

NORTH CAROLINA STATE UNIVERSITY

Department of Chemistry

Name _____

Physical Chemistry CH437

Problem Set #4

Due Date: September 22, 2015

Using a Fourier Transform Infra-red (FTIR) spectrometer we can obtain sufficiently high resolution data to resolve the rotational fine structure of the rotation-vibration transitions of HCl. Structural information about the molecule can be obtained from an analysis of this spectrum. We can begin with the identification of P, Q and R branches shown in Figure 1.

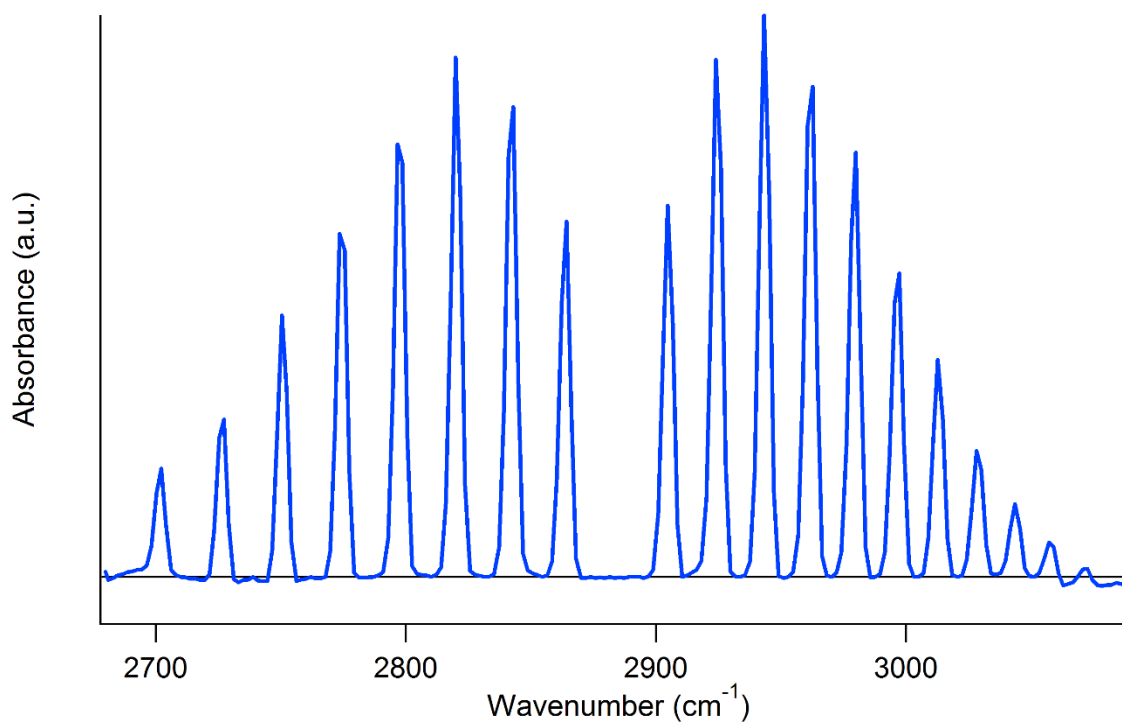


Figure 1. FTIR spectra data obtained on HCl in a 10 cm pathlength cell.

Task 1. Please indicate the P, Q and R branches on the figure. Sketch a diagram showing the change in the rotational quantum number for each transition.

We notice that spacing of the rovibrational lines is not exactly even. Instead, they appear to be getting closer together in the R branch and moving further apart in the P branch. There are two higher order effects that combine to give this appearance. These are anharmonicity and centrifugal distortion. Anharmonicity arises from the fact that the true potential energy surface is not harmonic. Centrifugal distortion arises from the changing bond length of the molecule during rotation. Clearly the rigid rotator approximation is not applicable to a real molecule and the chemical bond acts like a spring that alters the distance between the nuclei. The moment of inertia increases with the bond length squared and therefore the rotational constant decreases as the bond length increases. We can express this phenomenon as a correction to the rotational energy.

$$F(J) = \tilde{B}J(J+1) - \tilde{D}J^2(J+1)^2$$

where \tilde{D} is the centrifugal distortion constant. \tilde{D}_e is related to the vibrational wavenumber,

$$\tilde{D}_e = \frac{4\tilde{B}_e^3}{\tilde{\nu}_e^2}$$

When the above factors are accounted for, the actual energy of a rovibrational state is

$$S(v, J) = \tilde{\nu}_0 \left(v + \frac{1}{2} \right) + \tilde{B}_e J(J+1) - \tilde{\alpha}_e \left(v + \frac{1}{2} \right) J(J+1) - \tilde{D}_e [J(J+1)]^2$$

Where $\tilde{\alpha}_e = x_e \tilde{\nu}_e$ is the anharmonicity. Using equation (1) we can calculate the change in the transition energy given the rotational selection rule:

$$\Delta J = \pm 1$$

$$\Delta F(J) = F(J+1) - F(J)$$

We already know the solution for the \tilde{B} term is $2\tilde{B}(J+1)$. For the centrifugal distortion we have:

$$\tilde{D}[(J+1)^2(J+2)^2 - J^2(J+1)^2] = \tilde{D}[J^2 + 4J + 4 - J^2](J+1)^2 = 4\tilde{D}(J+1)^3$$

Our first level of analysis yields the following empirical relationship that can be used to explain the series of spectral lines.

$$\tilde{\nu}_{obs} = \tilde{\nu}_e + 2\tilde{B}_e m \quad (1)$$

The definition of $m = J+1$ for the R branch, where $\Delta J = +1$ and $m = J-1$ for the P branch where $\Delta J = -1$. If we include anharmonicity ($x_e \tilde{\nu}_e$) and the rotation-vibration interaction ($\tilde{\alpha}_e$) terms the same treatment yields:

$$\tilde{\nu}_{obs} = \tilde{\nu}_e + 2(\tilde{B}_e - \tilde{\alpha}_e)m - \tilde{\alpha}_e m^2 \quad (2)$$

which we can write as

$$\tilde{\nu}_{obs} = a_0 + a_1 m + a_2 m^2$$

with the definitions

$$a_0 = \tilde{\nu}_0$$

$$a_1 = 2(\tilde{B}_e - \tilde{\alpha}_e)$$

$$a_2 = -\tilde{\alpha}_e$$

For the analysis of data using linear least squares the centrifugal distortion term can be included in a cubic fit to the data:

$$\tilde{\nu}_{obs} = a_0 + a_1 m + a_2 m^2 + a_3 m^3$$

where

$$a_3 = 4\tilde{D}_e = \frac{16\tilde{B}_e^3}{\tilde{\nu}_e^2}$$

Definitions:

$\tilde{\nu}$ = the observed vibration frequency in *wavenumbers* cm^{-1} (as indicated by the tilde ~).

$\tilde{\nu}_0$ = the frequency for a vibrational transition for $\Delta J = 0$, i.e. the (absent) Q branch.

\tilde{B}_e = the rotational constant for the equilibrium bond length R

$\tilde{\alpha}_e$ = vibration-rotation interaction.

\tilde{D}_e = centrifugal distortion constant.

The unit of cm^{-1} is the most common unit in spectroscopy. If you want to convert it to s^{-1} you need to use the speed of light, but the units must be cm/s ($c = 2.99 \times 10^{10} \text{ cm/s}$). To convert cm^{-1} to Joules use the conversion factor hc , where h is Planck's constant.

CALCULATION OF MOLECULAR PARAMETERS

We will analyze only the R branch in this assignment. First let us analyze the *frequencies (peak positions)* in the first column of the data.

2904.8
2924.1
2943.3
2962.7
2980.0
2997.4
3012.8
3028.2
3043.7

Task 2. Using an Excel spreadsheet applied to the infrared vibration-rotation spectrum of HCl in terms of the theoretical model discussed above. First try a linear regression fit of the equation:

$$\tilde{\nu}_{obs} = a_0 + a_1 m$$

The linear regression in Excel can be carried out using the LINEST function.

=LINEST(B1:B9,A1:A9,1,1)

To employ a linear fit using LINEST you need to make two columns in A and B as follows

1	2904.8
2	2924.1
3	2943.3
4	2962.7
5	2980.0
6	2997.4
7	3012.8
8	3028.2
9	3043.7

Then outline a square of 4 spaces (2x2) somewhere on the spreadsheet and LINEST will output the slope, intercept and standard errors for both parameters based on linear least squares fitting. Then use **<ctrl> + shift + enter** to implement the linear regression. Report the predicted frequency for the HCl vibrational band, $\tilde{\nu}_o$, and the rotational line spacing, \tilde{B}_e

Task 3. Use a residual plot to show that it is necessary to add a term a_2m^2 to the model. Now the model has the form:

$$\tilde{v}_{obs} = a_0 + a_1m + a_2m^2$$

The linear regression including a quadratic term can also be carried out using the LINEST function.

=LINEST(C1:C9,A1:B9,1,1)

Note that in this case, in order to employ a linear fit that includes a quadratic term using LINEST you need to make three columns in A, B and C as follows

1	1	2904.8
2	4	2924.1
3	9	2943.3
4	16	2962.7
5	25	2980.0
6	36	2997.4
7	49	3012.8
8	64	3028.2
9	81	3043.7

Then outline a square of 6 spaces (2x3) (rows x columns) somewhere on the spreadsheet and LINEST will output the parameters a_2 , a_1 and a_0 their standard errors based on linear least squares fitting. Report the values of \tilde{v}_o , \tilde{B}_e and $\tilde{\alpha}_e$.

Task 4. Examine the residuals. If you look closely you can see that the residuals are not random. Add another term to the polynomial and investigate whether the centrifugal distortion - $\tilde{D}_e J^2(J+1)^2$ could be responsible for such a term.

$$\tilde{\nu}_{obs} = a_0 + a_1 m + a_2 m^2 + a_3 m^3$$

The linear regression including a quadratic term can also be carried out using the LINEST function.

=LINEST(D1:D9,A1:C9,1,1)

Note that in this case, in order to employ a linear fit that includes a quadratic term using LINEST you need to make four columns in A, B, C and D as follows

1	1	1	2904.8
2	4	8	2924.1
3	9	27	2943.3
4	16	64	2962.7
5	25	125	2980.0
6	36	216	2997.4
7	49	343	3012.8
8	64	512	3028.2
9	81	729	3043.7

Then outline a square of 8 spaces (2x4) somewhere on the spreadsheet and LINEST will output the parameters a_3 , a_2 , a_1 and a_0 their standard errors based on linear least squares fitting. From these data please calculate and report $\tilde{\nu}_o$, \tilde{B}_e , $\tilde{\alpha}_e$ and \tilde{D}_e .

Task 5. From \tilde{B}_e you can calculate the moment of inertia I and the bond length R.