Rotational constants obtained from spectroscopic measurements of gas phase molecules can be used to determine extremely accurate values for bond lengths and bond angles. This problem concerns the determination of the CH and CC bond lengths of acetylene (HCCH), a linear molecule, from measurement of its gas phase rotation-vibration spectrum with infrared absorption spectroscopy.

a) (5 pts) How many normal modes of vibration does acetylene have?

b) (5 pts) The quantized rotational energy levels based on the rigid-rotor model are given by

\[ E(J) = B_e J(J+1) \]  

where \( B_e \) is the rotational constant and \( J \) the rotational quantum number, which can be any non-negative integer, \( \ldots, J = 0, 1, 2, 3, \ldots \). What is the rotation selection rule for a linear molecule?

c) (5 pts) 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

\[ B_e = \frac{\hbar}{8\pi^2 c I_e} \]

where the moment of inertia is defined by

\[ I_e = \sum_{i=1}^{N} m_i r_i^2 \]

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. What is the value of the \( N \) (the limit of the sum) in the equation for \( I_e \) for acetylene?

d) (5 pts) To a first approximation, we can just add the energy expressions for the harmonic oscillator and rigid rotor to get \( E(v,J) \), the vibrational-rotational energy, as follows:

\[ E(v,J) = h\nu(v+\frac{1}{2}) + B_e J(J+1) \]

However, this is a 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 \( \alpha_e \). When \( \alpha_e \) is included, what is the energy level...
expression for \( E(v,J) \)?

e) (5 pts) We can also take into account vibration-rotation interaction by introducing an effective rotational constant, \( B_v \). Note that \( E(v,J) \) can be rewritten in terms of an effective rotational constant, \( B_v \), which is different for each value of \( v \). Give an expression for \( B_v \) in terms of \( B_e, \alpha_e \) and \( v \).

f) (20 pts) In the vibration-rotational spectrum of linear molecules, the higher wavenumber branch (the R branch) corresponds to the \( \Delta J = +1 \) transitions. The R branch lines are given by:

\[
\nu_R(J) = \nu_0 + (B_0 + B_1)(J+1) - (B_0 - B_1)(J+1)^2
\]

The P branch lines correspond to the \( \Delta J = -1 \) transitions. Give an expression for \( \nu_P(J) \), analogous to the one above for \( \nu_R(J) \).

g) (20 pts) From the expressions for \( \nu_R(J) \) for \( \nu_P(J) \), we can obtain equations that depend only on \( B_0 \) or \( B_1 \). For example, an equation that depends only on \( B_1 \) is:

\[
\nu_R(J) - \nu_P(J) = 2B_1(2J + 1).
\]

Obtain an analogous expression for \( \nu_R(J) - \nu_P(J + 2) \) that depends only on \( B_0 \). Explain how these two equations can be used to obtain values of \( B_e \) and \( \alpha_e \).

h) (10 pts) To calculate \( r_e \) of the CH and CC bonds, the distance to the center of mass of the molecule (rotation axis) has to be determined.

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

\[
R_H = 1/2 \text{ CC bond} + \text{C-H bond length} (r_{CH}).
\]

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

\[
R_C = 1/2 \text{ CC bond length} (r_{CC})
\]

Figure 2 defines \( r_{CH} \) and \( r_{CC} \).
Inserting the radius of $R_H$ and $R_C$ into the equation for the moment of inertia (eq 3) gives:

$$I_e = 2m_H R_H^2 + 2m_C R_C^2$$

Obtain an equation for $I_e$ in terms of $m_C$, $m_H$, $r_{CH}$ and $r_{CC}$.

i) (5 pts) By measuring the spectrum for DCCD, we obtain a different $B_e$, but the bond lengths will be the same. Write an equation for the moment of inertia for DCCD in terms of $m_C$, $m_D$, $r_{CC}$, and $r_{CD}$.

j) (20 pts) From your answer to i), give two equations that would allow you to solve for $r_{CC}$, and $r_{CD} = r_{CH}$.