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# The Infrared Spectra of C<sub>2</sub>H<sub>2</sub> and C<sub>2</sub>D<sub>2</sub>

## An experiment on molecular structure and symmetry

It is a fundamental postulate of the quantum mechanics that atomic particles of the same kind are indistinguishable. Even so, the undergraduate rarely does an experiment for himself which supports the need for this postulate. Therefore one of the goals of the search for undergraduate experiments in spectroscopy was to find an exercise, such as this one, which clearly focuses attention on the importance of symmetry in determining the properties of molecules.

In the present experiment the student obtains and analyzes a portion of the near infrared absorption spectra of C<sub>2</sub>H<sub>2</sub> and C<sub>2</sub>D<sub>2</sub>. The rotational lines in each band show a marked intensity alternation due to the molecular symmetry. In addition, by calculating the rotational constants for the two isotopically different molecules, the student obtains enough data to solve for the C≡C and C—H bond lengths. This provides an example of the standard spectroscopic method of determining the structure of polyatomic molecules.

For a variety of reasons, in addition to those listed above, the  $\nu_1 + \nu_3$  bands of acetylene were chosen for this experiment. One of the most important is that since C<sup>12</sup> has a nuclear spin quantum number equal to zero, the calculation of the statistical weights of the rotational states of acetylene is exactly parallel to that for *ortho*- and *para*-hydrogen. Therefore this experiment fits well with a common topic in physical chemistry lectures. In addition, the  $\nu_1 + \nu_3$  bands fall in a region of the spectrum which is easily observed in high resolution on the commonly available ultraviolet-visible spectrophotometers whose range extends into the near infrared. Also the bands are intense enough that a small sample cell can be used, and are relatively free from overlapping bands.

### The Experiment

The spectra shown in Figures 1 and 2 were recorded on a Cary Model 14 spectrophotometer and reproduced photographically. In both figures the zero of absorbance is arbitrary. In Figure 1 the acetylene was diluted with air to obtain a better looking trace, but the experimental data were taken with the gases at 1 atm pressure and a chart scale of 15 Å/in. This made it possible to read the relative positions of the absorption lines to 0.5 Å or better. Since it is the spacing of the lines which is of primary concern in this experiment, no attempt was made to obtain an absolute

calibration of the wavelength scale of the spectrophotometer.

The gases were prepared by mixing calcium carbide and either H<sub>2</sub>O or D<sub>2</sub>O right in the absorption cell. After the reaction subsided, the cell was loosely corked (because some gas evolution continued) and the windows were warmed a bit to evaporate the moisture which had condensed there. (A hot surface would be safer for this than a flame.) There is no point in drying the calcium carbide because the isotopic purity of the acetylene is not important and the water or D<sub>2</sub>O vapor in the cell does not produce interfering absorptions.

### Theory

Acetylene and C<sub>2</sub>D<sub>2</sub> are linear, symmetrical molecules. Therefore the selection rule for the  $\nu_1 + \nu_3$  band, in which the fluctuations in the dipole moment are parallel to the molecular axis, is that the rotational quantum number  $J$  may change by only  $\pm 1$ . This results in a band which has the same appearance as a rotation-vibration band for a diatomic molecule, and the theoretical treatment of the band is also very similar (1a). Since this kind of spectrum has been described in many textbooks as well as articles in THIS JOURNAL (2, 3), it is not necessary to discuss it in detail here. Instead, the results of the theoretical analysis will simply be asserted along with references to places where the derivations can be found.

For any given state specified by quantum numbers  $v$  and  $J$ , the vibrational plus rotational energy in wavenumbers of a linear molecule can be represented with sufficient accuracy by the formula

$$G(v) + F(J) = G(v) + B_v J(J+1) - DJ^2(J+1)^2 \quad (1)$$

where  $G(v)$  is the vibrational energy,  $B_v$  is the rotational constant, (which varies with the vibrational quantum state), and the constant  $D$  describes the centrifugal distortion of the molecule (1b, 4a). By combining the selection rule  $\Delta J = \pm 1$  with eqn. (1), it can be shown that all the rotational lines in the band resulting from a transition from one vibrational state to another can be fit by the cubic equation:

$$\nu = \nu_0 + (B_v' + B_v'')m + (B_v' - B_v'')m^2 - 2Dm^3 \quad (2)$$

where  $\nu_0$  is the change in vibrational energy,  $B_v'$  and  $B_v''$  are the rotational constants for the upper and lower states respectively, it is assumed that  $D' = D''$ , and  $m$  is a serial number assigned as in the figures (4b). (In the *R* branch,  $m = J'' + 1$ ; in the *P* branch,  $m = -J''$ ). Therefore by fitting a cubic equation to the wavenumbers of the lines in the band, it is possible to obtain the coefficients of  $m$  and  $m^2$  and hence the

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rotational constants for the upper and lower states,  $B_v'$  and  $B_v''$ .

If the calculations are to be done by hand, there is a simpler way of obtaining the rotational constants (1c). When describing this method, it is traditional to number the lines according to the value of  $J''$ , the rotational quantum number in the lower state of the transition giving rise to the line. Thus  $P(5)$  is the line in the  $P$  branch in which  $J'' = 5$ . For a given value of  $J''$ , the lines  $R(J'' - 1)$  and  $P(J'' + 1)$  have the same upper state, and therefore the difference between the wavenumbers of these lines is equal to the energy difference of the states  $J'' + 1$  and  $J'' - 1$ . In other words, by taking this difference, the properties of the upper vibrational state have been eliminated. Furthermore, by using eqn. (1) it can be shown that this difference is equal to

$$\begin{aligned}\Delta_2 F'' &= F''(J + 1) - F''(J - 1) \\ &= (4B'' + 6D'')(J + 1/2) + 8D''(J + 1/2)^3 \quad (3) \\ &\approx 4B''(J + 1/2) + 8D''(J + 1/2)^3\end{aligned}$$

where the last approximation is justified by the fact that  $D$  is usually about  $10^6$  times smaller than  $B$ . Therefore a plot of  $\Delta_2 F''$  versus  $J + 1/2$  should give a line with an initial slope of  $4B''$ . In the case of the  $\nu_1 + \nu_3$  acetylene bands, the cubic term in eqn. (3) remains small enough that it can be neglected without serious error. As a result  $\Delta_2 F''/(J + 1/2)$  has the constant value of  $4B''$ , so that calculating its average value from all possible pairs of lines gives a good value for  $B''$ . The method of obtaining bond lengths from the rotational constants for  $C_2H_2$  and  $C_2D_2$  is discussed by Herzberg (1d).

The intensity alternation in the acetylene spectrum is due to the fact that there are three times as many molecules in the rotational states with odd  $J$  as in the states with even  $J$ . At high enough temperatures, this is also true for normal hydrogen, and is explained in terms of the quantum mechanical postulate that particles of the same kind are indistinguishable. As has already been mentioned, the business of working out the statistical weights of the rotational levels is exactly parallel for hydrogen and acetylene (1e). Since the hydrogen case has been well described (4c, 5, 6), it is not necessary to repeat the analysis here. The statistical weights for the rotational levels of  $C_2D_2$  are also the same as for  $D_2$ , and the population of the  $J$  even levels is twice that of the  $J$  odd levels.

### Student Procedures

The sample preparation is simple enough that each student can obtain his own spectrum if the spectrophotometer is available. However the important part of the experiment is having the student derive the equations used in analyzing the spectra and carry out the analysis.

Assigning quantum numbers to the  $C_2D_2$  spectrum is not entirely straightforward because of the presence of hot bands, which are due to absorption by molecules in excited vibrational states, and are discussed more below. However there should be no trouble with  $C_2H_2$ . Once this spectrum has been assigned, the student should observe the intensities of the lines, paying particular attention to the comparison of lines in the  $P$  and  $R$  branch with the same value of  $J''$ . Since the dominant factor in determining the relative

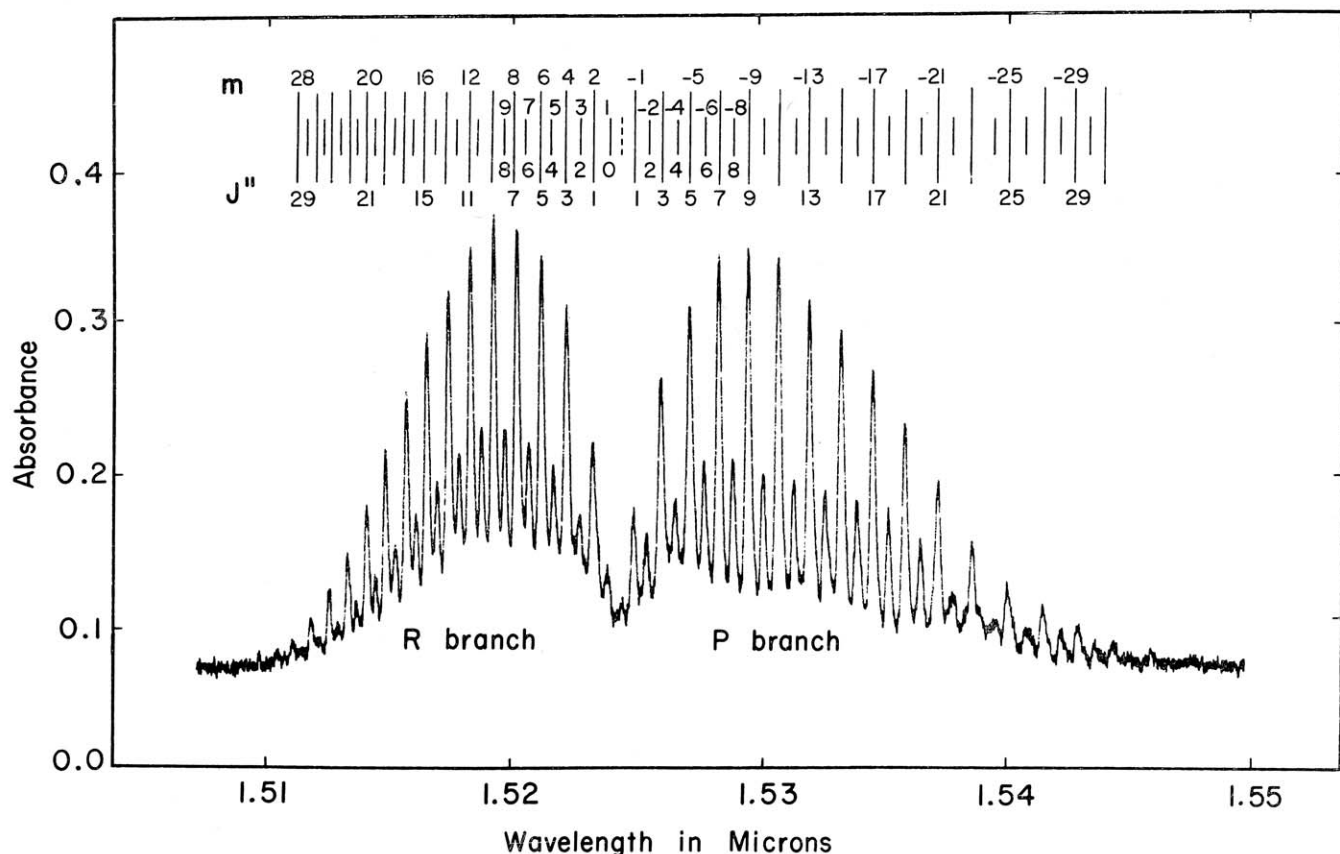


Figure 1. The  $\nu_1 + \nu_3$  band of  $C_2H_2$  observed with about 1/2 atm in a 10 cm cell. The zero of absorbance is arbitrary.

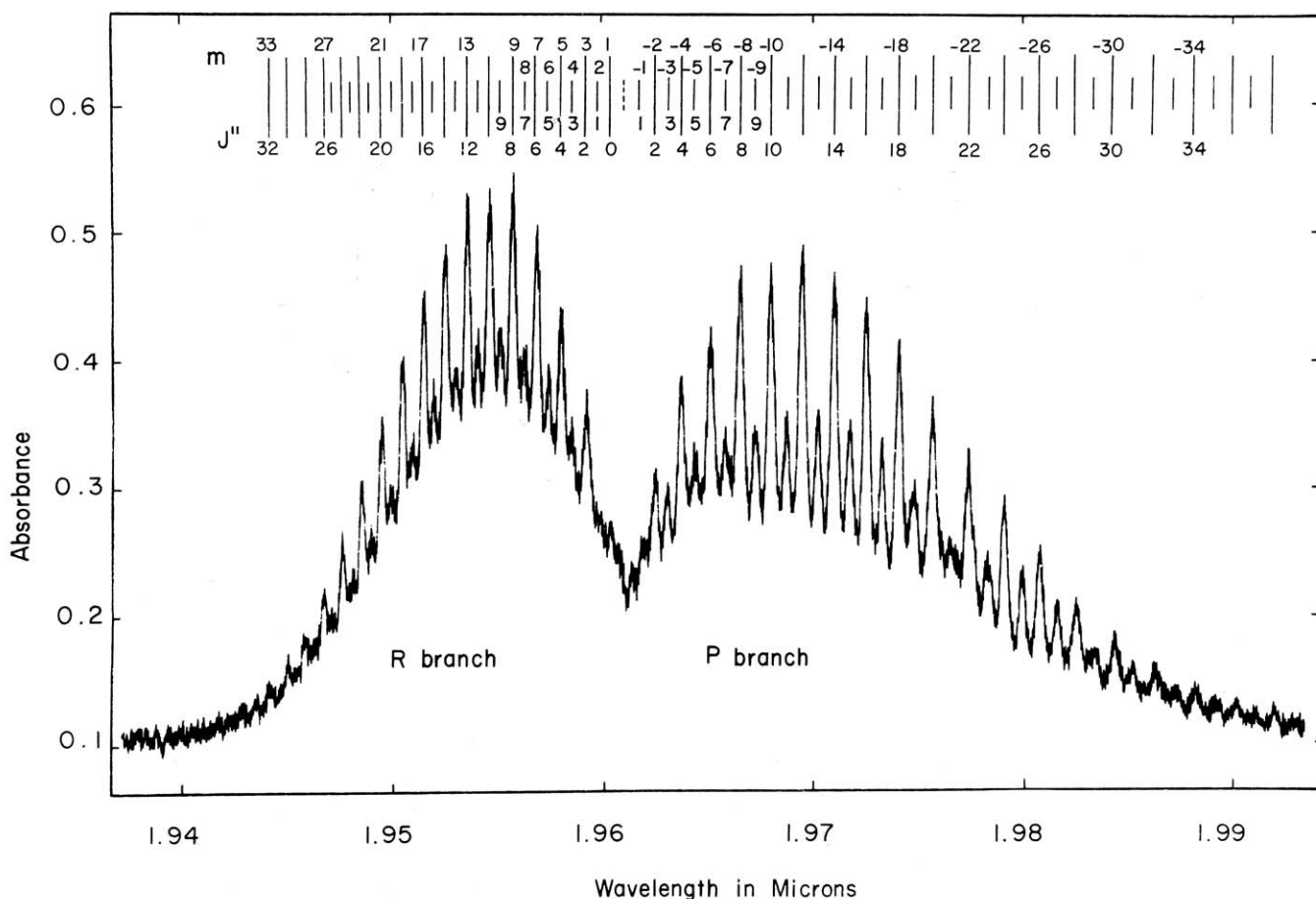


Figure 2. The  $\nu_1 + \nu_3$  band of  $\text{C}_2\text{D}_2$  observed at a pressure of about 1 atm in a 10 cm cell.

intensities is the distribution of molecules over the various rotational levels of the lower vibrational state, these pairs of lines have nearly the same intensity. However the intensities in the *R* branch are slightly larger because the multiplicity of the upper state is larger for a given  $J''$  (4*d*). Once the student has become familiar with this pattern of intensities, assigning the  $\text{C}_2\text{D}_2$  spectrum becomes simple.

The business of fitting a cubic equation to the data is tedious enough that this is best done by computer. Programs for fitting polynomial expressions are commonly available, or a program which has been written specifically for this task by the author can be used (3). The advantages of the specialized program are that it is designed for efficient use by a laboratory class, it converts wavelengths to wavenumbers, and it prints out a table indicating how well the calculated equation fits the spectrum, which makes it easy to spot errors in the data.

If the calculations are to be done by hand, the student should be allowed several hours time with a desk calculator to obtain successively the reciprocal of the wavelength of 50 to 60 lines for each isotope, 25 to 30 differences  $\Delta_2 F''$ , the same number of quotients  $\Delta_2 F''/(J'' + 1/2)$ , and then the average of these quotients.

If the student has already examined the spectrum of several isotopically substituted HCl molecules, he has seen evidence that the *equilibrium* bond lengths in a molecule do not change on isotopic substitution. However he also realizes that the effective bond lengths in

the ground vibrational state are slightly different. Unfortunately, in this experiment it is not practical for the student to obtain the dependence of the rotational constant on the number of quanta in each of the four normal modes and then calculate the equilibrium rotational constant for each isotope. Therefore it is necessary to make the good approximation that the bond lengths are the same in the ground vibrational state for  $\text{C}_2\text{H}_2$  and  $\text{C}_2\text{D}_2$ .

## Results

One important result is immediately apparent: the spectra show an intensity alternation due to the different statistical weights of the rotational levels with odd and even values of  $J$ , and the odd levels are favored in  $\text{C}_2\text{H}_2$  while the even levels are favored in  $\text{C}_2\text{D}_2$ . It would also be interesting to obtain the  $\nu_1 + \nu_3$  band of  $\text{C}_2\text{HD}$  and observe that destroying the molecular symmetry also destroys the intensity alternation. Unfortunately this band is not easily recorded because it is quite weak. However a good reproduction of it is widely available (7), along with a table giving the wavenumbers of each of the rotational lines, so the student can easily see what kind of results are obtained with a specialized spectrograph and even make use of the data himself.

The experiment is also accurate enough to produce good data for bond lengths. Using a least squares fit of a cubic equation to spectra like those shown in Figures 1 and 2 resulted in rotational constants in the ground vibrational state of  $1.1742 \text{ cm}^{-1}$  for  $\text{C}_2\text{H}_2$

and  $0.8478\text{ cm}^{-1}$  for  $\text{C}_2\text{D}_2$ . These are to be compared with recent values (8) of  $1.17654 \pm 0.00004\text{ cm}^{-1}$  and  $0.84794 \pm 0.00005\text{ cm}^{-1}$ . The rotational constants obtained here lead to bond lengths of  $r_{\text{CC}} = 1.213\text{ \AA}$  and  $r_{\text{CH}} = 1.055\text{ \AA}$ , which are within 0.5% of the recent values of  $1.2088 \pm 0.0002$  and  $1.0566 \pm 0.0003\text{ \AA}$  (8). These effective bond lengths in the ground vibrational state should not be confused with the equilibrium bond lengths, which are  $r_{\text{CC}} = 1.203_1\text{ \AA}$  and  $r_{\text{CH}} = 1.060_8\text{ \AA}$  (9).

As has been mentioned, the  $\nu_1 + \nu_3$  bands are overlapped by hot bands, and this is particularly severe in the case of  $\text{C}_2\text{HD}$  (7). Plyler and Gailer have published a high resolution spectrum of the  $\nu_1 + \nu_3$  band of  $\text{C}_2\text{D}_2$  which clearly shows the presence of a hot band that explains the puzzling appearance of Figure 2 in the region near  $m = 0$  and the strange shape of the  $m = -21$  line (10).

If there is time to do so, it would also be interesting for the student to record the  $\nu_1 + \nu_5$  band of acetylene which appears between  $2.4$  and  $2.5\mu$ . This is a perpendicular band (the fluctuations in the dipole moment have a component perpendicular to the molecular axis) and therefore transitions with  $\Delta J = 0$  are allowed and give rise to a  $Q$  branch (1a). Here again the  $P$  and  $R$  branches are easily resolved so that the intensity alternation can be seen, but the lines of the  $Q$  branch are so closely spaced that they appear as one very strong absorption line. Observing this spectrum would acquaint the student with the common form of infrared bands.

For the student who is gifted in understanding theoretical arguments, it would be possible to become familiar with the derivation which shows that finding bands with intensity alternation and no  $Q$  branch such as in Figures 1 and 2 proves that acetylene must be linear and symmetrical (1f). Hence these two spectra, together with the carbon-hydrogen analysis, molecular weight and atomic weights, serve to completely determine the molecular structure.

#### Further References

A person wishing to become familiar with the litera-

ture on the infrared spectra of acetylene and the isotopically substituted acetylenes should begin with Reference (9), which provides a good key to earlier work. A table of the wavenumbers of the lines in the  $\nu_1 + \nu_3$  band of  $\text{C}_2\text{D}_2$  has been published by Allen, Blaine, and Plyler (11). No such table has been found for  $\text{C}_2\text{H}_2$ , but tables for many other bands involving the ground vibrational state of  $\text{C}_2\text{H}_2$  have been published by Wiggins, Plyler, and Tidwell (12). The presence of hot bands in the  $\nu_1 + \nu_2$  band of  $\text{C}_2\text{H}_2$  is shown by a portion of a very high dispersion spectrum given by Rank, *et al.* (13).

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