Chapter XIV  Spectroscopy

APPARATUS

Medium- or high-resolution infrared grating or FTIR spectrometer; gas cell with sapphire, NaCl, or KBr windows; vacuum line (with pressure gauge) for filling cell; cylinder of HCl gas with needle valve; three-neck round-bottom flask; reflux condenser; glass-stoppered dropping funnel; two traps, one with a stopcock on each arm; oil bubbler; exhaust hood; heating mantle; CO and CH$_4$ gas for calibration check (optional).

Heavy water (2.5 mL at least 95 percent D$_2$O); benzoyl chloride (70 g); ice or Dry Ice and isopropanol; liquid nitrogen; or a 5-L flask of DCl gas (available from Cambridge Isotope Laboratories, 20 Commerce Way, Woburn, MA 01801, and other suppliers of isotopically substituted compounds).

REFERENCES


GENERAL READING


EXPERIMENT 38

Vibrational–Rotational Spectra of Acetylenes

In this experiment, several vibrational-rotational infrared bands of C$_2$H$_2$ and C$_2$D$_2$ will be recorded at medium to high resolution (~1 cm$^{-1}$). These spectra will be analyzed to extract rotational constants for use in the calculation of accurate values for the C—H and C—C bond lengths. The role of symmetry and nuclear spin in determining the activities
and intensity patterns of the spectral transitions is also examined. From such considerations, the infrared bands can be assigned to specific modes of vibration and values can be deduced for the fundamental vibrational frequencies of C\textsubscript{2}H\textsubscript{2} and C\textsubscript{2}D\textsubscript{2}.\textsuperscript{1,2}

### THEORY

**Vibrational Levels and Wavefunctions.** Acetylene is known to be a symmetric linear molecule with \( D_{\text{ab}} \) point group symmetry and \( 3N - 5 = 7 \) vibrational normal modes, as depicted in Table 1. Symmetry is found to be an invaluable aid in understanding the motions in polyatomic molecules, as discussed in detail in Refs. 3 through 9. Group theory shows that each vibrational coordinate and each vibrational energy level, along with its associated wavefunction, must have a symmetry corresponding to one of the symmetry species of the molecular point group. The \( D_{\text{ab}} \) symmetry species corresponding to the different types of atomic motion in acetylene are indicated in the table. Motions that retain the center of inversion symmetry, such as the \( \nu_1, \nu_2, \) and \( \nu_4 \) modes of Table 1, are labeled \( g \) (gerade, German for even), while those for which the displacement vectors are reversed on inversion are labeled \( u \) (ungerade, odd). Modes involving motion along the molecular axis (\( z \)) are called parallel vibrations and labeled \( \Pi \), while those involving perpendicular motion are labeled \( \Sigma \) and are doubly degenerate since equivalent bending can occur in either \( x \) or \( y \) directions. From the appearance of the nuclear displacements, it can be seen that only the \( \nu_3 \) and \( \nu_5 \) modes produce an oscillating change in the zero dipole moment of the molecule and hence give rise to infrared absorption.

From the harmonic-oscillator model of quantum mechanics, the term value \( G \) for the vibrational energy levels for a linear polyatomic molecule can be written as

\[
G(u_1, u_2, \ldots) = \sum_{i=1}^{3N-5} \frac{\hbar^2}{2m_i} (u_i + \frac{1}{2}) (1)
\]

### TABLE 1 Fundamental vibrational modes of acetylene

<table>
<thead>
<tr>
<th>Normal mode</th>
<th>Symmetry species</th>
<th>Description</th>
<th>Activity, band type(^a)</th>
<th>( \text{C}_2\text{H}_2 )</th>
<th>( \text{C}_2\text{D}_2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>H—C=C—H</td>
<td>( \Sigma^+ )</td>
<td>Sym. CH stretch</td>
<td>Rp, ( \parallel )</td>
<td>3372.8</td>
<td>2705.2</td>
</tr>
<tr>
<td>H—C=C—H</td>
<td>( \Sigma^+ )</td>
<td>CC stretch</td>
<td>Rp, ( \parallel )</td>
<td>1974.3</td>
<td>1764.8</td>
</tr>
<tr>
<td>H—C=C—H</td>
<td>( \Sigma^+ )</td>
<td>Antisym. CH stretch</td>
<td>IR, ( \parallel )</td>
<td>3294.8</td>
<td>2439.2</td>
</tr>
<tr>
<td>H—C=C—H</td>
<td>( \Pi^+ )</td>
<td>Sym. bend (gerade)</td>
<td>Rd( \parallel )</td>
<td>612.9</td>
<td>511.5</td>
</tr>
<tr>
<td>H—C=C—H</td>
<td>( \Pi^+ )</td>
<td>Antisym. bend (ungerade)</td>
<td>IR, ( \perp )</td>
<td>730.3</td>
<td>538.6</td>
</tr>
</tbody>
</table>

\(^a\) The designations IR or R indicate that the fundamental transition for the mode is infrared- or Raman-active, respectively, and the labels \( \rho \) and \( dp \) give the polarization of the Raman band (see Exp. 35 for a detailed discussion). Parallel bands (\( \parallel \)) have \( PR \) branches, while perpendicular bands (\( \perp \)) show \( PQR \) branches.

\(^b\) The frequencies are from compilations in Refs. 1 and 2.
where \( \tilde{\nu}_i = \nu_i/c \) is the vibrational frequency of mode \( i \) in cm\(^{-1} \) when \( c \) is the speed of light in cm s\(^{-1} \). Additional anharmonicity corrections, analogous to \( \tilde{\nu}_i x_i \) for diatomic molecules (see Exps. 37 and 39), can be added; but these are usually small (1 to 5 percent of \( \tilde{\nu}_i \)) and will be neglected in this discussion. The energy levels of some of the states of acetylene are shown in Fig. 1. Each level is characterized by a set of harmonic oscillator quantum numbers \( y_1 y_2 y_3 y_4 y_5 \), shown at the left of the figure. The fundamental transitions from the ground state are those in which only one of the five quantum numbers increases from 0 to 1; the two infrared-active fundamentals \( \nu_3 \) and \( \nu_5 \) are indicated with bold arrows in the figure.

The set of quantum numbers of a level also serves to define the corresponding wavefunction, which in the usual approximation is written as a product of one-dimensional harmonic oscillator functions,

\[
\psi_{v_1v_2v_3v_4v_5} \ldots = \phi_{v_1}(Q_1) \phi_{v_2}(Q_2) \phi_{v_3}(Q_3) \ldots
\]  

The latter have the form

\[
\phi_{v_i}(Q_i) = \left( \frac{\gamma_i}{\pi} \right)^{1/4} \exp\left( -\frac{\gamma_i Q_i^2}{2} \right) \quad (3a)
\]

\[
\phi_1(Q) = \left( \frac{4\gamma_1}{\pi} \right)^{1/4} \exp\left( -\frac{\gamma_1 Q_1^2}{2} \right) \gamma_1^{1/2} Q_1 \quad (3b)
\]

\[
\phi_2(Q) = \left( \frac{\gamma_1}{4\pi} \right)^{1/4} \exp\left( -\frac{\gamma_1 Q_1^2}{2} \right) (2\gamma_1 Q_1^2 - 1) \text{ etc.} \quad (3c)
\]

where \( \gamma_i = k_i/k_i\tilde{\nu}_i \) and \( k_i \) is the quadratic force constant for the mode of frequency \( \tilde{\nu}_i \). The function \( \phi \) is an even or odd polynomial in the normal coordinate \( Q \), depending on the evenness or oddness of the quantum number \( v_i \). In general \( Q \) is a combination of bond-stretching and angle-bending coordinates that all oscillate in phase and at the characteristic
frequency $\nu_i$. The precise combination is obtained by solution of Newton's equations as described in Refs. 4 through 9, but here we restrict our analysis to a consideration of the role of symmetry in limiting the possible mix of coordinates and the transitions between vibrational levels.

**Symmetry Relations.** Each normal coordinate $Q_i$ and every wavefunction involving products of the normal coordinates, must transform under the symmetry operations of the molecule as one of the symmetry species of the molecular point group. The ground-state function in Eq. (3a) is a Gaussian exponential function that is quadratic in $Q$, and examination shows that this is of $\Sigma_g^+$ symmetry for each normal coordinate, since it is unchanged by any of the $D_{sh}$ symmetry operations. From group theory the symmetry of a product of two functions is deduced from the symmetry species for each function by a systematic procedure discussed in detail in Refs. 4, 5, 7, and 9. The results for the $D_{sh}$ point group applicable to acetylene can be summarized as follows:

\[
g \times g = u \times u = g \quad g \times u = u \times g = u \\
\Sigma^+ \times \Sigma^+ = \Sigma^- \times \Sigma^- = \Sigma^+ \quad \Sigma^+ \times \Sigma^- = \Sigma^- \\
\Sigma^+ \times \Pi = \Sigma^- \times \Pi = \Pi \\
\Pi \times \Pi = \Sigma^+ + \Sigma^- + \Delta \quad \Delta \times \Delta = \Sigma^+ + \Sigma^- + \Gamma \\
\Pi \times \Delta = \Pi + \Phi
\]

(4)

Application of these rules shows that the product of two or more $\Sigma_g^+$ functions has symmetry $\Sigma_g^+$, hence the product function for the ground-state level (00000) is of $\Sigma_g^+$ symmetry.

From Eq. (3b) it is apparent that the symmetry species of a level with $\nu_1 = 1$ is the same as that of the coordinate $Q_i$. In the case of a degenerate level such as (00001), there are two wavefunctions involving the degenerate $Q_5$, $Q_5$ pair of symmetry $\Pi_v$. The symmetry of combination levels involving two different degenerate modes is obtained according to the above rules, and for example, for the (00011) level, one obtains $\Sigma_u^+ \times \Sigma_u^+ \times \Pi_y \times \Pi_y = \Sigma_u^+ + \Sigma_u^- + \Delta_u$. Thus one sees that the product of two degenerate functions gives rise to multiplets of different symmetries. For overtone levels of degenerate modes, a more detailed analysis\(^7,9\) is necessary in which it is found that levels such as (00020), (00003), and (00004) consist of multiplets of symmetry $\Sigma^+ + \Delta, \Pi + \Phi$, and $\Sigma^+ + \Delta + \Gamma$, respectively.

From such considerations the symmetry species of each wavefunction associated with an energy level is determined, and these are indicated at the right in Fig. 1. It is important to realize that this symmetry label is the correct one for the true wavefunction, even though it is deduced from an approximate harmonic-oscillator model. This is significant because transition selection rules based on symmetry are exact whereas, for example, the usual harmonic-oscillator constraint that $\Delta \nu = \pm 1$ is only approximate for real molecules.

**Selection Rules.** The probability of a transition between two levels $i$ and $j$ in the presence of infrared radiation is given by the transition moment $P_{ij}$ [see Eq. (35-8)],

\[
P_{ij} = \left| \psi_i \mu \psi_j \right| d\tau
\]

(5)

For a given molecule, $P_{ij}$ is a physical quantity with a unique numerical value that must remain unchanged by any molecular symmetry operation such as rotation or inversion. Hence, to have a nonzero value, $P_{ij}$ must be totally symmetric: that is, $\Gamma(\psi_i) \times \Gamma(\mu) \times \Gamma(\psi_j) = \Sigma_g^+$, where $\Gamma(\psi_i)$ denotes the symmetry species of $\psi_i$ etc. The dipole moment component $\mu_z$
and the equivalent pair \( \mu_x, \mu_y \) are of symmetries \( \Sigma_u^+ \) and \( \Pi_g \) respectively, for the \( D_{sh} \) point group and are usually indicated in point-group (or character) tables. From this and the rules of Eq. (4), it follows that, for a transition between two levels to be infrared allowed, it is necessary that the symmetry species of the product of the two wavefunctions be the same as one of the dipole components. Thus, from the \( \Sigma_g^+ \) ground state of acetylene, transition to the \( \Sigma_u \) or \( \Delta_g \) members of the (00011) multiplet is forbidden while that to the \( \Sigma_u^+ \) level is allowed by the \( \mu_x \), dipole component. Transitions involving \( \mu_x \) are termed parallel bands, while those involving \( \mu_y, \mu_z \) are called perpendicular bands.

In the case of a Raman transition, the same symmetry arguments apply, except that the dipole function \( \mu \) must be replaced by the polarizability tensor elements \( \alpha_{x,y} \) \( \alpha_{x',y'} \) etc. [see Eq. (35–7)]. For molecules of \( D_{sh} \) symmetry, these elements belong to the symmetry species \( \Sigma_g^+ \), \( \Pi_g \), and \( \Delta_g \) so that the condition for a Raman-active transition is that the product \( \Gamma(\psi_1) \times \Gamma(\psi_2) \) include one of these species. Thus, from the \( \Sigma_g^+ \) ground state of acetylene, Raman transitions to the (10000) \( \Sigma_g^+ \), (01000) \( \Sigma_g^+ \), and (00010) \( \Pi_g \) levels are allowed and can be used to determine the \( \nu_1, \nu_2 \), and \( \nu_3 \) fundamental frequencies, respectively. As can be seen in Table 1, these three modes do not produce a dipole change as vibration occurs, and thus these transitions are absent from the infrared spectrum. This is an example of the “rule of mutual exclusion,” which applies for IR/Raman transitions of molecules with a center of symmetry.

Although direct access to the (10000), (01000), and (00010) levels from the (00000) ground-state level by infrared absorption is thus rigorously forbidden by symmetry, access from molecules in the (00010) or (00001) levels can be symmetry allowed. For example \( \Gamma'(00001) \times \Gamma(00000) = \Pi_g \times \Sigma_g^+ = \Pi_u = \Gamma(\mu_x) \), and so the transition between these levels, termed a difference band, \( \nu_1 - \nu_3 \), is not formally forbidden. As can be seen in Fig. 1, the frequency \( \nu_1 - \nu_3 \) can be added to the fundamental frequency \( \nu_3 \) to give the exact value of \( \nu_1 \), the (10000)–(00000) spacing. Similarly, the \( \nu_2 - \nu_3 \) and \( \nu_3 - \nu_4 \) difference bands are infrared-active and can be combined with \( \nu_5 \) and \( \nu_3 \) to deduce \( \nu_2 \) and \( \nu_4 \), respectively. Such difference bands are detectable for acetylene but will of course have low intensity because they originate in excited levels that have a small Boltzmann population at room temperature. The intensity of such bands increases with temperature, hence they are also termed “hot-band” transitions.

Other nonfundamental bands often appear in infrared spectra and can be used to obtain an estimate of the fundamental frequencies. For example, from the ground state of acetylene, an infrared transition to the (00011) level is permitted and is termed the \( \nu_1 + \nu_3 \) combination band. The difference \( \nu_4 + \nu_3 - \nu_5 \) can be used as an estimate of \( \nu_5 \), but it should be noted that this is actually the separation between levels (00011) and (00001) and not the true \( \nu_4 \) separation between (00010) and (00000). Because of anharmonicity effects, these two separations are not identical and hence the determination of fundamental frequencies from difference bands is preferred.

**Force Constants of Acetylene.** From the vibrational frequencies of the normal modes, one can calculate the force constants for the different bond stretches and angle bends in the \( C_2H_2 \) molecule. In the most complete valence-bond, harmonic-oscillator approximation, the potential energy for \( C_2H_2 \) can be written as:

\[
U = \frac{1}{2} k_r (r_1^2 + r_2^2) + \frac{1}{2} k_R R^2 + \frac{1}{2} k_\delta (\delta_1^2 + \delta_2^2) + k_\alpha \alpha_1 \alpha_2 + k_R R (r_1 + r_2) + k_\delta \delta_1 \delta_2
\]

where \( r \) and \( R \) refer, respectively, to the stretching of the CH and CC bonds and \( \delta \) represents bending of the H—C—C angle from its equilibrium value. The interaction constants \( k_\alpha, k_R \), and \( k_\delta \) characterize the coupling between the different vibrational coordinates and are usually small compared to the principal force constants \( k_r, k_R \), and \( k_\delta \).
The normal modes are combinations of $r$, $R$ and $\delta$ coordinates that provide an accurate description of the atomic motions as vibration takes place. These combinations must be chosen to have a symmetry corresponding to the symmetry species of the vibration. Consequently, for example, there is no mixing between the orthogonal axial stretches, and the perpendicular bending modes and $U$ contains no cross terms such as $r\delta$ and $R\delta$. The process of finding the correct combination of coordinates, termed a normal coordinate analysis, involves the solution of Newton’s equations of motion. This solution also gives the vibrational frequencies in terms of the force constants, atomic masses, and geometry of the molecule.\(^4\)\(^9\)

Such an analysis yields the following relations for acetylene:\(^5\)\(^8\)

$$4\pi^2\nu_1^2 + 4\pi^2\nu_2^2 = \left( k_r + k_r \right) \left( \frac{1}{m_H} + \frac{1}{m_C} \right) + \frac{2(k_R - 2k_R)}{m_C}$$ \hspace{2cm} (7a)

$$4\pi^2\nu_3^2 \times 4\pi^2\nu_4^2 = \frac{2(k_r + k_r)k_R - 2k_R^2}{m_Hm_C}$$ \hspace{2cm} (7b)

$$4\pi^2\nu_3^2 = \left( k_r - k_r \right) \left( \frac{1}{m_H} + \frac{1}{m_C} \right)$$ \hspace{2cm} (7c)

$$4\pi^2\nu_4^2 = \left( k_\delta - k_\delta \right) \left[ \frac{1}{R_{HH}m_H} + \left( \frac{1}{R_{HH}} + \frac{2}{R_{CC}} \right) \frac{1}{m_C} \right]$$ \hspace{2cm} (7d)

$$4\pi^2\nu_5^2 = \left( k_\delta + k_\delta \right) \frac{1}{R_{HH}^2} \left( \frac{1}{m_H} + \frac{1}{m_C} \right)$$ \hspace{2cm} (7e)

When C\(_2\)D\(_2\) frequencies are used, $m_H$ should be replaced by $m_D$. The force constants for acetylene can be calculated from these relations using the measured vibrational frequencies, and the bond lengths can be determined from the rotational analysis described below. If one expresses the frequencies in cm\(^{-1}\) units and the masses in appropriate isotopic mass units, the factors $4\pi^2$ should be replaced by $4\pi^2c^210^{-3}N_0^{-1} = 5.8918 \times 10^{-5}$ (this includes a factor of $10^{-3}$ kg/g mass conversion). This substitution gives the force constants $k_r$, $k_\delta$, $k_r$, and $k_rR$ in N m\(^{-1}\) units and the bending constants $k_\delta$ and $k_\delta\delta$ in units of N m.

**Rotational Levels and Transitions.** The vibrational–rotational energy levels for a linear molecule are similar to those for a diatomic molecule and to a good approximation are given in cm\(^{-1}\) units by the sum $G(v_1v_2\ldots) + F_v(J)$, where\(^5\)

$$F_v(J) = B_v[J(J + 1) - l^2] - D_v[J(J + 1) - l^2]^2$$ \hspace{2cm} (8)

The general label $v$ characterizes the set $v_1v_2v_3\ldots$ and is added to $F_v$ to account for the fact that the rotational constant $B$ and centrifugal distortion constant $D$ change slightly with vibrational level. $B_v$ is related to the moment of inertia $I_v$ by the equation

$$B_v = \frac{h}{8\pi^2cI_v}$$ \hspace{2cm} (9)

where

$$I_v = \sum_{i=1}^{N} m_ir_i^2$$ \hspace{2cm} (10)

and the sum is over all atoms in the molecule, having mass $m_i$ and located a distance $r_i$ from the center of mass of the molecule. The quantum number $l$ characterizes the vibrational angular momentum about the linear axis and is 0, 1, 2, \ldots for levels of symmetries.
Chapter XIV  Spectroscopy

\[ \Sigma, \Pi, \Delta, \ldots, \] respectively. This angular momentum derives from a rotary motion produced about the linear axis by a combination of the degenerate \( x \) and \( y \) bending motions. For acetylene there are two bending modes, requiring \( I_4 \) and \( I_5 \) quantum numbers, which are sometimes shown as superscripts to the \( y_4 \) and \( y_5 \) labels.

The allowed changes in the rotational quantum number \( J \) are \( \Delta J = \pm 1 \) for parallel (\( \Sigma^+ \)) transitions and \( \Delta J = 0, \pm 1 \) for perpendicular (\( \Pi \)) transitions.\(^3,5,7,8\) Parallel transitions such as \( \nu_3 \) for acetylene thus have \( P(\Delta J = -1) \) and \( R(\Delta J = +1) \) branches with a characteristic minimum between them, as shown for diatomic molecules such as HCl in Fig. 37-3 and for the HCN \( \nu_3 \) mode in Fig. 2. However, perpendicular transitions such as \( \nu_3 \) for acetylene and \( \nu_2 \) for HCN (Fig. 2) have a strong central \( Q \) branch (\( \Delta J = 0 \)) along with \( P \) and \( R \) branches. This characteristic \( PQR\)-versus-\( PR \) band shape is quite obvious in the spectrum and is a useful aid in assigning the symmetries of the vibrational levels involved in the infrared transitions of a linear molecule.

The individual lines in a \( Q \) branch are resolved only under very high resolution, but the lines in the \( P \) and \( R \) branches are easily discerned at a resolution of 1 cm\(^{-1}\) or better. As discussed in Exp. 37, it is possible to represent both \( P \) and \( R \) transition frequencies with a single relation:

\[
\tilde{\nu}_m = \tilde{\nu}_0 + B'\nu_2 - B''\nu_2 + (B' + B'')m + (B' - B'')m^2 - 4D_m m^3
\]

(11)

Here \( \tilde{\nu}_0 \) is the rotationless transition frequency corresponding to \( \Delta G \), the spacing between the two vibrational levels with \( J = 0 \). \( B' \) and \( B'' \) are the rotational constants of the upper and lower states, respectively, and the index \( m = -J \) for \( P \) branch lines, \( J + 1 \) for \( R \) branch lines. The centrifugal distortion constants are extremely small (typically \( 10^{-6} \) cm\(^{-1}\)), and it is assumed that \( D'_c = D''_c = D_c \).

FIGURE 2
Portions of the infrared absorption spectrum of HCN. The \( \nu_2 \) bending vibration is a perpendicular band and therefore has allowed \( P, Q, \) and \( R \) branches. The \( \nu_3 \) [C-H stretching] vibration is a parallel band with \( P \) and \( R \) branches only.
Intensities and Statistical Weights. The absolute absorption intensity of a vibrational–rotational transition is proportional to the square of the transition moment $P_{ji}$ times the population in the lower state. $P_{ji}$ varies only slightly for different rotational levels, so the principal factors determining the relative intensity are the degeneracy and the Boltzmann weight for the lower level,

$$I_j \propto g_l g_f \exp \left[ -\frac{\hbar B(J+1)}{kT} \right]$$  \hspace{1cm} (12)

The rotational degeneracy $g_f$ is $2J+1$, and the nuclear-spin degeneracy $g_l$ varies with rotational level only when the molecule contains symmetrically equivalent nuclei.

A complete discussion of the factors that determine $g_l$ is beyond the scope of this book but can be found in Refs. 5 and 7. Briefly, the total wavefunction $\Psi_{tot}$ for molecules with equivalent nuclei must obey certain symmetry requirements upon exchange, as determined by the Pauli principle. Exchange of nuclei with half-integral spin, such as protons ($I = \frac{1}{2}$), must produce a sign change in $\Psi_{tot}$. Such nuclei are termed fermions and are distributed among energy levels according to Fermi–Dirac statistics. Nuclei with integral nuclear spin, such as deuterium ($I = 1$), obey Bose–Einstein statistics and are called bosons; for these the sign of $\Psi_{tot}$ is unchanged by interchange of the equivalent particles. The total wavefunction can be written, approximately, as a product function,

$$\Psi_{tot} = \psi_{elec}\psi_{vib}\psi_{rot}\psi_{ns}$$  \hspace{1cm} (13)

For the ground vibrational state of acetylene, $\psi_{elec}\psi_{vib}$ is symmetric with respect to nuclear exchange, so $\psi_{rot}\psi_{ns}$ must be antisymmetric for $\text{C}_2\text{H}_2$, symmetric for $\text{C}_2\text{D}_2$. For linear molecules the $\psi_{rot}$ functions are spherical harmonics that are symmetric for even $J$, antisymmetric for odd $J$.

The $\psi_{ns}$ spin-product functions for two protons consist of three that are symmetric ($\alpha\alpha, \alpha\beta + \beta\alpha, \beta\beta$) and one that is antisymmetric ($\alpha\beta - \beta\alpha$), where $\alpha$ and $\beta$ are the functions corresponding to $M_f$ values of $+\frac{1}{2}$ and $-\frac{1}{2}$ (see Exp. 32). Thus for $\text{C}_2\text{H}_2$, it follows that $g_f$ is 1 for even $J$, 3 for odd $J$, and the $P$ and $R$ branch lines will alternate in intensity. For $\text{C}_2\text{D}_2$, with spin functions $\alpha, \beta, \gamma$ representing the $M_f$ values of $+1, 0, -1$, there are six symmetric nuclear spin combinations $(\alpha\alpha, \beta\beta, \gamma\gamma, \alpha\beta + \beta\alpha, \alpha\gamma + \gamma\alpha, \beta\gamma + \gamma\beta)$ and three that are antisymmetric to exchange $(\alpha\beta - \beta\alpha, \alpha\gamma - \gamma\alpha, \beta\gamma - \gamma\beta)$. Consequently the even $J$ rotational lines are stronger in this case. The experimental observation of such intensity alternations confirms the $D_{nh}$ symmetry of acetylene, and in the present experiment serves as a useful check on the assignment of the $J$ values for the $P$ and $R$ branch transitions.

**Experimental**

An infrared grating or Fourier-transform (FTIR) spectrometer covering the spectral region from 600 to 4000 cm$^{-1}$ is sufficient for this experiment, although extension to 4000 cm$^{-1}$ is desirable if the $v_5$ band of $\text{C}_2\text{D}_2$ at about 540 cm$^{-1}$ is to be studied. Table 2 indicates the spectral regions of interest and the approximate pressures that give satisfactory intensities. These pressures may require some adjustment depending on the resolution capabilities of the instrument, since the peak absorbance of a narrow line increases as the spectral resolution improves. For the survey scan, a resolution of 4 cm$^{-1}$ is adequate to permit rapid data collection at reasonable signal-to-noise ratio. The regions to be studied in detail should be examined at an expanded scale to permit accurate frequency measurements. A resolution of at least 1.5 cm$^{-1}$ is needed to resolve the rotational structure of the
acetylene bands, and a value of 0.5 cm\(^{-1}\) or better is desirable. (The effect of resolution on the \(\nu_5\) mode of \(\text{C}_2\text{H}_2\) can be seen in Fig. XIX-28.) Detailed instructions for operating the spectrometer will be given in the laboratory.

The \(\text{C}_2\text{H}_2\) sample can be taken from a commercial gas cylinder\(^\dagger\) in the manner described in Exp. 37 or a sample can be synthesized as described below for \(\text{C}_2\text{D}_2\). Acetylene is flammable; there should be no flames in the filling or synthesis area, which, if feasible, should be in a hood. A 10-cm cell fitted with KBr windows should be filled to a pressure of about 300 Torr for a survey scan and for expanded traces of the weak difference band regions as indicated in Table 2. The cell pressure should then be reduced to about 25 Torr so that the strong \(\nu_3\) and \(\nu_5\) fundamentals and the \(\nu_4 + \nu_5\) combination band have a more reasonable intensity. Expanded scans of the latter bands are recorded according to Table 2, preceded by a second survey scan.

\(\text{C}_2\text{D}_2\) can be synthesized by addition of \(\text{D}_2\text{O}\) to calcium carbide using the apparatus shown in Fig. 3. About 2.5 g of calcium carbide is placed in flask \(F\), which is then evacuated to remove traces of \(\text{H}_2\text{O}\); 0.5 mL of \(\text{D}_2\text{O}\) is added with a syringe to flask \(F\) through the rubber septum, and the entire system up to the vacuum stopcock \(V\) is allowed to “cure” at room temperature for about 5 to 10 min to allow deuterium exchange with \(\text{H}_2\text{O}\) adsorbed on the walls of the system. The pressure should be monitored and kept below 1 atm during this period, reducing it if necessary by opening and closing \(V\).

The system is then evacuated, after which the cold traps are put in place and 0.5 mL of \(\text{D}_2\text{O}\) is added to flask \(F\). The pressure will rise and then drop as the \(\text{C}_2\text{D}_2\) is condensed in the storage vessel cooled by liquid nitrogen. When the pressure drops to a few Torr, another increment of \(\text{D}_2\text{O}\) is added and the procedure is repeated until a total of 4 mL has been added. When gas evolution has slowed or stopped, stopcock \(A\) is closed and the reaction flask and water trap are placed in the hood, open to allow any further reaction to occur harmlessly.

\(^\dagger\)Commercial acetylene is widely used for welding purposes and is shipped dissolved in acetone, in which it is extremely soluble. The acetone is retained by a porous filler material within the cylinder so that the discharged acetylene is typically \(>99\) percent. If desired, residual traces of acetone can be eliminated by passage through a Dry Ice/isopropanol trap. In its free state, acetylene may decompose violently; the stability decreases at higher pressures. At pressures below 1 atm, the sampling conditions of this experiment, the gas can be handled safely but one should of course wear safety glasses and exercise reasonable judgment. Unalloyed copper, silver, and mercury should never be used in direct contact with acetylene, particularly when wet, owing to the possible formation of explosive acetylides.
To fill the infrared cell, the system is evacuated with the liquid nitrogen trap still in place. Stopcock $V$ is then closed and the nitrogen Dewar is lowered to allow the storage vessel to warm slowly until the pressure is about 300 Torr. The stopcocks $C$ leading to the infrared cell are then closed, and as warming continues, the system pressure is monitored and adjusted with stopcock $V$ if necessary to keep it below 1 atm. When room temperature is reached, stopcock $B$ can be closed to save some residual $\text{C}_2\text{D}_2$ as “insurance” until all cell pressure adjustments and spectral measurements are completed. The spectral regions of $\text{C}_2\text{D}_2$ indicated in Table 2 should be scanned in the same manner as for $\text{C}_2\text{H}_2$.

Do not open stopcock $B$’ to air with the storage vessel in liquid nitrogen, since liquid oxygen will condense on top of the acetylene, forming a potentially explosive mixture. At the end of the experiment, the acetylene in the infrared cell and in the storage vessel can be disposed of by simply exhausting it through the roughing pump of the vacuum system.

**CALCULATIONS AND DISCUSSION**

**Vibrational Assignments and Fundamental Frequencies.** Examine your survey spectra for $\text{C}_2\text{H}_2$ and $\text{C}_2\text{D}_2$ and note the striking difference between parallel and perpendicular bands. Determine the frequencies of as many of the transitions shown in Fig. 1 as your data allow. In doing this take the $Q$ branch maximum of each expanded spectrum of the $\nu_3$, $\nu_1 - \nu_5$, $\nu_2 - \nu_5$, and $\nu_3 - \nu_4$ perpendicular bands as a measure of these vibrational frequencies. The $Q$ branch of the $\text{C}_2\text{D}_2$ $\nu_2 - \nu_3$ band may be difficult to detect, since it overlaps some of the rotational structure of the $\nu_4 + \nu_5$ band of $\text{C}_2\text{HD}$, an inevitable impurity in $\text{C}_2\text{D}_2$.†

The parallel bands are expected to show a gap between the $P$ and $R$ branches at the position of the missing $Q$ branch as in Fig. 37-3, but in fact such a gap is not seen for the

---

†A higher D/H ratio can be achieved by adding the acetylene to a storage bulb containing 5 mL of 99+ percent D$_2$O and about 1 g of basic alumina. The latter serves to promote the exchange of acidic protons on $\text{C}_2\text{H}_2$ with the D$_2$O and thereby improves the D content of the acetylene. For best results the protons on the basic alumina should first be exchanged by adding a few milliliters of D$_2$O and evacuating the storage bulb prior to addition of more D$_2$O and acetylene. After exchange at room temperature for a few hours, the storage bulb can be cooled in a Dry Ice/isopropanol bath and the enriched C$_2$D$_2$ distilled into the infrared cell.
acetylenes owing to overlap with combination and difference bands. For example, in the expanded trace of the \( \nu_3 \) region of \( \text{C}_2\text{D}_2 \), a weak feature seen at the \( Q \) branch position is not a consequence of a violation of selection rules but rather is due to overlapping \( R(J' = 2) \) branch lines of the difference bands \((\nu_3 + \nu_4) - (\nu_4) \) and \((\nu_3 + \nu_2) - (\nu_2) \). This line happens to be the one of minimum intensity between the \( P \) and \( R \) branches and may be taken as a good approximate value of \( \nu_3 \) for \( \text{C}_2\text{D}_2 \). The corresponding \( \nu_3 \) region for \( \text{C}_2\text{H}_2 \) is more complicated owing to additional overlapping absorption by a combination band \( \nu_2 + \nu_4 + \nu_3 \), and the \( \nu_3 \) value given in Table 1 can be used for subsequent calculations.

Use your data to obtain as many of the fundamental transition frequencies of acetylene as possible, and compare the results with the literature values listed in Table 1. Use these values to assign other combination or difference bands that you observe in the \( \text{C}_2\text{H}_2 \) spectra, using band shapes and symmetry arguments as a guide. Draw a vibrational energy-level diagram from 0 to 4000 cm\(^{-1} \) and show all the vibrational transitions you observe for \( \text{C}_2\text{H}_2 \). For \( \text{C}_2\text{D}_2 \), such an assignment task is more difficult because of \( \text{C}_2\text{HD} \) impurities, for which all the fundamental transitions are allowed because of the lower symmetry. One clue serving to identify the transitions of the latter species is the absence of intensity alternation in the \( P \) and \( R \) branches, since there is no longer exchange symmetry for the protons.

**Rotational Analysis.** The \( \nu_4 + \nu_3 \) parallel combination bands of \( \text{C}_2\text{H}_2 \) and \( \text{C}_2\text{D}_2 \) should be analyzed to obtain the ground-state \( \tilde{B} \) values for each species.† Note the alternation of line intensities and use the intensity predictions from the nuclear spin statistics as an aid in assigning an \( m \) value to each line in the \( P \) and \( R \) branches. The feature that appears at the \( Q \) branch position is due to overlapping \( R \) lines of the difference bands \((2\nu_4 + \nu_3) - (\nu_3) \) and \((2\nu_5 + \nu_3) - (\nu_3) \). These overlapping branches also cause the alternating intensity ratios to differ somewhat from the values of 3:1 and 6:3 predicted for \( \text{C}_2\text{H}_2 \) and \( \text{C}_2\text{D}_2 \).

Tabulate the transition frequencies and fit them to Eq. (11) using a least-squares method. Since this is a parallel transition between two \( \Sigma \) states, \( l' \) and \( l'' \) are zero in this equation. (If a perpendicular fundamental such as \( \nu_5 \) is to be analyzed, a value of \( l' = l'' = 1 \) should be substituted.) Compare your rotational constants for the ground state with the literature values \( B'(\text{C}_2\text{H}_2) = 1.176608 \text{ cm}^{-1} \), \( B'(\text{C}_2\text{D}_2) = 0.847887 \text{ cm}^{-1} \) cited in Refs. 1 and 2. Assume that the structure is unchanged by deuteration and, using Eqs. (9) and (10), calculate the \( \text{C}---\text{H} \) and \( \text{C}---\text{C} \) bond lengths. Use the uncertainties from the least-squares analysis to calculate the uncertainty in these bond lengths and compare your results with values of \( R_{\text{CH}} = 1.0625 \text{ Å} \), \( R_{\text{CC}} = 1.2024 \text{ Å} \) that correspond to the equilibrium positions of the atoms on the potential energy surface.‡

**Force-Constant Determination.** Calculate the force constants for acetylene using Eqs. (7) with the fundamental frequencies and the \( \text{C}---\text{H} \) and \( \text{C}---\text{C} \) bond lengths that you have determined. The bending force constants \( k_b \) and \( k_{bb} \) have units of energy, N m, when the angular displacements are in (dimensionless) radians. Compare values of \( k_b \) and \( k_{bb} \) obtained with \( \text{C}_2\text{D}_2 \) frequencies with those calculated for \( \text{C}_2\text{H}_2 \); how good is the assumption that the force constants are independent of isotopic substitution?

Compute the stretching force constants \( (k_a, k_{aa}, k_{ab}, k_{bb}) \) and discuss their magnitudes in terms of the strengths of the chemical bonds and the likely interactions among these. Two independent determinations of the quantity \( k_a - k\varepsilon \) are obtained using the isotopic data and Eq. (7c), but the calculation of \( k_a + k\varepsilon, k_{aa}, \) and \( k_{ab} \) requires the combined

†The \( \nu_3 \) band of \( \text{C}_2\text{D}_2 \) and the \( \nu_3 \) perpendicular band for both isotopic species are also suitable for analysis. In addition the \( \nu_2, 2\nu_3, \) and \( \nu_3 \) bands of HCN seen in Fig. 2, along with the DCN counterparts, can serve as alternatives for a similar vibrational–rotational study.

‡The \( \nu_3 \) band of \( \text{C}_2\text{D}_2 \) and the \( \nu_3 \) perpendicular band for both isotopic species are also suitable for analysis. In addition the \( \nu_2, 2\nu_3, \) and \( \nu_3 \) bands of HCN seen in Fig. 2, along with the DCN counterparts, can serve as alternatives for a similar vibrational–rotational study.
solution of Eqs. (7a) and (7b) for both isotopic species. In fact, Eq. (7b) for C₂D₂ is redundant and places no new constraint on the force constants, since these factor out of the ratio of Eq. (7b) for the two isotopes:

\[
\frac{v_2^2(D)v_3^2(D)}{v_1^2(H)v_3^2(H)} = \frac{1/m_b + 1/m_c}{1/m_a + 1/m_c}
\]

Equation (14) is an example of a relation derived from a general product rule⁵,⁸ that provides a useful method of checking frequency assignments without doing a detailed normal-coordinate analysis.

**Theoretical Calculations.** Because of its simple structure and limited number of electrons, acetylene is a good candidate for an ab initio quantum mechanical computation using a program such as Gaussian. Examples of such calculations at various levels are described in Foresman and Frisch¹³ and in Hehre et al.¹⁴ Compare your values for the CH and CC bond lengths with those obtained from ab initio calculations. In making comparisons of vibrational frequencies, it should be noted that the quantum calculations yield harmonic values that the molecule would have for motion about the equilibrium position. For C₂H₂ the harmonic frequencies, derived by correcting the experimental values for anharmonicity, are 3497, 2011, 3415, 624, and 747 cm⁻¹ for modes 1 to 5, respectively.⁷ Theoretical values for these from ab initio calculations are generally high by about 10 percent, but agreement with experiment improves as the basis set and level of calculation increase. The vibrational frequencies can also be calculated using semiempirical methods such as PM3 in the program HyperChem, which also provides an animated display of the normal modes.

The spectroscopic value of the C₂H₂(g) heat capacity \(\tilde{C}_v\) can be calculated if desired by using the vibrational partition function and the resulting \(\tilde{C}_v\) (vib) harmonic-oscillator expression given in Eqs. (37-19) and (37-20). Since C₂H₂ has seven normal modes, \(\tilde{C}_v\) (vib) is of course given by an appropriate sum of Eq. (37-20) over the seven values of \(\nu = \hbar \nu/kT\). The experimental value of \(\tilde{C}_p\) for C₂H₂(g) at 298.15 K is 43.93 J K⁻¹ mol⁻¹; thus \(\tilde{C}_v = \tilde{C}_p - R = 35.62\) J K⁻¹ mol⁻¹.

**SAFETY ISSUES**

The acetylene cylinder must be chained securely to the wall or laboratory bench. Work on a vacuum system requires a preliminary review of procedures and careful execution in order to avoid damage to the apparatus and possible injury from broken glass; in addition, the liquid nitrogen used for cold traps must be handled properly (see Appendix C). Safety glasses must be worn. Acetylene is flammable; no flames can be permitted in the synthesis area. Take great care not to allow oxygen condensation to occur in the presence of acetylene (potentially explosive). Carry out as many operations as possible in a fume hood. Dispose properly of excess CaC₂.

**APPARATUS**

Infrared-grating or FTIR instrument with a resolution of 1.5 cm⁻¹ or better; 10-cm gas cell with KBr windows; vacuum line with pressure gauge for synthesis and for filling cell, located in a hood if feasible; cylinder of acetylene.
Round-bottom flask (250 mL) with septum port; syringe; 5 mL D$_2$O (99+ percent); calcium carbide (3 g); D$_2$O trap and 1-L storage flask with stopcocks; two Dewars; Dry Ice/isopropanol slurry; liquid nitrogen; basic alumina (optional).

**REFERENCES**


2. Ibid., p. 912.


**GENERAL READING**


**EXPERIMENT 39**

**Absorption and Emission Spectra of I$_2$**

Although the electronic spectra of condensed phases are typically quite broad and unstructured, the spectra of small molecules in the gas phase often reveal a wealth of resolved vibrational and rotational lines. Such spectra can be analyzed to give a great deal of information about the molecular structure and potential energy curves for ground and excited electronic states. The visible absorption spectrum of molecular iodine vapor in the 490- to 650-nm region serves as an excellent example, displaying discrete vibrational bands at moderate