> **Massachusetts Institute of Technology**
> **Department of Chemistry**
> **5.33 Advanced Chemical Instrumentation**
> **Fall 2007**

Experiment #1: Molecular Spectroscopy of Acetylene

I. Introduction

While in freshman chemistry, you may have wondered how scientists figured out that HCl has a bond length of 127 pm (1.27 Å). How do you measure something that small to any kind of precision? You are about to find out! Spectroscopy is one of the most powerful methods available for determining the structure of molecules.

The infrared range of the spectrum covers wavelengths $\lambda = 2$–25 μm, or energies per photon $E = hc/\lambda$, expressed in "wavenumber" (cm^{-1}) units as $E/hc = 1/\lambda = 400$–5000 cm^{-1}, where h is Planck's constant and c is the speed of light. Infrared spectroscopy probes the vibrational and rotational energy levels of molecules, and is widely used by chemists to study the structure, dynamics, and concentrations of chemical compounds. In this experiment, you will use infrared spectroscopy to measure the carbon-carbon and carbon-hydrogen bond lengths in a simple linear molecule, acetylene (and its mono- and di-deuterated derivatives). You will be able to determine force constants of the bonds and the quantum energy levels of the molecule, and explore other aspects of infrared absorption phenomena.

II. Experimental Procedure

Experimental work should be done by all **three lab partners** working together**.** Although the experimental part of this lab is not particularly difficult, it is imperative that you understand the procedure before performing it. In addition, you should at least skim through the theory section of this lab so that you have some idea of why you're bothering to do all of this and have some understanding of the spectra that you take. **<u>Do not come into lab unprepared!</u>**

Plan on two days for the experimental work. The glassware required for the experiment will be available in the laboratory. The C_2H_2 section is probably the easiest

because it involves no synthesis; the acetylene is taken directly from a tank. You should plan your work so that the C_2H_2, C_2HD, and C_2D_2 spectra can be taken during this two-day period. Keep in mind that C_2D_2 and C_2HD readily exchange D and H with materials they are in contact with, and thus *cannot* be stored overnight.

The syntheses will be performed in Room 4-474, using the vacuum line already set up in the hood and the Nicolet FT-IR spectrometer. The acetylenes are very flammable gases with an irritating odor due to impurities. Therefore, all work is to be done in the hood, and absolutely **NO SMOKING or OPEN FLAMES** are allowed in the room.

A.   Basic Set-Up

The vacuum line (see Fig. 1) is set up in the hood, along with the glassware pieces that must be oven-dried prior to use. These include:

1. one 3-neck round-bottom flask, 100-mL size
2. one glass stopper
3. glass adapter ($\bar{\top}$ 19/22 to $\bar{\top}$ 14/20)
4. rubber septa (to fit $\bar{\top}$ 14/20)
5. two plastic clips to fit $\bar{\top}$ 14/20 (stock room)

All glassware should be clean and oven-dried. It is not necessary to dismantle and clean the vacuum line already set up in the hood. Assemble the glassware as indicated in Fig. 1 (note that because you are doing non-deuterated acetylene first, you do not need to attach the 3-neck flask or the trap that it is connected to). Use a light film of vacuum stopcock grease on the female parts of the O-ring joints, then clamp the O-ring joints with the clamps provided (the T.A.'s will demonstrate this somewhat tricky part). Pressure in the system is monitored with Wallace and Tiernan dial gauges (dual range, 0 – 1 atm and 0 – 50 Torr; be sure you know which is which.)

The gas IR cells are in the glass desiccator near the hood. The ends of the cells are KBr windows, which do not absorb IR radiation. However, fingerprints and water do absorb IR radiation. When using the cell on the vacuum line, keep the salt plate ends covered with rubber septa (also in the desiccator) to prevent the KBr windows from absorbing water and "clouding" over.

The FT-IR and the computer are always on and should be never be turned off! Further description of the operating principles of the FT instrument are given in Appendix A of this manual.
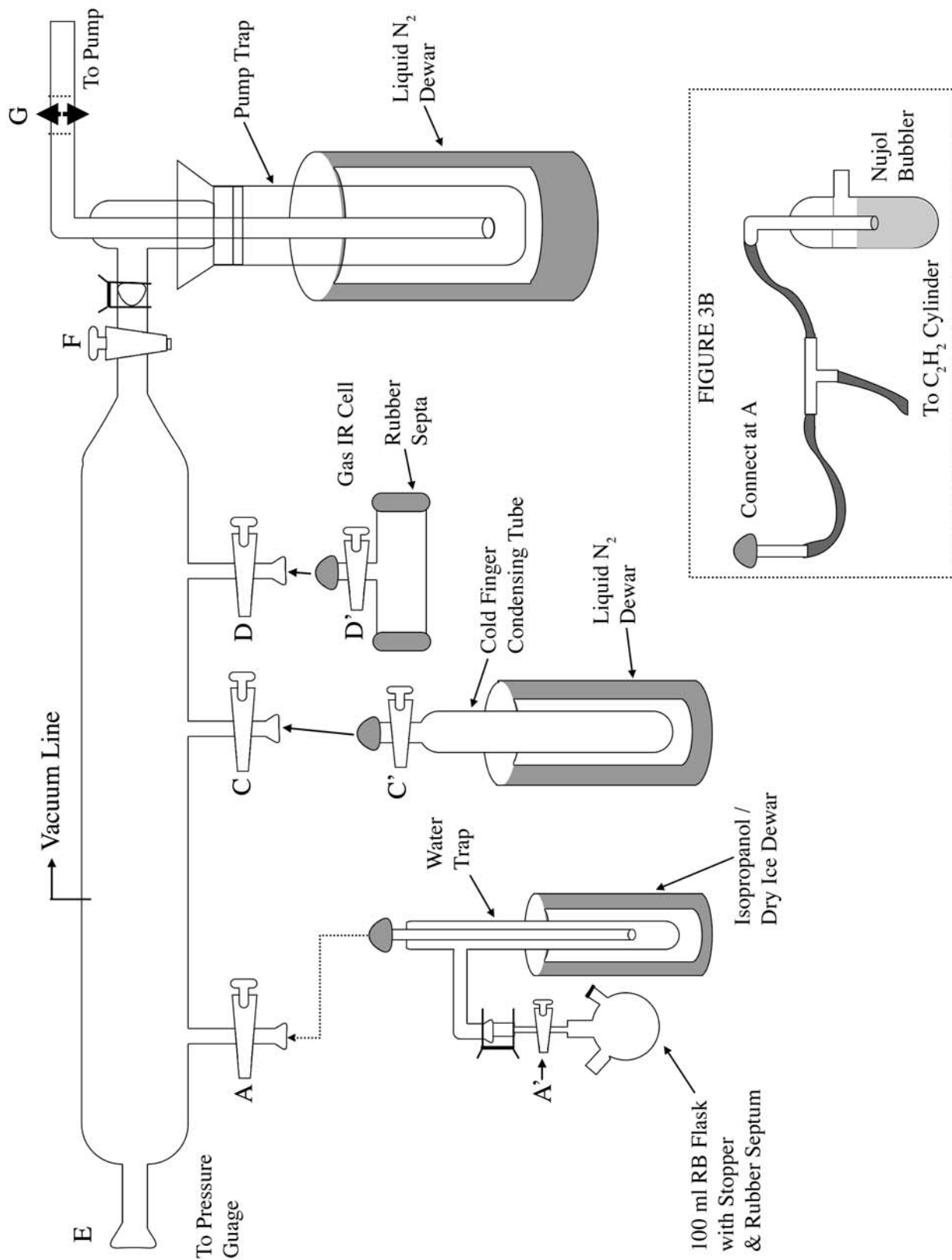
Figure by MIT OpenCourseWare.

B. Synthesis and Spectrum of C_2H_2

Close stopcocks **F** and **G** and turn on the vacuum pump by plugging it in. Close stopcocks **A, A', C, C', D**, and **D'**. Open stopcocks **G** and then **F**. After pumping and waiting a minute, open stopcocks **D, D', C, and C'**. Place one of the Dewars around the pump trap and clamp it in place. Fill the Dewar slowly with liquid nitrogen – let it cool as you fill it to avoid splashing the liquid nitrogen, as it will cause skin burns. The short delay before cooling the trap is to allow most of the air to be pumped out; otherwise, it would liquefy in the pump trap. **Liquid air is very corrosive and reactive. It could cause organic compounds, like acetylene, to burn when the trap is later warmed!** Wait until the pressure gauge reads less than 0.5 Torr.

The pressure gauge should read less than 0.5 Torr after a few minutes. Close stopcocks **D, D', C, and** C'. Then close stopcock **F** and wait a few minutes. The pressure should not rise more than 1 Torr. This is called leak-testing the vacuum line. If the pressure is stable, then open, one by one, stopcocks **D, D', C, and C'**. After each of these stopcocks is opened, the total system pressure should not rise much and should be stable. If the pressure jumps up and increases, then a leak has been found. If any stopcocks or O-ring joints are leaking, then (a) close the stopcock above the leak to keep a vacuum in the rest of the system, (b) re-pressurize the faulty part by taking apart the joint or stopcock, (c) clean and re-grease the joint, and (d) reassemble the joint, pump out the part, and see if it holds a vacuum.

When all stopcocks have been opened and any leaks in the system have been repaired, the pressure should stabilize below 0.5 Torr, and this vacuum should be stable for at least 5 minutes with stopcock **F** closed.

The source of the acetylene will be a gas cylinder. Using a glass tube ending in an O-ring joint, connect the tank to inlet **A**. [See Fig. 1B] With **A** still closed, open the valve on the C_2H_2 tank until the bubbler rate is about 3 bubbles/second. Close the valve to the bubbler. Slowly raise the third Dewar (filled with liquid N_2) around the cold finger at **C'** and clamp it in place. Be careful not to freeze C_2H_2 in the neck of the cold finger. Close stopcock **F**. Slowly open **A**, and allow C_2H_2 to solidify in trap **C'**. If the pressure rises too quickly, slow the C_2H_2 flow by closing the tank valve slightly. After a few minutes, close **A** and disconnect the glass tube.

Close **C** and evacuate the remaining gas by opening **F**. Insure that **D'** and **D** are closed. Remove the cell from the apparatus and collect a background scan using the FT-IR. You need to take a background scan to eliminate absorbance due to the cell and the air in the FT-IR. Carbon dioxide and water are IR-active and must be purged with

nitrogen which is not IR-active. The nitrogen never gets rid of all the CO_2 and H_2O, but in 30 seconds the system will equilibrate.

Open OMNIC. A **Smart Accessory Change** window will appear and select **5.33 IR Exp** in the drop-down menu so that the correct experimental parameters are used. Press **OK**. Click on the **Exp Set** icon in the upper left to check the experimental parameters. You may change the number of scans from the default of 16 if you want, but you should leave the resolution at 0.5 cm^{-1}, the highest resolution setting. Take note of the data point spacing, as this will be important in the error analysis. The final format should be absorbance and under Background Handling it should be set to collect a background before every sample. Press OK when you are done. Now you are ready to collect a spectrum.

Place the empty cell (after removing the rubber septa from each end) in the cell holder by opening the top-sliding window on the instrument. Click on the **Col Smp** icon. A window comes up asking to collect a Background spectrum. Close the window on the instrument, wait approximately one minute (this allows time for water and CO_2 to be purged from the chamber), and then press OK. After a few seconds a Single Beam Spectrum will appear on the screen. This does **not** indicate data collection is complete. The number of scans completed can be monitored in the lower left of the screen. A window will appear asking to collect the sample spectrum when data collection is complete. Do **not** press OK yet. Remove the cell from the instrument and close the top window. Replace the rubber septa and put the cell back on the vacuum line to fill it with Acetylene.

Evacuate the IR cell again by opening **D** and **D'**. Now close **F**, open **C**, and partially lower the liquid N_2 Dewar, allowing the upper half of the trap to warm up. Allow the pressure to rise slowly, using the height of the Dewar around the trap to control the rate. When the pressure reaches about 80 Torr, close stopcocks **D'** and **D**, then close stopcock **C**, and immediately raise the Dewar around the cold finger. Open stopcock **F**, and pump out the remaining C_2H_2 in the system. The IR cell may now be removed and the spectrum recorded.

Leave the Dewar around the cold finger in case another sample of C_2H_2 is needed. When you are pleased with your spectrum, pump the remaining C_2H_2 out of the cold finger by opening **C** and lowering the liquid N_2 Dewar.

When the cell is filled with the sample gas, place it back in the instrument positioned just as before. Close the top window and wait one minute (it is more important to wait the same amount of time you waited for the empty cell spectrum than it is to wait exactly one minute). Now press OK to collect the sample spectrum. When

data collection is complete, a window will appear where you can enter the spectrum title. Press OK. Then press Yes to add to Window1.

When the computer is done transforming the data, you will need to save the file. Scans can be saved with the .CSV extension, which is an ASCII text file.

Once the spectrum is saved, label the peaks and print it over a range of 4000-500 cm^{-1}. The x-axis limits can be changed by going to **View** and selecting **Display Limits**. You can label individual peaks by clicking on the **T** at the bottom of the window, and then clicking on the peak of interest. Print this labeled spectrum. Next, as summarized in Table 1, obtain a high resolution display from 1420 to 1220 cm^{-1} by changing the limits, and then label the frequencies of these peaks by going to **Analyze** and clicking **Find Peaks**. Click to move horizontal line up or down to label the peaks of interest. Then click **Replace** in the upper right to work with your labeled spectrum. You may create a chart of the peak frequencies and intensities that can be copied and pasted into spread sheet format by going to **Analyze** and clicking on **Resolve Peaks**. Ask the TA how to get a good fit, and then copy the peak and intensity information and you can save it in WordPad. Print this if necessary. For C_2H_2 and C_2HD, the computer analysis is identical except, of course, the limits of the high resolution expanded region.

After the spectra have been recorded, reattach the IR cell to the vacuum line and empty out the cell using the vacuum pump. If the sample pressure was too low or too high, the IR cell may be filled by adding more C_2H_2, or some of the gas may be pumped out. Alternatively if enough solidified C_2H_2 remains, the cell may be completely pumped out and a new sample made at the desired pressure

C.   Synthesis and Spectrum of C_2D_2

Add to the round-bottom flask 2.5 g CaC_2 (kept in a desiccator or in the hood). The CaC_2 should look like little black rocks. If it is coated with a lot of grayish dust, you may need to get a fresher sample of calcium carbide. Replace the glass stopper, and check to make sure the rubber septum is tight. Connect the third cold trap and the round-bottom flask as described in Figure 1.

Fill another Dewar with an isopropanol/dry ice bath: fill the Dewar 1/2 full of isopropanol and add dry ice in small amounts until the violent bubbling stops and the mixture is viscous.

When the vacuum pressure has stabilized, slowly raise the isopropanol/dry ice Dewar around the water trap and clamp it in place. Close **D** and **D'.**

Since C_2D_2 is slightly acidic, it could exchange protons with any stray sources in the system (such as excess grease). Therefore, the system must be "deuterated" before any C_2D_2 is collected. To do this, close stopcock **F** and inject 0.5 ml D_2O into the flask through the septum. Do not leave the cap off the D_2O bottle for long, as it will exchange protons with atmospheric water vapor. The CaC_2 should bubble violently and the pressure will rise as C_2D_2 is produced. Do not let the pressure rise above atmospheric pressure, otherwise parts of the system might burst. If too much D_2O is injected and the pressure rises near atmospheric pressure, open stopcock **F** and let the pump withdraw the excess. It will be trapped in the pump trap. Wait about 5 minutes with **F** closed to allow exchange with any available protons. Open **F** and pump out the gas. The vacuum will probably not be as good as before, since the CaC_2 will keep producing small amounts of C_2D_2 for a long time. However, the pressure should be less than 0.8 Torr.

Slowly raise the third Dewar (filled with liquid N_2) around the cold finger and clamp it in place. Be careful not to freeze C_2D_2 in the neck of the cold finger. Close stopcock **F**. Inject 0.5 mL D_2O into the flask. The pressure will rise and then fall slowly as the C_2D_2 is solidified in the trap at **C'**. When the pressure has fallen below ~10 Torr, make another 0.5 ml injection. Repeat this procedure until a total of 4.0 mL D_2O has been injected.

Close **C** and evacuate the remaining gas by opening **F**. Insure that **D** and **D'** are closed. Remove the cell from the apparatus and take a background scan through it using the FT-IR.

While taking the scan, close **A** and remove the flask and water trap; first remove the isopropanol/dry ice Dewar, then detach the water trap and reaction vessel from the system. The flask must be left <u>open</u> in the hood to allow C_2D_2 to escape. The water trap should also be left in the hood to warm up. The CaC_2 waste should be dumped in the labeled waste container in the hood.

Replace the cell and open **D** to allow the pump to remove the air. Close **D** when the pressure is down. Now the IR cell can be filled by "boiling off" C_2D_2 from the cold finger. Close **F** and open **C, C', D** and **D'**. Lower the liquid N_2-filled Dewar, allowing the cold finger to warm up slightly. When the pressure reads about 200 Torr, close stopcock **C** and <u>quickly</u> raise the Dewar around the cold finger. Wait a few minutes, then open **F** and evacuate the system to below 0.1 Torr, if possible. This procedure allows any air which has liquefied to boil off, and also deuterates the IR cell.

Now close **F**, open **C**, and partially lower the liquid N_2 Dewar, allowing the upper half of the trap to warm up. Allow the pressure to rise slowly, using the height of the Dewar around the trap to control the rate. When the pressure reaches 50 Torr, close

stopcocks **D** and **D'**, then close stopcock **C**, and immediately raise the Dewar around the cold finger. Open stopcock **F**, and pump out the remaining C_2D_2 in the system. The IR cell may now be removed and the spectra recorded. Leave the Dewar around the cold finger in case another sample of C_2D_2 is needed.

When all spectra have been run, remove the cell, cold finger and cold trap; the IR cell must be placed in the desiccator with its rubber spectra caps. The cold finger condenser and cold trap must be left in the hood to warm up **WITH THE STOPCOCK REMOVED**.

Although variations on the above procedure are possible**, it is extremely important that no closed vessel containing solidified acetylene be allowed to warm up beyond the boiling point of the gas**. This includes the pump trap, which will contain some liquefied air as well. Any such rise in pressure above 760 Torr will cause glassware to burst and/or stopcocks to fly out of their bores.

D. Synthesis of C_2HD

Samples of C_2HD may be prepared by following the C_2D_2 directions with two modifications. Approximately two scoops of alumina from the wide end of a mid-sized spatula should be mixed with the CaC_2. The alumina promotes the production of C_2HD over C_2H_2 and C_2D_2. Instead of injecting 4 mLof D_2O, 4 mL of a 50/50 mixture of D_2O and H_2O should be used. The spectrum should be recorded with 250 torr of C_2HD.

TABLE 1 - EXPERIMENTAL SUMMARY

Compound	Source	High Resolution Pressure (Torr)	Expanded Region[*]
C_2H_2	tank	~75	1420-1220 cm^{-1}
C_2D_2	synthesis with 100% D_2O	~75	1100-1000 cm^{-1}
C_2HD	synthesis with 50/50 D_2O/H_2O	~250	1260-1140 cm^{-1}

[*] All major peaks must be "blown up" on the computer screen to determine the frequency of the Q branch, (hence the vibrational mode) accurately, but these do NOT have to be printed out.

III. Theory

The challenge of the analysis for this lab is to relate the absorption spectrum of acetylene to its structure. This section is intended to be a guide from first principles to your IR spectrum of acetylene. Virtually all of the theory that you need to understand in order to analyze your spectrum is presented in this section; however, basic concepts such as the harmonic oscillator and rigid rotor models are paraphrased, and rigorous derivations and many theoretical details are omitted. Spectroscopy is a vast field, and the theory in this section only provides a glimpse at molecular spectroscopy. You are encouraged to consult the references listed at the end of the manual for a deeper understanding of the material.

A.   The Born-Oppenheimer Approximation

The Born-Oppenheimer approximation is the paradigm through which we understand the spectra and dynamics of molecules. Thus, an understanding of the Born-Oppenheimer approximation is crucial to your understanding of this lab and will be discussed fully below. First we will discuss the approximation qualitatively and then provide a more rigorous, mathematical discussion.

We start with the full Hamiltonian $\mathcal{H}$ for all the nuclei and electrons, whose coordinates are represented by R and r respectively.

$$H(r,R) = -\sum_A \left(\frac{h^2}{2m_A}\right)\nabla_A^2 - \sum_i \left(\frac{h^2}{2m_e}\right)\nabla_i^2 - \sum_{A,i} \left(\frac{q_A e^2}{r_{Ai}}\right) + \sum_{A>B} \left(\frac{q_A q_B e^2}{r_{AB}}\right) + \sum_{i>j} \left(\frac{e^2}{r_{ij}}\right)$$

$$= T_N(R) + T_e(r) + V_{eN}(r,R) + V_{NN}(R) + V_{ee}(r) \tag{1}$$

The Hamiltonian includes the kinetic energy terms for the nuclei and electrons (the first and second terms respectively, in which the sums are taken over the nuclei A and the electrons i) and the potential energy terms describing electron-nuclear attractions, nuclear-nuclear repulsions, and electron-electron repulsions.

The complete Schrödinger equation is

$$\mathcal{H}(r,R)\ \Psi(r,R) = E\ \Psi(r,R) \tag{2}$$

We would like to separate the electronic and nuclear coordinates, i.e. to write $\mathcal{H}(r,R) = \mathcal{H}_N(R) + \mathcal{H}_e(r)$ with separate electronic and nuclear parts. Then we could write the wavefunction as a product of separate electronic and nuclear wavefunctions, $\Psi(r,R) = \psi_N(R)\psi_e(r)$, and separate Schrödinger equations could be written as

$$\mathcal{H}_e(r)\,\psi_e(r) = E_e\,\psi_e(r)$$

$$\mathcal{H}_N(R)\,\psi_N(R) = E_N\,\psi_N(R)$$

with $E_e + E_N = E$. Unfortunately this cannot be done rigorously because the Coulomb attractions that hold the molecule together, described by $V_{eN}(r,R)$, depend on both nuclear and electronic coordinates which determine the distances r_{Ai}.

However, we can treat the situation approximately by recognizing that the nuclear masses m_A greatly exceed the electron mass m_e, i.e. $m_A/m_e > 1000$. This mass difference allows the electrons to move much faster than the nuclei. We can imagine that the electron distribution (the electron "cloud") always adjusts itself instantaneously to the current nuclear geometry. This is actually the basis for any kind of molecular "potential energy curve" that you have ever seen! Such a curve, as illustrated below, is a plot of electronic potential energy versus nuclear position. The x-axis could be, for example, interatomic distance for a diatomic molecule, or more generally it could represent motion of atoms along any molecular vibrational coordinate (C–O stretch, various bending modes, etc; note that the actual form of the curve will depend on exactly which vibrational motion is examined). The curve assumes that for any particular value of R there is a single value of potential energy. This means that only the instantaneous positions of the nuclei (the instantaneous value of R) matter; it doesn't matter where the nuclei were immediately before reaching those positions. For example, in a diatomic molecule which is vibrating it doesn't matter if the interatomic distance reaches some value while the molecule is stretching or compressing. What if the electrons really couldn't move much faster than the nuclei? Then the electron distribution would be continuously lagging behind and trying to "catch up" with the positions of the nuclei. In that case the electron distribution (and so the electronic energy) at a given value of R would depend on whether that value was reached during stretching or compression. Starting with introductory chemistry (5.11 level), you have seen lots of potential energy curves describing bonding and antibonding orbitals. It was never stated explicitly, but those curves only have meaning in the context of the Born-Oppenheimer approximation which lets you assign a single electronic energy to each nuclear configuration!

Let's take a closer look at how a potential energy curve is calculated. The strategy is to fix R, and then to calculate the electronic energy at that configuration. This calculation involves no approximation; whether or not it is physically realistic, we certainly can do a quantum-mechanical calculation of electronic energy for a bunch of fixed nuclei and moving electrons. The result will be some energy $E_e(R)$ and some eigenfunction $\Psi_e(r;R)$ (the semicolon indicates a parametric dependence on R for the wavefunction). (Note that there will actually be a whole set of eigenfunctions and eigenvalues, but we're only concerned with the lowest-energy one, i.e., the electronic ground state.) To continue with this strategy, the electronic energy is calculated at a bunch of fixed values of R, and the results are plotted to form a molecular "potential energy curve" like the one shown above. This curve, whose values were all calculated with fixed values of R, is then used as a function of the *variable* R to solve for the behavior of the (moving) nuclei. This is where the approximation comes in, since we have no guarantee *a priori* that the electronic energies we calculated at fixed R are accurate for the molecule when R is varying rapidly.

POTENTIAL ENERGY

VIBRATIONAL COORDINATE R
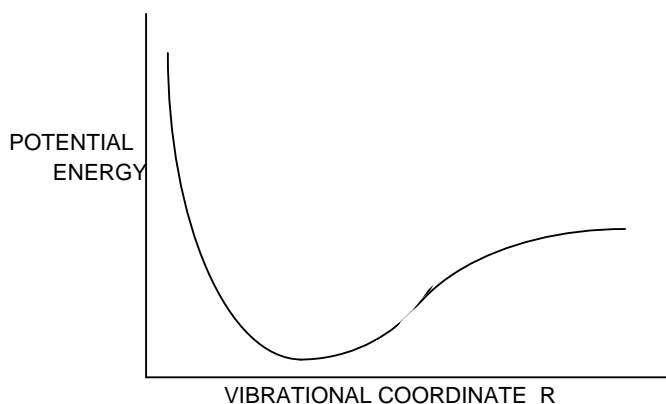
This approximation can be written mathematically as

$$\mathcal{H}(r,R) \approx T_N(R) + H_e(r;R)$$
$$\psi(r,R) \approx \psi_N(R)\psi_e(r;R)$$

and these expressions can be inserted into the Schrödinger equation, which becomes

$$[T_N(R) + \mathcal{H}_e(r;R)]\, \psi_N(R)\psi_e(r;R) = E\, \psi_N(R)\psi_e(r;R)$$

Let's examine each of the two terms of the left hand side. The second term is

$$\mathcal{H}_e(r;R)\, \psi_N(R)\psi_e(r;R) = \psi_N(R)\, \mathcal{H}_e(r;R)\, \psi_e(r;R) = \psi_N(R)\, E_e(R)\, \psi_e(r;R)$$

No approximation has been made here. $\mathcal{H}_e(r;R)$ has fixed R and therefore doesn't operate on $\psi_N(R)$. The operation of $\mathcal{H}_e(r;R)$, the electronic Hamiltonian for fixed R, on $\psi_e(r;R)$, the electronic wavefunction for the same fixed R, yields the electronic energy $E_e(R)$ for that value of R. The first term on the left-hand side above is

$$T_N(R)\ \psi_N(R)\psi_e(r;R) \approx \psi_e(r;R)\ T_N(R)\ \psi_N(R)$$

This is the central approximation. It is based on the idea that operation of $T_N(R)$, which contains the nuclear mass terms $1/m_A$, on $\psi_e(r;R)$ yields a result that must be very small compared to the operation of $\mathcal{H}_e(r;R)$, which includes $T_e(r)$, on the same wavefunction since $T_e(r)$ contains the electronic mass term $1/m_e$. Since the nuclear mass exceeds the electron mass by about 1000 even for a proton, we neglect the operation of $T_N(R)$ on $\psi_e(r;R)$. This is the mathematical embodiment of the more qualitative discussion above. The Schrödinger equation becomes

$$\psi_e(r;R)\ T_N(R)\ \psi_N(R) + \psi_N(R)\ E_e(R)\ \psi_e(r;R) = E\ \psi_N(R)\psi_e(r;R)$$

There are no operators acting on $\psi_e(r;R)$, which can be cancelled from each term to yield

$$[T_N(R) + E_e(R)]\ \psi_N(R) \equiv [T_N(R) + U(R)]\ \psi_N(R) \equiv \mathcal{H}_N(R)\ \psi_N(R) = E\ \psi_N(R)$$

where we have just re-labeled the electronic energies as U(R) to emphasize the fact that these are the potential energies which control the motions of the nuclei. The nuclear kinetic and potential energy terms together give us the nuclear Hamiltonian $\mathcal{H}_N(R)$. That's it! We now have an equation in only nuclear coordinates whose solutions give us the nuclear wavefunctions and the total molecular energies.

B.   The Nuclear Wavefunction for Polyatomic Molecules

The nuclear Schrödinger equation describes the nuclear energy due to molecular vibration, rotation, and translation. However, as derived above, the nuclear wavefunction is a function of 3N Cartesian coordinates, three for each nucleus. Although all of the motions of the molecule could be described in terms of these 3N coordinates, these coordinates do not present an intuitive means of thinking about the dynamics and energetics of the molecule. The standard technique for giving intuitive meaning to the nuclear Schrödinger equation is to transform the 3N Cartesian coordinates on each atom into 3N coordinates that describe the translation, rotation, and vibration of the molecule.

The molecule as a whole possesses 3 translational degrees of freedom in (xyz)-space. In addition, for nonlinear molecules, 3 mutually perpendicular axes are needed to describe the rotations of the molecule. The remaining 3N - 6 degrees of freedom appear as vibrations of the molecule. (Linear molecules possess only two degrees of rotational freedom, because they have no moment of inertia with respect to rotation along the molecular axis. Thus, linear molecules are expected to possess 3N-5 vibrational degrees of freedom.) The net result of this coordinate transformation is that the nuclear wavefunction can be written as a product of separate translational, rotational, and vibrational wavefunctions, and the energy can be written as a sum of translational, rotational, and vibrational energies.
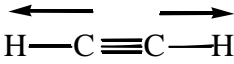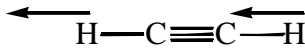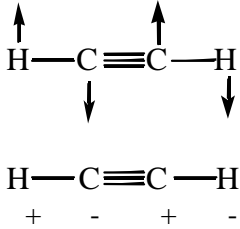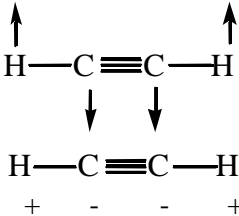
Note that this separation of the nuclear wavefunction into translational, rotational, and vibrational parts does involve approximations. Rotational and vibrational motion are coupled because vibrations change the moment of inertia of the molecule and hence affect the rotations. However, the approximation is generally a good one when the amplitude of the vibrational motion is small, i.e., low vibrational energy states, and correction factors can be added using perturbation theory to correct for the vibration-rotation coupling (more below on this topic).

C.   The Vibrational Wavefunction

The 3N-6 (or 3N-5) vibrational coordinates arising out of the separation of the nuclear wavefunction discussed are known as normal modes of vibration. A normal vibrational mode has the special property that all of the atoms oscillate in phase and with the same frequency. Normal modes are chosen to be orthogonal, and thus all vibrational motions can be described as superpositions of normal vibrational modes. The process of determining what the normal modes of a particular molecule look like is called a normal mode analysis (see references 4, 7, 9 and 10).

The normal modes of acetylene are shown in Table 2:

Table 2. Fundamental vibrational modes of acetylene (see Steinfeld, p. 245-248)

Mode	Description	Symmetry	Normal Mode
ν_1	Symmetric C-H stretch	Σ_g^+	$\longleftarrow$ H—C≡C—H $\longrightarrow$
ν_2	Symmetric CC stretch	Σ_g^+	H—C≡C—H
ν_3	Asymmetric C-H stretch	Σ_u^+	H—C≡C—H
ν_4	Symmetric bend	Π_g	H—C≡C—H H—C≡C—H + - + -
ν_5	Asymmetric bend	Π_u	H—C≡C—H H—C≡C—H + - - +

The symmetry designations will be discussed later in the section on Group Theory. Note that the bending vibrations are doubly degenerate; the displacements must be along either of two directions which are perpendicular to each other and to the linear axis.

The normal modes of C_2D_2 are virtually identical to those of acetylene. (Why? In what way do they differ?) The normal modes of C_2HD are fundamentally different (see Table 3).

Table 3. Fundamental vibrational modes of C_2HD (see ref. 4, p. 292)

Mode	Description	Symmetry	Normal Mode
ν_1	C-H stretch	Σ^+	H—C≡C—D
ν_2	CC stretch	Σ^+	H—C≡C—D
ν_3	C-D stretch	Σ^+	H—C≡C—D
ν_4	Symmetric bend	Π	H—C≡C—D H—C≡C—D + - + -
ν_5	Asymmetric bend	Π	H—C≡C—D H—C≡C—D + - - +

Note that the normal modes drawn in this diagram and the one for acetylene are approximate. Normal modes of vibration involve all of the atoms in the molecule; however, some of the atoms vibrate with larger amplitudes than other, and we are frequently able to describe the normal mode motions approximately as "C-H stretches" etc. The arrows in the diagrams above refer to the most significant motions in the molecule.

The solution of each of the 3N-6 (or 3N-5) normal vibrational wavefunctions depends on the exact nature of the potential energy U(Q) along the normal mode coordinate Q. In theory, the potential U(Q) could be calculated by solving the electronic energy problem (as discussed in the Born-Oppenheimer section above). However, in practice this calculation is usually extremely difficult. A more generally useful technique is to describe vibrational motion of small amplitude about the equilibrium geometry, where the potential can be approximated by a quadratic expression of the form

$$U(Q) = \frac{1}{2}kQ^2 \tag{3}$$

where Q is the displacement from the equilibrium position of the vibration and k is a constant. This form of the potential leads directly to harmonic oscillator wavefunctions and energies, which take the form

$$E(v) = \left(v + \frac{1}{2}\right)h\nu \tag{4}$$

where v is the vibrational quantum number, h is Planck's constant, and ν is the frequency constant for the oscillator, which is related to the masses and force constants (more on this in the Analysis section). Under the harmonic oscillator approximation, the total vibrational energy of the molecule, G_v, consists of a sum of the energies of each vibrational mode, i.e.,

$$G_v = \sum_{i=1}^{3N-6(or5)} \left(v_i + \frac{1}{2}\right)h\nu_i \tag{5a}$$

More generally, anharmonicities of the potential wells cause a small amount of coupling between the vibrational modes, and the vibrational energy is more accurately modelled by

$$G_v = \sum_{i=1}^{3N-6(or5)} \left(v_i + \frac{1}{2}\right)h\nu_i + \sum_{i>j}x_{ij}\left(v_i + \frac{1}{2}\right)\left(v_j + \frac{1}{2}\right) \tag{5b}$$

where the constants x_{ij} are anharmonic coupling constants. These anharmonic constants are generally quite small compared to the harmonic oscillator energy ($h\nu$), but the importance of the anharmonicity increases at higher vibrational levels because the anharmonic term depends on two vibrational quantum numbers. (Classically, when vibrational motion along one mode reaches large amplitudes, coupling to other modes

may become important and some motion along other modes may take place.) In your experiment you will be concerned with low vibrational levels of acetylene, and anharmonic coupling effects should be minor.

D.   Infrared Absorption and Vibrational Excitation

Classically, molecules absorb infrared light because the oscillating electric field of the light drives polar vibrational modes. Power from the oscillating electric field is absorbed by the vibrations most efficiently when the light frequency matches the resonant vibrational frequency. Thus the absorption spectrum has peaks which match the molecular vibrational frequencies.

Quantum mechanically, light absorption leads to transitions between different vibrational energy levels. However, not all transitions between vibrational levels are "allowed", i.e., can be induced by light absorption. Selection rules, which dictate those transitions that are actually observed, are derived using time-dependent quantum mechanics, which is well-discussed in most standard textbooks. The selection rules for the harmonic oscillator are well known

$$\Delta v = \pm 1$$

However, anharmonicity in the potential well allows other transitions to occur. Transitions from the ground state to the first excited state of a normal mode lead to "fundamental" bands in a spectrum. Transitions from a ground state to the second excited state (or higher) lead to "overtone" bands. In polyatomic molecules, one photon may also excite more than one vibrational mode simultaneously. Bands arising from these transitions are called "combination" bands. Finally, oftentimes not all molecules at room temperature are in the ground vibrational state, and vibrational bands called "hot bands" may arise from a transition from one excited vibrational state to another. How should the intensity of a hot band change with temperature?

Another set of selection rules for vibrational transitions is based essentially on the symmetry of the molecule. The best-known selection rule of this sort, understandable in terms of the classical description given above, states that for a fundamental vibrational transition to be allowed, the vibrational mode excited must induce a change in the dipole moment of the molecule. You should be able to predict which fundamentals of acetylene are allowed by inspecting the table of normal modes of acetylene. However, this qualitative technique is not applicable to determining whether overtone, combination, and

difference bands are allowed. The most powerful means of determining whether any vibrational transition is IR allowed is to use group theory, which is the mathematics of symmetry. The application of group theory to this lab is discussed in an Appendix to this Experiment.

E.   The Rotational Wavefunction

Rotation of a linear molecule can be described to a good approximation by the rigid rotor model, the energy levels of which are given by starting with the classical expression,

$$E = |\mathbf{M}|^2/2I \tag{6}$$

where $\mathbf{M}$ is angular momentum (a vector quantity) and I is the moment of inertia, and using the angular momentum quantization rule (one of the fundamental results of quantum mechanics)

$$|\mathbf{M}| = h[J(J + 1)]^{1/2} \tag{7}$$

where J is the rotational quantum number. The result is

$$E(J) = hcB_eJ(J + 1) \tag{8}$$

where B_e is the rotational constant (in wave numbers, or cm^{-1}) and c is the speed of light. The rotational constant B_e depends in turn upon the moment of inertia, I_e, of the molecule at its equilibrium geometry:

$$B_e = \frac{h}{8\pi^2 cI_e} \tag{9}$$

The equilibrium moment of inertia is defined by

$$I_e = \sum_{i=1}^{N} m_i r_i^2 \tag{10}$$

where r_i refers to the distance between a given nucleus and the center of mass, and i is an index over the atoms of the molecule. Note that the formulas for rotational energy given above apply only to linear molecules. The models describing rigid rotation of nonlinear

molecules are more complex because nonlinear molecules rotate about three axes, whereas linear molecules carry rotational energy only about two axes, both of which are perpendicular to the molecular axis.

Just as the harmonic oscillator model does not provide a completely accurate description of the vibrations of polyatomic molecules, the rigid rotor is only an approximation of the rotational behavior of linear molecules. No molecule is completely rigid, and correction factors describing deviations from rigid rotor behavior can be introduced using perturbation theory. The two most important correction terms are the vibration-rotation coupling and centrifugal distortion.

Vibration-rotation interaction accounts for the fact that molecular vibrations may change the average moment of inertia of a molecule. (Which of the normal modes of acetylene would you expect to generate the largest vibration-rotation interaction terms? What relation would you expect anharmonicities of the potential surface to have with vibration-rotation interactions?). The vibration-rotation interaction is typically treated as a correction to the equilibrium rotational constant B_e:

$$B_v = B_e - \alpha_e \left(v + \tfrac{1}{2} \right) \tag{11}$$

where α_e is the vibration-rotation coupling constant, which is positive for most molecules. (Why?) Note that the constant B_e refers to the rotational constant of the molecule with all of the atoms at their equilibrium positions, whereas B_v is a mean rotational constant for a vibrating molecule. Using this notation, the rotational energy of the molecule is $hcB_vJ(J+1)$. Equation 11 is written for a diatomic (with one vibrational degree of freedom), but more generally one needs to sum vibrational-rotational couplings with each vibrational mode (see eq. 20).

Centrifugal distortion accounts for the change in the moment of inertia due to the rotations of the molecule. In other words, as a molecule rotates faster, the internuclear distance increases, so the moment of inertia increases and the effective rotational constant decreases. The centrifugal distortion is modeled by a correction term $-D_e[J(J + 1)]^2$ to the rotational energy, and can be conceptualized as another correction to the equilibrium rotational constant B_e of the magnitude $-D_e[J(J + 1)]$. Thus the rotational energy levels to this degree of approximation can be expressed by the equation

$$\frac{E(J)}{hc} = B_e J(J + 1) - \alpha_e J(J + 1)\left(v + \tfrac{1}{2} \right) - D_e \left[J(J + 1) \right]^2 \tag{12}$$

where both sides of the equation have units of wavenumbers.

The selection rules for the rigid rotor are given by

$$\Delta J = \pm 1$$

The rigorous justification for this rule, as for all selection rules, arises from time-dependent quantum mechanics. However, this rule can be understood qualitatively by considering conservation of angular momentum during the absorption of a photon. A photon carries one quantum of angular momentum. Thus, when a molecule absorbs a photon, its angular momentum must change by one quantum. One way for this to occur is for the molecule to gain or lose one quantum of rotational angular momentum.

F.   Vibrational Angular Momentum

Linear molecules like acetylene may change their angular momentum by another mechanism involving degenerate vibrational bending modes. A rigorous understanding of this vibrational angular momentum comes from solving the two-dimensional harmonic oscillator problem, which is discussed in several of the references (see Bernath, for example). However, vibrational angular momentum can be understood qualitatively in following manner: Imagine the bending vibrations of the H atom on acetylene. If the molecule is aligned along the z-axis, then the two degenerate vibrations correspond to the H atoms bending in the same direction along either the x-axis or the y-axis. You may recall from quantum mechanics that any linear superposition of two degenerate eigenfunctions is also an eigenfunction of the Hamiltonian. One simple case of superposition occurs when both degenerate vibrations act in phase; that is, the H atoms leave the z-axis along the x-axis and the y-axis at the same time. In this case the net motion is just a bending vibration at 45° between the two axes, and another similar linear superposition could be constructed for motion at –45°. These two modes are really the same as those we considered originally, but the coordinate axes have been rotated by 45°.

However, the vibrations along the x- and y-axes can also be out of phase. For example, imagine that the bending motion along the y-axis does not begin until the motion along the x-axis has reached its maximum, i.e., one-half the vibrational period after motion the motion along the x-axis began. In this case the two modes are 90° out of phase rather than in phase as we considered before, and each H atom appears to "sweep

out a cone" about the molecular axis, and thus contains angular momentum[1]. The presence of this vibrational angular momentum alters the selection rules for a molecule because during the absorption of a photon the molecule may change its vibrational angular momentum instead of its rotational angular momentum. The vibrational angular momentum is often designated by a quantum number l. A more precise statement of the selection rules for this case is that ΔJ may equal zero if $\Delta l = \pm 1$. Thus, in the vibrational IR spectrum there are some transitions in which the rotational angular momentum J changes by ± 1 quantum and some in which the vibrational angular momentum l changes by ± 1 quantum.

G.   Vibrational-Rotational Transitions

Purely rotational transitions can be induced using light in the microwave region of the electromagnetic spectrum. However, the rotational levels of a molecule can also be studied by vibrational (infrared) spectroscopy, because, as we have just seen, a vibrational transition in a molecule must be accompanied by a change of J of ± 1, except in the case of linear molecules, for which ΔJ may sometimes be 0. Remember that at room temperature, the molecule can initially be in many different rotational energy levels, and so many different rotational transitions can accompany a given vibrational transition. The diagram on the next page shows a few rotational transitions that can accompany a vibrational transition from v" to v'. Note that $\Delta J = 0$ transitions are not depicted here (you can draw them in). Note also that final rotational and vibrational states are conventionally designated by a 'single prime', whereas initial states are designated by a "double prime".

To understand the spectra you will be taking, it is helpful to predict what the energies of the various transition should be. Consider first the simplest model, in which the energy of the molecule is given by the harmonic oscillator and rigid rotor approximations with no correction terms:

$$E(v, J) = \left(v + \tfrac{1}{2}\right)h\nu + hcB_e J(J + 1) \tag{13}$$

You should work out for yourself that the energy of a $\Delta J = +1$ transition is given by

---

[1] Note that vibrational angular momentum can be understood through analogy with circularly polarized light. Special linear combinations of two orthogonal linear polarizations of light result in right- or left-circularly polarized light. Conversely, linearly polarized light can be considered a superposition of right- and left-handed circularly polarized light.
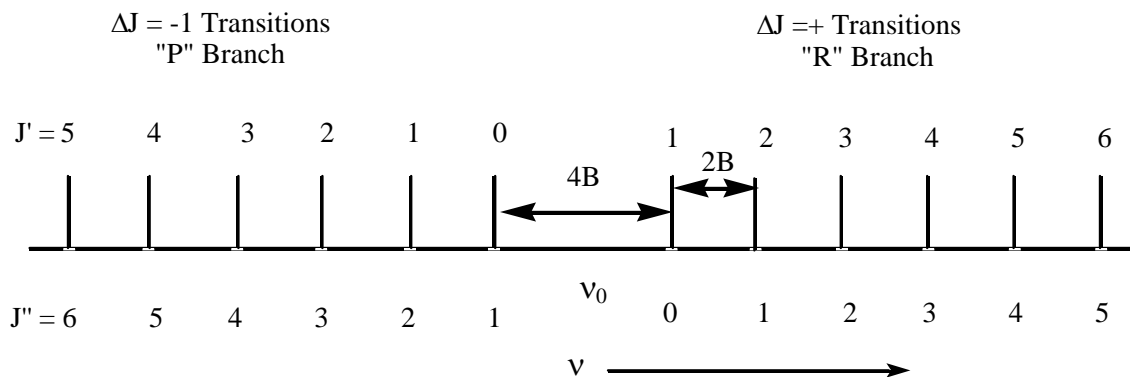
$$\Delta E = h\nu + 2hcB_e(J'' + 1) \tag{14a}$$

whereas the energy of a $\Delta J = -1$ transition is

$$\Delta E = h\nu - 2hcB_eJ'' \tag{14b}$$

The energy of a $\Delta J = 0$ transition, if it is allowed, is just the vibrational energy $h\nu$. Incorporating correction terms in the energy expression such as vibration-rotation coupling adds a level of complexity to this treatment that will be addressed in the Analysis section.
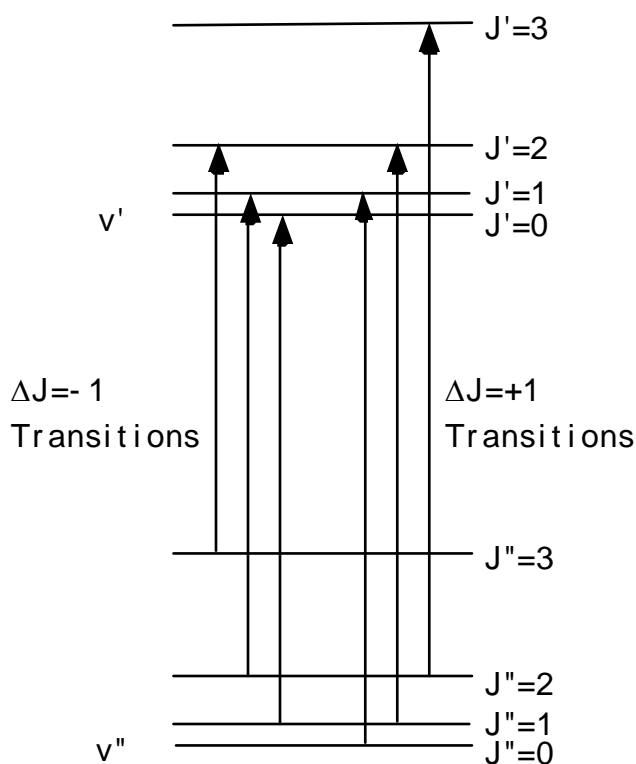
Each allowed transition results in an absorption line in the IR spectrum. The $\Delta J = -1$ and $\Delta J = +1$ transitions are referred to as P- and R-branch lines respectively. The energy difference between any two adjacent lines in the P and R branches is given by $2B_e$ (in wavenumbers). Thus, the spectrum has the following structure:

ΔJ = -1 Transitions
"P" Branch

ΔJ =+ Transitions
"R" Branch

J' = 5   4   3   2   1   0   1   2   3   4   5   6

4B   2B

ν_0

J" = 6   5   4   3   2   1   0   1   2   3   4   5

ν ⟶

The vibrational energy can be determined immediately as the midpoint of the first two transitions in the P and R branches. The rotational constant can be determined simply from the spacing between the adjacent lines in either branch. If a "Q" branch (corresponding to ΔJ = 0) were present, an absorption line would appear midway between the first P and R branch lines.

H.   Intensities of Absorption Lines

Important information can be gained from the relative intensities of the transitions. The intensity of an absorption line is proportional to 1) the number of molecules in the particular initial state and 2) the transition moment (i.e. the "strength") of the particular transition. The transition moment can be thought of as a probability that a molecule interacting with light of the appropriate frequency will actually absorb a photon and undergo a transition. The transition moment times the number of molecules in the initial state (times the intensity of light) is effectively a rate of conversion of initial state molecules to final state molecules. In case you're interested, the transition moment is calculated by an integral of the form $\langle m|\mu|n \rangle$ where μ is the transition dipole operator and m and n are the initial and final wavefunctions respectively.

The transition moment is typically difficult to calculate and it is often assumed that the transition moments for the rotational transitions in one vibrational band are all equal. This is usually a reasonably good assumption, and it will be utilized for the remainder of this section. However, in the Analysis section, expressions are provided for the rotational dependence of the transition moments of acetylene.

The number of molecules N_i in any given initial energy level i for a system at equilibrium is easily calculated from the Boltzmann equation,

$$N_i \propto g_i \left[\exp\left(-\frac{E_i}{kT} \right) \right] \tag{15}$$

where g_i is the degeneracy of the level, E_i is the energy referenced to some ground state, k is Boltzmann's constant, and T is the temperature. Neglecting degeneracy, higher energy levels have smaller populations than lower energy ones. If E_i is large compared to kT, then very few molecules exist in level i at equilibrium. This is the case for most vibrationally excited states of molecules. Thus, most molecules are in the vibrational ground state at room temperature.

On the other hand, for most molecules the energies separating rotational states is small compared with kT at ambient temperatures, and many rotationally excited states are populated at room temperature. Recall that for angular momentum states J, the degeneracy is

$$g_J = 2J + 1.$$

(Does this remind you of the degeneracies of the s, p, d and higher orbitals which correspond to electronic orbital angular momentum $l = 0$, 1, 2, etc.?) Thus the population of each rotational state in the rigid rotor approximation is

$$N_J \propto (2J+1)\exp\left(-\frac{hcBJ(J+1)}{kT} \right) \tag{16}$$

Because we are assuming that the transition moments are identical, the intensity profile of a vibrational band should look like the following:
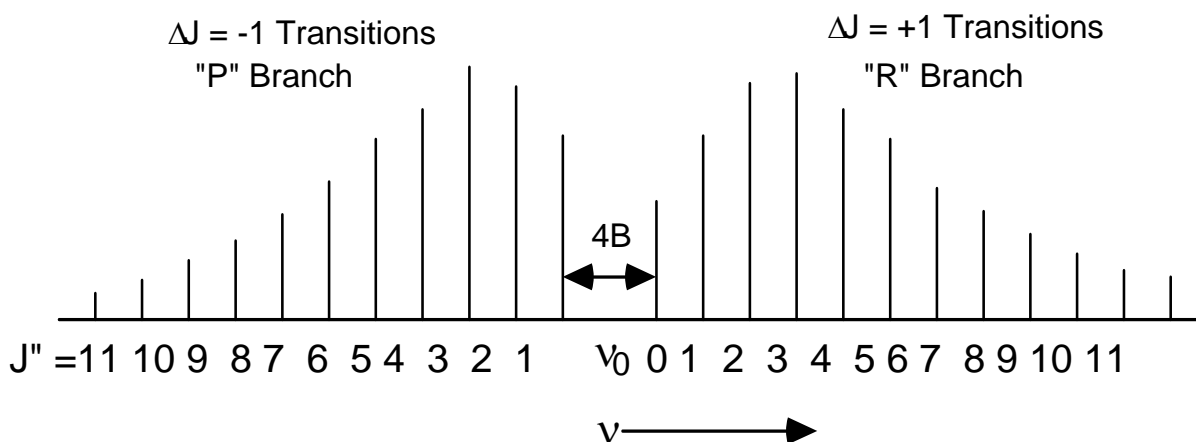
The intensity profile is the product of a linearly increasing function and an exponentially decreasing function. At large J the exponential decrease takes over, but at small J the

linear increase is important, and the maximum intensity line occurs at moderate J values. If the sample temperature were higher, would the maximum intensity move to higher or lower J?

I.   Nuclear Spin Statistics

In reality, the diagram and description above are accurate for C_2HD, but not for C_2H_2 or C_2D_2. The origin of the deviations of C_2H_2 or C_2D_2 from the above description is an extra source of degeneracy that arises from the nuclear wavefunction and must be included in the Boltzmann equation. Nuclear spin statistics are discussed in references (7, pp. 16-18) and (8, pp. 117-120).

Nuclear spin statistics are closely related to the Pauli principle. The Pauli principle as applied to polyatomic molecules states that the total wavefunction of any molecule must be either symmetric or antisymmetric with respect to exchange of any indistinguishable nuclei. Specifically, if the indistinguishable particles are *fermions* (e.g. any spin-1/2 particle like ^1H), then the wavefunction must be antisymmetric so that performing the symmetry operation reverses the sign of the wavefunction. If the particles which are interchanged are *bosons* (e.g. any spin-1 particle like ^2D), then the wavefunction must be symmetric so that performing the interchange leaves the sign of the wavefunction unchanged. Note that only the sign of the wavefunction can change when indistinguishable nuclei are interchanged. If any other changes to the wavefunction occurred, then the molecular structure (which depends on $|\psi|^2$) would change and the interchange would not yield an indistinguishable structure. In acetylene,the two hydrogens are fermions (spin one-half), and thus the overall wavefunction must be anti-symmetric with respect to exchange of the two hydrogens. [It turns out that we don't have to worry about the two carbons because they have zero spin.]

To understand how symmetry affects the wavefunctions of molecules, it is helpful to consider the total wavefunction as a product of electronic, vibrational, rotational, and nuclear spin parts which to a good degree of approximation are separable, i.e.,

$$\Psi_{TOT} = \psi_{elec}\psi_{vib}\psi_{rot}\psi_{ns}$$

where ns refers to the nuclear spin wavefunction. The Pauli principle states that the *total* wavefunction must be either symmetric or antisymmetric upon exchange of identical nuclei, but it does not specify how each part of the wavefunction must transform upon this exchange. As you will see below, for any molecule with two or more identical nuclei

with nonzero spin, there are always more than one possible nuclear spin wavefunction for the molecule. Some fraction of these nuclear spin wavefunctions will be symmetric upon interchange of the identical nuclei, while the rest will be antisymmetric. Since the overall wavefunction must remain either symmetric or antisymmetric, this implies that only the symmetric or the antisymmetric nuclear spin wavefunctions will be allowed by the Pauli principle, depending on what the symmetry of the rest of the wavefunction is. The analysis of the symmetry of the electronic, vibrational, and rotational parts of the wavefunctions is a somewhat subtle topic and will not be presented in full (the most lucid treatment is probably McQuarrie, *Statistical Thermodynamics*). The basic outcome of this analysis is that vibrational wavefunctions are symmetric with respect to exchange of nuclei, as are the ground electronic states of most molecules (including acetylene). The rotational wavefunctions alternate between symmetric and antisymmetric, and for acetylene, ψ_{rot} is even for even values of J and odd for odd values of J. Thus, acetylene molecules with even values of J must have antisymmetric nuclear spin functions, and vice versa, in order to satisfy the Pauli principle.

The nuclear spin wavefunction is best understood by example. Hydrogen nuclei have spin quantum number I=1/2. Unlike the rotational or electron orbital angular momentum quantum numbers, the spin quantum number of the proton is an intrinsic feature that never changes. The spin angular momentum vector **I** is given, just like the rotational angular momentum vector, by $|\mathbf{M}| = h[I(I + 1)]^{1/2}$, and the degeneracy is given, as usual, by $g_I = 2I+1$. For the hydrogen nuclei the degeneracy is therefore $g_I = 2$. The two degenerate spin levels are denoted by the spin sublevel quantum number $m_I = \pm 1/2$, whose value refers to the fact that when a magnetic field is applied (along what is denoted as the z-axis) the spin angular momentum vector becomes oriented such that the z-component of angular momentum is $M_z = hm_I$ with either possible value of m_I. The two orientations of the spin are normally referred to as spin up and spin down.

In order to satisfy the Pauli principle, the nuclear wavefunctions for the molecule as a whole must take the following symmetrized forms:

$$\uparrow(1)\uparrow(2)$$
$$\downarrow(1)\downarrow(2)$$
$$\frac{1}{\sqrt{2}}[\uparrow(1)\downarrow(2) + \downarrow(1)\uparrow(2)]$$
$$\frac{1}{\sqrt{2}}[\uparrow(1)\downarrow(2) - \downarrow(1)\uparrow(2)]$$

where 1 and 2 refer to the two hydrogens and the arrows represent spin up or down. [A wavefunction such as ↑(1)↓(2) cannot exist because interchanging the two nuclei results in a wavefunction that is distinguishable from the original and is neither symmetric nor antisymmetric.] The origin of these wavefunctions is entirely analagous to the electron spin wavefunctions for helium. Note that the first three are symmetric with respect to interchange of the nuclei and the last one is antisymmetric. This means that there are three possible spin wavefunctions that can be occupied for each odd value of J, and only one spin wavefunction that can be occupied for each even value of J. The nuclear spin degeneracy for the acetylene molecule is therefore
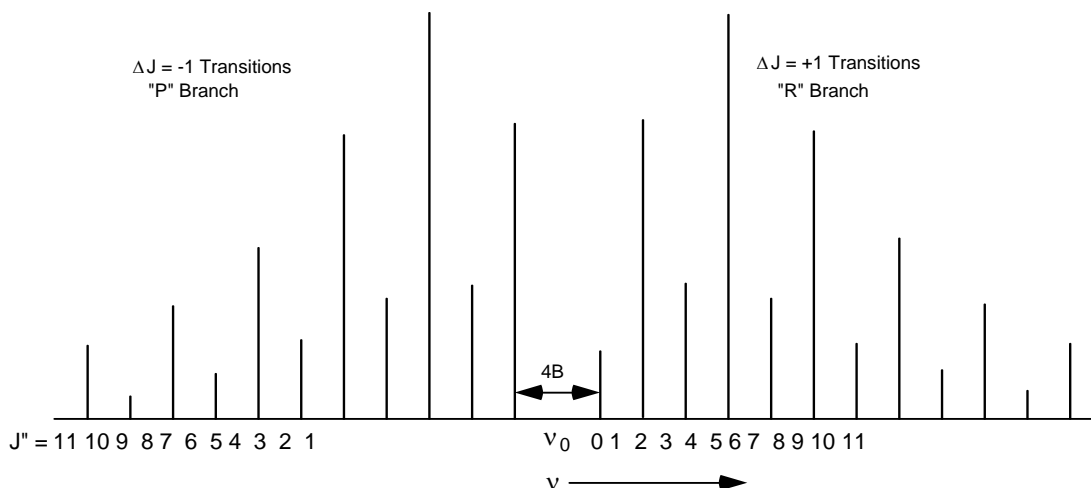
$$g_I = 3 \ (\text{J odd})$$

$$g_I = 1 \ (\text{J even})$$

The Boltzmann distribution including the nuclear spin degeneracy has the form

$$N_J \propto g_I (2J+1) \exp\left(-\frac{hcBJ(J+1)}{kT}\right) \tag{17}$$

What is the consequence in your spectrum? Each transition originating from an odd J value is three times more intense than it would be if J were even! So there is an alternation of intensities, as shown on the following page.

Another way of thinking about the molecular nuclear spin functions written above is in terms of vector addition of the two spin angular momenta. Specifically, constructive vector addition of the two spins gives a total spin angular momentum quantum number $I_{total} = 1$, and destructive vector addition to give a total spin quantum number $I_{total} = 0$. The degeneracy of the molecular nuclear spin angular momentum levels is, as usual, given by $g_I = 2I_{total} + 1$ which means that for $I_{total} = 1$ there are three sublevels with $m_I = \pm 1$ and 0 (in general $m_I = -I, -I+1, ..., I-1, I$) and for $I_{total} = 0$ there is only one state. Note also that the different energies of the spin angular momentum sublevels when a magnetic field is applied provide the basis for NMR, in which transitions between sublevels are measured. [However, for the $(2J + 1)$ sublevels of each J rotational level, there is no simple way to lift the degeneracy by applying an external field.]

From the discussion above, you should be able to deduce the ratio of intensities of alternate peaks in the C_2D_2 spectrum. The important information you need is that the deuterium nucleus has an intrinsic spin quantum number I =1.

ΔJ = -1 Transitions "P" Branch   ΔJ = +1 Transitions "R" Branch

4B

J" = 11 10 9 8 7 6 5 4 3 2 1 ν_0 0 1 2 3 4 5 6 7 8 9 10 11

$\nu \longrightarrow$

IV. Analysis

This section will guide you through a detailed analysis and assignment of your spectra. You should be aware that the analysis for this lab is lengthy and that some of the concepts involved are difficult. It will probably take you several days to complete the analysis. This does not include the amount of time that it may take you to understand the basic concepts presented in the Theory section or the time that it will take you to prepare your report. If you have any deficiencies in your understanding of quantum mechanics, they will handicap your efforts to complete the analysis, so be sure to address them right away. **Above all, do not hesitate to ask for help!**

For the numerical parts of the analysis, it is mandatory to propagate errors through all of your calculations and to compare all results (with errors) to literature values.

A.   Vibrational Analysis

(1) With the help of the density functional theory (DFT) calculations of the vibrational frequencies (See Appendix 2), assign each of the vibrational bands observed in each spectrum to a vibrational transition (an initial and final vibrational state of the molecule). The DFT calculation should allow a fairly straightforward assignment; however you should be able to assign virtually all of the bands yourself. You are expected to provide justification for your assignments beyond agreement with the

calculation. **Be certain to note where you relied on the DFT calculations or literature for assignments.**

Group theory is essential for assigning the spectrum (see the Appendix below). Here are some additional hints to help you with the assignments:

C_2H_2. Recall that only vibrational modes that result in an oscillating dipole moment absorb IR radiation strongly. How many of these modes are there in C_2H_2 and C_2D_2? From the frequencies, intensities, and band shapes you observe, assign the frequencies of these two <u>fundamental</u> vibrations. The prominent band in the 1300 cm^{-1} region (which you will shortly analyze in detail) is, in fact, a combination of the two bending modes $\nu_4(\pi_g)$ and $\nu_5(\pi_u)$. The symmetry of the combination state is the product of the symmetries of the fundamentals; since this includes Σ, the appearance of the band is that of a parallel band, with P and R-branches only. Identify as many other combination bands as you can find; by taking differences between the various bands, see if you can estimate the values of the three infrared-inactive normal modes.

C_2D_2. Be careful! Not all of the bands you observe arise from C_2D_2. In particular, you will probably observe a sharp peak near 680 cm^{-1} that results from an impurity in the C_2D_2 sample. What is the impurity? How can your C_2H_2 spectrum help you to assign your C_2D_2 spectrum? (See the section on Isotopic Substitution below.)

C_2HD. At this pressure, you should be able to see four of the five fundamental vibrations. It may be helpful to use the frequencies of the bands you have determined for C_2H_2 and C_2D_2 as upper and lower limits for the corresponding C_2HD band. You should also label C_2H_2 and C_2D_2 bands which appear in your spectrum.

(**2**) Compile a list of all the fundamental frequencies for each molecule based upon your assignments. Compare these to literature values. What are the sources of error in your values? What anharmonicity constants are you able to obtain from your data?

(**3**) The fundamental frequencies of the isotopomers of acetylene obey some interesting relationships. Recall that the Born-Oppenheimer separation of nuclear and electronic motion allows us to assert that the potential surface, and thus the equilibrium structure, remains unchanged upon isotopic substitution (why?). Isotopic substitution does, however, affect the nuclear wavefunction, and thus the vibrational and rotational constants. Using the harmonic oscillator model, you should be able to show that the vibrational frequencies for isotopically substituted diatomic molecules are related by

$$\left(\frac{v'}{v}\right) = \left(\frac{\mu}{\mu'}\right)^{\frac{1}{2}}$$

where μ is the reduced mass.

The counterpart of this equation for polyatomic molecules is the Teller-Redlich Product Rule. Its derivation is too technical to be developed here [see (4), pp. 231-235, for details]. The results for the infrared-active modes of acetylene include the following:

$$\frac{(v_3)_{C_2D_2}}{(v_3)_{C_2H_2}} = \left[\frac{m_H(m_C + m_D)}{m_D(m_C + m_H)}\right]^{\frac{1}{2}} \tag{18}$$

Test the prediction of Eq. (12) with your observed values of v_3. Also use the formula to calculate the expected position of v_5 for C_2D_2. Another Teller-Redlich relation (ref. 7, p.289) is the following:

$$\frac{(v_1 v_2 v_3)_{C_2HD}}{(v_1 v_2 v_3)_{C_2H_2}} = \left[\frac{m_H(2m_C + m_H + m_D)}{m_D(2m_C + 2m_H)}\right]^{\frac{1}{2}} \tag{19}$$

(4) To what extent can you rationalize the relative intensities of the different vibrational bands? If you increased or decreased the temperature, what effects would you expect on the intensities of the vibrational bands? Pick out one hot band and calculate the change in intensity that you would expect if you increased the temperature by fifty degrees Centigrade.

B.   Rotational Analysis

(1) You first need to assign each of the peaks in the rotationally resolved vibrational bands that you have printed out. Each of the peaks corresponds to the same vibrational transition but to a different rotational transition, so you need to determine the initial and final rotational states for each peak. For C_2H_2 and C_2D_2 the intensity alternations will aid in making the assignments, but depending on the quality of the spectrum there may still be some ambiguity. If this is the case, talk to your TA.

(2) Just by looking at your spectrum you should be able to get an estimate of B, the rotational constant. However, you will notice that the lines are not evenly spaced, as would be the case for a rigid rotor, so we can hope to extract vibration-rotation and centrifugal distortion constants. A very useful and general technique for determining rotational constants is Combination Differences. Notice that you can find pairs of lines (one in the P-branch and one in the R-branch) which share either a common upper state or a common lower state. Consider first all pairs of lines which share a common lower state:
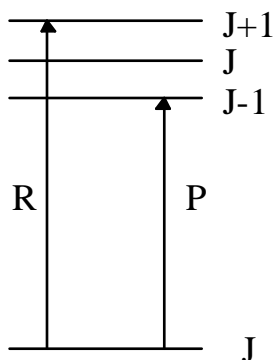
Traditionally, the upper state is denoted by single primes and the lower state by double primes, so the upper and lower state rotational energies are

$$B'J'(J'+1) \text{ and } B''J''(J''+1)$$

respectively. The rotational constants B' and B" for the vibrationally excited and vibrational ground state, respectively, depend on the vibrational state due to vibration-rotation coupling. A good approximation for B' is

$$B' = B_e - \sum_{i=1}^{3N-5} (\alpha_e)_i \left[v_i + \frac{1}{2} \right]$$

(20)

and therefore

$$B'' = B_e - \frac{1}{2} \sum_{i=1}^{3N-5} (\alpha_e)_i$$

(21)

where i is an index over vibrational modes and B_e is the rotational constant of the molecule at equilibrium, which is related to its equilibrium moment of inertia. Note that

each vibrational mode has a different vibration-rotation coupling constant. If we take the difference between the R- and P-branch transitions, which is equivalent to the difference between the two upper state energy levels, we obtain

$$4B'\left(J+\frac{1}{2}\right)$$

where J refers to the common lower rotational state. Thus, by plotting the combination differences vs. J we can obtain the value of the upper state rotational constant. Examine your plot carefully. Does there appear to be any significant curvature in the plot? If so, this is an indication of significant centrifugal distortion. You can obtain this value by nonlinear regression (ask your TA if you don't know how).

Perform a similar analysis to obtain the rotational and centrifugal distortion (if possible) constants for the ground state. Are the rotational constants significantly different for the upper and lower states? Estimate the vibration-rotation constants, if possible.

Make certain to obtain uncertainties for all constants that you calculate. The best way to do this is to use a statistics/graphing package that will calculate the errors for you. You can use the "Excel" package on MIT Server or another mathematical or statistical software package, but make sure you can get the error estimates out of the program, or you can use the analytic expressions in Appendix B of this Manual;

(3) How should the rotational constants of the three molecules be related to each other? Quantitatively compare them.

(4) Compare the intensity profile in your spectra to that predicted by the Boltzmann equation. In order to obtain a better fit, incorporate the fact that the transition probabilities are not equal for all rotational transition in the same vibrational band. Rather, the transition probabilities are proportional to $(J'' + 1)/(2J'' + 1)$ for $\Delta J = +1$ (R-branch) and $J''/(2J'' + 1)$ for $\Delta J = -1$ (P-branch).

Also derive an expression for the peak that you would expect to have maximum intensity in both branches (neglecting intensity alternation). Compare with experiment.

(5) How close is the intensity alternation to that predicted by nuclear spin statistics? Why?

(6) Use your rotational constants to obtain the moments of inertia. Use α_e to calculate B_e. Next use the moments of inertia to solve for the bond lengths. (Why can you assume that all three have the same bond lengths? What does this have to do with the Born-Oppenheimer principle?) One way of doing this, following ref. 7, p. 397, involves defining two distances: $a = \frac{1}{2} r_{CC}$ and $b = \frac{1}{2} r_{CC} + r_{CH}$, as shown in the following figure:
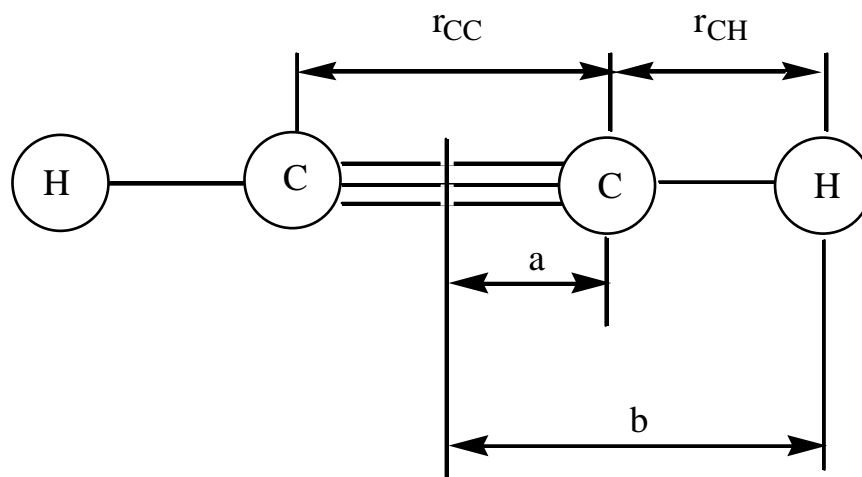
Solve for the moments of inertia of two of the isotopomers in terms of these distances and then solve these equations simultaneously. Report the bond lengths with errors and compare to literature values. Be careful with units; report your values and literature values in the same set of units. Compare the bond lengths to typical values for C-H and C≡C bonds. Would you have been able to calculate the bond lengths if you had only taken the spectrum of one isotopomer?
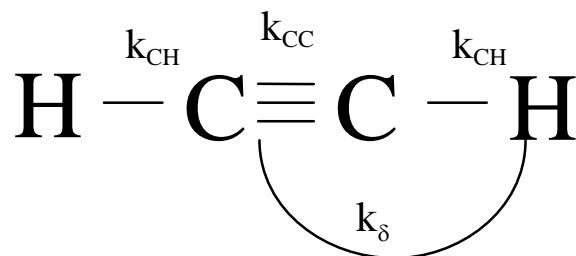
C.   Force Constants

(1) Force constants are one of the best ways to describe the electronic structure of a molecule in an intuitive fashion. We typically think of force constants as a description of the strength of a bond. A somewhat more rigorous understanding of force constants is that they help to describe the potential energy surface of a molecule near its equilibrium geometry. Consider the harmonic oscillator. The force constant associated with the oscillator completely describes the potential energy, which is given by

$$V = \frac{1}{2}kx^2$$

In a real diatomic molecule with anharmonicities, one force constant is insufficient to completely describe the potential, but can be interpreted as the second derivative of the potential around the equilibrium position.

In a polyatomic molecule, to the extent that the normal mode/harmonic oscillator approximation is valid, one could approximate the potential of the molecule with one 'force constant' for each normal mode vibration. However, these 'force constants' would have little intuitive meaning. Instead, the potential is often described in terms of the distances and angles between atoms.

$$H \overset{k_{CH}}{-} C \overset{k_{CC}}{\equiv} C \overset{k_{CH}}{-} H$$
$$k_\delta$$

To a very crude approximation, the potential energy can be described by three force constants, k_{CH}, k_{CC}, and k_δ. If we define deviations from equilibrium bond lengths as x_A and x_B for the two C-H stretches and y for the C≡C stretch, and deviations from the linear bond angles as δ_A and δ_B then the potential energy of the molecule would be modeled as

$$V = \frac{1}{2}\left[k_1 y^2 + k_2\left(x_A^2 + x_B^2\right) + k_\delta\left(\delta_A^2 + \delta_B^2\right) \right]$$

[Like bond lengths, the force constants should be the same for all three isotopomers. Why?] This potential can be made more accurate by including coupling terms, such as

$$k_{\delta'}\delta_A\delta_B$$

These coupling terms are less easy to understand intuitively. The $k_{\delta'}$ force constant, which will be included in the analysis below, can be understood roughly as a coupling between the two bending motions; in contrast to normal vibrational modes, there is no reason to expect the two bending motions to be independent, as reflected by the dependence of the potential on the product of the two coordinates.

Below are presented equations that relate the force constants to the normal mode vibrational frequencies. You have more than enough spectral information to calculate these force constants; they are overdetermined and thus you should be able to check the internal consistency of your results. It will be convenient to define $\lambda_i = 4\pi^2\nu_i^2$ where ν_i is the frequency of the ith vibrational mode. The λ_i can be thought of as normal mode force constants divided by normal mode reduced masses.

The equations for C_2H_2 are

$$\lambda_1 + \lambda_2 = \left(2k_{CC}/m_C\right) + \left(1 + (m_H/m_C)\right) \cdot \left(k_{CH}/m_H\right) \tag{22a}$$

$$\lambda_1 \lambda_2 = 2k_{CC}k_{CH}/m_C m_H \tag{22b}$$

$$\lambda_3 = \left(1 + \frac{m_H}{m_C}\right)\left(\frac{k_{CH}}{m_H}\right) \tag{22c}$$

$$\lambda_4 = \frac{k_\delta - k_{\delta'}}{r_{CC}^2 r_{CH}^2}\left[\frac{r_{CC}^2}{m_H} + \frac{\left(r_{CC} + 2r_{CH}\right)^2}{m_C}\right] \tag{22d}$$

$$\lambda_5 = \left(1 + (m_H/m_C)\right) \cdot \left((k_\delta + k_{\delta'})/m_H r_{CH}^2\right) \tag{22e}$$

Results for C_2D_2 are identical except that m_D replaces m_H. The results for C_2HD would be very different, however, because the normal modes are entirely different.

(2) Noting that two of the normal modes in C_2HD (shown in the theory section) look essentially like simple C-H and C-D stretches, estimate both of these force constants directly from the frequencies of these modes. What approximations must you make in order to perform this calculation? How should the two frequencies be related? Is it possible to perform this sort of calculation for C_2H_2 and C_2D_2?

V. Notebook, Discussion, and Written Report

Record all procedures and observations in your laboratory notebook as they occur in the laboratory. "Incorporate" all spectra and computer printouts into your notebook. Clearly explain who did what in lab. The notebook of each lab partner should have all the data obtained from measurements of the spectra. <u>All calculations are to be done independently</u>. If they get too messy, add summary versions to make your work clear to the TAs. Print out spreadsheets and incorporate them into your notebook. Make sure the formulas used in your spreadsheets are the correct ones. Include all calculations and discussion described above. Be sure that your spectra are clearly labeled and turn them in with the notebook pages. The following table summarizes the required data and analysis for the written report.

	C_2H_2	C_2D_2	C_2HD
<u>Vibrational Analysis</u>			
Density Functional Theory calculations of vibrations	X	X	X
$4000 - 500$ cm^{-1} spectra with fundamental, combination, difference, and overtone bands assigned	X	X	X
Values for each individual mode, $\nu_1 - \nu_5$	X	X	X
Evaluate the vibrational isotope effect		X	
Percent C_2HD in C_2D_2		X	
<u>Rotational Analysis</u>			
Assign rotational transitions to peaks	X	X	(qualitative)
Plot $\Delta\nu(m)$ vs m with linear regression	X	X	
B_e, α_e	X	X	
$C\equiv C$ bond distance		X	
C–H (C–D) bond distance		X	
Evaluate rotational isotope effect		X	
Bar graphs of calculated and experimental intensities	X	X	
<u>Force constants</u>			
k_1, k_2, $k_{\delta\delta'}$	X	X	

In your report, present the quantitative results for the molecular constants enumerated above *with experimental uncertainties derived from your data*. If you need some reminders on how to carry out the error analysis, see Appendix B, "Some Topics in Data Analysis", in this manual. <u>There is **no** need to repeat either the experimental</u>

directions or the theoretical development in this write-up in your report; simply refer to the appropriate part of the write-up as reference. If you vary the experimental procedure, that should be described. Also, refer to the appropriate theoretical expression when it is used; if you have used additional references for the theory (textbooks, etc.), those should also be cited. You should include a concise discussion of the following points:

A.   Vibrational Spectrum

How pure was your C_2D_2? Discuss source of C_2HD contamination.

Discuss the reliability of your assignment of the vibrational bands you have observed in the acetylene molecule. What additional experiments could be done to directly observe non-infrared-active fundamentals in C_2H_2 and C_2D_2?

Discuss your results in terms of quantum vs. classical descriptions of molecular structure and behavior. In what respect(s) does this work show the failure of classical theory? To what extent is classical theory adequate?

B.   Rotational Spectrum

Discuss the accuracy of your results. Estimate the error in your measurements of line positions. Estimate the error in the final derived values of the molecular parameters. Compare these parameters with literature values. Do they agree within the estimated error range? What are the largest sources of error in this experiment?

Compare the value your found for the C≡C triple bond distance with textbook values for the C=C double bond and C–C single bond distances (cite the source you used!). How do you explain these values? Compare the C–H bond distance in acetylene with that in methane or ethane (again, cite the source). What (if anything) does this imply about the electronic structure of acetylene?

VI. References

1. D. P. Shoemaker, *et al*, "Experiments in Physical Chemistry," Sixth Edition, McGraw-Hill (New York) 1989. This is the single most helpful source. **<u>Read it!</u>** On pages 404–416 is "Vibrational-Rotational Spectrum of Acetylene." Other helpful chapters are experiments 35, "Infrared Spectroscopy: Vibrational Spectrum of SO_2," pp. 383–388 and 37, "Rotation-Vibration Spectrum of HCl and DCl," pp. 397–404. Refer to chapter 22, "Vacuum Techniques," pp. 615–643, on the experimental procedure. Chapter 22, "Least-Squares Fitting Procedures," pp. 710–732, should be consulted when you do the analysis.

2. P.F. Bernath, "Spectra of Atoms and Molecules", Oxford University Press (Oxford) 1995. Introduction to spectroscopy at the first-year graduate level.

3. McQuarrie, D. A., "Quantum Chemistry," University Science Books (Mill Valley) 1983. This will not get you all the way through this lab, but it is great place to start. If you were not assigned this book for 5.61, you should probably take a look. It is very well written and has great examples.

4. Herzberg, G., "Molecular Spectra and Molecular Structure. II. Infrared and Raman Spectra," Van Nostrand, 1945. (This will be referred to as HII, for quick reference.) Despite its age, this work is an excellent and readable source for a deeper understanding of the details of this experiment. This is still the bible of IR spectroscopy!

5. Steinfeld, J.I., "Molecules and Radiation: An Introduction to Modern Molecular Spectroscopy," 2nd edition, M.I.T. Press, 1993. An exceptionally well written source for this lab.

6. Herzberg, G., "Molecular Spectra and Molecular Structure. I. Spectra of Diatomic Molecules," Van Nostrand, 1950. Another fine Herzberg work. It covers many of the details you will explore.

7. Levine, I. N., "Molecular Spectroscopy," Wiley-Interscience, 1975. Another solid source.

8. Barrow, G. M., "Introduction to Molecular Spectroscopy," McGraw-Hill (New York) 1962.

9. Wilson, Jr., E. B., J. C. Decius, and P. C. Cross, "Molecular Vibrations," McGraw-Hill (New York) 1955. Graduate level. If all else fails, or if you are digging deep. Good stuff.

10. Pauling, L., and Wilson, E.B., Jr., "Introduction to Quantum Mechanics", McGraw-Hill, New York 1935 (*<u>on reserve</u>*). A classic which covers the basics in exquisite detail.