

### 5.33 Advanced Chemical Instrumentation NMR Spectroscopy Supplement

These notes are intended to help you understand the origin of magnetic resonance spectroscopy. There is also a discussion of chemical kinetics and thermodynamics.

#### Quantization of Angular Momentum

This is one of the most important results of quantum-mechanics. It cannot be rationalized in terms of classical mechanics. The main result is the following.

$$M = \hbar[J(J + 1)]^{1/2} \quad \text{or} \quad M^2 = \hbar^2 J(J + 1) \quad \text{with } J = 0, 1, 2, \text{ etc.}$$

where  $M$  is angular momentum, a vector quantity. The result shows that angular momentum is quantized in units of  $\hbar$ . Here we have used  $J$  as the quantum number, which is conventional for rotational angular momentum. In this case the rotational energy is  $E_{\text{rot}} = M^2/2I$  (same as the classical expression, but with the quantized magnitudes of  $M$ ) where  $I$  is the moment of inertia. This gives our familiar  $J(J + 1)$  rotational energy level dependence on the angular momentum quantum number.

Another familiar result is the one for electron orbital angular momentum. In this case the quantum number is usually given the symbol " $l$ ". The  $l=0, 1, 2, 3$  etc. states correspond to the familiar s, p, d, f etc. orbitals.

Note the degeneracies! There are  $(2l + 1)$  orbitals (one s, three p, five d, etc.) for orbital angular momentum quantum number  $l$ . Similarly, in treating IR spectroscopy we saw that there are  $(2J + 1)$  states for each energy level given by quantum number  $J$ . These sublevels correspond to the quantized values of the *components* of angular momentum along a unique axis (usually taken as the z-axis). So there is an angular momentum quantum number, e.g.  $l$  for electron orbital angular momentum, and also a quantum number for the z-component of angular momentum, e.g.  $m_l$ . The z-component is quantized as follows.

$$M_z = m_l \hbar \quad \text{with } m_l = -l, -l + 1, \dots, l - 1, l.$$

The z-component quantum number runs from  $-l$  to  $l$  in unit steps, yielding  $(2l + 1)$  distinct sublevels in all. In the absence of an applied field or perturbation which affects them, the sublevels all have the same energy and the levels are  $(2l + 1)$ -fold degenerate.

Now we come to electron and nuclear spin, which are the focus of our attention in magnetic resonance experiments. The two main results stated above are the same, with different symbols used for the quantum numbers. For electron spin,

$$\begin{aligned} S^2 &= \hbar^2 s(s + 1) & s &= 1/2 \\ S_z &= m_s \hbar & m_s &= \pm 1/2 \end{aligned}$$

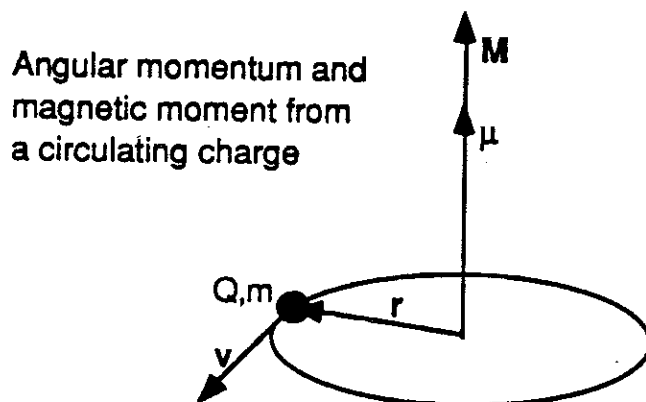
where  $S$  is electron spin angular momentum,  $S_z$  the z-component, and  $s$  and  $m_s$  the corresponding quantum numbers. Unlike the case for orbital or rotational angular momentum, for which the quantum numbers can vary, the spin quantum number is a fundamental property of an elementary particle. As indicated, for the electron  $s = 1/2$  and so  $m_s = \pm 1/2$ . For nuclei,

$$\begin{aligned} I^2 &= \hbar^2 I(I + 1) & I &= 1/2 \text{ for } ^1\text{H} \\ I_z &= m_I \hbar & m_I &= \pm 1/2 \text{ for } ^1\text{H} \end{aligned}$$

where  $I$  is nuclear spin angular momentum,  $I_z$  the z-component, and  $I$  and  $m_I$  the corresponding quantum numbers. The proton also has spin quantum number of  $1/2$ . Larger nuclei containing many protons can have other spin quantum numbers, determined by the superposition of the proton spins. Particularly important in NMR are the results that  $^{12}\text{C}$  has no spin ( $I = 0$ ), while  $^{13}\text{C}$  has  $I = 1/2$ . Thus carbon ordinarily does not play a role in NMR spectra, but  $^{13}\text{C}$ -NMR spectra can be recorded using isotopically enriched samples.

### Magnetic moments

A charged particle with angular momentum produces a magnetic dipole moment  $\mu$  parallel to  $M$ . Classically, the situation as shown below is that a particle with charge  $Q$  and mass  $m$  is travelling in a circular orbit with radius  $r$  and linear velocity  $v$ .



The classical angular momentum is  $M = m(\mathbf{v} \times \mathbf{r})$ , with magnitude  $M = mvr$ . The classical magnetic moment is given by the current  $i$  that is flowing and the area  $a$  of the circular orbit, i.e.  $\mu = ia/c = [Q(\mathbf{v} \times \mathbf{r})/2\pi r^2](\pi r^2)/c$ , in the same direction as  $M$  and with magnitude  $\mu = Qvr/2c$ . So  $M$  and  $\mu$  are parallel, and proportional to each other with a proportionality constant which is called the gyromagnetic ratio  $\gamma$ :  $\mu = (Q/2mc)M = \gamma M$ .

The spin angular momentum of an elementary particle like an electron or a proton can be derived through a relativistic quantum mechanical treatment. The spin angular momentum and associated magnetic moment are still proportional to each other, but the gyromagnetic ratio is slightly different from that predicted classically. For the electron,

$$\mu_e = -(e/2m_e c)(g)S = -\gamma S$$

where  $e$  is the charge and  $m_e$  the mass, and  $g$  is the "electron g-factor", essentially a quantum-mechanical correction to the gyromagnetic ratio, which is equal to 2.0. For a nucleus,

$$\mu_N = (e/2m_p c)(g_N)I = \gamma_N I$$

where  $m_p$  is the proton mass,  $g_N$  is the nuclear g-factor, and  $\gamma_N$  is the nuclear gyromagnetic ratio. For the proton,  $g_H = 5.6$ . Comparing magnitudes, we note that because of their masses nuclei have much smaller magnetic moments than electrons even though they have roughly the same angular momentum. This means that an applied magnetic field interacts much more strongly with electrons, as we will see below.

We will want to consider the effect of an applied magnetic field along what will be defined as the z (unique) axis. To do this we write the z-component of the magnetic moment as

$$(\mu_e)_z = -(e/2m_e c)(g)S_z = -\gamma S_z = -\gamma \hbar m_s = -\mu_0 g m_s$$

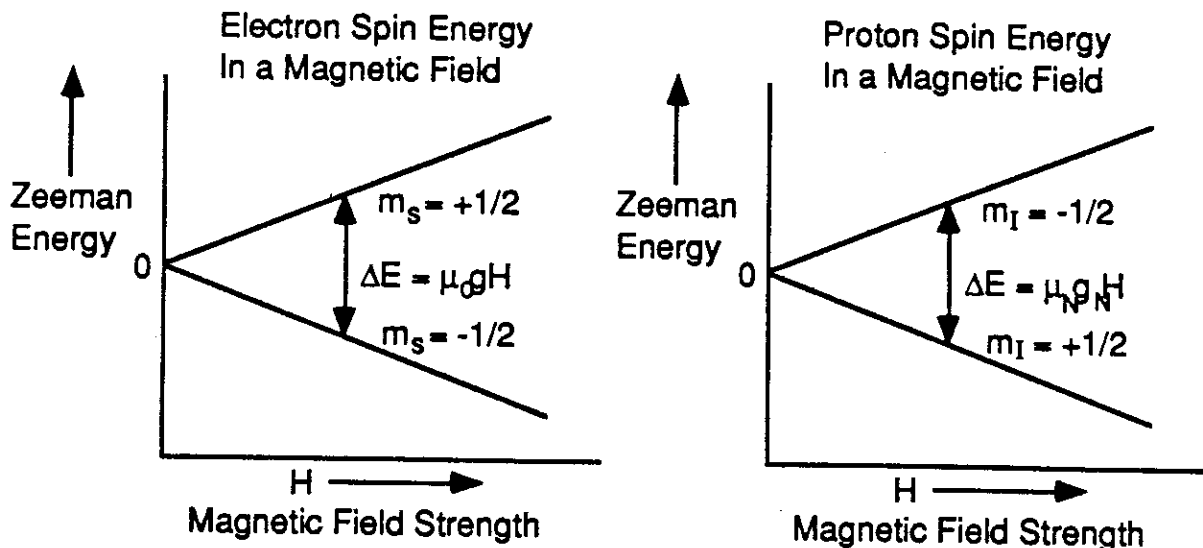
where we have recalled that  $S_z = m_s \hbar$  and defined the *Bohr magneton*  $\mu_0 = e\hbar/2m_e c = 0.9 \times 10^{-20}$  erg/gauss. For nuclei,

$$(\mu_N)_z = (e/2m_p c)(g_N)I_z = \gamma_N I_z = \gamma_N \hbar m_I = \mu_N g_N m_I$$

where  $\mu_N = e\hbar/2m_p c = 0.5 \times 10^{-23}$  erg/gauss is the *nuclear magneton* which, unlike  $\gamma_N$ , has the same value for all nuclei since the nuclear g-factor is separate from it.

### Spin energies in an applied magnetic field

In the absence of an applied field or perturbation, the spin sublevels are degenerate. An applied magnetic field  $H$ , along what we will define as the z (unique) axis, changes their energies since they have different degrees of alignment with the field. The magnetic interaction energy is  $E_{int} = -\mu \cdot H = -\mu_z H = \mu_0 g m_s H$  (for the electron) or  $= -\mu_N g_N m_I H$  (for the proton or other nucleus). This shows that the electron or proton spin sublevels with  $m_s$  or  $m_I = \pm 1/2$ , which are degenerate in the absence of a field, become split once a field is applied. The splitting, called the "Zeeman" splitting, increases linearly with the field magnitude  $H$ , as shown below.



Since  $\mu_0 \gg \mu_N$ , the splitting of electron spin sublevel energies is much greater than that of the nuclear spin sublevels for the same magnitude applied field.

### NMR and ESR Spectroscopy

Given an energy difference  $\Delta E$  between lower and upper sublevels, electromagnetic radiation can be absorbed to induce transitions between the levels. The energy of the absorbed photons is equal to energy difference between the two levels,  $\Delta E = \mu_0 g H$  for the

electron or  $\Delta E = \mu_N g_N H$  for the proton. So magnetic resonance spectroscopy is similar to other spectroscopies in which light whose energy matches the difference between two levels is absorbed, but in this case the energy difference between the levels exists because of an applied field. The spin levels on nuclei or electrons can be measured in nuclear magnetic resonance (NMR) or electron spin resonance (ESR) spectroscopy respectively.

A small NMR or ESR machine has a magnetic field strength of about 10 kG (kilogauss). For NMR, the corresponding electromagnetic radiation is in the radiofrequency (RF) range of about 60 MHz. For ESR, microwave frequencies of about 30 GHz are used. The difference of about a factor of 1000 reflects the fact that  $\mu_0 \gg \mu_N$ .

Note that in either case the frequency is given by  $\Delta E = h\nu = \hbar\omega$  where  $\nu$  is in units of cycles/sec or Hz (hertz) and  $\omega$  is in units of radians/sec or just  $\text{sec}^{-1}$ . (There was a short-lived attempt to introduce the "Avis" unit for the latter ~~unit which was squelched by journal editors~~.) In practice, the spectrum can be collected by either fixing the magnetic field strength  $H$  and varying the radiation frequency, or by fixing the radiation frequency and varying the field strength. Alternatively, the spectrum can be collected in the time domain. In this case, which is called "Fourier transform NMR" or FTNMR, the field strength  $H$  is fixed along the  $z$  axis and a short RF pulse is applied along the  $x$  axis. This induces the magnetic spins to precess about the  $z$  axis, with a precession frequency  $\nu$  (given by  $\Delta E = h\nu$ ). A magnetic coil is used to measure the net magnetic moment along the  $x$  or  $y$  axis, which oscillates at the precession frequency. The data appear as damped oscillations whose frequency is  $\nu$  and whose damping rate,  $\gamma$ , corresponds to the linewidth of the NMR feature in the frequency domain.

The "Avis" still lives!

The discussion thus far might suggest that when an NMR or ESR spectrum is recorded there appears exactly one line, corresponding to the proton or electron spin energy level splitting. In fact different protons on a molecule have different characteristic NMR frequencies, and this is what makes NMR a useful spectroscopic tool. The reason for the differences is that the actual magnetic field felt by a proton depends on not just the applied field  $H$ , but also on nearby magnetic moments (due mainly to electron orbital angular momentum) which can counteract the applied field and so reduce the field at the proton. This is called "screening" of the proton from the applied field. The effective field strength at the proton is then

$$H_{\text{eff}} = (1 - \sigma)H$$

where  $\sigma$ , the screening constant, is on the order  $10^{-6}$ . The value of  $\sigma$  depends in detail on the environment of the proton, and so different types of protons have measurably different NMR frequencies. Similar effects occur in ESR spectra since the electron spins feel an "effective" field which is moderated slightly by the electron orbital magnetic moments.

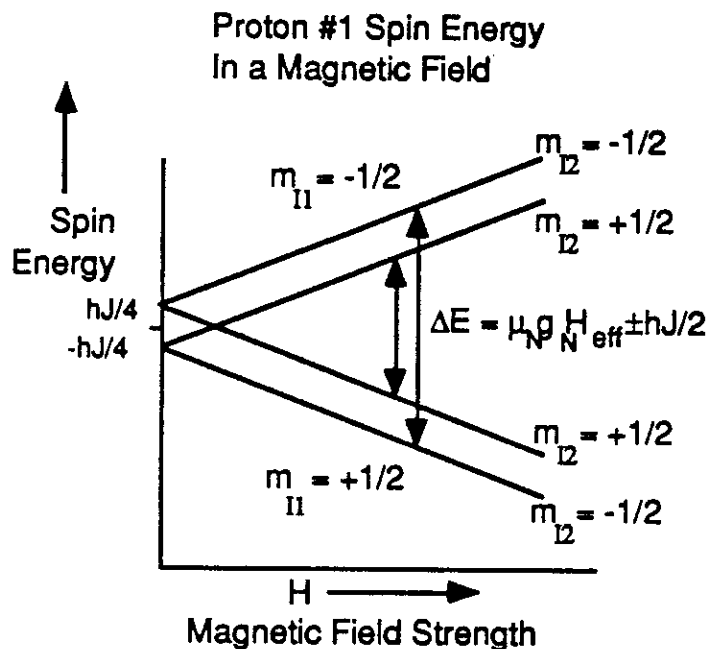
Now we can understand how different protons show different NMR frequencies, but this still would indicate that each proton gives rise to just one NMR line. Of course you are familiar with NMR doublets, triplets, etc. They arise because different spin magnetic moments interact with each other. The interaction energy is just like that indicated earlier for an applied field, except that this time the field comes from another spin. The energy is proportional to the dot-product of the two spin magnetic moments, and can be written as

$$E_{\text{int}} = hJ_{ij}m_{ij}m_{j}$$

for the spins on nuclei  $i$  and  $j$ .  $J_{ij}$  is a proportionality constant called the nuclear spin-spin coupling constant, and typically  $hJ_{ij}$  is about 1-10 Hz. Since the  $m_l$  values can be either  $+1/2$  or  $-1/2$ , an interaction of this type gives rise to two values of the energy, i.e.  $\pm hJ_{ij}/4$ , for each spin state of nucleus  $i$ . That is, the total spin energy of proton #1 if there is one nearby proton (#2) is

$$-\mu_N g_N m_{I1} H_{\text{eff}} \pm hJ_{12} m_{I1} m_{I2}.$$

For each of the two values of  $m_{I1}$ , there are two values of the spin energy corresponding to  $m_{I2} = \pm 1/2$ . This is illustrated below. Note that the illustration is not "to scale"! The energy difference  $\Delta E = -\mu_N g_N H \pm hJ_{12}/2$  is dominated by the first term at ordinary applied fields.



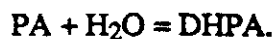
The effect of this is to produce *two* transitions at different frequencies corresponding to the energy differences shown. Note that only two transitions are allowed since the photon, which carries one quantum of angular momentum, can change only one spin state. This shows how one spin-spin interaction can produce an NMR doublet. It is straightforward to extend to several interactions and to generate triplets and more complex patterns.

Note that the part of this diagram that is directly relevant to your NMR spectrum is that which has a substantial field (i.e. 10 kG or more) applied. For this regime, the diagram is accurate. However the diagram as drawn above is not accurate for the zero-field regime. A worthwhile "extra-credit" effort (after you've mastered the basics) would be to find out what is wrong and explain the correct result!

Finally, as you know spectral "lines" really have measurable widths which tell you about damping ("lifetime"), pure dephasing, and/or inhomogeneous dephasing. In your experiment you are to assume that the linewidths give you lifetimes which correspond to the time that the molecule itself exists before it is transformed into another chemical species. In this way the NMR linewidth directly yields a chemical reaction rate.

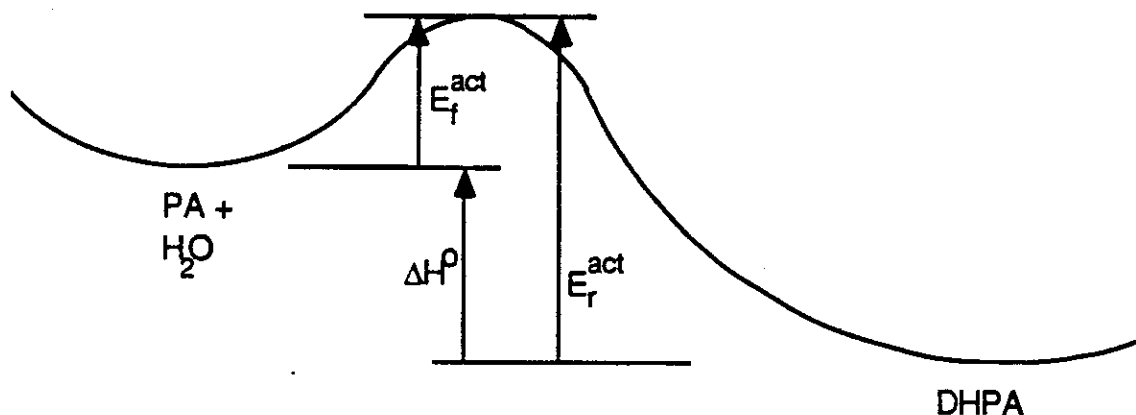
### Some notes on chemical kinetics

You will study the chemical equilibrium between pyruvic acid (PA) and dihydroxypropanoic acid (DHPA). The reaction is



By measuring the linewidths of the methyl protons on PA and DHPA, you determine the lifetimes, i.e. the amount of time each molecule lives before undergoing chemical conversion to the other species. The linewidths therefore give you the forward and reverse chemical reaction rates,  $k_f$  and  $k_r$  respectively.

You then use the results of Arrhenius reaction rate theory to determine from the rate constants the activation energies for the forward and reverse reactions ( $E_f^{\text{act}}$  and  $E_r^{\text{act}}$  respectively). The energy diagram is sketched below.



The Arrhenius result

$$k = A \exp(-E^{\text{act}}/RT),$$

which holds for the reaction rate and activation energy in either direction, shows you that at higher temperatures the rate constant increases. In particular, the important quantity is the ratio of the activation energy to the product  $RT$ . This is similar to what we found in the IR experiment for the probability that a molecule is in a state with rotational energy  $J$ :  $P_J \propto \exp(-E_J/k_B T)$ , where  $k_B = R/N_A$  is the Boltzmann constant. The Arrhenius result just expresses the probability that a molecule is in a "transition state" whose energy is at the top of the barrier to reaction. Arrhenius rate theory *assumes* that the reaction rate is proportional to this probability. Note that the expression for  $P_J$  is the same except that the molecular rather than molar energy is used.

You will determine the forward and reverse rate constants as functions of temperature from your NMR linewidths. The Arrhenius result can be rewritten in the form

$$d(\ln k)/d(1/T) = -E^{\text{act}}/R$$

which shows that  $E^{\text{act}}$  can be determined from the slope of an "Arrhenius" plot.

Given the forward and reverse activation energies, you can deduce the enthalpy of reaction  $\Delta H^0$  from their difference, as indicated in the figure. (Note that the energy and enthalpy are essentially interchangeable here since there is no pressure-volume work done.)

Note that none of the quantities  $E_{\text{act}_f}$ ,  $E_{\text{act}_r}$ , or  $\Delta H^0$  are temperature-dependent! The temperature influences the kinetics because hot molecules can get over the barrier faster, not because the barrier height or any of the energetics are changed.

Finally, you can deduce the free energy of reaction  $\Delta G^0$  and the equilibrium constant  $K_{\text{eq}}$  from your results. Note that these quantities *are* temperature-dependent since  $\Delta G = \Delta H - T\Delta S$ . Neither  $\Delta H$  nor  $\Delta S$  changes substantially with temperature, but since  $\Delta S$  is multiplied by  $T$  to determine  $\Delta G$  the free energy does change. There are two ways to deduce  $\Delta G$  and  $K_{\text{eq}}$  from your results. First, you measure the areas under the peaks which immediately gives you the relative concentrations of the two species. These concentrations, i.e. the reaction equilibrium, are governed by free energy (not just by energy - entropy matters!). The expression for the equilibrium constant is

$$K_{\text{eq}} = [\text{DHPA}]/[\text{PA}] = \exp(-\Delta G^0/RT) \text{ or } \ln(K_{\text{eq}}) = -\Delta G^0/RT.$$

So from the areas you determine the equilibrium constant and the free energy of reaction at each temperature. Separately, you determine the forward and reverse rate constants at each temperature from the linewidths as discussed above. The ratio of rate constants gives you the equilibrium constant:

$$k_f/k_r = K_{\text{eq}}.$$

To understand this, recognize that at equilibrium the net concentrations are not changing at all, but there is rapid interconversion of the two species. To maintain an equilibrium which, for example, favors PA, the relatively large number of PA molecules must undergo conversion much more slowly than the relatively small number of DHPA molecules. The ratio of rates determines the ratio of concentrations, i.e. the equilibrium constant.

Finally, since you determine both  $\Delta H^0$  and  $\Delta G^0$  you can also get  $\Delta S^0$ , the entropy of reaction. From the reaction formula, it should be obvious which side of the reaction is favored by entropy. As temperature increases, the equilibrium should shift to this side. Note that because entropy plays an important role, it is not necessarily the case that the species which is lower in energy (DHPA, according to the sketch above which is not guaranteed to be accurate) is favored at equilibrium. It is the case that at very low temperature the lower-energy species is favored since then the entropy effects become less important.

You also determine the rate constants as functions of catalyst (acid) concentration, at fixed temperature. Does a catalyst affect the thermodynamics or only the kinetics?

### Molecular interpretation of the entropy

The discussion above is sufficient to understand all of your results. Here is an "extra" discussion which may add some insight. It is based on the microscopic interpretation of entropy which is the basis for statistical mechanics. The result, deduced by Boltzmann (and inscribed on his tombstone!),<sup>\*</sup> is

$$S_J = k_B \ln(g_J)$$

It says that the entropy  $S_J$  of a state in energy level  $J$  is given by the degeneracy of that level. Qualitatively, it is understandable since the degree of order is very high if a system is in an energy level with only one possible state. The degree of order is much lower if there

<sup>\*</sup> actually,  $S = k \ln W$

are many possible states the system could be in, even if the energy is known. Now let's go revisit the Arrhenius rate constant expression,  $k = A \exp(-E^{\text{act}}/RT)$ , and also the relation between the rate constants and the equilibrium constant,  $k_f/k_r = K_{\text{eq}} = \exp(-\Delta G^0/RT)$ . The first expression holds for each rate constant, and from the expression for each we can calculate the ratio:

$$k_f/k_r = A_f \exp(-E^{\text{act}}_f/RT) / A_r \exp(-E^{\text{act}}_r/RT) = (A_f/A_r) \exp(-\Delta H^0/RT).$$

But we already have the result

$$k_f/k_r = K_{\text{eq}} = \exp(-\Delta G^0/RT) = \exp(-\Delta H^0/RT) \exp(\Delta S^0/R)$$

which shows that the ratio of "preexponential" factors,  $(A_f/A_r)$ , is determined by the entropy of reaction. (This result does not draw on statistical mechanics.) We can go further by defining forward and reverse "activation entropies" similar to the corresponding activation energies, with  $E^{\text{act}}_f - E^{\text{act}}_r = \Delta S^0$ . Then we can write for each of the rate constants

$$k = A \exp(-E^{\text{act}}/RT) = \exp(S^{\text{act}}/R) \exp(-E^{\text{act}}/RT) = \Delta g \exp(-E^{\text{act}}/RT)$$

where  $\Delta g$  is the change in the degeneracy, i.e. in the number of possible molecular configurations, between the transition state and the reacting species. This says that the reaction rate is favored by a low activation barrier, but also by a large number of possible transition state structures any one of which could be reached to get over the barrier. This makes sense, and is reminiscent of the full expression (including the degeneracy  $g_J$ ), from your IR experiment, for the population of rotational levels with energy  $E_J$ :

$$P_J \propto g_J \exp(-E_J/k_B T) = \exp(S_J/k_B) \exp(-E_J/k_B T)$$

where the Boltzmann expression for entropy has been used. This shows too that energy levels are more highly populated not just if the energy is low but also if the degeneracy is high. The Arrhenius theory says that the reaction rate is proportional to the probability that transition state energies can be reached, and this probability depends on both how high those energies are and how many distinct "transition" states with those energies exist.

### Summary

For your experiment, you should have a good understanding of the basics of NMR [what the experiment is all about, how spectra are recorded in either the time or frequency domain, why there are NMR lines with different positions and splittings, what the linewidths tell you and why (especially for this experiment), which features can be explained classically and which cannot], the basics of ESR, and the details of the chemical kinetics and the chemical thermodynamics (including energy, entropy, and free energy) that you determine. There are a few "extras" that you might explore given mastery of the basics. These include "what is wrong" at zero field with the spin energy diagram sketched above for the case of two interacting protons, and the understanding of entropy and the rate constants in microscopic terms with the Boltzmann expression.

Finally, in the midst of all the theory don't neglect to do a careful analysis and presentation of your data! You might give some thought to the assumption that your linewidths are due entirely to the reaction rates. Is part of the linewidth due to any other causes? For example, how wide are "ordinary" lines of species (especially methyl or ethyl groups) at the same temperatures which don't undergo reaction?