Molecular Spectroscopy of Acetylene

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1. Introduction

Molecular spectroscopy is one of the most powerful tools available for determining molecular structure. The very high precision with which spectroscopic transitions of gas phase molecules can be measured allows us to determine with high accuracy the bond lengths and bond angles of small molecules. In this experiment you will use a Fourier transform infrared spectrometer to measure infrared absorption spectra of normal acetylene (C_2H_2) and deuterium substituted acetylene (C_2D_2). The infrared region of the electromagnetic spectrum spans wavelength ranges of roughly $\lambda = 2$ to 25 µm (1 µm $= 1 \times 10^{-6}$ meter). Rather than wavelength, the related quantity, wavenumber, is often used in infrared spectroscopy. Wavenumber is simply the reciprocal of the wavelength, $\bar{v} = 1/\lambda$, and the unit of wavenumber is cm^{-1}. The infrared region of 2 to 25 µm is equivalent to 400 to 5000 cm^{-1}. Other equations related to electromagnetic radiation are:

(frequency) × (wavelength) = speed of light, $\lambda v = c$

Energy = (Plank's constant) × (frequency), $E = hv = hc/\lambda = hc\,\bar{v}$

Note that both frequency and wavenumber are proportional to energy and for convenience we often use units of cm^{-1} to describe energies in spectroscopy, even though cm^{-1} is not a proper energy unit. If we need to convert a value in cm^{-1} units to an energy unit, such as joule, we use the above equation.

The energy of infrared radiation is sufficient to cause transitions between quantized vibrational energy levels of molecules. Hence, infrared spectroscopy is often called vibrational spectroscopy. Molecules also have quantized rotational energies that are roughly two orders of magnitude smaller than vibrational energies. When a molecule changes vibrational state, it can also change rotational state, which leads to rotational fine structure that accompanies each vibrational transition. In this experiment, you will analyze the rotational fine structure on one of the vibrational transitions that appears in the infrared spectrum of acetylene. From your analysis you will be able to determine the precise values of the C–H and C≡C bond lengths of acetylene.

2. Theoretical background

The peaks that you will measure are due to transitions between different energy levels in the acetylene molecule. Hence, to predict the wavenumber position of a peak, you need to know the initial and final state energies of the molecule. These states are specified by a vibrational

quantum number, υ, and a rotational quantum number, J. If we use cm^{-1} units for the energy levels, then the position of a line in our spectrum is given by

$$\bar{\nu} = E_f(\upsilon_f, J_f) - E_i(\upsilon_i, J_i) \tag{1}$$

where i and f refer to the initial and final states, respectively. We start by using a Born-Oppenheimer separation of the vibrational and rotational energies and treat them as independent so that the total energy is the sum of the two. This is an approximation, but correct for the inaccuracies due to this approximation by adding a small correction term.

The vibrational energies are based on the harmonic oscillator approximation, which gives a series of evenly spaced levels given by

$$E(\upsilon) = h\nu(\upsilon + \tfrac{1}{2}), \text{ where } \upsilon = 0, 1, 2, 3, 4, 5, ... \tag{2}$$

and where the separation between any two adjacent levels is given by

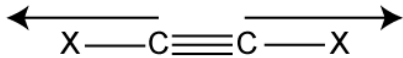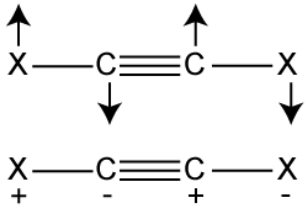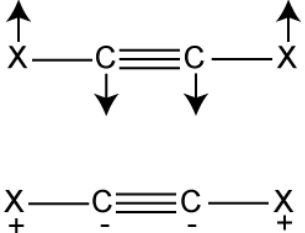$$E(\upsilon+1) - E(\upsilon) = h\nu. \tag{3}$$

The selection rule for harmonic oscillators are such that in an *absorption* spectrum (as opposed to an emission spectrum) only transitions for which the υ quantum number increases by 1, *i.e.*, $\Delta\upsilon = +1$, are allowed. This would correspond to a peak in the IR absorption spectrum at $h\nu$, in proper energy units, or at E/hc in wavenumber units. As presented below, most molecules are in their ground vibrational state at room temperature and so the infrared absorption spectrum consists of only $\upsilon = 0 \rightarrow \upsilon = 1$ transitions, which are known as vibrational fundamentals. For a diatomic molecule, the stretching of the bond corresponds to the displacement in the harmonic oscillator model. For a polyatomic molecule, there are multiple bonds that can be stretched as well as bond angles that can bend as the molecule vibrates. If we make what is called the harmonic approximation, then there are only a certain number of distinct ways the molecule can vibrate and these ways are called normal modes. The number of normal modes for a molecule consisting of N atoms is given by one of the following two equations for the number of vibrational degrees of freedom:

$3N$-5, linear molecules

$3N$-6, non-linear molecules

Since diatomic molecules are linear, the formula correctly gives 1 normal mode for diatomics. Acetylene is also linear, so we expect 7 normal modes of acetylene. Not all of these modes are IR active. For a normal mode to be IR active, the molecule's dipole moment has to change during the vibration. For some molecules all of the normal modes are IR active, while for others only a few of the modes are. The question of which modes are IR active depends on the symmetry of the molecule and can be addressed through the use of group theory. For acetylene, two fundamentals appear in the IR spectrum at 3281.9 and 730.3 cm^{-1}. Besides the fundamental

stretch and bending modes that appear in the IR spectrum, other transitions can also appear such as combination bands (two fundamental modes added together). In this experiment, you will be analyzing the combination band of the two bending (asymmetric and symmetric) modes at 1328.18 and 1048.49 cm^{-1} for C_2H_2 and C_2D_2, respectfully. A table showing the atomic displacement patterns of the normal modes of acetylene is shown below. Only five modes are shown because the bending modes come in degenerate pairs, *i.e.*, there are two equivalent modes with the same frequency. The partners to the bending modes shown involve bending out of the plane of the page (as represented by the + and – signs).

Mode	Description	Normal Mode	Band (cm^{-1})
ν_1	Symmetric C-X stretch	X—C≡C—X	X=H, 3373.7 X=D, 2700.5
ν_2	Symmetric CC stretch	X—C≡C—X	X=H, 1973.8 X=D, 1762.4
ν_3	Asymmetric C-X stretch	X—C≡C—X	X=H, 3281.9 X=D, 2439.3
ν_4	Symmetric bend	X—C≡C—X X—C≡C—X + - + -	X=H, 612.9 X=D, 505
ν_5	Asymmetric bend	X—C≡C—X X—C≡C—X + - - +	X=H, 730.3 X=D, 536.9

Table 1. Fundamental frequencies for C_2H_2 for all normal modes.

The quantized rotational energy levels are based on the rigid rotor model and are given by

$$E(J) = B_e J(J+1) \qquad (4)$$

where B_e is the rotational constant and J the rotational quantum number, which can be any non-negative integer, *i.e.*, $J = 0, 1, 2, 3, ...$. The rotational selection rule is $\Delta J = \pm 1$. The rotational constant, in wavenumber units, is related to the masses of the atoms in the molecule and to the molecular geometry through the moment of inertia, I_e, by

$$B_e = \frac{h}{8\pi^2 c I_e} \tag{5}$$

where the moment of inertia is defined by

$$I_e = \sum_{i=1}^{N} m_i r_i^2 \tag{6}$$

In these equations the subscript "e" refers to the equilibrium geometry. In the equation for I_e, the sum is over all the atoms in the molecule. For a linear molecule like acetylene, the r_i refer to the distance of an atom from the center of mass, which for acetylene is located at the midpoint between the two carbon atoms. From analysis of the spectra, you can obtain a value for B_e from which you can calculate I_e. Since you know the masses of the atoms, you can then obtain the r_i and hence the bond length. Figure 1 shows a rotational energy level diagram with the $\Delta J = \pm 1$ transitions marked by the arrows.
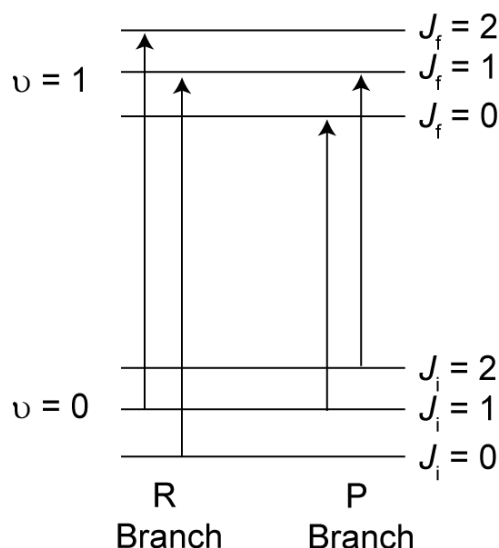
Figure 1. Energy diagram showing the first two transitions in the R and P branches, respectively.

To a first approximation, we can just add the energy expressions for the harmonic oscillator and rigid rotor to get $E(\upsilon, J)$, the vibrational rotational energy. However, this is little too drastic an approximation and we need to add a term that takes into account that vibration and rotation are not entirely independent and interact to some extent. The vibration-rotation interaction constant is α_e and when it is included the energy level expression that we need can be written as

$$E(\upsilon, J) = h\nu(\upsilon + \tfrac{1}{2}) + B_e J(J+1) - \alpha_e J(J+1)(\upsilon + \tfrac{1}{2}) \tag{7}$$

Note that this can be rewritten in terms of an effective rotational constant, B_υ, which is different for every vibrational level of the molecule. The idea that the effective rotational constant

depends on vibrational level is another way of saying that vibration and rotation are not entirely independent and have some interaction. In terms of B_υ, the energy expression is then

$$E(\upsilon,J) = h\nu(\upsilon+\tfrac{1}{2}) + B_\upsilon J(J+1) \qquad (8)$$

where

$$B_\upsilon = B_e - \alpha_e(\upsilon+\tfrac{1}{2}). \qquad (9)$$

We have neglected a couple of terms in this expression that are not important for this experiment: the anharmonicity and the centrifugal distortion. Anharmonicity accounts for deviations from an ideal harmonic oscillator, which would be important for a vibrational analysis of acetylene, and centrifugal distortion, which is mainly important for much higher values of J than we are considering. For a vibrational fundamental, $\upsilon = 0 \rightarrow \upsilon = 1$, the rotational lines in the spectrum occur at lower (the P branch) wavenumber positions than the pure vibrational transition (which occurs at ν_0) for $\Delta J = -1$, and at higher wavenumber positions (the R branch) for the $\Delta J = +1$ transitions. From the above energy level expression, we can write the following two equations for the peak positions in the R and P branches of a vibrational fundamental

$$\nu_R(J)= \nu_0 + (B_0+B_1)(J+1) - (B_0-B_1)(J+1)^2 \qquad (10)$$

$$\nu_P(J)= \nu_0 - (B_0+B_1) J - (B_0-B_1)J^2 \qquad (11)$$

These two equations will be used for the data analysis.

In addition to knowing the equations that describe the peak positions, we need to know what determines the relative intensities among the rotational transitions. The basic answer is that the intensity of a rotational line in either the P or R branch, depends on the number of molecules in the initial energy level, J, which is given by

$$N_J = g_J\exp\left\{\frac{-E_J}{kT}\right\} \qquad (12)$$

where the exponential term is the Boltzmann factor from thermodynamics. It tells us that if the energy is very high relative to the thermal energy available at an absolute temperature T (in Kelvin), then there will be relatively few molecules with that energy. If the energy is comparable to or lower than the thermal energy, then the probability will be high. Since rotational energies are small relative to kT at room temperature, there are many molecules with J values between 0 and about 30 or so. The second factor, g_J, refers to the degeneracy, which is the number of different states of the same energy. For a linear molecule, the energy depends on the quantum number J, but there is another quantum number associated with rotation, M_J, which the energy does not depend on. There are $2J+1$ different M_J values for each J value, so the degeneracy associated with the different M_J values is $2J+1$. (The J and M_J quantum numbers

are exactly analogous to the angular momentum and magnetic quantum numbers in the hydrogen atom, l and m_1, respectively.)

In addition to the degeneracy associated with the different M_J values, symmetric molecules, such as acetylene, can have an additional degeneracy associated with what are known as nuclear spin statistics. In fact, observing the effects of nuclear spin statistics, which can have a large effect on relative intensities, is one of the main points of the acetylene IR experiment. The reason nuclear spin has anything to do with infrared spectroscopy is due to one of the most fundamental principles of quantum mechanics, the Pauli Principle. This principle states that the probability density, given by $|\Psi_{total}|^2$, must be unchanged upon the exchange of identical particles. This means that the exchange either does not change Ψ_{total}, or changes it to $-\Psi_{total}$. These two behaviors, symmetric and antisymmetric with respect to exchange, correspond to two types of particles, fermions and bosons. For fermions, the total wavefunction changes sign and is antisymmetric upon exchange, whereas for bosons the wavefunction does not change sign and is symmetric. Nuclei, such as H, that have a nuclear spin angular momentum quantum number of ½, are fermions, whereas nuclei such as D with a spin quantum number of 1, are bosons. Because of nuclear spin statistics, the relative intensities of the rotational lines in the IR absorption spectrum of C_2H_2 and C_2D_2 are qualitatively different. For the molecule C_2HD, the two hydrogen atoms are not identical, so nuclear spin statistics do not affect the intensities. Although the carbon atoms are identical, ^{12}C has a nuclear spin of zero, which means the degeneracy of the nuclear spin wavefunction is one, which in turn means there is no effect on the relative intensities.

To understand why H and D affect the relative intensities differently, we need to consider that the total wavefunction for internal motion

$$\Psi_{total} = \psi_{elec}\psi_{vib}\psi_{rot}\psi_{ns} \tag{13}$$

can be factored into separate electronic, vibrational, rotational, and nuclear spin wavefunctions. In general, vibrational wavefunctions are symmetric with respect to exchange of identical nuclei and so are the electronic wavefunctions of the ground states of most molecules, including acetylene. Therefore, for acetylene, the symmetry of the total wavefunction with respect to exchange depends only on the rotational and nuclear spin wavefunctions. Depending on the nuclear spin angular momentum quantum number, there can be several different nuclear spin wavefunctions, all of the same energy, so that the degeneracy of the initial state in a vibration-rotation transition depends on nuclear spin. If the nuclear spin quantum number is I, then the nuclear spin degeneracy is $2I+1$ for each nucleus. (Note: quantum mechanically all angular momenta obey the same general rules; the degeneracy for the angular momentum of the hydrogen atom is $2l+1$, the degeneracy for the rotational angular momentum of the rigid rotor is $2J+1$, and the degeneracy for the nuclear spin angular momentum is $2I+1$). The nuclear spin degeneracy can be thought of as the number of different orientations of the nuclear spin angular momentum vector. For an $I = ½$ particle such as an H atom or an electron, the degeneracy is 2,

Figure 2 below shows the simulated spectra
3/11/2014

corresponding to spin up and spin down. When equivalent nuclei are involved, such as for acetylene, then the spins of each nucleus are independent and the total nuclear spin degeneracy is $(2I+1)^2$, *i.e.*, this is the number of different wavefunctions possible. Of these nuclear spin wavefunctions, $(2I+1)(I+1)$ are symmetric with respect to exchange of the equivalent nuclei and $(2I+1)I$ are antisymmetric. So for two identical particles with $I = ½$, there are three symmetric spin functions and one antisymmetric function. For $I = 1$, there six symmetric functions, and three antisymmetric functions.

The symmetry of the rotational wavefunction with respect to exchange of identical nuclei is simply determined by the rotational quantum number. For $J =$ even, the rotational wavefunction is symmetric with respect to exchange, while for $J =$ odd, it is antisymmetric. To make Ψ_{total} antisymmetric with respect to exchange, as it must be for fermions like H, the odd J states must be combined with even nuclear spin states, and the even J states must combine with antisymmetric nuclear spin states. Therefore, the nuclear spin degeneracy for even J states for C_2H_2, is 1, while for odd J states it is 3. For C_2D_2, the even J states must combine with the symmetric nuclear spin wavefunctions, and the odd J states must combine with the antisymmetric nuclear spin states to make the overall wavefunction symmetric with respect to exchange. Therefore the nuclear spin degeneracy for the even J states of C_2D_2 is 6, and the degeneracy for even J values is 3. The important observable is the relative degeneracies, and this reasoning indicates that there with be a 3:1 relative intensity ratio for the rotational lines of C_2H_2 for initial J states of odd number relative to initial states with even Js. For C_2D_2, the ratio will be 2:1, with the states with even initial Js more intense. Figure 2 below shows the simulated spectra of the rotational fine structure of a linear molecule, such as acetylene, without and with the inclusion of effect of nuclear spin statistics.
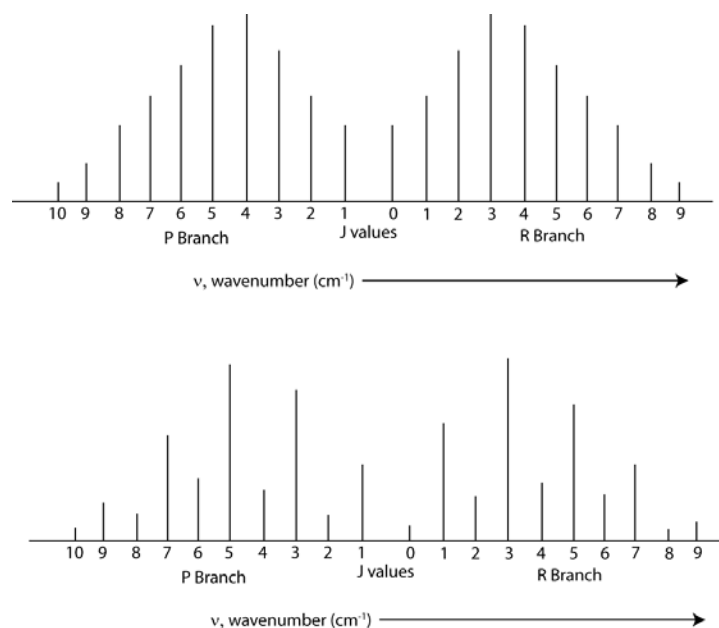

Figure 2. Simulated Spectra of C_2H_2 without and with the inclusion of nuclear spin statistics.

Acetylene IR Experimental Procedure

A. Reaction to produce C_2H_2/C_2D_2

For this experiment, you will be synthesizing acetylene (C_2H_2) and deuterated acetylene (C_2D_2) from calcium carbide (CaC_2) and DI-water (H_2O) and deuterium oxide (D_2O).

$$CaC_2 + 2\ H_2O \longrightarrow C_2H_2 + Ca(OH)_2$$

$$CaC_2 + 2\ D_2O \longrightarrow C_2D_2 + Ca(OD)_2$$
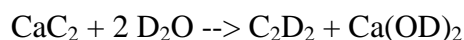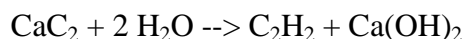
C_2H_2 and C_2D_2 are highly flammable gases and can react with oxygen (O_2), checking for leaks in the manifold is crucial before starting the synthesis.

B. Steps for safe laboratory work

Please review the following steps before starting the experiment.

1. All valves are closed on the manifold when entering and exiting the laboratory except G.

2. Your TA will check to make sure you are using the appropriate amounts of CaC_2 and H_2O/D_2O. Using excess CaC_2 will create a high pressure of C_2H_2, which could cause an explosion in the manifold.

3. When the experiment is over, open the flask in the fume hood. This will prevent flammable/noxious gases from entering the laboratory.

4. Always wear safety goggles, you will not be allowed to perform the experiment without them. Taking them off will also result in a performance point deduction and you may possibly be asked to leave the laboratory for the day.

C. Synthesis of C_2H_2/C_2D_2 and acquiring IR spectra

1. The following procedure is the same for C_2H_2 and C_2D_2.
2. Your TA will provide liquid nitrogen to fill the dewar for the cold trap.
3. Review and familiarize yourself with the figure below.
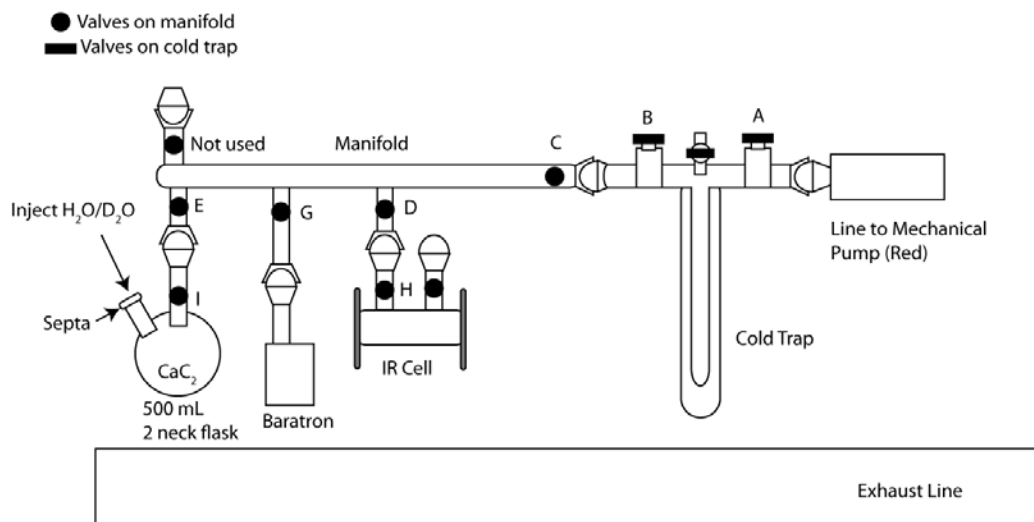
Figure 3. Vacuum line for sample cell preparation.

4. Fit the cold trap between the hose that leads to the mechanical pump and valve C. Make sure valves A and B are open. Attach the spring clips across the two joints but do not tighten them. Make sure valves are in the open position.

5. Place the empty dewar under the cold trap, raising it until it covers most of the trap. Wrap both chains around dewar to secure it.

6. Tighten the spring clips across the joints of the trap.

7. Weigh out ~0.4 ± 0.1 g of CaC_2 (one or two piece(s) of CaC_2) for C_2H_2 synthesis and put into 500 mL flask. For C_2D_2, you need ~0.8 ± 0.1 g of CaC_2. Do not crush CaC_2.

8. Put septum on open 14/20 fitting on 500 mL flask, attach flask to manifold.

9. Remove the IR cell from the dessicator.

10. Fit the inlet ball of the IR cell into the socket under valve D, and place a spring clip across the joint. You may need to use a clamp to support the cell. The valves on the IR cell should be closed.

    Note: Do not allow the NaCl windows of the IR cell to come into contact with any moisture. Placing fingers on the window surfaces will cause damage.

11. Open valve D, H, E, and I. Turn on mechanical pump (switch on surge protector located on the side by the red vacuum line) and slowly open valve C. Valve C should be closed when entering and exiting the laboratory. Fill cold trap with liquid nitrogen.

12. Wait until the pressure reaches ~ 0.6 Torr. If the pressure reading is not going down, check to make sure the valve (valve G), to the baratron is open.

13. Check for leaks by isolating the manifold by closing valve C. Then open valve C and close valve A. This ensures no oxygen enters the system through a leak to the atmosphere. If pressure rises after each check, there is a leak in the manifold/cold trap. After checking for leaks, make sure valves C and A are open.

14. Close valve E, then close H and D. Remove IR cell and acquire background spectrum on the Bruker Tensor 27 FTIR. See next section for instructions.

15. While taking a background scan, make an ice bath with $CaCl_2$ and H_2O. Submerge in bucket up to the neck (right below septum) of the flask.

16. After background scan is complete, attach IR cell back to manifold (valve H), open D, then H. Wait for the pressure to drop in the manifold.

17. Open valve E.

18. Fill syringe with 3.0 mL/5.5 mL of H_2O/D_2O. Make sure there isn't any air by tapping syringe and purging it of all bubbles.

19. Close valves C and I. This isolates the manifold from the cold trap and pump and flask from manifold preventing water vapor from entering the cell.

20. Inject H_2O/D_2O into the flask. Open valve I about 30 seconds after injection. When the pressure starts rising in the manifold, you are synthesizing C_2H_2. You need 50-100 Torr of C_2H_2 and 150-200 Torr for C_2D_2.

21. After reaction is finished, close valve H and A. Open valve C slowly and the pressure should drop, all remaining C_2H_2/C_2D_2 in the manifold will be contained in the cold trap.

22. Open valve A after pressure has stabilized.

23. Close valve D, remove IR cell.

24. Take sample spectrum.

25. While acquiring spectrum, close E and I.

26. Remove flask and put it back in fume hood. Open valve I and remove septum.

27. Fill flask halfway with H_2O, this will dissolve some of the $Ca(OH)_2$ and any remaining CaC_2 will react. While filling with H_2O, close fume hood window leaving just enough space to work. Only pour the first washing of the flask into the waste labeled FTIR.

28. Use sonicator and 0.1 M HCl if $Ca(OH)_2$ residues cannot be removed from the flask.

29. Pour rest of wasted down the drain and flush with water.

30. After spectrum is acquired, remove IR cell from instrument and fit back onto manifold.

31. Open valves H and D to evacuate cell. After pressure stabilizes in manifold, close both valves and remove from manifold.

32. Close valves C, B, and A. Turn off pump and remove cold trap. Leave cold trap in liquid nitrogen while carrying it to the fume hood. Remove all valves from cold trap in fume hood and lower fume hood window.

Instrument Operation for the Bruker Tensor 27 FTIR

I. Loading the Software.

1. The IR software that is used for this experiment is OPUS 7.2.139.1294. To start the program, double click on the 'OPUS 7.2.139.1294' icon on the windows desktop. Click login, no password is required for the program. If the screen does not appear as the same as the print screen available on the website, click on File, Open, and click on the WORK folder. Click on the pchem_343 file. The appearance of the program should now resemble that of the print screen. Before any scans can be completed, the pchem_343.xpm file must be initiated. To do this, go to the tool bar, which is located on the top of the screen, and click on the test tube icon. Under Basic tab, make sure the pchem_343.xpm file is loaded for the experiment (Do not click save). Change the sample description to your names and the date, and sample form to either c2h2 or c2d2. In the Advanced tab, go to the File Name. Put date and both of the students' names in the box. Even though the file is saved after each spectral scan automatically, you will not have access to it after running the experiment. Go back to Basic tab to run background scan.

II. Running a Background Scan

2. A background scan allows the user to easily subtract out the contributions of the sample holder, solvent, instrument, and atmosphere inside the instrument from the spectra. For every run, different solvent, or different technique of acquiring a spectrum, you must first acquire a background spectrum. The same background, however, may be used for many spectra. A new background should be acquired after ~60 minutes has elapsed, to account for any change in the instrument over time.

3. To open the sample compartment, lift cover to sample compartment (light blue part of instrument). Fit cell into the transmission holder slot. Close the sample compartment. You want to minimize the amount of time the compartment remains open to reduce the purge time.

4. Wait 5 minutes after closing sample compartment to allow all of the water and carbon dioxide (CO_2) to be purged from the instrument before acquiring a scan.

5. Under the Basic tab (after clicking on the test tube icon), click on Run Background Scan. Then click 'Accept and Exit'. NOT SAVE. Nothing will appear on the screen for the background scan.

III. Running a Sample Scan

6. Click on test tube icon and under Basic tab click Sample Scan. The box will close opening up a new measurement window. On the lower left hand corner of the window, click 'Start Measurement'.

7. Once the spectrum appears on the screen, check if it is acceptable. If acceptable, you can remove the cell from the sample holder and go to step 30 in the experimental section.

IV. Printing Results

8. Click on the peak picking icon to the right of the test tube (it looks like three upside down Gaussian peaks). Click on Frequency Range tab and set the limits as 1380 to 1280 for C_2H_2 and 1080 to 1020 for C_2D_2. Then click Peak Picking. The peak number should show up on the plot.

9. Click on the print button (located right next to the peak picking button). Make sure layout file is acetyleneprintlayout.PLE. Go to frequency range tab. It should read for the x startpoint and endpoint 1410 and 1250 for C_2H_2 and 1080 and 1000 for C_2D_2, respectively. For the y minimum, it should be 0 and the y maximum is the top of spectrum (on previous screen). This will change in regards to the pressure in the cell. Click on Options tab. Output to printer and click print at the bottom of the box.   You should have two sheets of paper, one with the spectrum and scan settings, the other with the peak positions in wavenumbers and their corresponding intensities. These will be used for the data analysis.

10. Before leaving lab, close OPUS software and make sure spectrometer sample compartment is closed.

Spectral Analysis

I. Labeling peaks with respective *J* values
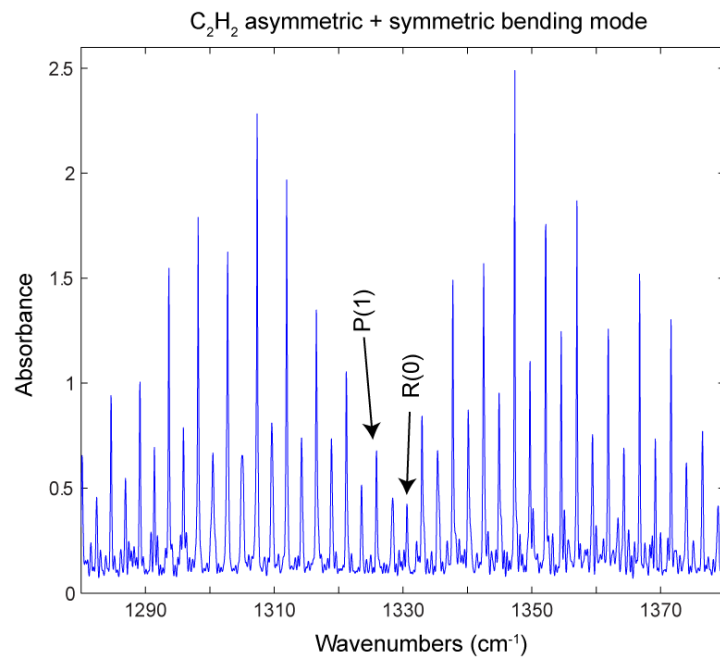
**Figure 4.** Spectrum of C_2H_2
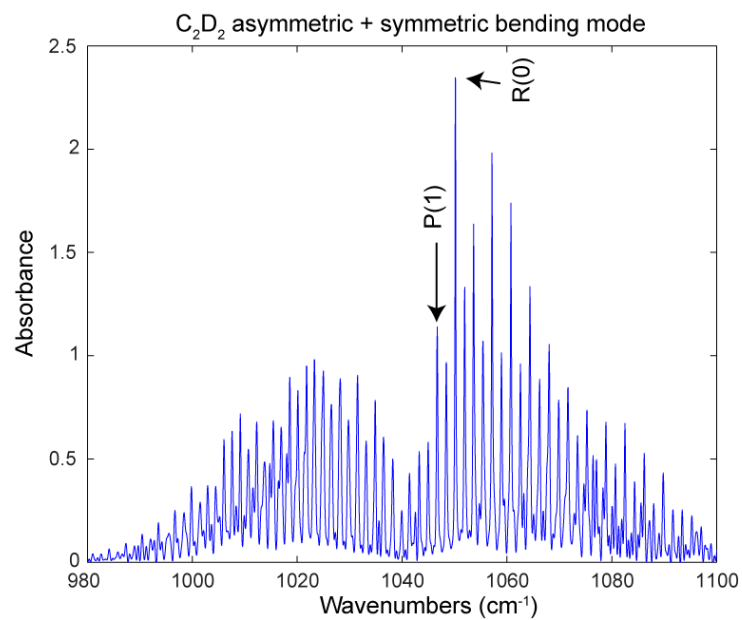
Figure 5. Spectrum of C_2D_2

Data Analysis

(a) Make a table of J values and the corresponding experimental frequencies from the R and P branches. (Check out sample spectra, figs. 4 and 5 as guide, should provide frequency values up to $J = 10$)

(b) Plot $\frac{1}{2}[v_R(J)+v_P(J+1)]$ (using equations 10 and 11) against $(J+1)^2$ and draw the best straight line through the points. This is function $f = f[(J+1)^2]$. Use Origin, SigmaPlot, or other statistic software to calculate a linear regression.

(c) Compute the function $f = f[(J+1)^2]$ using Eqs. 10 and 11 to determine what the slope and the intercept represent.

(d) Plot $[v_R(J)-v_P(J+1)]$ against $4(J+1)$ and draw the best straight line through the points. This is function $g = g[4(J+1)]$. Use Origin, SigmaPlot, or other statistic software to calculate a linear regression.

(e) Do the same as in (c) for $g = g[4(J+1)]$.

(f) Calculate I_e, the moment of inertia and r_e, the internuclear distance. See next page for information needed to calculate r_e.

(g) Tabulate the values of v_0, B_e, α_e, I_e, and $r_{e_{CH}}$ and $r_{e_{CC}}$. Compare with results from Tidwell, etc. These are located on the last page of this manual.

(h) Compare peak intensities in the C_2D_2 and C_2H_2 spectra for even and odd J values. What are the ratios for the even/odd C_2D_2 and C_2H_2 peaks? How does this correlate to the nuclear spin for the hydrogen and deuterium atoms?

R_e calculation - C_2H_2, C_2D_2
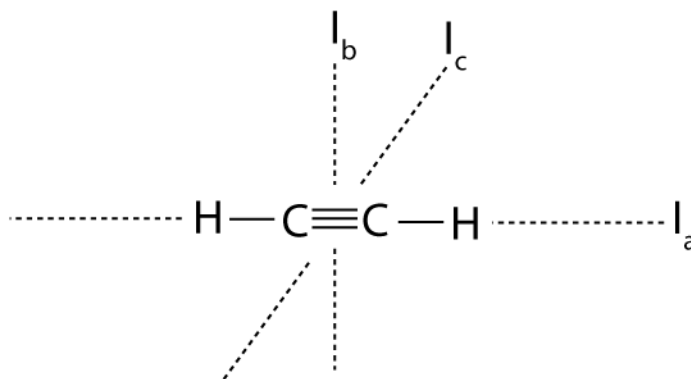
Figure 8. Moments of Inertia for C_2H_2.

Acetylene is a linear molecule, so $I_a = 0$ and $I_b = I_c$

To calculate r_e of the CH and CC bonds, the distance to the central of the molecule (rotation axis) has to be determined.

Rotational Axis
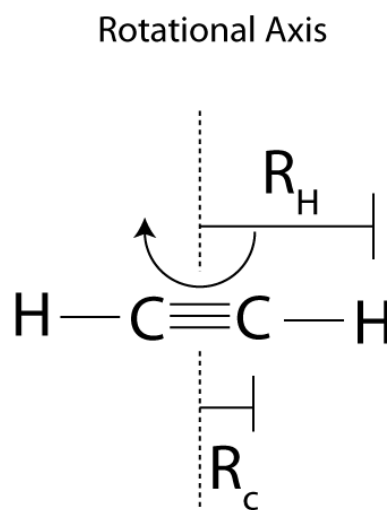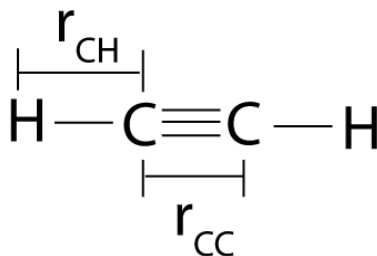

Figure 9. Drawing of C_2H_2 molecule with R_H and R_C.

The radius R_H (the distance of the hydrogen atom the center of the molecule) is:

R_H = 1/2 CC bond + C-H bond

The radius R_C (the distance of the carbon atom the center of the molecule) is:

R_C = 1/2 CC bond

Using these two radii and equation (4), you can find r_{CH}, and r_{CC}.

Figure 10. Drawing of C_2H_2 molecule with r_{CC} and r_{CH}.

Inserting the radius of R_H and R_C into equation 4 gives:

$$I_e = \mu R_H{}^2 + \mu R_C{}^2$$

After performing some simple algebra, it reduces to:

$$I_e = 1/2\ \mu_C r_{CC}{}^2 + 2\ \mu_H (r_{CH} + 1/2 r_{CC})^2$$

Remember that the length for carbon-deuterium (CD) bond is the same as the length for carbon-hydrogen (CH) bond.

Discussion Questions

1. Why is the vibrational-rotational interaction constant, α_e, negative?

2. If you increase the temperature of the cell, how does the population of rotational states change?

3. At the end of the experiment, you end up with a grayish precipitate. What is this precipitate? Provide one way to completely dissolve it.

4. How can you increase the signal (or absorbance) experimentally in the IR spectrum?

Table of Molecular Constants

Isotope	V_0 (cm^{-1})	B_e (cm^{-1})	B_0 (cm^{-1})	α_e (cm^{-1})	I_e (g cm^2)
C_2H_2	1328.18	1.1751	1.1769	-0.003586	2.368×10^{-39}
C_2D_2	1048.49	0.8458	0.84794	-0.004240	3.291×10^{-39}

r_{eCC} (Å)	1.203
r_{eCH} (Å)	1.061

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