eta m. \qquad (2)$$

Demonstrate how you can calculate the z component of a bulk magnetic moment, M_z for a sample containing N nuclear spins *I* of a gyromagnetic ratio γ. (Hint: use population P_α, P_β)

(C) List three parameters that affect the strength of the bulk magnetic moment in NMR based on your answer in (B).

(D) In general, ^{1}H NMR gives higher sensitivity than ^{13}C NMR for most organic compounds. List three reasons why you can obtain the higher sensitivity for ^{1}H NMR.

Q2. Answer the following questions [30 points; A-C 10 point each]

(A) Bloch equation in the laboratory frame is given by

$$(d\mathbf{M}(t)/dt)_{Lab} = \mathbf{M}(t) \times \gamma\mathbf{B}(t). \qquad (3)$$

When a strong static magnetic field is applied along the z-axis, $\mathbf{B}(t) = \mathbf{B}_0 \square (0, 0, B_0)$. If a magnetic moment at t = 0 is prepared along the z-axis, as $\mathbf{M}(0) = (0, 0, M_0)$, what kind of motion of $\mathbf{M}(t)$ is expected in the static field ? Give good reasoning for your answer using eq. (3).

(B) Fill Q1-Q4 with an appropriate formula.

In the frame rotating along the z-axis at the angular frequency of □ (*rotating frame*), it is known that $d\mathbf{M}_r(t)/dt$ is given by

$$(d\mathbf{M}_r(t)/dt)_{Rot} = \underline{(d\mathbf{M}(t)/dt)_{Lab}} + \mathbf{M}_r(t) \times \boldsymbol{\square}, \qquad (4)$$

where $\mathbf{M}_r(t)$ denotes a magnetic moment observed in the rotating frame. By substituting eq. (3) to the underline of eq. (4), we have

$$(d\mathbf{M}_r(t)/dt)_{Rot} = \mathbf{M}_r(t) \times (\boldsymbol{\square} + \gamma\mathbf{B}(t))$$

$$= \mathbf{M}_r(t) \times (\gamma\mathbf{B}_{\mathbf{eff}}(t)) \qquad (5)$$

$$\gamma\mathbf{B}_{\mathbf{eff}}(\mathbf{t}) = \boldsymbol{\square} - \{\ \mathbf{Q1}\ \} \qquad (6)$$

Now, suppose that $\mathbf{B}(t) = \mathbf{B}_0 + \mathbf{B}_1(t)$ and $\mathbf{B}_1(t)$ is an oscillating RF magnetic field given by

$$\mathbf{B}_1(t) = [2B_1\cos(\square t), 0, 0]. \qquad (7)$$

Then, in the laboratory frame, the effective field, $B_{eff}(t)$ is given by

$$\gamma\mathbf{B}_{\mathbf{eff}}(t) = [2B_1\gamma\cos\square t, 0, (Q2)\ ] \qquad (8)$$

In the rotating frame, the effective field is given by

$$(\gamma\mathbf{B}_{\mathbf{eff}}(t))_{Rot} = [(Q3), 0, \square + \gamma B_0]. \qquad (9)$$

The Bloch equation in the rotating frame is

$$(d\mathbf{M}_r(t)/dt)_{Rot} = \mathbf{M}_r(t) \times (\boldsymbol{\square} + \gamma\mathbf{B}(t))$$

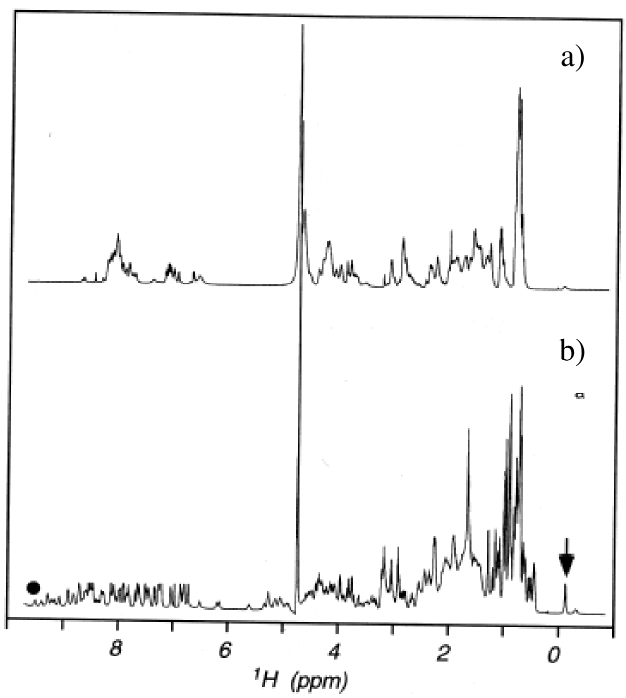
$$= \mathbf{M}_r(t) \times (\gamma\mathbf{B}_{\mathbf{eff}}(t))_{Rot} \qquad (10)$$

In general $|B_1| << |B_0|$, hence the effect of B_1 is negligible, compared with large field, B_0, as shown in (9). However, equationd (9, 10) show that when □ = [Q4], $\mathbf{B}_1(t)$ produces non-negligible effects on $\mathbf{M}_r(t)$, causing NMR transitions.

(C) When $\mathbf{M}_r(0) = [0, 0, M_0]$ and $(\square\mathbf{B}_{\mathbf{eff}}(t))_{Rot} = [\square_1, 0, 0\ ]$, what kind of motion do you expect on $\mathbf{M}_r(t) = [M_{Xr}(t), M_{Yr}(t), M_{Zr}(t)]$?

Q3 Misc. Questions. [30 points; A-C, 10 point each]

(A) One of the ^1H NMR spectra below (a, b) was obtained for a protein in a folded state while the other was for the same protein but in an unfolded state. Which is the spectrum for the folded protein? Give good reasoning for your answer.



(B) What are the purposes of applying a window function in 1D FT NMR? List two.

(C) Explain the principle of 2D FT NMR using 2D $^{13}C/^1H$ correlation NMR within two paragraphs. Describe how the data are acquired, and then processed to obtain the 2D spectrum. Draw a diagram, a time-domain signal (FID), and a spectrum if necessary.

Q4. Today's seminar speaker, Prof. Tatyana Polenova at Univ. Delaware introduced interesting work. Summarize her work in two paragraphs (include the name of the samples, method, and the main results). (10 points)