MASSACHUSETTS INSTITUTE OF TECHNOLOGY
Department of Chemistry
5.35 Introduction to Experimental Chemistry

Module 1: <u>FUNDAMENTALS OF SPECTROSCOPY</u>

It's amazing how much we can learn about molecules and materials by shining light on them! In spectroscopy, we use light to determine a tremendous range of molecular properties, including electronic, vibrational, rotational, and electron and nuclear spin states and energies. From this information, we can often deduce a great deal of additional insight, including:

- Molecular identities – what is the sample composed of?
- Molecular conformations, geometries, and sizes
- Chemical equilibria
- Effects of liquid or solid-state surroundings on molecules
- Dynamics, including the rates of chemical reactions, interchange among different molecular conformations, relaxation of molecular excited states, photosynthetic energy transfer, protein folding, etc.

We also can use light to control, as well as study, some molecular properties and events. In photochemistry, light may be used for generation of new chemical products, sometimes with selectivity or yields that cannot otherwise be achieved. We depend on a wide range of photophysical processes like those in photosynthesis and vision. Modern laser sources allow the use of intense light pulses to manipulate materials and molecules in unique ways, inducing phase transitions, ablating material, initiating nuclear fusion, and so on. Laser micromachining and CD recording are examples of applications of these processes.

There are a great many ways in which spectroscopy may be conducted. In some cases, light of different wavelengths is shined on a sample and the wavelengths that get absorbed most strongly are measured. In others, you let the sample first absorb light and then measure the wavelength of light emitted. In yet others, you shine a pulse (or a sequence of pulses) of light on the sample and measure various time-evolving responses. There are countless variations on these themes, some routine and commercialized, others highly specialized and carried out only in scattered research labs around the world. Through an understanding of the general principles of spectroscopy, you can understand the way most spectroscopic measurements work and begin to think creatively about the broad range of spectroscopic possibilities.

Purpose

This module is designed to introduce the basic concepts of spectroscopy and to provide a survey of several of the most common types of spectroscopic measurement. You will conduct the following measurements.

- UV-VIS (ultraviolet-visible) spectroscopy of electronic states
- Fluorescence spectroscopy of electronic states
- IR (infrared) vibrational spectroscopy
- NMR (nuclear magnetic resonance) spectroscopy of nuclear spin states

In most cases, you will be able to see the insides of the spectrometers and develop an understanding of how they work. You will use your spectra for chemical identification, study of electronic properties of organic molecules and semiconductor quantum dots, assessment of how electronic energy levels are affected by their surroundings in a solid, and other purposes. In the process of conducting the experiments, you will learn methods of sample preparation, operation of the spectrometers, and interpretation of the various types of spectra that you will record.

Safety

Chemicals: The chemicals involved in this experiment should be handled with care to avoid harm to your or your colleagues. These include deuterated solvents such as acetone-d_6 or chloroform-d_3 that are used for NMR spectroscopy so that the signals from protons in the compounds of interest are not obscured by protons of the solvent.

Glass: In preparing NMR samples, you will use glass pipettes and NMR sample tubes. In placing a rubber bulb on the pipette or a plastic cap on the sample tube, the experimenter should hold the tube immediately below the point of attachment to avoid breakage of the glass.

Magnetic Fields: The field generated by an NMR magnet can have deleterious effects on watches (battery-powered watches with liquid crystal displays are an exception), magnetic credit cards (VISA, AmEx, etc.), and similar items. When working in the vicinity of an NMR spectrometer, leave these items in an alternate location. The magnetic field can also influence cardiac pacemakers and other medical devices. Discuss any such devices with your instructor and take the necessary precautions.

Reading

1. Hore, P. J. *Nuclear Magnetic Resonance*, Oxford University Press, Oxford, 1998.
2. Mohrig, J.R.; Hammond, C.N.; Schatz, P.F.; Morrill, T.C. *Techniques In Organic Chemistry* W.H. Freeman: New York, 2003. Chapter 19.
3. Pavia, D. l.; Lampman, G. M.; Kriz, G. S. *Introduction to Spectroscopy: A Guide for Students of Organic Chemistry*, Saunders: Fort Worth, 1996. Chapters 3-5.

General Background
Light and Matter

What happens when a sample is irradiated by light? From introductory chemistry courses, you might have a quantum mechanical picture of light absorption, which emphasizes that light energy comes in quantized units, called photons, and that a molecule's energy also comes in quantized units or "quanta", so when a molecule absorbs a photon, it takes up the photon's energy to reach an "excited state" of some sort. Your picture of light absorption might look like this.
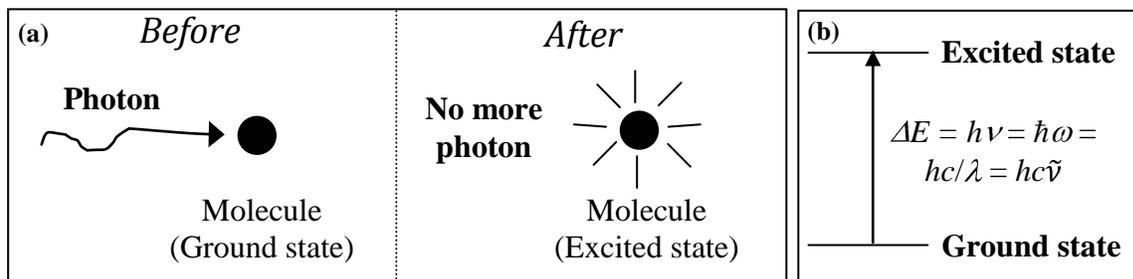

Figure 1. Optical absorption.

Both of these depictions get one crucial element correct: conservation of energy. The photon energy does indeed get turned into molecular energy. Also, since molecular energy is quantized, there are only molecular excited states at certain discrete energy levels. The photon energy has to be equal to the difference ΔE between some pair of energy levels of the molecule in order for absorption to occur. There are many types of states that these energy levels could correspond to, but in this module you will only consider electronic, vibrational, and spin states.

> *Exercise 1.* What are the names, values, and units of h and $\hbar$? How about ν, ω, λ and $\tilde{\nu}$? What are their values for visible and infrared light and for the MIT radio station frequency?

Figure 1 also contains some grave simplifications. Its biggest problem is that it suggests that the molecule is in a static, or (in quantum mechanical terms) stationary, excited state after irradiation. The accuracy of this description varies, but in your NMR experiments you will see graphic evidence that it is not complete. In those experiments, you will irradiate a sample with a pulse of radiation at radio frequencies (RF) and you will measure the time-dependent, oscillating state of the proton spins in the sample, long after the RF pulse is gone. Similarly, time-dependent molecular vibrations that occur during and after irradiation by an IR pulse can be measured, although their time scale is so fast that ultrashort laser pulses are required to observe the individual vibrational oscillations. Time-dependent oscillations in molecular electronic charge distribution due to visible or UV light are even faster, but there are ways of measuring them too.

> *Exercise 2.* Express the frequency values ν that you found from Exercise 1 in reasonable units, i.e. megahertz (MHz), gigahertz (GHz), or terahertz (THz). Now calculate the time T required for a single oscillation period in each case, again expressed in appropriate units of

microseconds (μs), nanoseconds (ns), picoseconds (ps), or femtoseconds (fs). These are the frequencies and oscillation periods of the RF, IR, and visible radiation and also of the respective spin, vibrational, and electronic responses of molecules that have energy levels whose differences match the radiation frequencies. When molecules are irradiated at a frequency that matches a transition between two energy levels, we say that the radiation is *on resonance* with the molecular transition frequency.

Exercise 3: Indicate what types of molecular energy level transitions are involved in the following spectroscopic techniques: NMR, IR, UV-Vis, Fluorescence.

These *dynamical*, time-dependent responses can be expressed in the most accurate and general terms through time-dependent quantum mechanics, which isn't treated in undergraduate courses. Fortunately, it can be expressed with excellent accuracy in most cases in the framework of *classical* mechanics. And this is something for which you have a lifetime of experience and intuitive understanding.

Figure 2 is an alternate depiction of light absorption. This picture is very different from those in Figure 1! Light is now depicted as a propag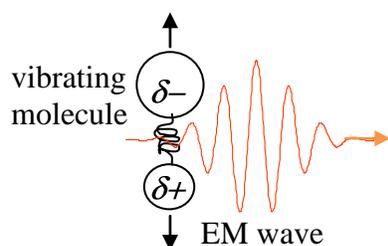ating wave, not a particle. The molecule is now shown as a classical harmonic oscillator, suggesting any possible vibrational amplitude, rather than only a set of discrete states. Which picture is right?

The answer is that both pictures are correct, and both can offer important insights. Figure 2 correctly suggests that light is a propagating electromagnetic wave. The molecule does indeed respond to the light much as a harmonic oscillator would. For example, a polar molecule like HCl responds to an oscillating electric field by alternately stretching and compressing, that is, through well-defined vibrational oscillations induced at the frequency of the field. The induced oscillation amplitude is proportional to the amplitude of the light field. If the light frequency is on or near the molecular vibrational resonance frequency, the induced oscillations are larger in amplitude than if the light frequency is far off resonance. Experiments can be conducted that permit direct observations of these time-dependent vibrational oscillations.

Figure 2. Optical absorption.

If we can view the irradiated molecule as a classical oscillator responding to a classical force exerted by a classical electromagnetic field, what about the quantum mechanical view? The details of this discussion will have to wait until 5.61 and even beyond, but the basic results can be described here. The molecule does indeed have well defined *stationary* states with well defined, discrete energies, as depicted in Fig. 1b. Molecular and light energy do come in discrete *quanta* as that figure suggests. But the fact that the molecule has time-independent, stationary states does not mean that the molecule always must be in one of those states. The molecule may be in a *time-dependent* state, which is not one of the stationary states but is described mathematically as a linear combination of stationary states. The time-dependent state may be very much like a classical oscillator, and any

oscillation amplitude is possible. This may seem to suggest that any vibrational *energy* is possible, in contrast to the laws of quantum mechanics. But it turns out that if you make a measurement of molecular vibrational energy, you always get one of the discrete energy values corresponding to one of the stationary states. Similarly, it is accurate to describe the light coming from a lamp or a laser as an oscillating electromagnetic field that can drive oscillating molecular responses. But if you measure the energy taken up by a molecule when it absorbs light, you find that the energy comes in indivisible quanta – what we call photons.

The reconciliation of time-dependent, classical molecular vibration and classical electromagnetic waves with quantized molecular energy levels and photons is a subtle point, but rest assured that the two apparently contrasting views presented in Figures 1 and 2 are indeed compatible. And that means we should not disregard Figure 2, for which life in the classical world has provided us ample intuition. Infrared light really does drive molecular vibrational oscillations. Visible and UV light drive electron clouds to move in an oscillatory fashion about their host nuclei. RF radiation drives magnetic dipoles in an oscillatory fashion, as any oscillating magnetic field drives a bar magnet. Where possible, we will use classical mechanics to explain spectroscopy.

Electromagnetic Radiation and the Electromagnetic Spectrum
Since light can be described as an electromagnetic wave, we should be able to depict it and understand parameters like those of Figure 1, applied to individual photons, in terms of wave motion. Imagine a wave propagating through space in what we will define as the x direction. We can describe the electric field as follows;

$$\mathbf{E}(x,t) = \hat{\mathbf{\varepsilon}} E_0 \cos(kx - \omega t) \tag{1}$$

Let's look at this equation. First, the field is a **vector** (**bold**); it is directional. On the RH side, first we see a unit vector $\hat{\mathbf{\varepsilon}}$ that indicates the direction along which the field is pointed. Here we've written $\hat{\mathbf{\varepsilon}}$ as time-independent for simplicity. Next we see an amplitude E_0, which we also have chosen to make time-independent. This describes a never-ending wave of light with a time-independent amplitude; later we'll describe pulses of light whose amplitudes are time-dependent. Finally, we have the oscillatory cosine term that indicates that the field is an oscillating function of both position and time. If we pick any position in space (fix the value of x) we see that the field that passes through that point oscillates in time. If we pick a fixed time, we see that the field oscillates in position.

Exercise 4. Plot the field as a function of time at a fixed position and vice versa. Indicate the amplitude E_0 and the oscillation period T for the first plot and the wavelength λ for the second. What are the relationships between T and ω and ν and between λ and k, the wavevector?

Absorption of Light

How do we describe how light interacts with molecules? Sticking with our classical picture, let's start with $F = ma$. In this case, the force exerted is the time-dependent, oscillating electromagnetic field. Let's consider the molecular vibrations of a polar, diatomic molecule like HCl. Treating it as a harmonic oscillator, we can write its equation of motion including three force terms: the Hooke's Law restoring force due to the spring, a frictional damping term proportional to the velocity, and the external force applied by the light. The result is

$$\mu \frac{d^2Q}{dt^2} + b \frac{dQ}{dt} + KQ = aE_0 \cos(\omega t) \qquad (2)$$

where Q, the vibrational coordinate, is the deviation from the equilibrium length of the spring (or the equilibrium bond length), μ is the reduced mass of the molecule, b is a friction coefficient, K is the force constant, and a is a coupling constant that measures how effectively the light drives the molecular vibration. We don't need to include propagation of the light or the position of the molecule explicitly in this equation; we can just solve it for any position (i.e., $x = 0$), and assume it will be the same everywhere else. Also note that the bigger a is, the larger the amplitude of vibration. We won't go into detail about this coupling constant here, except to mention that it depends on how polar the vibration is. The dipole moment of the molecule has to change as a result of the vibrational motion for the mode to be *IR-active*, that is, for it to absorb any IR light at all. Therefore, vibrations in homonuclear diatomics like H_2 and Br_2 do not appear in IR spectra (in our equation of motion, $a = 0$). The molecules vibrate but there is no change in dipole moment when they do. The result is that an electric field does not exert a force that affects the bond.

Extra Credit Exercise 1. This is your chance to "do the math." It is the fundamental classical mechanics of a driven, damped oscillator, which is an important problem that comes up in myriad contexts. It is somewhat time-consuming but straightforward since you are expected to use a text or online treatment from which you can follow the derivations and transcribe them directly. However, it is expected that you understand clearly anything you turn in.

Find a treatment of the classical mechanics of a driven, damped harmonic oscillator.

1. Show for a mass m that is connected by a spring of force constant K to an infinitely massive, immovable wall, that Newton's Law $F = ma$ along with Hooke's Law $F = -KQ$ (where Q measures the stretching of the spring, starting from its length with the mass at rest) yield the equation of motion $m \frac{d^2Q}{dt^2} + b \frac{dQ}{dt} + KQ = 0$ where the second term, which you will see describes damping, has simply been added in. Then show that for two masses, m_1 and m_2, on the two ends of the spring, the equation of motion has the same form, $\mu \frac{d^2Q}{dt^2} + b \frac{dQ}{dt} + KQ = 0$, where the mass m has been replaced by the reduced mass μ for which you should derive an expression.

2. Show that with no friction, i.e. $b = 0$, the solutions are oscillatory at the *resonance frequency* $\omega_0 = \sqrt{\frac{K}{\mu}}$. If you stretch the oscillator by some amount Q_0 and then let go (i.e. set initial conditions $Q = Q_0$, $dQ/dt = 0$), the solution takes the form $Q(t) = Q_0 \cos(\omega_0 t)$.

3. Show that for weak friction, the solutions are exponentially damped oscillations: $Q(t) = Q_0 e^{-\gamma t} \cos(\Omega t)$, where $\gamma = \frac{b}{2}$ is the *damping constant* and the oscillation frequency $\Omega = \sqrt{\omega_0^2 - \gamma^2}$ is slightly lower than the resonance frequency.

How does the harmonic oscillator respond to a periodic driving force like that exerted by light? It is possible to use eq. (2) to derive the response of the damped harmonic oscillator to an oscillating driving force at the driving frequency ω. The result is

$$Q(t) = A(\omega)sin(\omega t + \beta), \tag{3}$$

with the vibrational amplitude A increasing as the driving frequency approaches the resonance frequency ω_0. The vibrational amplitude depends on the driving field amplitude and on the driving frequency,

$$A(\omega) = \frac{aE_0/\mu}{\left(\left(\omega^2 - \omega_0^2\right)^2 + 4\gamma^2\omega^2\right)^{1/2}}. \tag{4}$$

Finally, the amount of power that is absorbed from the driving field by the damped oscillator is given in classical mechanics by the expression *power = force * velocity*. Using our expressions above and neglecting oscillations that are very rapid in comparison to the length of the measurement (that is, averaging over an oscillation period), we get

$$P(\omega) = \frac{(aE_0)^2}{\mu} \frac{\gamma \omega^2}{\left(\omega^2 - \omega_0^2\right)^2 + 4\gamma^2\omega^2} \approx \frac{(aE_0)^2}{4\mu} \frac{\omega^2}{(\omega - \omega_0)^2 + \gamma^2} \tag{5}$$

assuming weak damping and a driving frequency that is near resonance. Maximum power absorption occurs on resonance, and the power absorbed far from resonance is negligible. In an absorption spectrum, you measure how much power $P(\omega)$ from a light source is absorbed by the sample as a function of the light frequency. The functional form on the RH side of eq. (5) is called a *Lorentzian* function. Its peak is at the resonance frequency ω_0 and its width is given by the damping constant γ. Thus the basic parameters of the sample can be determined directly from the absorption spectrum. Note that the power absorbed depends on the field amplitude squared, or the light intensity, which, averaged over the cycles of the field, is the light power. That is, the amount of power absorbed is proportional to the amount of power that hits the sample.

Extra Credit Exercise 2. Plot the time-dependent displacement of the damped harmonic oscillator $Q(t)$. Plot the frequency-dependent vibrational amplitude and power absorption for the driven oscillator with $\gamma = \omega_0/10$ and $\omega_0/100$. Indicate the parameters ω_0 and γ on the frequency plots. What changes in these plots as γ changes?

Note that in the treatment above, we wrote that the driving force oscillates as $\cos(\omega t)$ while the driven response oscillates as $\sin(\omega t + \beta)$. The frequencies are the same, but the vibrational phase may not be. When the vibrational phase factor β is $\pm\pi/2$, $\sin(\omega t + \beta) = \cos(\omega t)$ and the driving force and the response are **in phase**. This happens whenever the

driving frequency is **far off resonance**. On the other hand, when β = 0, the response is 90° **out of phase** with the driving force and the driving frequency is **exactly on resonance**. This is one way of thinking about the power absorbed from the driving force: it is largest when the frequency is on resonance because the force is always driving the oscillator out of phase, and therefore always meeting substantial resistance.

In the classical damped harmonic oscillator, the time-dependent oscillations and the vibrational energy are damped at a rate given by γ. When damping is complete, there are no significant further oscillations and the vibrational energy is zero. We say that the well-defined time-dependent oscillations treated above are *phase-coherent*, because their timing—their vibrational phase, β—is well defined. It turns out that the absorption linewidth γ really measures the loss of vibrational phase-coherence, or *dephasing* (sometimes called "decoherence"). In some cases the dephasing rate and the energy decay rate are the same, but in many cases dephasing is much faster. This is the case with electronic and spin states as well as vibrations. The absorption linewidths tell us about how long it takes for the coherent oscillations in vibrational displacement, electronic charge distribution, or magnetic moment to decay, but not about how long the vibrational, electronic, or spin energy is retained by the molecule (vibrational, electronic, or spin state *lifetimes*).

We should not forget entirely the quantum mechanical picture, e.g. Fig. 1b. The resonance frequency ω_0 that we associate with classical time-dependent oscillations also gives us the energy difference, $\Delta E = \hbar\omega_0$, between the ground state and an excited state of the molecule. The reason that energy might remain in the molecule long after coherent oscillations are fully damped is that the molecule at that point may be left in the excited state – a stationary state. The energy lifetime is just the lifetime of the molecule in that state. Eventually the molecule will return to the ground state by some mechanism – emission of light (fluorescence) or a nonradiative mechanism in which the energy is lost to thermal energy of the surroundings.

Experiments 1-2: UV-Vis Absorption Spectroscopy

Absorbance is measured using a *spectrophotometer*. The intensity I of the light that is transmitted through the sample of a known thickness l is compared to the "reference" intensity I_0 of light that did not go through the sample. In practical spectroscopy, the power absorption labeled $P(\omega)$ in the discussion of fundamentals above is often called the *absorbance* and labeled $A(\nu)$. The absorption of light in a suitable concentration range can be described by Lambert-Beer's law,

$$A(\nu) = -\log\left(\frac{I}{I_0}\right) = \varepsilon(\nu) * c * l \tag{7}$$

where ε is the extinction coefficient and c is the sample concentration. In order to get the dependence of the absorbance on the wavelength, the sample is irradiated by light composed of all the wavelengths of interest and the transmitted light is then dispersed using a grating. The separated frequency components are measured in different parts of a CCD detector.

*Exercise 5.* Derive Beer's Law—it's easy to find in textbooks and online.

In one experiment, we will use the relationship between absorbance and concentration to determine the concentration of an absorbing molecule of interest. One measures the absorbance of a series of solutions of known concentrations to determine the relationship between the absorbance and concentration (that is, to determine the value of ε), usually through a linear fit. Once this is known, then from measurement of the absorbance of a solution of unknown concentration, the concentration can be determined. The measurement error can be minimized by adjusting the concentrations and/or sample length such that the absorbance is between 0.3 and 1, ensuring that the absorption is strong enough to yield a significant difference between I_0 and I, but not so strong that there is too little transmitted light to measure.

Image removed due to copyright restrictions. Please see: Ocean Optics. USB4000 Fiber Optic Spectrometer Installation and Operation Manual. Document Number 211-00000-000-02-201201. Appendix C, p. 27.

Quantum mechanical particle-in-a-box model of electronic excited state energies
We've seen how absorption spectra have peaks at the resonance frequencies ω_0 of electronic, vibrational, or spin states of molecules. Can we calculate the values of the frequencies from first principles? The answer is yes – if we can calculate the energies of the quantum mechanical electronic, vibrational, and spin states. In general this may require sophisticated numerical calculations, but in some cases we can use simple models to get approximate values of the energies.
You will record UV-Vis absorption spectra of electronic transitions in a series of aromatic hydrocarbons illustrated below.

Figure 4.
Aromatic hydrocarbons.
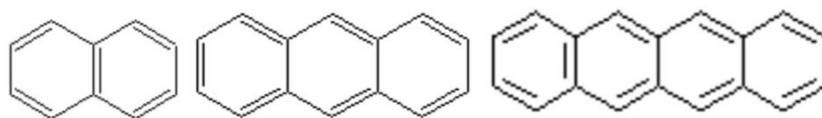
naphthalene   anthracene   tetracene (naphthacene)

The pi electrons can move freely throughout the molecules. A very simple model that describes the electrons is a quantum mechanical "particle-in-a-box." In this model, the potential is infinitely high outside the box and zero inside the box. The model is applied to the molecules by assuming that the molecule size is the box size. For a 1-dimensional particle in a box, the energy of the nth level is given by
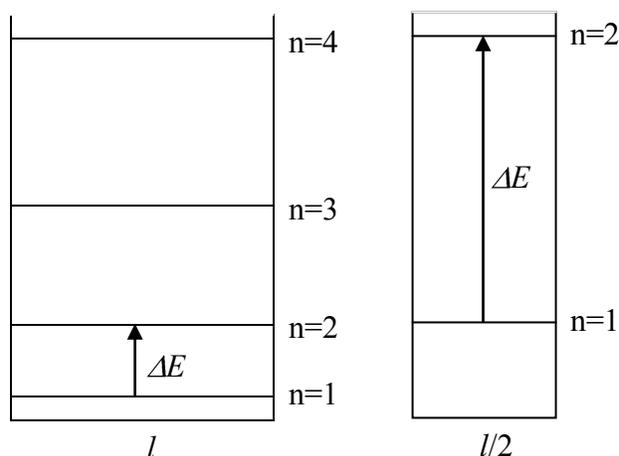
Figure 5. Particle in a box energy levels for boxes of lengths l and $l/2$. In the smaller box, the energy levels are separated by larger amounts and transitions require more energy.

$$E_n = \frac{n^2 h^2}{8ml^2}, \quad n = 1,2,3,\ldots \qquad (8)$$

where m is the mass of the particle and l is the length of the box. The smaller the box, the larger the spacing between the energy levels. Therefore, a smaller box requires light with a higher photon energy (and higher frequency) to induce transitions between the ground state (level 1) and the first excited state (level 2) as shown in Fig. 5. You should observe a shift in the absorption spectral peaks toward lower frequencies, described approximately by Eq. (8), as the number of rings increases.

Experiments 4-5: Fluorescence spectra

A fluorescence measurement is similar to the one described above except that the measured light is emitted by the sample, rather than transmitted through it. Although fluorescence is emitted in all directions, typically we measure the emission at a 90° angle relative to the incoming radiation path in order to minimize the amount of transmitted or reflected light that reaches the detector. Since the fluorescence is much weaker than the incident light, fluorescence signal is easily overwhelmed by stray incident light.

Fig. 6. Fluorescence.
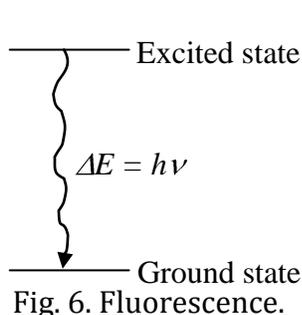
Once energy gets absorbed by a molecule, what happens? Clearly the molecule doesn't retain the extra energy forever. The molecule will eventually return to the ground state. One way this happens is for the molecule to *emit* light at the resonance frequency—to *fluoresce*, either spontaneously or by stimulation.

Spontaneous Emission

In this type of fluorescence, the molecule spontaneously emits a photon and loses the associated energy *ΔE*. In spontaneous emission (indicated by the wavy line), emitted light can go off in any direction. There is no driving light field; spontaneous emission is a purely quantum mechanical process that leaves the molecule in a stationary state, not a time-dependent oscillating state. Still, if we analyze the emitted light as a function of frequency, we discover that the maximum of the spectrum occurs on resonance and the spectral width is given by the dephasing rate, just like in the absorption spectrum.

In our fluorescence experiment we use the particle in a box model to study quantum dots fabricated by the Bawendi research group. Quantum dots are semiconductor crystals of nanometer sizes over which an excited electron is delocalized. In a bulk semiconductor, there is an energy gap E_g (the "bandgap") between the valence band, where the electrons

are in the ground state, and the conduction band. A *band* state simply means that the electrons are not localized on individual atoms or molecules, but rather are delocalized over a large area of the crystal—in the case of quantum dots, the entire dot. Due to the finite size of the dot, allowed energies of the electron are quantized approximately by the particle in a box expression, so the lowest-energy excited state is separated from the ground state by the gap energy plus the lowest ($n = 1$) particle-in-a-box energy. Both fluorescence and absorption lines should shift as a function of nanoparticle size. In this experiment we will look at fluorescence and absorption from three solutions of quantum dots (CdSe with trioctylphosphine ligands in hexane/toluene solvent) and observe the shift of the maxima as a function of the size of the dot. From the wavelengths at which the maxima appear, it is possible to estimate the size of the dots using the formula in the previous section.

Stimulated Emission

Although emission can occur spontaneously, it also can be stimulated by an incident light field, just like absorption. In stimulated emission, the emitted light has several interesting properties that differentiate it from spontaneous emission: it is exactly the same as the incident light in its direction, polarization, frequency, and phase. This is why stimulated
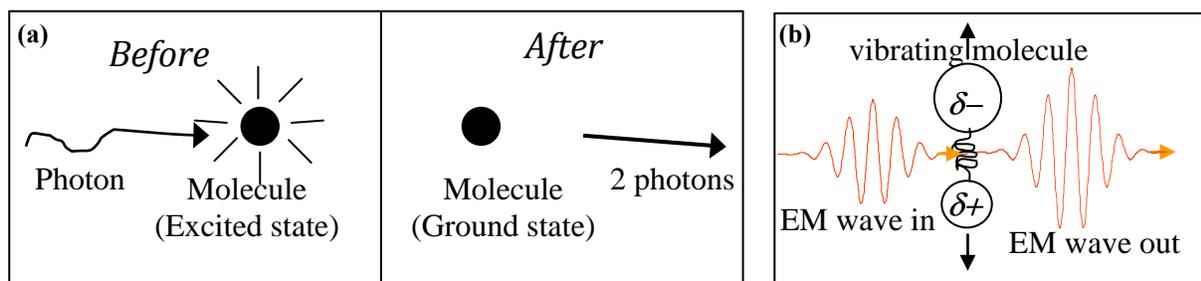

Figure 7. Stimulated emission.

emission is used in lasers and laser amplifiers. If laser light enters a population of excited molecules, it may stimulate emission and emerge with substantially increased power. In general, light that is resonant with a molecular transition frequency may induce absorption or stimulated emission. If all the molecules are in the ground state, then only absorption occurs. If some molecules are in the excited state, then stimulated emission can also occur, and if 50% of the molecules are in each state, then there is no net gain or loss of optical power (though many individual molecules may absorb or emit). If more than 50% of the molecules are in the excited state—a population "inversion"—then there is more stimulated emission than absorption, and more light emerges than entered. A population inversion cannot occur in molecules *at thermal equilibrium*, but there are many ways to introduce energy into selected levels and to maintain a population inversion for long enough to extract the energy as stimulated emission.

Exercise 6. What does LASER stand for?

<div align="center">**Fourier Transform Spectroscopy**</div>

Spectroscopy in the time domain

In UV-Visible spectroscopy, you measured absorption and fluorescence spectra in the *frequency domain* using spectrometers with diffraction gratings that separated the different frequencies of light that is either absorbed or emitted. The amount of light at each frequency was detected using a CCD detector; the measurement was made directly as a function of frequency. An alternative to collecting data in the frequency domain is to carry out a measurement in the *time domain*. For example, a short pulse of light can be used to initiate an oscillatory response. After the pulse is gone, the system will continue to oscillate until dephasing is complete. (See Exercise 5, part 3.) If we can measure the oscillations directly as a function of time, then we can work out what ω_0 and γ are, just as we did in the frequency domain. The time-domain measurement may be advantageous for a number of reasons. One key advantage is that a single pulsed measurement yields the information in a very short time, even including the time spent in repeating the measurement and averaging to obtain a good signal/noise ratio. A second important reason for making the time-domain measurement is that it can sometimes yield additional information that cannot be extracted from a simple frequency-domain absorption measurement.

It often is convenient and useful to display the results of a time domain measurement as a function of frequency. One could fit the measured oscillations, extract the values of ω_0 and γ from the fit, and then plot a Lorentzian function using the extracted values, thereby providing a display of the frequency-domain spectrum. However, there is a much more direct way of going between the time domain and the frequency domain. It's called *Fourier transformation*, and it yields the *Fourier transform $F(\omega)$* of a function *f(t)*. The Fourier transformation is executed as follows[1]:

$$F(\omega) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} f(t) \cos(\omega t) \; dt \tag{6}$$
$$f(t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} F(\omega) \cos(\omega t) \; d\omega$$

We'll only use the first of these relations, but it's useful to see that one could go either way between time and frequency domains. Let's imagine that *f(t)* is our measured time-dependent response $Q(t) = Q_0 e^{-\gamma t} \cos(\omega_0 t)$, where we have approximated that the dephasing rate is very small. This approximation is not necessary to get the correct result, but it simplifies the discussion. Now imagine trying the top integral above with different values of the frequency ω. First try $\omega = \omega_0$. This will give a large positive result because $\cos(\omega t)$ becomes $\cos(\omega_0 t)$, and this multiplies the same oscillatory function that is part of *f(t)*. When one factor of $\cos(\omega_0 t)$ is positive or negative, so is the other one, so the product is positive at all times. Therefore the integral over all time yields a large positive result. On the other hand, if ω is substantially different from ω_0, then $\cos(\omega_0 t)$ and $\cos(\omega t)$ will oscillate between being in and out of phase, yielding both positive and negative

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[1] These formulae work for a cosine function, but if the oscillation phase were different, e.g. sinusoidal, there would be problems. There is a more general version, but it is not necessary for our purposes.

contributions which will average out to a neglibily small value with time. Eventually, the exponential decay will end any significant contributions to the integral.

Now consider $\omega \approx \omega_0$. In this case the oscillations will stay in phase for many cycles, yielding a large positive result for a substantial portion of the integral. Eventually the oscillations will go out of phase, and this could yield negative values that might substantially cancel the positive contribution. But if the exponential decay basically ends $f(t)$ before the oscillations of $\cos(\omega_0 t)$ and $\cos(\omega t)$ go out of phase, then these negative values are insignificant. This is the case as long as $|\omega_0 - \omega| \ll \gamma$. What this tells us is that for frequencies at or near the resonance frequency, we have large values of $F(\omega)$, and as the frequency moves farther off resonance in either direction, $F(\omega)$ becomes small in value. In fact, it's not too hard to show that $F(\omega)$ is precisely the Lorentzian function we saw before – the absorption spectrum – with center frequency ω_0 and linewidth γ.

Our example above is a Lorentzian function, but in fact the FT relation holds much more generally, even for spectra that are not Lorentzian. For example, imagine several spectral lines that are very close together, so they merge into one very broad line with a width much greater than any of the individual linewidths γ. This spectrum will have an irregular shape, the details of which depend on the relative strengths of the different absorption peaks, how far apart their central frequencies are, and their linewidths. The corresponding time-domain response also will be irregular, since the driving force will start all the oscillators going and they will get out of phase rather quickly since they will be oscillating at different frequencies. The details of the decay of the oscillations in signal will depend on the relative amplitudes of the different responses, how far apart their resonant frequencies are, and their individual decay rates. But the time and frequency domain responses $Q(t)$ and $P(\omega)$ still will be related through Fourier transformation.

Extra Credit Exercise 3. Calculate the Fourier transform numerically or analytically (the definite integrals in this particular case are available in tables) of your damped oscillatory functions from *Extra Credit Exercise 3*, with $\gamma = \omega_0/10$ and $\gamma = \omega_0/100$. Then calculate the FT of the sum of two or three oscillatory functions, and repeat this with a few different choices of frequency values. Plot both the time-domain and frequency-domain functions. Try to develop some intuition for what the Fourier transforms look like for different cases.

When you make the measurement in the time domain, you use a short pulse of light and measure the sample's oscillating response. The pulse is centered at some frequency ω_p, and it has some duration τ. For example, the pulse might have a Gaussian envelope function, so the field may be given by $E(t) = e^{-(t/\tau)^2} \cos(\omega_p t)$, a bit like the pulse sketched in Fig. 2. In this expression, it appears that the field simply oscillates at the frequency ω_p, which would render our experiment ineffective—if there is no light at a certain frequency (all frequencies except ω_p), we can't determine how much light at that frequency gets absorbed, regardless of the domain. In fact, the measurement works because *the frequency components are all contained within the short light pulse*. The key to understanding this is to realize that the Gaussian pulse can be written as a sum of many different frequency components, with a Gaussian spectrum of frequencies centered at ω_p. The width of the

frequency spectrum, δ, is given by the inverse of the pulse duration, τ. Therefore, the shorter the pulse duration, the greater range of frequencies it contains! At the center of the pulse, at time $t = 0$, the oscillations of all the different frequencies are in phase, so there is a large total field and a large intensity. At a short time before or after the center of the pulse, the oscillations of the different frequency components are somewhat out of phase with each other, so the total field and intensity are lower. At a longer time before or after the center of the pulse, all the oscillations of the different frequency components are completely out of phase and the superposition of all the components yields no net field or intensity. This is an important concept, and it may be worth your while to sketch out four or five different frequencies on graph paper that all have maxima at the origin. Now, in a different color, try adding them up. You should get a feeling for how the sum of many frequencies results in a train of pulses; if we sum (actually integrate) over a continuous set of frequencies rather than a few discrete frequencies, there is only one pulse.

The Fourier transform relations between a light pulse and its frequency spectrum are similar to those that we saw before between a harmonic oscillator response and its absorption spectrum. In both cases, a rapid decay of oscillation amplitude corresponds to a broad frequency range and a slow decay of oscillations corresponds to a narrow frequency range.

Recalling eq. (1) for the light field, the oscillating term $\cos(kx - \omega t)$ suggests that not only can frequency ω and time t be interchanged through Fourier transformation, but so can wavevector k and position x. And since the wavevector is related to the wavelength, i.e. $k = 2\pi/\lambda$, then just as time-domain data can be Fourier transformed to yield the frequency-dependent spectrum, so can position-domain data be Fourier transformed to yield the wavelength-dependent spectrum. And of course the spectrum written as a function of wavelength or frequency is the same since the two are simply related by the speed of light in air.

Can we really record data in the "position domain"? What would that mean? It suggests that we could examine a "snapshot" of the light field, like the one you generated in Exercise 3, and see just how it had been affected by passing through the sample. Is this possible?

The answer is: *almost*. We don't have a way of recording a snapshot of a rapidly varying field directly, but as you'll see, in FTIR spectroscopy we measure the superposition of two fields *and then translate one field spatially relative to the other*. Imagine two identical plots like yours from Exercise 3, showing snapshots of the same field. Now imagine adding the two fields together. If they are exactly in phase, the result will be constructive interference and the field amplitude will double and the intensity of the light, which is the square of the field, increases everywhere fourfold. So does the power, which is just the integrated or time-averaged intensity over one or more cycles of the field. This is what is measured. Now imagine shifting one of the fields spatially, forward or backward. If you move it by half the wavelength, then the two fields are exactly opposites at all times. Their superposition yields destructive interference, and there is no light intensity or power at any time. If you continue to move it by another half-wavelength, the two fields are back in phase and the

original power is back. So the power oscillates between a maximum value and zero as we shift the relative phase of the fields.

A plot of the power vs. relative displacement *X* between the two interfering fields is called an *interferogram*. It provides "almost" a snapshot of the field. For a light field like the one we've been discussing, this function, which we can call $g(X)$, oscillates as $cos(kX)$ and its Fourier transform is zero for any value of *K* other than *k*, the light wavevector. This is the idealized limit of a never-ending light wave with a single frequency, except now the analysis is in terms of the wavelength and position-dependence (accounting for how we make the measurement) rather than the frequency and time-dependence. If instead we have many wavevector components, then their oscillations won't stay in phase for long, so when we shift one field relative to the other, at first they will go in and out of phase like before, yielding oscillations in the measured power, but after a short displacement they will no longer interfere constructively or destructively and we will just measure the average power of each separate field (half the maximum power). This situation is closely analogous to the time-frequency case we considered above. When the range of wavevector components is very narrow, it will take a long distance for them to get out of phase. When the range of wavevector components is very broad, they will get out of phase very quickly. The wavevector and spatial domains have the same relationship that the frequency and time domains have.

> *Exercise 7*: Explain in your own words the function of a Fourier transform and why it is a useful technique for spectroscopy.

Experiments 6-7: Fourier Transform Infrared Spectroscopy

The technique you will use to measure IR absorption spectra differs from the one described above for UV-VIS spectra. Instead of using a grating to disperse the light, the FTIR spectrometer uses an *interferometer*, as depicted below. The light beam from an IR source is split by a 50% reflector (thick dashed line in the figure) into two beams. These are directed toward mirrors that reflect them back to the 50% reflector, at which each of the beams may be partially reflected and partially transmitted, going back toward the IR source or toward the detector. One of the mirrors is mounted on a movable stage so the path length traveled by the reflected field can be varied, allowing us to control the phase of one beam relative to the other. When the beams return to the 50% deflector, one of two things can happen: if the beams are in phase, the light goes back to the source, and if they are out of phase, the light goes to the detector. A good way to think of this is through time-reversal symmetry: if you draw the wave originally hitting the 50% reflector and the two waves emerging from it, and then reverse the direction of time, the picture should look the same. Of course, if you had put the IR source where the detector is and done the same thing, that picture also should look the same. In practice, the source emits light throughout the IR spectrum, covering a wide range of wavelengths, so the interferogram recorded by moving the stage and measuring the power at the detector shows a limited number of oscillation cycles and then, at large values of *X*, no further interference. The Fourier transform of the interferogram yields the IR light intensity at each wavelength. When a sample is placed in

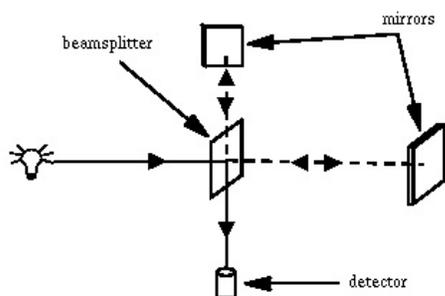front of the detector, some wavelengths are absorbed and this changes the interferogram

and its Fourier transform. The difference between the Fourier transforms of interferograms recorded with and without the sample present gives the sample's absorption spectrum. It is necessary to record the "reference" spectrum with no sample present each time the spectrometer is used because both water and CO_2 (whose concentrations in the air may vary over time) will absorb strongly in this region, and our spectrum will be corrupted if we fail to subtract their contributions.

Figure 9: Interferometer (image from NIST, National Institute of Standards and Technology). For another example of an Interferometer, please see http://www.physics.mq.edu.au/ ~goldys/optmicroweb/ftir

IR spectra are often used to determine the structure of a molecule, since the frequency of molecular vibrations is dependent on the stiffness of bonds and on the masses of atoms. In order to illustrate how we get information about properties of a molecule using FTIR, you will record the interferogram of chloroform and then calculate its Fourier transform, which will give you its vibrational spectrum in the region of 500 – 4000 cm^{-1}. Next, you will use FTIR spectroscopy to look at the structures of limonene and carvone, which differ only in one functional group but nonetheless exhibit IR absorption spectra with differences sufficient to enable their identification.
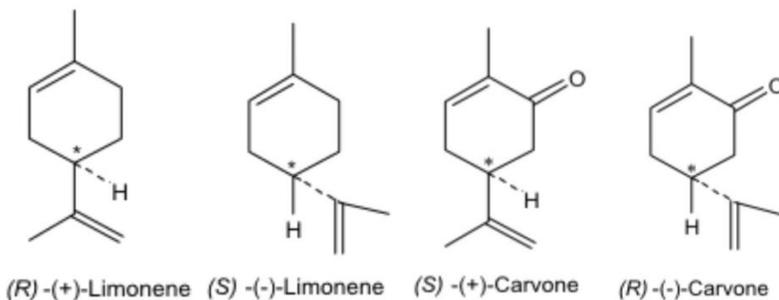

Figure 10. Limonene and carvone.

(R) -(+)-Limonene   (S) -(-)-Limonene   (S) -(+)-Carvone   (R) -(-)-Carvone

Aside from studying and identifying small molecules, FTIR is also important in biophysical studies where the molecular environment can shift vibrational frequencies. For example, hydrogen bonding from water molecules can decrease the force constant of carbonyl stretches, shiftint the resonance frequency by tens of cm^{-1}. In proteins and DNA, common building blocks form biopolymers with repeat structures whose similar environments lead to characteristic frequencies. We will investigate the Amide I vibration of proteins (primarily C=O stretch, 1600-1700 cm^{-1}), a vibration that is sensitive to secondary structure because structure-specific backbone hydrogen bonds affect the frequencies and because the vibrating atoms in nearby monomer units move in unison, which also affects the frequency and makes it particularly sensitive to molecular conformation. β-sheets are characterized by IR peaks at 1620-1635 and 1670-1680 cm^{-1} while α-helices show peaks at ~1650 cm^{-1} and random coils at ~1640 cm^{-1}. To avoid overlapping H_2O vibrational peaks, we will dissolve the proteins in D_2O, which exchanges with the solvent exposed N-H amino acid groups. This exchange results in a slight frequency downshift in Amide I, but a large

100 cm^{-1} shift in Amide II (C-N stretch and N-H or N-D bend) from 1550 to 1450 cm^{-1}. We will investigate the Amide I absorption spectrum of myoglobin, ribonuclease A, and lysozyme, an α-helical, β-sheet, and mixed protein, respectively. We will also watch the Amide I and Amide II regions of the spectrum to monitor the structural changes induced in ribonuclease A with heating.

Experiments 8-9: Nuclear Magnetic Resonance (NMR)

In NMR, the transitions are between different spin states of the proton. It turns out that every ^{1}H nucleus (as well as ^{13}C, various other nuclei, and the electron) has an inherent spin angular momentum and associated spin magnetic moment. This is a purely quantum mechanical effect, although the term "spin" is based on the wistful notion that the effect could be connected with the classical spinning of a charged particle. While electron orbital angular momentum and magnetic moments can be understood qualitatively in terms of circulating, charged particles, spin has no classical analog. Nonetheless, the response of the spin magnetic moment to an applied magnetic field can be understood substantially in classical terms.

Unlike electronic and vibrational levels which have inherently different energies, the two spin states of the proton ordinarily have the same energy (they are *degenerate*). In this case there is no spectroscopy possible, since there is no light frequency of transition between the two levels. However, when a static (dc) magnetic field **B** is applied, the two levels separate in energy because the spin magnetic moments **μ** align mostly parallel or mostly antiparallel to the direction of the applied field. When the field is applied, say along the *z* direction (all modern NMR spectrometers have the dc magnetic field aligned along *z*), the spin magnetic moments are not locked along this axis, but *measurement of their z-components always yields the same magnitude*, either positive or negative in sign, indicating alignment of the *z*-component either with the field ("up" or +1/2) or against the field ("down" or -1/2). The positive or negative values are those of the spin *z*-component quantum number, $m_I = \pm 1/2$, associated with *z*-components of the spin angular momentum, $I_z = \hbar m_I$, and the spin magnetic moment, $\mu_z = \hbar m_I \gamma_p$, where the proportionality constant $\gamma_p = 26.75 \times 10^7$ T^{-1}s^{-1} ("T" is Tesla, a unit of magnetic field) is called the proton *gyromagnetic ratio*. The energy in a magnetic field is given by $E = -\mathbf{\mu} \cdot \mathbf{B} = -\hbar m_I \gamma_p B = \pm 1/2 \hbar \gamma_p B$. When the magnetic field is on, transitions between the two spin levels are possible through absorption of radiation. The frequencies of this absorption are generally in the radiofrequency (RF) region, roughly on the order of the MIT radio station frequency.
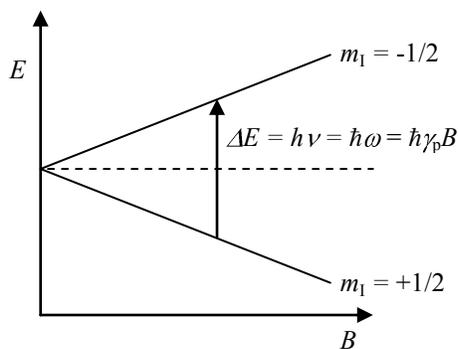
The NMR spectrum is an RF absorption spectrum. The magnetic field magnitude B is held fixed, but instead of scanning the RF frequency and recording how much RF power at each frequency gets through the sample, like in UV-VIS spectroscopy, the spin response is measured in the time domain. A short RF pulse is incident on the sample, inducing coherent oscillations of the spin magnetic moment which

$$m_I = -1/2$$
$$\Delta E = h\nu = \hbar\omega = \hbar\gamma_p B$$
$$m_I = +1/2$$

Figure 11. Proton spin energy levels as a function of applied magnetic field.

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continue for long after the pulse is gone. The decaying oscillations are recorded in real time with a magnetic coil. Fourier transformation of the time-dependent response, called *free induction decay* (FID), yields the NMR spectrum.

Exercise 8. Find the joke hidden somewhere in the paragraph that starts with "Unlike".

Exercise 9. The two NMR spectrometers you will use have RF frequencies of 15 MHz and 300 MHz. Calculate the magnetic field strength in each instrument using the relationship between the resonance frequency and magnetic field.

The dc magnetic field is aligned along the *z*-axis, as mentioned above. The pulsed magnetic field is polarized along the *y*-axis, tilting the spin magnetic moments along the *y* direction. Typically, the RF pulse amplitude is adjusted to tilt the magnetic moments by 90°, or $\pi/2$. Thus the magnetic moments are forced into the *xy*-plane, initially along the *y*-axis and then precessing about the *z*-axis. The net magnetic moment along the *x*-axis, which oscillates at the precession frequency (given by $h\nu$ as illustrated in the figure), is what is measured with a magnetic coil. Over time, the precessing moments begin to return toward the *z*-axis under the influence of the dc field in that direction. Thus the measured oscillation amplitude decays with time, yielding a frequency and a dephasing rate.

Interactions with electrons: Chemical shifts

The discussion thus far would suggest that every proton of a molecule in a magnetic field should show the same spin resonance frequency. If this were true, NMR would be of little spectroscopic value since every proton would yield the same signal. But the local magnetic field "B_{loc}" that is actually felt by each individual nucleus is not quite equal to the applied magnetic field because the applied field causes circulating currents in the electrons around the nucleus, and these give rise to a small magnetic field of opposite sign to the applied one. The induced field slightly shields the nucleus from the applied field, giving $B_{loc} = (1 - \sigma)B$ where σ is the *shielding constant*. Although this effect is small, it produces an easily measurable shift in the proton spin resonance frequency. Since the nature of the electron distribution varies from one part of the molecule to another, so does the magnitude of this *chemical shift*. The chemical shift often is expressed as a relative quantity, $\delta = \frac{\nu_0 - \nu_{ref}}{\nu_{ref}} * 10^6$, so that unlike the resonance frequency ν_0, it does not depend on the applied field magnitude. This permits convenient comparison of chemical shifts, irrespective of the NMR instrument that is used to measure them. The reference frequency ν_{ref} is given by
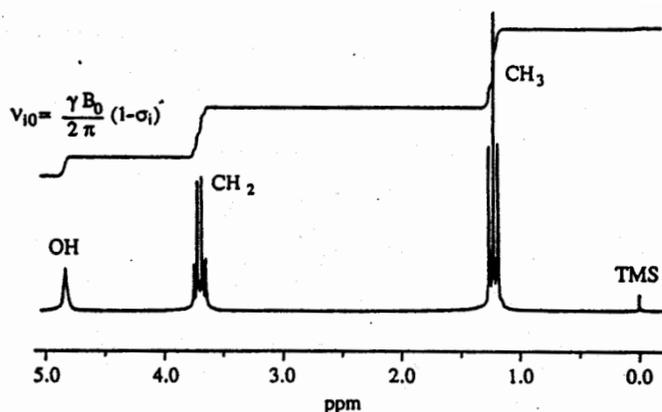

Figure 12. The proton NMR spectrum of ethanol. TMS (the most widely used reference signal) stands for tetramethylsilane ($Si(CH_3)_4$). The upper step-like curve is the integrated signal, proportional to the number of spins contributing to each set of peaks. From J.T. Arnold et al, *Journal of Chemical Physics* **19,** p. 507 (1951).

convention by the frequency of the single NMR line in tetramethylsilane (TMS), which shows very little chemical shielding. A simple illustration is provided by the NMR spectrum of methanol, shown in Fig. 12.

The spectrum reveals methyl, ethyl, and alcohol proton peaks in well separated regions of the spectrum, though the actual frequencies measured differ only by a few parts per million. The spectrum also includes a plot of the integrated areas under each set of peaks, thereby indicating the relative numbers of protons that contribute to them. Figure 13 shows commonly measured spectral shifts in NMR spectra of organic molecules.
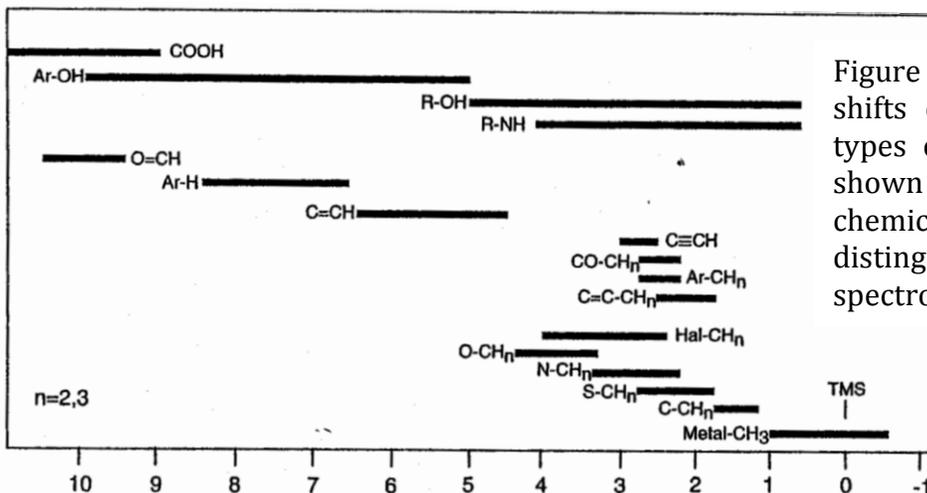

Figure 13. The chemical shifts expected for various types of ^1H resonances. As shown here, a wide range of chemical groups may be distinguished through NMR spectroscopy.

Interactions between proton spins: J-couplings and splittings

An interesting and important feature of the ethanol NMR spectrum has not yet been explained. The CH_3 and CH_2 spectral features consist of three and four components, respectively. The splitting of NMR lines arises from interactions between the spin magnetic moments on inequivalent, nearby nuclei. Like nearby bar magnets, the spin moments exert weak magnetic forces on each other. The result is that the spin energies due to nuclei a and b include a *spin-spin coupling* term $E_{ab} = hJ_{ab}m_I(a)m_I(b)$, with the coupling constant J typically only 1-10 Hz. If we examine the energy of a + ½ spin on nucleus a without an applied field and include the interaction due to b, there are now two possible values depending on what spin nucleus b has. Each of these two values is then changed by an applied field. The diagram below illustrates the possible spin combinations and allowed transitions; note that only one spin state may change when a photon is absorbed because a photon carries just one quantum of angular momentum.
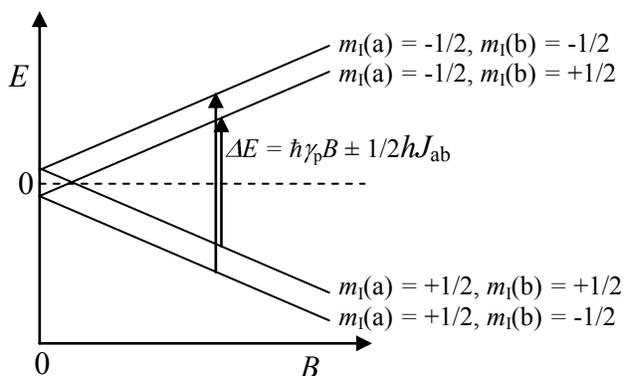

$m_I(a) = -1/2, m_I(b) = -1/2$
$m_I(a) = -1/2, m_I(b) = +1/2$

$\Delta E = \hbar \gamma_p B \pm 1/2 h J_{ab}$

$m_I(a) = +1/2, m_I(b) = +1/2$
$m_I(a) = +1/2, m_I(b) = -1/2$

Figure 14. Proton a spin energy levels as a function of applied magnetic field B, including interaction with nearby proton b.

So, the effect of one nearby proton is to split the NMR absorption line into two closely spaced lines of equal intensity. If we extend this treatment to include another proton c that is indistinguishable from b (e.g. on an ethylene group) and that therefore interacts in the same way as b with

proton *a*, then it is easy to see that there are three distinct spin energies associated with *a* including the spin-spin interactions: one with *b* and *c* both spin up, one (including two different states) with one spin up and the other down, and one with *b* and *c* both spin down. In this case there are three different spin transition frequencies in the intensity ratio 1:2:1. Similarly, if we consider a third indistinguishable proton *d* on a methyl group with *b* and *c*, we discover that there are four distinct spin transition frequencies for proton *a* in the ratio 1:3:3:1. These effects are apparent in the ethanol NMR spectrum. The singlet, doublet, triplet, and quartet spectral features are extremely useful for NMR interpretation and chemical identification.

Instrumentation

You will conduct NMR spectroscopy using two very different instruments. The TeachSpin 15-MHz NMR instrument is designed to expose the dc magnet and the workings of the spectrometer to your view and manipulation, so you can gain a clear understanding of what is going on in an NMR measurement. This instrument allows you to record free induction decays (FIDs) and other time-dependent responses in a simple and illustrative manner. In contrast, the Varian 300-MHz NMR spectrometer is a highly automated instrument. You still are able to control many of its functions, in particular the RF pulse sequences that are used to induce the sample responses, but the workings of the device are buried more remotely alongside the superconducting magnet which is perpetually cooled with liquid helium. Although its performance is more obscured from view, it is also clearly superior. The higher magnetic field results in far greater separation of peaks with different chemical shifts, and the better field uniformity across the sample results in linewidths that are not broadened instrumentally by having different parts of the sample subject to different field levels. You will use the 300 MHz instrument for eludication of chemical composition and molecular structure.

In your NMR measurements, you will mostly use a single pulse, adjusted to be a $\pi/2$ pulse, to initiate spin precession and free induction decay. As you have seen, the decay rate that you measure does not necessarily give you the dynamical dephasing rate γ, because in some samples local inhomogeneity leads to a wide range of absorption resonance frequencies. Each resonance might have a narrow linewidth γ, but since all the lines merge together you only measure a much broader *inhomogeneous linewidth Δ*. In the time-domain NMR measurement, the result is the same as in the frequency domain. A short $\pi/2$ pulse will tilt all the spins into the *xy*-plane and they will all start precessing about the *z*-axis, but after a few oscillation periods they will start to go out of phase because they precess at different frequencies. The higher-frequency spins will start to run ahead of those at the central frequency, and the lower-frequency spins will lag behind. But a second RF pulse could be applied (after a delay time τ following the first pulse) that is twice as strong as the first one. It is a "pi" pulse, and its effect is to flip all the spins by 180°. In this case the spins find themselves precessing about the *z* axis like before, but in exactly the opposite direction – so the higher-frequency spins find themselves lagging behind the average, and the lower-frequency spins find themselves ahead! After a few cycles, the higher-frequency spins will begin to catch up, and the lower-frequency spins will find their lead diminishing. After the same time period τ that separated the first two pulses, all the spins will be precessing in

phase again. In our measurement of net magnetization, we will see a maximum – the signal, instead of decaying away, will have built back up! This recurrence of signal is called a "spin echo." It is very useful because it makes it possible to measure the dynamical dephasing rate γ, even if the sample is inhomogeneous. This is accomplished by varying the time period τ and measuring the decay of the echo signal intensity. The π pulse and the spin echo measurement permit reversal of dephasing that occurs due to inhomogeneous variation in resonance frequencies but not due to dynamical processes, so the echo signal level decays with rate γ which can therefore be measured.

Recall that the lifetime, conventionally called T_1, or (its inverse) the energy decay rate γ_1, is not measured in the spin echo measurement, which gives the homogeneous dephasing rate γ, or the free induction decay, which gives the total dephasing rate which we'll call Γ and which is the sum of homogeneous and inhomogeneous rates, i.e. $\Gamma = \gamma + \Delta$. Some of the dynamical processes (interactions or "collisions" between molecules) that cause dephasing actually cause loss of the spin energy and relaxation back to the lowest-energy spin state, that is, they contribute to the energy decay rate γ_1. But many of these processes simply give the precessing spin a "kick" that changes its precessing phase, leaving the spin energy intact. In this case the affected spin no longer precesses in phase with those around it, so "pure" dephasing occurs without energy relaxation. The pure dephasing time is conventionally labeled T_2^*, and we'll label the pure dephasing rate (its inverse) γ_2^*. The homogenous dephasing rate is then a sum of two contributions, i.e. $\gamma = \gamma_1 + \gamma_2^*$. The lifetime T_1, or energy decay rate γ_1, can be determined by reversing the order of the π and $\pi/2$ pulses from the spin echo measurement. If the π pulse arrives first, it leaves the spins exactly flipped from their initial orientations, not precessing but stationary with a net orientation against the field direction. The $\pi/2$ pulse then brings them into the xy-plane where they start precessing, and a free induction decay can be measured. As the time τ between the pulses is increased, energy relaxation occurs, and the free induction decay signal level decreases at the rate γ_1 which can be measured. Thus all the contributions to the total dephasing rate $\Gamma = \gamma_1 + \gamma_2^* + \Delta$ can be determined.

Sequence	Variable Measured	Equation of Relaxation
$\pi/2$	Γ	$M(\tau)=M(\infty)[\exp(-\tau\Gamma)]$
$\pi/2 - \tau - \pi - \tau$	γ	$M(\tau)=M(\infty)[\exp(-2\tau\gamma)]$
$\pi - \tau - \pi/2$	γ_1	$M(\tau)=M(\infty)[1-2\exp(-\tau\gamma_1)]$

Finally, a note on shimming. The word "shim" was used to describe a bell tuner who would remove shims of metal from different places on the bell so that the bell produced a single sharp tone. Imagine a chemical species with only one proton. If we put a sample of this type in an NMR magnet we would expect one narrow line. But if the applied magnetic field is not uniform across the sample, then the resonance frequency will vary across the sample and the line will be broadened. This is similar to inhomogeneous broadening described above, except the inhomogeneity is in the applied field rather than the sample. The 15 MHz spectrometer has significant field inhomogeneity, but 300 MHz instrument allows us to adjust how strong the magnetic field is at different locations within the sample using *shim coils*. These coils have a small current running through them, which induces a magnetic

field. Each coil is located near the sample such that by changing the current, the magnetic field in the sample can be made homogeneous. A homogeneous magnetic field yields a narrow line, which helps prevent nearby peaks from overlapping and lets us determine the true dephasing rate.

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