Physical Chemistry Cumulative Exam October 4, 2018
Professor Trenary

100 points total.

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

$$E(J) = B_e J(J+1) \tag{1}$$

where B_e is the rotational constant and J the rotational quantum number, which can be any non-negative integer, *i.e.*, $J = 0, 1, 2, 3, \ldots$. 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

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

where the moment of inertia is defined by

$$I_e = \sum_{i=1}^{N} m_i r_i^2 \tag{3}$$

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 $E(\mathrm{v},J)$, the vibrational-rotational energy, as follows:

$$E(\mathrm{v},J) = h\nu(\mathrm{v}+½) + B_e J(J+1)$$

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 α_e. When α_e is included, what is the energy level expression for $E(\mathrm{v},J)$?

e) (5 pts) We can also take into account vibration-rotation interaction by introducing an effective rotational constant, B_v. Note that $E(\mathrm{v},J)$ 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, α_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:

$$\nu_\mathrm{R}(J) = \nu_0 + (B_0+B_1)(J+1) - (B_0-B_1)(J+1)^2$$

The P branch lines correspond to the $\Delta J = -1$ transitions. Give an expression for $\nu_\mathrm{P}(J)$, analogous to the one above for $\nu_\mathrm{R}(J)$.

g) (20 pts) From the expressions for $\nu_\mathrm{R}(J)$ for $\nu_\mathrm{P}(J)$, 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 α_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.

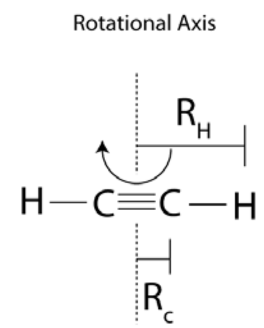

Figure 1. Drawing of C_2H_2 molecule with R_H and R_C.

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

$$R_\mathrm{H} = 1/2 \text{ CC bond} + \text{C-H bond length } (r_\mathrm{CH}).$$

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

$$R_\mathrm{C} = 1/2 \text{ CC bond length } (r_\mathrm{CC})$$

Figure 2 defines r_CH and r_CC.

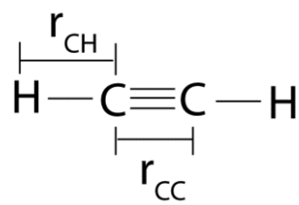

Figure 2. Definitions of r_{CH} and r_{CC}.

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 $r_{CD} = r_{CH}$.