Analysis of the FTIR spectrum of HCl

INTRODUCTION

Harmonic oscillator E=h v_e(v+½)

R-branch   P-branch

v_e

R_0

R

E

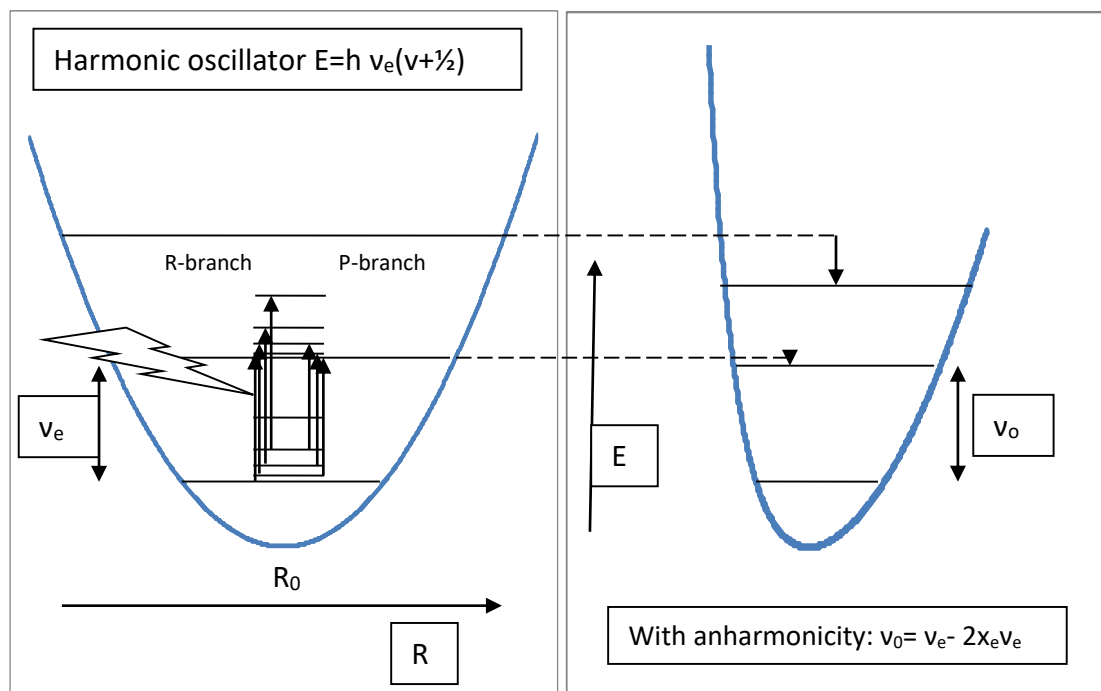v_0

With anharmonicity: v_0= v_e- $2x_ev_e$

Fig. E7.1 Energy diagram for the process of IR absorption by HCl

Using a Fourier Transform Infra-Red (FTIR) Spectrometer it is possible to resolve the rotational fine structure of the rotation-vibration transitions of a small linear molecule like HCl. Structural information about the molecule can be obtained from an analysis of this spectrum. Taking into account only harmonic and rigid terms McQuarrie and Simon derive two different expressions [13.12] for the R branch and [13.13] the P branch. However, they can be combined. Using the variable m, defined below McQ[13.12] and McQ[13.13] both yield:

$$\tilde{v}_{obs} = \tilde{v}_e + 2\tilde{B}m \tag{1}$$

$m \equiv J_i + 1$ for the R branch, where (ΔJ= +1), $m \equiv - J_i$ for the P branch, where (ΔJ= -1).

If we include anharmonicity (x_ev_e) McQ[13.21] and rotation-vibration interaction (α) McQ[13.17] terms the same treatment yields:

$$\tilde{v}_{obs} = \tilde{v}_o + 2(B_e - \alpha)m - \alpha m^2 \tag{2}$$

where:

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

$\tilde{\nu}_o$ = the frequency for a vibrational transition for $\Delta J = 0$, i.e. the (absent) Q branch.
B_e = the rotational constant for the equilibrium bond length R
α = vibration-rotation interaction.

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 x 10^{10} cm/s). To convert cm^{-1} to Joules use the conversion factor hc, where h is Planck's constant.

EXPERIMENT

In this experiment you will run the infrared spectrum of HCl in the vapor phase using an Excalibur Fourier Transform Infra-Red Spectrometer. The intensity of the absorption for each transition is a product of the population of the initial state and the absorption coefficient for the transition. You will use the integrated intensities to test the applicability of the Boltzmann distribution prediction of the populations of the initial states.

The HCl is introduced into a 10 cm quartz cell as two drops of hydrochloric acid, and the spectrum is taken of the vapor in equilibrium with this solution. Quartz transmits between 2500 and 3500 cm^{-1}. That allows the HCl fundamental to be observed, i.e. we will look at the frequency of light that causes the process:

$$HCl(v = 0 ; J_i) \rightarrow HCl(v = 1 ; J_f) \text{ where } J_f - J_i = \Delta J = \pm 1$$
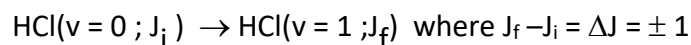
Since we will only look at (v= 0→1), the fundamental frequency, we can only find the energy difference between the ground state and the first excited (vibr.) state, $\tilde{\nu}_o$, not $\tilde{\nu}_e$, the frequency corresponding to the curvature at the bottom of the parabolic potential curve (see McQ[13.22]). For the lines we study, the accompanying rotational change is either $\Delta J = +1$ (for R) or $\Delta J = -1$ (for P).

A. CALCULATION OF MOLECULAR PARAMETERS

First let us analyze the *frequencies (peak positions)* in the first column of the data.

The major part of this assignment is an analysis of the infrared vibration-rotation spectrum of HCl in terms of the theoretical model discussed above
First try a regression fit of the equation: $\tilde{\nu} = a_0 + a_1 m + \varepsilon$
Use a residual plot to show that it is necessary to add a term $+ a_2 m^2$ to the model.
Compare this polynomial (actually quadratic) model with Eq. 2 to identity of the coefficients as:

$$a_0 = \tilde{\nu}_o \qquad\qquad a_1 = 2\,\tilde{B}_e - 2\alpha \qquad\qquad a_2 = -\,\alpha$$

This model allows for vibration-rotation interaction, but ignores the centrifugal distortion term $-D_eJ^2(J+1)^2$ (see McQ[13.23]) Show a plot of observed frequencies and the calculated ν *vs.* m and a residual plot.

If the residuals are not random, it may be necessary to add another term to the polynomial and investigate whether the centrifugal distortion $-D_eJ^2(J+1)^2$ could be responsible for such a term. Show a derivation along the lines of McQ[13.12/13] and use the definitions of m($\rightarrow$Introduction).

From these data you will calculate and report $\tilde{\nu}_o$, $\tilde{B}_e$ and α (and perhaps D_e). From $\tilde{B}_e$ you will calculate the moment of inertia I and the bond length R. Include calculated uncertainties with all calculated quantities using the method of propagation of uncertainties (or errors). Ignore possible covariance between the coefficients a_i in the polynomial model.

Hint: To do the error propagation, first express B_e, I and R in terms of the parameters a_0, a_1, and a_2. Then calculate weights for the variances ($s_e^2(a_{0,\,1,\,2,\,3})$) by taking derivatives. Make sure you report and use the correct units.

B. FITTING BOLTZMANN DISTRIBUTION

Secondly, let us analyze the *intensities* of the peaks. Your data contains two values, both height and area, but one is clearly a better measure than the other, just look at a graph of area vs. frequency and height vs. frequency. One is smoother than the other, take the best one. From the above analysis the value for *m* and thus the initial value of J (J_i) is known. We will indicate the intensity value for a line with a certain initial J value as I_J below.

We will go beyond simply finding the properties of the molecules to examine the prediction of the Boltzmann distribution and the *relative* intensities of the rotational lines. The population, N_J, of the level with rotational quantum number J (with degeneracy g_J) is given by:

$$N_J = (2J+1)exp\left\{\frac{hc\tilde{B}J(J+1)}{kT}\right\}$$

Using this formula we see that $N_0 = 1$ (at J=0). Therefore, the relative population is:

$$\frac{N_J}{N_0} = (2J+1)exp\left\{\frac{hc\tilde{B}J(J+1)}{kT}\right\} \tag{3}$$

The factor g_J is the degeneracy of the level J. Because rotation wave functions are identical to the rotational part of hydrogen wave functions $g_J = 2J+1$. (s, p, d, f, g,..)

The intensity of absorption of a rotational line departing from rotational level J, I_J, is given by:

$$I_J = \epsilon_J N_J \qquad (4)$$

For each line, the absorption coefficient ε_J is given by Herzberg as being *approximately* proportional to the line's frequency ν_J. Therefore the ratio of the intensity of a rotational line originating from rotational level J to that of a rotational level originating from the J = 0 level is:

$$\frac{I_J}{I_0} = \frac{\epsilon_J N_J}{\epsilon_0 N_0} \approx \frac{\nu_J N_J}{\nu_0 N_0}$$

$$(5)$$

And

$$\frac{I_J}{I_0} \approx \frac{\nu_J}{\nu_0}(2J+1)exp\left\{-\frac{hc\tilde{B}J(J+1)}{kT}\right\}$$

In this expression ν_0 is the frequency of the first transition (i.e. first rotational line in the R branch). The mean of the 0 here is that the transition originates from the zero state. It is a 0 -> 1 transition. In general, ν_J corresponds to a J -> J + 1 transition. From Equations 2 and 4 one can derive a formula to plot the relative intensities of different lines such that we should get a straight line. We can linearize the formula by taking the logarithm of both sides:

$$ln\left(\frac{I_J}{I_0}\frac{\nu_0}{\nu_J}\right) - ln(2J+1) = -\frac{hc\tilde{B}}{kT}J(J+1) \qquad (6)$$

This means that if you plot:

$$ln(2J+1) - ln\left(\frac{I_J}{I_0}\frac{\nu_0}{\nu_J}\right) \quad vs. \quad J(J+1)$$

You should get a straight line. From a regression you can extract the temperature. Be sure to include the error in the slope obtained from the fit and then to use propagation of error to obtain an error in your estimated temperature. The correct value should be less than 298 K since the building is usually not that warm during the winter months.

DISCUSSION

Compare calculated molecular parameters with those listed in Simon & McQuarrie p. 499 or another standard source.

Compare the calculated temperature with your best guess of the temperature in the sample chamber.

Why is there no absorption at $\tilde{\nu}_0$?

What is the difference between $\tilde{\nu}_0$ and $\tilde{\nu}_e$? [Cf. McQ & Simon Eq 13.21 (Remember v: 0→1) and see figure E7.1 above]

Infrared Spectroscopy folder is available in the laboratory and contains articles and tables of data dealing with the spectra of diatomic molecules.

Some Excel hints:

To do a quadratic regression create a column of the linear values of x (the A column), a column of the quadratic values of x^2 (the B column) and your y values (the C column). The select a range of 5 rows x 3 columns and type

=linest(C*first*:C*last*,A*first*:B*last*,TRUE,TRUE)

and use Ctrl+Shift+Enter to activate the formula. For the linear model you only need 2 columns, but for the quadratic model you will need three columns (e.g. for a model with ca term more use a column more.) The first row of the linest range contains the coefficients of the model *in reverse order*, i.e. for $Y = a + bX + cX^2$ you get c,b,a. In two additional columns, use these parameters to construct a fit value for each data point and, by subtraction, a residual. Graph the data plus the fit versus m.

Some useful constants:
m_H = 1.007825 au, m_{35} = 34.968853 au m_{37} = 36.965903 au, 1 au = 1.660540 10^{-27} kg.
h = 6.626076 10^{-34} Js, k_B = 1.38066 10^{-23} J/K. c = 2.99792458 10^{10} cm/s.
Careful: $\tilde{B}$ is in cm^{-1} (not m^{-1})

References:

1. Shoemaker, Garland, and Nibler, Experiment 38 and pages 758-763.
2. P. W. Atkins, *Physical Chemistry* (5th ed) 569-576.
3. McQuarrie & Simon, *Physical Chemistry,* Ch 13
4. Herzberg, G. *Infrared and Raman Spectra of Diatomic Molecules*
5. Pattacini, S.C., *J. Chem Educ.*, **1996**, 73, 822.