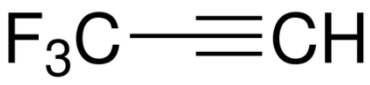
Homework 3, Due: Tuesday, April 1

1. Rotational Energy Levels of a Prolate Symmetric Top:

In this problem you will find rotational eigenvalues of a symmetric top **3,3,3-trifluoro-1-propyne** shown to the right. For this problem, we will assume the molecule is rigid. Choose the Cartesian z axis to be along the C-C bond.



a)- From the notes, the rotational Hamiltonian is:

$$\hat{H} = \frac{1}{2}\left(\frac{L_x^2}{I_{xx}} + \frac{L_y^2}{I_{yy}} + \frac{L_z^2}{I_{zz}}\right)$$

Us the symmetry of this molecule to write the Hamiltonian in terms of two moments of inertia $I_{\parallel}$ and $I_{\perp}$.

b)- Now we will find eigenvalues of this Hamiltonian. Remember that $L^2$and L_z share eigenfunctions. Thus it is convenient to write the Hamiltonian in terms of $L^2$and L_z. The rotational eigenfunctions have quantum numbers J (for angular momentum magnitude) and K (for angular momentum projection along the z axis). Write down the expression for energy in terms of these quantum numbers.

c)- Draw the structure of 3,3,3-trifluoro-1-propyne. For the value of **J=1** draw **<u>all</u>** possible rotational states of the molecule by superposing a vector on your drawing showing the direction of angular momentum vector and a circular loop with an arrow ↻ indicating the sense of rotation of the molecule. Do the same for **J=2**.

d)- Calculate the values of the two moments of inertia $I_{\parallel}$ and $I_{\perp}$ for this molecule given the following **approximate** values of bond lengths. **Assume** tetrahedral geometry around the *sp3* C (i.e. bond angle 109.5°).

sp C-H	108 pm
sp-sp C-C	137 pm
sp3-sp C-C	146 pm
C-F	134 pm

You may choose to do the above by finding the moment of inertia of each atom around an origin of your choice, adding up all moments of inertia matrices, and diagonalizing the resulting total moments of inertia matrix. If you choose the origin to be on the molecule axis, for example on the middle carbon, then the matrix will naturally come out to be diagonal. I suggest using a computer program such as matlab.

e)- Use the $I_{\parallel}$ and $I_{\perp}$ values from part (d) to calculate the energies of all rotational states with quantum numbers J=0 to J=10. To get an idea of the progression of energy levels, plot the energy as a function of the quantum number J. You may use the following matlab code.

```
figure(3)
hold on
for J=0:10
    for K=?:? % the corresponding range of K
        Energy = ?; % Your expression for energy as a function of J and K
        Energy = Energy/(hbar*2*pi)/10^9; % to convert to GHz
plot(J,Energy,'o','MarkerSize',2,'MarkerEdgeColor','k','MarkerFaceColor','k')
    end
end
```

f)- Calculate the **ambient energy at room temperature** in units of GHz and draw a line at that energy on your plot from previous part. At room temperature, roughly how many quanta of energy are found in the rotation of 3,3,3-trifluoro-1-propyne perpendicular to its main axis?

g)- **(Not Required)** Encouraged by this problem, you decide to calculate the energy levels of an **asymmetric top**. If you follow the above procedure, at which step do you get stuck? Why? Can you suggest any solutions?