Analytical Chemistry Cumulative --- October 2016
by Yoshitaka Ishii

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.

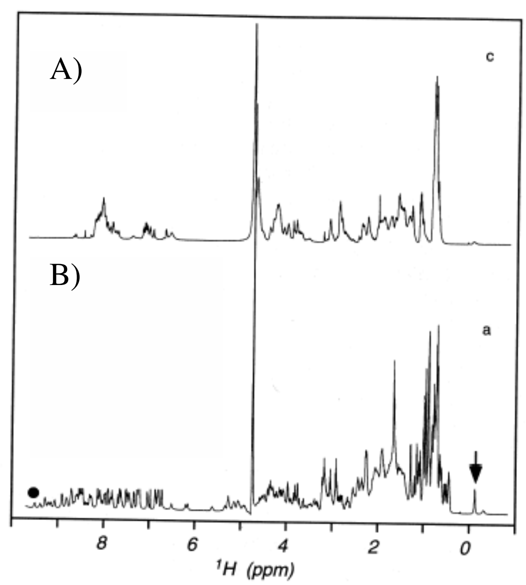
1. **Fourier transformation.** Answer the following questions.
 (a) 10 points (b) 10 points (c) 10 points

(a) For $s(t) = \exp(i\omega_0 t - \lambda t)$, show $S(\omega) = \int_0^{\infty} s(t)\exp(-i\omega t)dt = A(\omega) + i\,D(\omega)$, where $A(\omega) = \lambda/[(\omega - \omega_0)^2 + \lambda^2]$. Obtain the formula that describes $D(\omega)$.

(b) Based on the formula above, explain why the Fourier transform can converts a time-domain signal to a frequency-domain signal? Note that ω is an angular frequency defined by $\omega = 2\pi f$, where f is the frequency.

(c) Draw an approximate line shape of $A(\omega)$ by hand for ω_0 = 200 Hz for T_2 = 0.1 s. ($\lambda = 1/T_2$). Include the following information: the peak height, the line width at the half height, and the position of ω at the maximum peak position.

2. **Protein NMR and conformations.** Answer the following questions.
 (a) 5 points (b) 10 points (c) 15 points



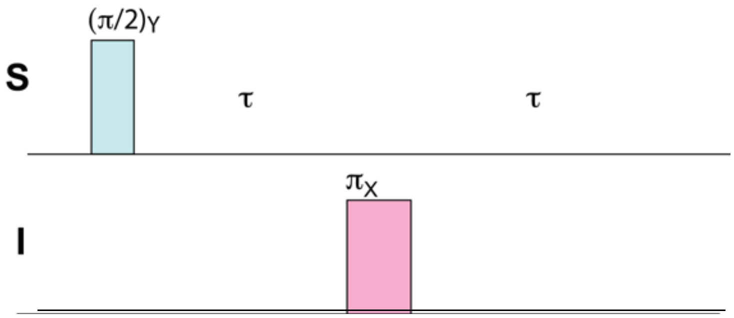
(a) The figures (A) and (B) in the right show ^{1}H NMR spectra of folded and unfolded proteins. Answer which spectrum corresponds to a folded protein.

(b) Then, explain what properties of the proteins make the differences in the spectra. Explain first what are folded and unfolded states.

(c) NMR is a rich source of conformational information for biomolecules. List three NMR parameters that can be used for determining conformations of proteins. Explain how each parameter can be converted into conformational information.

3. **Decoupling Experiments.** Answer the following questions. (a) 15 points (b) 15 points

(a) Explain what is a technique called ^{1}H decoupling? Explain the principle and effect of the experiment.



(b) For the above pulse sequence, the spin Hamiltonian is defined as $H = \Omega_S S_Z + 2\pi J I_Z S_Z$, where I and S are ^{1}H and ^{13}C, Ω_S denotes chemical shift of S, and J denotes a coupling constant between I and S. The time evolution of the density operator can be calculated using arrow notation as follows. <u>Give a formula that corresponds to [Q1-Q3]</u>

$S_Z \quad -\pi/2\, I_Y \rightarrow S_X$

$S_X \quad -2\pi J I_Z S_Z\, \tau \rightarrow$ [Q1] $+ 2S_Y I_Z \sin \pi J_S \tau$

[Q1] $+ 2S_Y I_Z \sin \pi J_S \tau \quad - \Omega_S S_Z\, \tau \rightarrow (S_X \cos \Omega_S \tau + S_Y \sin \Omega_S \tau)\cos \pi J_S \tau +$ [Q2] $\sin \pi J_S \tau$

$(S_X \cos \Omega_S \tau + S_Y \cos \Omega_S \tau)\cos \pi J_S \tau +$ [Q2] $\sin \pi J_S \tau \quad - \pi I_X \rightarrow$ [Q3]

[Q3] $\; - 2\pi J I_Z S_Z\, \tau \rightarrow S_X \cos \Omega_S \tau + S_Y \sin \Omega_S \tau$

$S_X \cos \Omega_S \tau + S_Y \sin \Omega_S \tau \quad - \Omega_S S_Z\, \tau \rightarrow S_X \cos 2\Omega_S \tau + S_Y \sin 2\Omega_S \tau$

4. **Nobel Prizes 2016.** Answer the following questions. 20 points

This year, the Nobel Prize in Chemistry was awarded to Jean-Pierre Sauvage (University of Strasbourg, France), Sir J. Fraser Stoddart (Northwestern University), and Bernard L. Feringa (University of Groningen, the Netherlands). The Nobel Prize in Physiology or Medicine 2016 was awarded to Yoshinori Ohsumi (Tokyo Institute of Technology, Japan). The Nobel Prize in Physics 2016 was divided, one half awarded to David J. Thouless (University of Washington), the other half jointly to F. Duncan M. Haldane (Princeton University) and J. Michael Kosterlitz (Brown University). Pick two awards. For each award, give a brief outline of what was done for the award and explain why the work has extraordinary importance and what kind of broad impact the work had or potentially has on the society.