

Introduction

This experiment is meant to illustrate principles involved in the vibration-rotation spectroscopy of polyatomic molecules. You will make use of a Perkin-Elmer Lambda 9 Spectrophotometer operating in the near infrared to record a particular vibration-rotation band for both C₂H₂ and C₂D₂. The rotational constants derived from an analysis of both spectra will then be used to calculate C≡C and C–H bond lengths. This lab also illustrates the use of isotopic substitution in bond length calculations.

Both spectra exhibit an interesting intensity alternation in the absorption lines. This intensity alternation can be understood by a consideration of the nuclear spin degeneracy of rotational states. The treatment makes use of a general form of the Pauli exclusion principle introduced in a restricted form for electrons in general chemistry.

You should come to this lab armed with a good understanding of the basic rotation-vibration spectroscopy of diatomic molecules (such as discussed in the theory section of the writeup for Experiment 2a, *Vibration-Rotation Spectra of HCl and DCl*), plus some knowledge of the Pauli exclusion principle. In addition to this write-up, the referenced sections in Winn and Barrow should be studied. References 3 and 4 are to applicable portions of Herzberg's classic works on molecular spectroscopy. This reading is a little tougher going than the Barrow reference but may be more satisfying to some of you.

References

1. J. S. Winn, *Physical Chemistry*, HarperCollins, 1995, Chapter 19, especially pp. 705–707, 712–717, and 743–745.
2. G. M. Barrow, *Introduction to Molecular Spectroscopy*, McGraw-Hill, 1962, Sections 5-4 and 5-5, pp. 96-103 and Sec. 7-4, pp. 142-146.
3. G. Herzberg, *Molecular Spectra and Molecular Structure. I. Spectra of Diatomic Molecules*, second edition, D. Van Nostrand, 1950, pp. 130-140.
4. G. Herzberg, *Molecular Spectra and Molecular Structure. II. Infrared and Raman Spectra of Polyatomic Molecules*, D. Van Nostrand, 1945, a) pp. 288-293, b) 390-398.
5. L. W. Richards, *J. Chem. Educ.*, 43, 644, (1966).

Theory

Acetylene is a linear molecule, and consequently its vibration-rotation bands bear a strong resemblance to those of a diatomic such as HCl. The quantum-mechanical treatment of rotation for any linear molecule always begins with the exact solution for the rigid-rotor problem with rotational energy levels given by

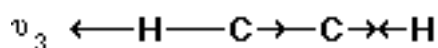
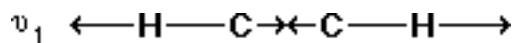
$$E_J = \frac{\hbar^2}{2I} J(J + 1) \quad (1)$$

where J is the rotational quantum number (0, 1, 2, ...) and I is the moment of inertia.

As described in detail in Section 7-4 in Barrow, the vibrational transitions of a linear molecule may give rise to either *parallel* bands or *perpendicular* bands in a vibration-rotation spectrum. Parallel bands are associated with an oscillating dipole moment parallel to the molecular axis; perpendicular bands are associated with a perpendicular oscillation of the dipole moment. Here, we are interested in the parallel band case for which the band has the same form as that for a heteronuclear diatomic—namely, P ($\Delta J = -1$) and R ($\Delta J = +1$) branches but no Q ($\Delta J = 0$) branch. This may seem reasonable to you if you will recall that the vibration-rotation band observed for HCl is by definition a parallel band.

Thus, provided we record a parallel vibration-rotation band for acetylene, the spectrum analysis will be closely analogous to that for HCl. We can use the rotational line spacings to calculate rotational constants, moments of inertia, and finally bond lengths.

Acetylene has $3N - 5 = (3)(4) - 5 = 7$ normal modes¹ of vibration, only five of which have independent frequencies. There are two doubly degenerate (equal-energy) bending vibrations. Among these five frequencies, there are two labeled ν_1 and ν_3 that arise from primarily CH stretching motions. (Mode ν_2 is a C≡C stretching vibration which we will not be concerned with.) Schematically, the nuclear motions in these two modes look like this:



¹ Normal modes of vibration are described on pp. 713–717 of Winn.

Mode ν_1 involves a *symmetric* stretching of the two CH bonds while ν_3 is an *anti-symmetric* CH stretching mode—one CH stretches while the other compresses. Mode ν_1 will not lead to absorption of radiation since it involves no oscillating dipole. The molecular dipole moment is zero at each instant during the symmetric vibration. Mode ν_3 does involve an oscillating dipole moment and is infrared active. It will give rise to a parallel band spectrum. Mode ν_3 is observed as a vibration-rotation band in the infrared around 3287 cm^{-1} (which is the transition energy of the "missing" pure vibrational transition—where the Q branch would be if it were allowed). This is in the working range of the Perkin-Elmer 1605 FTIR spectrometer that is used in the HCl, DCl experiment. The Lambda 9 spectrophotometer has far greater accuracy and resolution but can only be used for energies above about 4000 cm^{-1} . We can make use of this latter instrument by examining the combination band, $\nu_1 + \nu_3$, which arises from simultaneous (by a single quantum) excitation of the ν_1 and the ν_3 modes plus allowed rotational energy changes ($\Delta J = \pm 1$). The table below gives energies of the ν_1 (observed in Raman spectra) and ν_3 modes in C₂H₂ and C₂D₂. Use these to calculate the predicted energy of the $\nu_1 + \nu_3$ transition in the two molecules and the predicted center position of the two bands. You will need these two band locations when you come to lab.

<u>Pure Vibrational Energies</u>		
	$\nu_1\text{ (cm}^{-1}\text{)}$	$\nu_3\text{ (cm}^{-1}\text{)}$
C ₂ H ₂	3373.7	3278
C ₂ D ₂	2700	2427

The $\nu_1 + \nu_3$ combination band results in a parallel dipole moment oscillation and hence gives rise to a parallel band which you may easily assign and analyze. Note the interesting point that while excitation of the ν_1 mode alone is dipole forbidden it can be excited in combination with the dipole-allowed ν_3 mode excitation.

Actually we need concern ourselves little more about the character of the vibrational transition other than to ascertain its parallel nature. For our purposes, the vibrational transition can be looked at simply as the carrier of the rotational lines in the band. These rotational lines are in turn the quantities of interest in the experiment.

The analysis of the rotational fine structure for the purpose of bond length determinations is completely analogous to the procedure used for HCl. We may as usual express the total vibrational plus rotational energy for a linear molecule in some quantum state with vibrational quantum numbers denoted collectively by ν and a rotational quantum number J by writing:

$$E_{\nu,J}(\text{cm}^{-1}) = G(\nu) + B_{\nu} J(J + 1) - D_{\nu} [J(J + 1)]^2 \quad (2)$$

where

$G(v)$ = vibrational energy, a function of all the vibrational quantum numbers, e.g., in our case for the upper state:

$$v_{\nu_1} = 1, \quad v_{\nu_2} = 0, \quad v_{\nu_3} = 1, \quad v_{\nu_i} = 0 \text{ for } i = 4, 5$$

B_v = rotational constant in cm^{-1} . (The simple expression, $B_v = B_e - \alpha_e(v + 1/2)$, is no longer applicable since now each vibrational state is characterized by a set of quantum numbers.)

D_v = centrifugal distortion constant $\ll B_v$ (and will later be neglected).

Most importantly we may still write:

$$B_v = \frac{\hbar}{4\pi c I} \tag{3}$$

so that a determination of the rotational constant gives us immediately a value for the molecule's moment of inertia, I . It must be remembered that I is an average moment for the molecule in a particular vibrational state. For the lowest vibrational state of C₂H₂ and C₂D₂, we will calculate values of B_v which characterize the molecule with all five normal modes executing their zero point vibrations.

Neglecting centrifugal distortion, we may use Eq. (2) to write down the transition energy between some lower state (double primed) and an upper state (single primed):

$$E' - E'' = G(v') - G(v'') + B_v J'(J' + 1) - B_v J''(J'' + 1)$$

Recalling the selection rule $\Delta J = \pm 1$, we may write explicit expressions for the R branch and the P branch rotational lines:

$$\mathbf{R \text{ branch: } \Delta J = +1, \quad J' = J'' + 1}$$

$$(E' - E'')_R \equiv \nu_R(J'') = G(v') - G(v'') + B_v(J'' + 1)(J'' + 2) - B_v J''(J'' + 1)$$

$$\mathbf{P \text{ branch: } \Delta J = -1, \quad J' = J'' - 1}$$

$$(E' - E'')_P \equiv \nu_P(J'') = G(v') - G(v'') + B_v J''(J'' - 1) - B_v J''(J'' + 1)$$

We are interested in the ground state value of the rotational constant, B_v in our

case, so that we may use the method of combination differences. With a judicious choice of R branch and P branch lines we can perform a subtraction that eliminates any terms involving $B_{v'}$. Rewriting the ν_P expression in terms of $J'' + 2$ and subtracting it from $\nu_R(J'')$ gives

$$\nu_R(J'') - \nu_P(J'' + 2) = B_{v''}(J'' + 2)(J'' + 3) - B_{v''}J''(J'' + 1)$$

or

$$\Delta''(J'') \equiv \nu_R(J'') - \nu_P(J'' + 2) = B_{v''}(4J'' + 6) \quad (4)$$

where Δ'' is used to denote the combination difference containing the lower state's B value. Using Eq. (4), many values of $B_{v''}$ may be calculated from each spectrum that you will record. These may be averaged in order that a good value for I may be calculated using Eq. (3). The only remaining problem is the calculation of CH and CC bond distances from the I values for C₂H₂ and C₂D₂. For linear polyatomic molecules, the general expression for I is

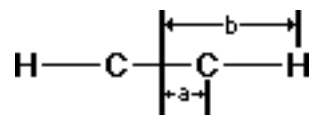
$$I = \sum_i m_i r_i^2 \quad (5)$$

where r_i is the distance of the *i*th nucleus from the center of mass and m_i is the atomic mass of the *i*th atom. This assumes that the electrons associated with an atom are all located at the same point as the nucleus which, because of the relative masses of electrons and nuclei, is a very good approximation.

Using Eq. (5) we may write the following explicit expression for the moment of inertia of C₂H₂:

$$I = 2m_C a^2 + 2m_H b^2 \quad (6)$$

where the distances **a** and **b** are indicated in the following figure:



Obviously, substitution of m_D for m_H yields the correct expression for $I_{C_2D_2}$. Eq. (6) is an equation in two unknowns, **a** and **b**. If we assume that **a** and **b** have the same value in C₂D₂ as in C₂H₂, then using Eq. (6) and the corresponding expression for $I_{C_2D_2}$ we have two equations in two unknowns. These can be quickly solved for **a** and **b** and hence for the CH and CC bond lengths. This method illustrates the value

of isotopic substitution to the determination of bond lengths in polyatomic molecules.

The second major point of this experiment is to illustrate, using the intensity alternation of the rotational lines, the consequences of identical particle indistinguishability. Barrow discusses this in Sections 5-4 and 5-5, and Winn covers it on pp. 743–745. Several key points are reemphasized and extended slightly in what follows here.

Consider a homonuclear diatomic molecule or, for that matter, any linear molecule with a center of symmetry such as C₂H₂. Let the wave function of the molecule be ψ and consider the effect of the parity or inversion operator \hat{P} on this function. Take the origin of the coordinate system at the center of symmetry. The parity operator has the effect of replacing each coordinate q_i by $-q_i$:

$$\hat{P}\psi(x_1, y_1, z_1, \dots) = \psi(-x_1, -y_1, -z_1, \dots) .$$

If we apply \hat{P} to both sides of this equation, we obtain:

$$\hat{P}^2\psi(x_1, y_1, z_1, \dots) = \hat{P}\psi(-x_1, -y_1, -z_1, \dots) = \psi(x_1, y_1, z_1, \dots) .$$

Considering this last expression as an eigenvalue equation with p^2 the eigenvalue of the operator \hat{P}^2 we see that $p^2 = 1$; therefore, the two possible eigenvalues of the operator \hat{P} are $p = \sqrt{1} = \pm 1$. To summarize, we can write

$$\hat{P}\psi(x_1, y_1, z_1, \dots) = p\psi = \pm\psi(x_1, y_1, z_1, \dots) ,$$

and we say **$p = +1$** means ψ has **even parity** while **$p = -1$** means ψ has **odd parity**.

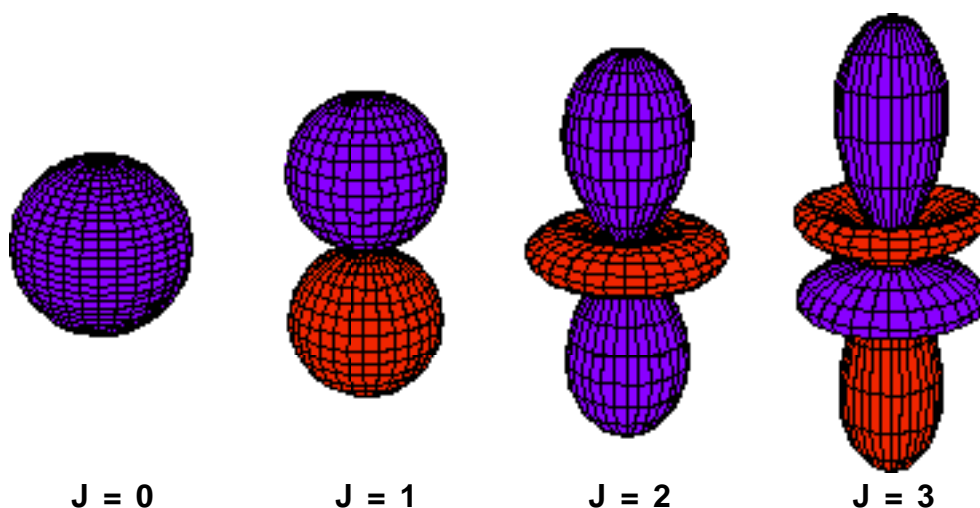
All of this symbolism is a bit more than necessary, and the ideas involved are easily expressed in words. For the molecules considered, since the particles are indistinguishable, the inversion operation gives back the identical configuration. The square of the wave function for this inverted configuration must be identical with that for the original configuration. Therefore ψ can go into either plus or minus itself under the inversion operation, leaving ψ^2 unaffected.

Thus for centro-symmetric linear molecules, ψ is an eigenfunction of \hat{P} with eigenvalue $+1$ or -1 . The complete wavefunction for the molecule must have either $p = +1$ or $p = -1$, and we can classify wavefunctions according to their parity.

To proceed with this classification we write

$$\Psi = \Psi_{\text{el}} \Psi_{\text{vib}} \Psi_{\text{rot}}$$

We then discuss the effects of \hat{P} on Ψ_{el} , Ψ_{vib} , and Ψ_{rot} independently. So long as Ψ_{el} is totally symmetric (i.e., a Σ_g^+ state, as is the case for the ground state of C₂H₂), Ψ_{el} is unchanged by the inversion operator. (The g subscript in the molecular term symbol Σ_g^+ tells you this.) The Ψ_{vib} factor is also unchanged by the inversion operator since it is a function of internuclear coordinates only. Thus the parity of Ψ_{rot} determines the over-all parity of Ψ . The rigid-rotor wavefunctions (the spherical harmonics) give the parity of Ψ_{rot} :



Inspection of these functions shows that Ψ_{rot} is + with respect to inversion if J is even (0, 2, 4, etc.) while Ψ_{rot} goes into $-\Psi_{\text{rot}}$ on inversion for odd J. Thus the parity of Ψ is completely determined by J.

The parity operator has the effect of interchanging both nuclear and electronic coordinates for centro-symmetric linear molecules. In applying the Pauli Principle (defined below) to C₂H₂ and C₂D₂ we will, however, be interested in wavefunction sign changes that accompany the interchange of identical nuclei only. For acetylene and other molecules that have Σ_g^+ ground states, the electronic wavefunction is symmetric to inversion of the electronic coordinates alone as we remarked earlier. Thus for molecules like acetylene the parity of Ψ (+ or -) gives directly the sign change that accompanies interchange of identical nuclei. For even J, the C₂H₂ spatial wavefunction is called symmetric (**s**) with respect to nuclear interchange, while for odd J, Ψ is antisymmetric (**a**).

Before considering the influence of nuclear spin, it is a good idea to see what the Pauli Principle in its most general form says about the nuclei in our molecules.

Pauli Principle

The total wave function for a system of Fermions² must be antisymmetric (change sign) for any pairwise interchange of identical Fermion space and spin coordinates. For a system of Bosons, the interchange must leave the wavefunction unchanged.

The principle is empirical (it works, but nobody knows why) and reduces in the case of electrons to the special case you have heard of earlier: no two electrons in an atom can have the same set of values for all four quantum numbers.

We have already succeeded in deducing the (**s**) or (**a**) character of the C₂H₂ (or C₂D₂) wavefunction with respect to interchange of the space coordinates of the nuclei. The effect of spin coordinate interchange must now be dealt with.

Many nuclei have an intrinsic spin angular momentum and spin quantum number, *I*, where the spin angular momentum magnitude is $\hbar^2 I(I + 1)$; an equation of the same sort is applicable to any sort of quantized angular momentum.

The ¹²C nuclei have zero spin (*I* = 0) and make no contribution to nuclear spin for C₂H₂ and C₂D₂. Our considerations are thus reduced to exactly those involved in determining nuclear spin wavefunctions for H₂ and D₂. The H₂ case is treated in detail in both Winn and Barrow by analogy with the electron spin wave functions for He. One sees that for H₂ where *I* = 1/2 for each proton one can write three symmetric and one antisymmetric nuclear spin function. Consider now the total wavefunction:

$$\Psi = \Psi_{el} \Psi_{vib} \Psi_{rot} \Psi_{nuc}$$

Except for the Ψ_{nuc} factor we have already succeeded in classifying ψ on the basis of whether *J* is even or odd. Now the Pauli Principle requires that $\psi \rightarrow -\psi$ for pairwise interchange of space *and* spin coordinates of the ¹²C nuclei and the ¹H nuclei. (No sign change for ¹²C interchange times sign change for ¹H interchange.) To satisfy the requirement we must combine the (**a**) spin function with the (**s**) space functions (*J* even) and the (**s**) spin functions with the (**a**) space functions (*J* odd). The net result of all of this is that for H₂ or C₂H₂ the states with odd *J* have a nuclear spin degeneracy of 3 (there are three symmetric spin functions) while the spin states for

² Fermions are particles with half-integral spin (e.g., electrons, protons, neutrons, etc.) while Bosons are particles of integral or zero spin (photons, ²H = D nuclei, ¹²C nuclei etc.).

even J are non-degenerate. In your C₂H₂ spectrum you should find that the states with odd J" are three times as heavily populated as those with even values of J". The more heavily populated states (J" = odd for C₂H₂) are designated³ *ortho*; the others are *para*.

One may use the general theory of angular momentum to summarize the nuclear spin results for H₂ or C₂H₂ and then extend the results by analogy to D₂ and C₂D₂. For each proton in H₂ or C₂H₂, $I = 1/2$. The two spins can be combined to yield a total spin angular momentum quantum number, T, where $T = 2I, 2I - 1, \dots, 0$. For H₂ this results in just two values of T: 1 and 0, or spin parallel and spins opposed, respectively. Analogous to the rigid rotor case where states have angular momentum quantum number J, the levels of different T have a degeneracy given by $2T + 1$. Thus, the spin parallel levels with $T = 1$ are triply degenerate while the $T = 0$ levels are nondegenerate.

It is a bit involved, but one can show that in the general case the intensity ratio, R, of the strong and weak lines is given by:

$$R = \frac{I + 1}{I} \quad (7)$$

With $I = 1/2$, Eq. (7) obviously predicts the correct intensity ratio for C₂H₂.

For C₂D₂, since both sets of identical nuclei are Bosons, the Pauli Principle insists that $\psi \rightarrow +\psi$ on pairwise interchange of nuclei. In this case, the even J space functions must be combined with (**s**) nuclear spin functions, the odd J functions with (**a**) spin functions. Again, it can be shown in general that the set of functions with $T = 2I$ is always symmetric, the set with $T = 2I - 1$ is antisymmetric, and so on in alternating fashion. Notice that this assignment works in the case of H₂.

One can use Eq. (7) to deduce the nuclear spin of ²H = D from the intensity alternation which you will observe in the C₂D₂ spectrum. The Pauli Principle can then be confirmed in the case of C₂D₂ by noting that the even J levels are associated with (**s**) nuclear spin functions while the odd J levels are associated with (**a**) spin functions.

³ Note that this use of *ortho* and *para* has nothing in common with the use of these terms in organic nomenclature!

Experimental

A 5 cm quartz window gas cell is available for use in the near IR. The instructor will demonstrate use of the Lambda 9. You should be familiar with all controls before you begin solo operation.

Both spectra will be recorded under the highest resolution conditions consistent with an acceptable signal to noise ratio. As was the case with HCl, the natural rotational line width is far less than the resolution limit of the instrument. We will strive to record the peak positions as accurately as possible while separating adjacent rotational lines as much as possible. The various parameters that govern the attainable resolution of the instrument will be discussed during the laboratory period.

C₂H₂ is readily synthesized by reacting calcium carbide, CaC₂, and H₂O. Substitution of D₂O for H₂O yields C₂D₂.

Calculations

Compute for both C₂H₂ and C₂D₂ at least 12 values of B_v⁰. Centrifugal distortion effects may be noticeable in the B_v⁰ values computed from lines of higher J⁰. Compute mean values of B_v⁰ and the uncertainty of both mean values at the 95% confidence limit (see S & G, p. 32). Compute I_{C₂H₂} and I_{C₂D₂} and finally r_{CH} and r_{CC} each with its uncertainty (derived from the uncertainty in mean B_v⁰).

Choose a series of six or so adjacent rotational lines in the P branch of each spectrum. Compute the mean value of the odd J⁰ peak heights and the mean value for the even J⁰ peak heights for this series of adjacent lines. The P branch is chosen because individual lines are better separated; the average of 3 or 4 either even or odd J⁰ lines is computed to approximately correct for the Boltzmann factor weighting of the individual lines. Next, compute the ratio of mean peak heights for the series. As discussed above, the odd J⁰ to even J⁰ ratio should be three for C₂H₂.

Discussion

Do you note any consistent trend with increasing J⁰ in the values of B_v⁰ calculated for either C₂H₂ or C₂D₂? A trend which depends strongly on J⁰ (i.e., ∝ J^{0 3}) would be evidence that you have observed centrifugal distortion and that your B_v⁰ values for high J⁰ are in error because of failure to correct for stretching.

How do your values of the ground state bond lengths and their calculated

uncertainty limits compare with the literature values⁴ of $r_{CC} = 1.2088 \pm 0.0002 \text{ \AA}$ and $r_{CH} = 1.0566 \pm 0.0003 \text{ \AA}$?

Use your calculated value of the intensity ratio, R , for C₂D₂ along with Eq. (7) to compute I for the deuterium nucleus. Your value may be too large because the measured R is too small as the result of band overlap. Use the true value of $I = 1$ and the general discussion given in the theory section to calculate allowed values of T for C₂D₂. What is the degeneracy of each state of given T ? Recalling that it is the value of T which determines whether a state is (**s**) or (**a**), what are the total number of (**s**) and the total number of (**a**) nuclear spin states for C₂D₂? Does the ratio of these totals agree with your observed R ? Are the (**s**) and (**a**) nuclear spin functions associated with the proper values of J'' to validate the Pauli Principle in the case of C₂D₂?

⁴ W. J. Lafferty, E. K. Plyler, and E. D. Tidwell, *J. Chem. Phys.* **37**, 1981 (1962).