

NAME OF PRACTICAL

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Category

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Atul Singh Arora: *Name of Practical*, Category,

*Every honest researcher I know admits he's just a professional amateur.  
He's doing whatever he's doing for the first time. That makes him an  
amateur. He has sense enough to know that he's going to have a lot of  
trouble, so that makes him a professional.*

— Charles F. Kettering (1876-1958) (Holder of 186 patents)

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CHEMISTRY NOTES

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October 19, 2012

## 1.1 PEAK BROADENING

1.1.1 *Natural (Lifetime)*

$$\Delta E \tau = \hbar/2\pi$$

$$\hbar \Delta \nu \tau = \hbar/2\pi$$

1.1.1.1 *Collisions*

Collisions can cause the lifetime to reduce. Some gasses will collide and go away, but in some, as you increase the pressure, the width will increase, and the intensity will decrease simply because a lot of electrons are unable to emit. It's the area under the peak that's constant, not the peak. Not only is the width increase, also there's a loss of intensity for reasons stated earlier.

But the average lifetime decreases. So remove other gasses and reduce the pressure, you're suppressing collisional broadening.

Every other broadening mechanism when removed, then you're left with the natural width of the peak. Collisions are inelastic, because its not just change of kinetic energy, because there's a change in potential energy (How?)

Its not dropping the intensity, there's no physical way you can understand that, but you need to understand FT. Increase in energy, causes increase in temperature also (Biplob Question)

Temperature rise is not like you can boil water on it. That class of spectroscopy is called photo thermal spectroscopy. Also called thermal lensing, photo acoustic. What they do is measure the heat (not certain about this..)

1.1.1.2 *Doppler*

Molecular motion that's always happening. By maxwell boltzman distribution, you have the nice bell shaped curve. When you increase the temperature, the same thing just becomes wider. Then there's a greater distribution of speeds. Classic example of the fact that frequencies observed are different (speed in this case) for a moving observer (or source), is a train sound (car sound). If the sodium is moving towards a source of 590 nm, then the sodium atom would not absorb because for the sodium atom, the wavelength is less than 590

nm. So if the source emits various wavelengths, then the sodium atom would absorb at different wavelengths because of doppler effects and this causes peak broadening called doppler broadening.

If I make liquid sodium or solid sodium, then that will add to complications. So you must cool it without solidifying or liquefying it. 10 K everything is solid, except helium etc., but you must cool these without them interacting with each other.

Need to know mean free path, pressure etc. to calculate things.

Doppler shift you know quantitatively. If you put it in the Maxwell Boltzman distribution, you get the width of the doppler broadening (don't memorize this) is given by  $\Delta\nu_D = 7 \times 10^{-7} \nu \sqrt{\frac{T}{M}}$ . This explains why Raman has a huge doppler, therefore the peaks are so very broad. Plus you have a root of T. Higher the molecular weight, the distribution gets smaller, therefore the doppler width becomes smaller. (not certain)

When you're stuck with doppler broadening, you've to cool the guy (because for a given technique your frequency is fixed), without freezing.

One method is to put the water in an Argon matrix (Biplob question) and this will be cooled. Also you can use the super cooling thing sir had talked about in one of his talks (figure out the precise name of the technique). Adsorption (Prashansa Question), the doppler's then gone, but the interaction with solid mustn't be strong otherwise pointless. But it could be used, take graphite its not that bad. But others like magnesium etc. can NOT be used.

#### 1.1.1.3 Others

Electric Field, perturbation Time of Flight Pressure Broadening



## REMOVING DEGENERECY

November 2, 2012

## 2.1 INTRODUCTION

2.1.1 *Nuclear Spin*

Electron has a spin half. If  $s = 1/2$ , then length of the vector would be  $\sqrt{1/2(1/2 + 1)}\hbar/2\pi$ . Electron spins, thus it generates a magnetic moment. Thus you can relate the magnetic moment, to its angular momentum.  $\mu$  is proportional to  $S$ . So for a proton, everything would be the same, except the charge. Now  $\mu$  is related to  $I$ , the angular momentum of the charged particle. ( $\mu$  is the angular momentum).  $\mu = g\beta_N I \text{ JT}^{-1}$ ,  $g$  depends on the nucleus. There's no need to remember that number, where  $\beta_n = \frac{e\hbar}{4\pi m_p}$ . It defines the magnetic moment the angular momentum will produce. The  $g$  value is different for Carbon and Hydrogen. Very characteristic of the nucleus you're looking at. That's important because it tells you where it'll lie in the spectrum.

To make the plus half

$$E = B_z \cdot \mu_z$$

$$E = -B_z g \beta_n I_z$$

$$\Delta E = g B_z \beta_n$$

The population difference will be as small as 10 in 2 million. When would a molecule absorb? Detour: Lets consider a system in which all atoms are in ground state. When you give energy, the first will go up. So say initially there were ten, now there are nine ground, one excited. Now as the population becomes small, the probability of stimulated emission becomes the same as probability of stimulated absorption and a dynamic equilibrium is reached. Now here, if the population of the excited state becomes high enough, then it will relax back due to quenching and thus the experiment can go on. However, the point anyway is the population difference is very small. When you go to higher fields, then you can more sensitively see better. 9 Tesla for a 400 MHz. In solids, the spectra will get extremely broadened (because life time will become extremely small). Therefore we don't use solids, and don't use gasses because they don't have any quenching. In liquids it's ideal and that's what we used. In gasses, first getting the experiment to work will be more difficult since the number density will be very low.

You can always express,  $\Delta E$  in Herts, so if  $B_z$  is 9, then for Hydrogen,  $\nu = 400$  MHz. You had to wait for superconductors for getting 9 Tesla. Even today, people who sell us 60 MHz machine, had come.

Suppose there's a bare proton, this is what I see (400 MHz). But supposing I take  $\text{CH}_4$ , but it's a proton with electrons surrounding it, and they will change the  $\Delta E$ . The electrons also have their own intrinsic spin (when the magnetic field is applied), then these two spins will start to cancel, then the number of electrons will decide how much of the magnetic field reaches the proton. So if you apply 9 Tesla, then it'll probably see less field. So they won't absorb at 400 MHz, but it'll instead absorb at less than 400 MHz. Now if you take  $\text{CH}_3\text{OH}$ , then the oxygen will take away most of the electrons, thus the H in OH will get a field closer to what you've applied. This is the electrons shielding. Thus NMR is so powerful as it can tell you about the environment around it. (Srijit: Wouldn't the protons of other atoms in the molecule interfere?) You have two absorptions, thus you can tell the molecule in many cases. With infra-red, it's hard even for the expets to tell which molecule it is. If you pin it to the wall and tell him to figure out the exact molecule, he'll say shoot me. So even with a molecular formula, you should be able to tell the structure, using NMR. It's almost always unambiguous. Of course then why aren't we just doing NMR? Well it can't tell you how strong the bond is, the forces etc., that's why you need other techniques

It's always easy to change the magnetic field, so you start with 9 Tesla, and keep dropping. So the first guy that hits, would be OH's H and then the  $\text{CH}_3$ 's H.

Today we of course don't do it this way. FT is used today. Nobody today does sweeping magnetic fields.

Only if  $I \neq 0$  do you get something. It's like a closed shell system giving you a singlet sigma system. If you take carbon 12, 6 proton, 6 neutron, thus its NMR inactive. If Odd + Even =  $1/2$  integral spins.

November 7, 2012

## 3.1 INTRODUCTION

3.1.1 *Splitting the degeneracy*

You can't calculate the  $g$  value for nucleus so easily, as compared to for electrons.  $h$  you must always know.  $g$  and  $\beta_n$  and  $h$  should be known,  $\beta_z$  must be known. In a way spin of the electron and spin of the proton, is very similar. So whatever you learn for a proton, you can apply the same for an electron. Shell structure for electron is very simple, but for a proton is not very simple, but there's a complicated shell structure.  $\nu = |g\beta_n\beta_z|$ . In vibrations, your energy spacing becomes very high, much greater than  $KT$ , and thus the population difference is very large. Almost equal population in this case, because the energy difference is very small. The population difference is only in ppm. If you apply a stronger magnetic field, the frequency corresponding to the separation becomes much larger. Srijit's doubt: The only way I can have single state,  $2S + 1 = 1$ , then  $S$  has to be zero. There's no bare proton. If I take a hydrogen atom, the electrons would also respond to the spinning charge. They would respond differently than the proton. They would try to oppose the field. So say if I apply 2 Tesla, then the proton feels 1.998, the field is not what you've applied, but somewhat less than that. Total angular momentum is what we're talking about. You apply the field, and you get to two levels, then its not the field you applied, its much smaller, I shouldn't say much smaller, its smaller.  $B_{\text{actual}} = B_z - B_{\text{induced}}$   $B_{\text{induced}} = \sigma B_z$  so then  $B_{\text{actual}} = B_z(1 - \sigma)$ , where  $\sigma$  is the electron density.  $\text{CH}_3 - \text{CBrH} - \text{CH}_2\text{Cl}$ , so the most electronegative Cl, will suck away the electron density, thus the proton will experience the least  $B_{\text{induced}}$ . The next will be the proton near Br, where you will have a slightly higher  $B_{\text{induced}}$  and the methyl will have the max  $B_{\text{induced}}$ .  $\text{CH}_3 - \text{OH}$ , acidity is manifested in the levels. The one experiencing the least shielding will talk first. This depends on  $\sigma$ . So if there are two guys, with 2.3T and 4.6T, with 100 MHz and 200 MHz, the difference would be in the ratio of 1:2. Brooker, or Glassgow, for UV its the same. So for NMR also we want a standard we can use. So we use the difference and divide it by the frequency of the machine that you're using. SO you go as  $\frac{100\text{Hz}}{100\text{MHz}} = 1 \times 10^{-6} = 1\text{ppm}$  and for the other machine also you'll have  $\frac{200\text{Hz}}{200\text{MHz}} = 1 \times 10^{-6} = 1\text{ppm}$ .

The actual frequency difference will be different but their difference normalized will be different. I will give you exercises where you calculate and convince yourself its accurate. In reality, I use a reference compound. So in my sample, I add a reference compound, which will give me a known peak at a given magnetic field. So lets say the difference in frequency is  $\Delta\nu = 100\text{Hz}/100\text{MHz} = 1\text{ppm}$ . So I report the peak appears 1 ppm away from the beginning. We use TMS, tetramethyl silane. It is nice because, Silicon is electropositive, so it's protons will be highly induced and therefore the peak would be very far away from the usual organic compounds. So this will show up at the highest magnetic field! Lithium Hydride say for instance, the peak will show up even more right on the spectrum. By definition, TMS would be at zero ppm. We had a Tau scale now it's Delta scales. High field machines have a greater split. So high field means high resolution. Therefore in high machines, you have these peaks more spread on the frequency scale. Also one peak is given. Volatile also, just heat the mixture and you could recover the analyte. Also has 12 protons, and so it'll have a large peak and would be soluble in it.  $\text{CDCl}_3$  is the solvent. Peak broadening, with increase in intensity, so if you take chloroform, it will swamp all the spectra because it'll sit right in the centre. If you had to do an experiment where TMS is not soluble, then you could use a different method. Then sir summarized the whole thing. We will harp on a little more and then we'll see the second order effects. You also get information about it's neighbours.

November 8, 2012

If the lower had 1, then the upper would have 0.99998, so the ratio would be 0.99998/1.99998. Do the assignments twice. But you sit down to doing it, you'll find there're many places where you can make mistakes and therefore should practice instead of losing time in the exam.

The spacing is so very small for carbon, that its difficult to observe. In the case of carbon, each carbon has 6 protons and 6 neutrons, and in such cases, the spins cancel out. For  $\text{C}^{13}$  though, its not NMR inactive.  $g$  is intrinsic to the particle, doesn't depend on magnetic fields. You can't quite guess  $g$  anyway.

TMS concept was reiterated.  $B_{\text{actual}} = B_0(1 - \sigma)$ , so the difference depends on the value of  $B_0$ . Now say in a 100 MHz machine you got a difference of  $326 \times 10^{-6} \text{T}$ . Now we know that 2.3487 T. Gradients had no concern at the times of 60MHz machines. There're times when you're not clear about weather you're clear or not. Good part of the questions will be from what i teach you in this module.

Splits will not depend on the magnetic field. The splitting patterns remain the same. Hydrogen talks in NMR, and the spin comes in the picture, becaues there's a resultant angular momentum and therefore it has a magnetic field.  $^{12}\text{C}$  has 6 protons and 6 neutrons. They pair up and there's no angular momentum they posses. Its nice that carbon

decided not to talk, therefore it's cool.  $^1\text{H}$  1p/on Odd Z, even N  $^{13}\text{C}$  6p/7n, Even Z, odd N  $I=1/2$   $^{12}\text{C}$  6p/7n, Even Z, odd N  $I=1/2$   $^2\text{H}$  1p/1n, Odd Z, odd N,  $I=1$  (integer)

$I=1$ , splits into a triplet, it goes 1, 0 and -1. Selection rules (find out)

Carbon 13 is very small statistically, so organic chemists would start using Carbon 13 as labels.

Area under the curve would be proportional to the number of protons

November 14, 2012

$\text{CH}_3 - \text{CH}_2 - \text{OH}$ , now for  $\text{CH}_2$ , there are two sets of inequivalent, then couple the strong ones, and then couple the weaker ones. So if  $\text{CH}_3$  has a stronger spin, you'll first split into four, and then split into two. If you have more s character in the bond, then the electrons will be closer to the nucleus, and therefore the nature of the bond decides the coupling. In 2(bromomethyl)-1-chloro-3-iodo propane, you see triplet of a triplet of a triplet. Double radiation experiment, with carbon being only 1 percent in natural abundance. They're very small in number the abundance is very little. Carbon 12 is silent in NMR. We know how to handle that, because we use Fourier transform NMR, so the sensitivity will be high enough. If you have  $\text{R}_3\text{CH}$ , you'll get one peak for the tertiary carbon and that'll be split into two. If the splitting is too much, then it might just get lost in the noise, since the intensity has to get distributed, which is anyway too small. Now to avoid splitting, you give the protons a radiation of 1400 MHz, the proton levels get saturated, basically a dynamic equilibrium is reached between the population of the two states. Since this is very rapid, the carbon sees only an average, therefore splitting doesn't happen. Don't have to worry about C 13 when you're doing hydrogen because C 13 is very small in number. Also, apply the broadband pulse because the protons get split at slightly different levels. Relaxation mechanisms are rapid, the state is restored because of environmental, lattice etc. So if you put a molecule in a higher state, it comes down to a lower state. The absorptions will depend on the population in the ground state, so if the relaxation is faster, then the peak will be intenser. For a proton, the relaxation time scales are the same. So from the peak, you can predict the number of protons. For carbon though, they're not the same, so you can't quite tell the number of carbons.



*If you want to hit on a geeky girl, try: We're degenerate nuclei; we couple but don't split*



*Check out Einstein's equation about rate of stimulated emission and that of absorption*

### 3.2 AMAZING EXAMPLES

$\text{CH}_3$  0.9,  $\text{C} = -\text{C} - \text{H}$  2  $\text{C} = \text{CHR}$  4, Benzene 6. With the benzene

November 21, 2012

## 3.3 I CAME LATE

$E = g\beta_N B_z I_z$  for a proton, for an electrons we have  $E = gg\beta_1 B_z J_z$ . If i want to calculate the g value of an electron we have

$$g = \frac{3}{2} + \frac{S(S+1) - L(L+1)}{2J(J+1)} \quad (1)$$


For a  $^2S_{\frac{1}{2}}$ , we have

$$g = \frac{3}{2} + \frac{1/2(1/2+1)}{2(1/2)(1/2+1)} \quad (2)$$

For a  $^2P_{\frac{1}{2}}$ , we'll have  $L = 1$ , we plug it in, to get  $\frac{2}{3}$ . Splitting the total Js into it's corresponding components. For atoms, L and S give me J, for molecules, we add the molecular rotation, so with the nuclear spin, we have to add that too. We then get,

$J + I \dots J - I$ , so for  $^2S_{\frac{1}{2}}$ , we'll have  $1/2 + 1/2 = 1$ , and  $1/2 - 1/2 = 0$ , so you get a slit, which is about 21cm, which is what revolutionized astronomy. The population difference in normal temperatures is zero, but in inter-galactic spaces, the temperature is so very low, the population difference is significant.

For the usual states, you use the schrodinger's equation to solve. Now you use approximation methods, with certain perturbations. Thus you can't use very strong fields, because then the quantum mechanics you use to predict things, won't be valid.



*I was complaining about it being cold in Delhi and was talking to my colleague, he's like you shouldn't complain about the temperature you do cold molecule spectroscopy and I was like I like my molecules to be cold, not MY molecules to be cold*

## 3.4 ESR

Here you end up using 0.3 Tesla and so on. It'll be in the giga hertz region, the frequencies. Simply because the nuclear magneton (magnetron is inversely proportional to the mass) is 1000 times less than that of the electron. The electrons are so very mobile, that their life-times are very small, thus the peak is very broad compared to NMR, in which the nucleus takes a long time to get restored. In NMR you don't want any unpaired electrons, no paramagnetic material. So the electron can come really close to the nucleus and lose energy, thus the time periods are small, thus it's broad, the line width. We normally plot the derivative, since the peaks are very broad. Also, the electron couples with the nucleus, and the peak splits into two.

You keep the frequency constant, (4600 MHz), and sweep the magnetic field, you'll get the spacing between the frequency as 0.05 for 0.32 T. For the splitting, the usual ways go. (missed out a bunch of examples, specially naphthalene, with pentant of a pentate).

$$a = R\rho \quad (3)$$

So for a hydrogen atom, if the value is 0.05 T, then for a methyl ion, the value will be smaller because the electron spends smaller time

with each nucleus, as the time is spent on various atoms. For the hydrogen, the split is max because the electron doesn't have anywhere to go. For the methyl radical, it'll be smaller (viz. 2.3 mT)! For benzene it becomes 0.38 mT.





## COLOPHON

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