

CHEM 354: Absorption of Iodine - An Experiment in Molecular Spectroscopy

Objective : Calculate molecular parameters for the ground and excited state of I_2 using UV/Vis absorption spectroscopy.

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1 Background

1.1 Theory

Solid iodine crystals produce a violet vapor above them at room temperature. The gaseous I_2 absorbs light in the yellow region of the visible spectrum resulting in the purple color. The transitions that give rise to this occur between the ground electronic state, X , and an excited electronic state, B . At room temperature, most of the molecules are in the ground vibrational state, $v'' = 0$. These transitions then, for the most part, are from

$$v'' = 0 \rightarrow v' = n$$

where n can range from 0 to ∞ .

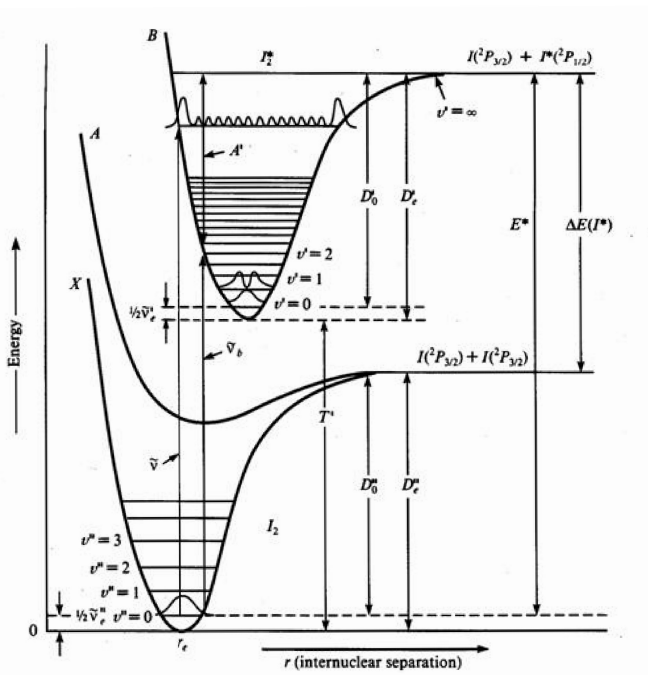


Figure 1: The two Morse potential wells for an I_2 molecule in the ground state (X) and the first excited state (B) displayed beside one another. The notation used in this figure corresponds almost exactly to the notation used here, any changes will be noted in the context they are introduced.

When discussing these transitions it is common practice to work with their wavenumbers, $\tilde{\nu}$ (cm^{-1}) as opposed to wavelengths, λ (nm.).¹ The energy of a molecule in one of the two states is given by the sum of the electronic, vibrational, and rotational energies of the molecule.

$$E_{state} = E_{elec} + E_{vibr} + E_{rot}$$

Rotational energies will be ignored for this experiment. The ΔE for a transition is then given by

$$\Delta E(v', v'') = E_B(v') - E_X(v'') \quad (1)$$

The energy of the electronic states are independent of the vibrational quantum number and will be denoted T'' and T' where the double prime refers to the ground state and the single prime refers to the excited state. The vibrational energy terms will be a function of the vibrational quantum number and will be denoted by $G(v'')$ and $G(v')$. Setting T'' to zero allows $T' = \tilde{\nu}_e$, the distance between the two minima on the potential energy curves (See Figure 1). This allows (1) to be rewritten in a more useful form. Recall that the energy of a photon is given by $E_p = \frac{hc}{\lambda} = hc\tilde{\nu}$. Substituting the above definitions and dividing (1) through by hc gives

$$\tilde{\nu}_{transition} = \tilde{\nu}_e + G(v') - G(v'') \quad (2)$$

1.2 Directly Calculated Parameters

Equation (2) is still useless without expressions for $G(v'')$ and $G(v')$. In a harmonic oscillator, the vibrational energy term can be written as

$$G(v) = \omega_e(v + 1/2)$$

where ω_e is the frequency for infinitesimal amplitudes of vibration² [6]. In practice, the Morse potential is a better fit to real molecules than the harmonic oscillator, we will therefore add in an anharmonicity constant to account for this:

$$G(v) = \omega_e(v + 1/2) - \omega_e\chi_e(v + 1/2)^2$$

Notice that this term implies that the spacings of the energy levels will get smaller as the quantum number increases, this is easy to verify visually in Figure 1. Substituting these forms for $G(v)$ into (2) yields the critical relation for this experiment.

$$\tilde{\nu}_{transition} = \tilde{\nu}_e + \omega'_e(v' + 1/2) - \omega'_e\chi'_e(v' + 1/2)^2 - \omega''_e(v'' + 1/2) + \omega''_e\chi''_e(v'' + 1/2)^2 \quad (3)$$

1.3 Indirectly Calculated Parameters

Convergence Limit E^*

E^* is the energy of the transition from $v'' = 0$ to the top of the excited state potential well (See Figure 1). It is therefore calculated by summing all the vibrational quanta above v to the maximum v_{max} . The energy of the vibrational quanta is given by $G(v + 1) - G(v)$ implying that

$$E^* = \tilde{\nu}_e + \sum_v (G(v + 1) - G(v))$$

¹These symbols may be used interchangeably, but will always be specified by either their units or symbols. It is also important to note that sometimes a value of energy is given in nm. or cm^{-1} , as opposed to the traditional joules or calories.

² ω_e is analogous to ν_o where $\nu_o = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}}$

From the previous section $G(v+1) - G(v) = \omega'_e - 2\omega'_e\chi'_e(v+1)$ and it therefore follows that $v_{max} = \frac{\omega'_e}{2\omega'_e\chi'_e} - 1$. The convergence limit is therefore

$$E^* = \tilde{\nu}_e + \frac{1}{2}[\omega'_e - 2\omega'_e\chi'_e(v+1)][v_{max} - v] \quad (4)$$

E^* should be calculated for each observed $\tilde{\nu}_{transition}$ and a mean and standard deviation reported. The derivation here is paraphrased from [6]

1.3.1 Dissociation Energy D_e

The energy required to separate the molecule into individual atoms is the dissociation energy, D_e . The ground state dissociation energy, D''_o is the distance from the $v'' = 0$ level of the X potential well to the height where it levels out. This is given by the Convergence Limit E^* energy minus the difference in energy between a ground state iodine atom and an excited state atom, $E(I^*)$. This energy has a value of 7859 cm^{-1} [4]. The ground state dissociation energy, D''_o , measured from the bottom of the potential well differs from D''_e by the zero point energy. In the approximations for the anharmonic oscillator used here, this zero point energy is $(\omega''_e/2) - (\omega''_e\chi''_e/4)$. For the dissociation energy of the excited state we simply subtract the distance from the bottom of the ground state potential well from the $v'' = 0$. These results were taken from [6], in summary:

$$\begin{aligned} D''_o &= E^* - E(I^*) \\ D''_e &= D''_o + \frac{\omega''_e}{2} - \frac{\omega''_e\chi''_e}{4} \\ D'_o &= E^* + \frac{\omega'_e}{2} - \frac{\omega'_e\chi'_e}{4} \\ D'_e &= E^* - \tilde{\nu}_e + \frac{\omega''_e}{2} - \frac{\omega''_e\chi''_e}{4} \end{aligned}$$

1.3.2 Force Constant

If the molecule is thought of as two masses attached to a spring, then Hooke's law will apply. As the bond is stretched, there is a force resisting this expansion. This restoring force is given by

$$F = -k(r - r_e)$$

where $r - r_e$ is the extension and k is the force constant. This constant is related to the curvature of the potential energy well and can be calculated by the following from [3]³

$$k = \frac{4D_e}{\omega_e}$$

1.3.3 Excited State Bond Length r'_e

Recall that instead of the harmonic oscillator potential, the Morse potential is a better fit to most diatomic molecules, and has been shown to be an especially accurate fit for iodine [2].

$$U(r - r_e) = D_e(1 - e^{-\beta(r-r_e)})^2 \quad (5)$$

³Depending on whether D''_e and ω''_e or D'_e and ω'_e are used, the force constant for both the ground state molecule or excited state can be calculated.

The three parameters in this model are D_e , β , and r_e . It has been shown previously how to calculate D_e . It can also be shown that⁴

$$\beta = \pi\omega_e\sqrt{2\mu c/D_e h}$$

where h is planck's constant, μ is the reduced mass in kg, and c is the speed of light in cm/s. According to the Franck-Condon principle [2], the most intense absorption band occurs at the transition from the maximum of $\psi_{v''=0}^2$ to the maximum of an excited state $\psi_{v'}^2$. These wavefunctions are shown graphically in Figure 1 where visually this occurs when $r = r_e''$. This maximum is also related to the absorption intensities by the Frank-Condon Principle

$$\frac{I(\nu)}{\nu} \propto |\psi_{v''=0}(R)|^2$$

where ν is the frequency of the vertical transition originating from the internuclear distance R . The maximum of $\frac{I(\nu)}{\nu}$ occurs when $R = r_e''$ as explained in [2]. The quantum number v' for this transition will be denoted v_m . If the Morse potential of the excited state is used (i.e. D_e' , β') then the value of that function at $r = r_e''$ is also given by

$$U(r_e'') = \tilde{v}(v'' = 0 \rightarrow v_m) + \frac{\omega_e''}{2} - \tilde{v}_e$$

. Using this value for $U(r_e'')$ and rearranging the Morse potential for the excited state to solve for r_e'' results in the following

$$r_e' = r_e'' + \frac{1}{\beta'} \left[\ln \left(1 + \sqrt{\frac{U(r_e'')}{D_e'}} \right) \right] \quad (6)$$

In order to use (6), a value for the ground state equilibrium bond distance is needed, from [2] $r_e'' = 2.666 \times 10^{-10}$ m.

1.4 Pre-Lab

1. The absorption spectrum of Br₂ has a peak occurring at a wavelength of $\lambda = 543.75$ nm. What is the corresponding wavenumber and ΔE of this transition? (Use traditional units)
2. The force constant for bromine is $k = 350$ N/m [5] Predict whether the force constant of I₂ be larger or smaller? (Explain)
3. Hypothesize whether the equilibrium bond distance will be longer or shorter for the excited state vs the ground state of I₂.
4. In the calculations for this lab, a multivariate linear regression will be employed. This can be accomplished through Excel⁵ Suppose a certain physical property, f , can be written as a linear combination of two known factors x_1 and x_2 . Given the following data, what is the equation for $f(x_1, x_2)$?

$f(x_1, x_2)$	x_1	x_2
0	0	0
69.666	1	18
71.298	2	19
72.930	3	20

⁴This expression comes from [6] and is not a trivial derivation.

⁵See the references section for a link to a tutorial on using the Excel Data Analysis package.

2 Experimental

Safety Warning: Iodine is volatile and corrosive to the skin. Use gloves and adequate eye protection when handling it. Work in a well-ventilated hood

2.1 Equipment

The lab is equipped with a high resolution Perkin Elmer Lambda 850 UV/Vis Spectrometer. Required materials in addition to this are:

- Crystalline iodine
- 50.0 mm cuvette
- 10.0 mm cuvette
- Parafilm
- Access to data analysis software such as Microsoft Excel or an equivalent program.
- USB Drive⁶

2.2 Procedure

1. Place a few crystals of iodine in the bottom of a 50.0 mm cuvette and add the lid to the top.
2. Secure the lid loosely in place with a small amount of parafilm to minimize any gas leakage. The vapor pressure of iodine at room temperature should be sufficient to saturate the cell with gaseous iodine. If necessary, run the cuvette under warm water to aid in saturating the cell.
3. After switching on the PerkinElmer UV/Vis Spectrometer, turn on the PC and open up the UV WinLab Explorer by clicking on the desktop icon.
4. Double click on the method titled "CHEM 354 Iodine". It should be listed towards the bottom of the list of methods. (See Figure 2 on next page)

⁶The PC with the instrument software is not connected to the internet for security reasons. Therefore, a physical way to take the data out of the lab is necessary.

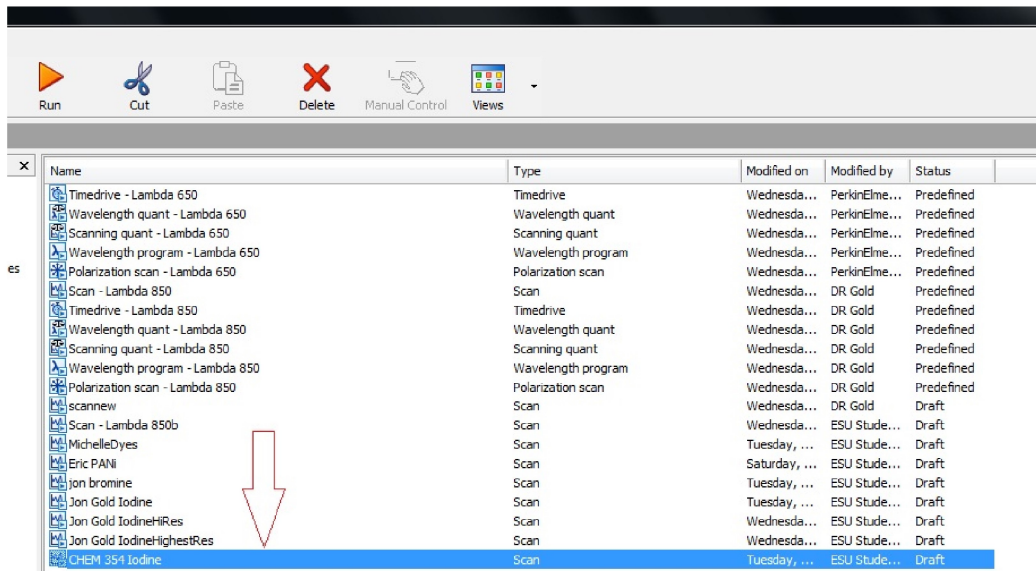


Figure 2: The figure above shows the initial WinLab Explorer screen. Highlighted in blue and in the direction of the red arrow is the method for this experiment.

5. After clicking on the method, the following main screen of the program should appear:

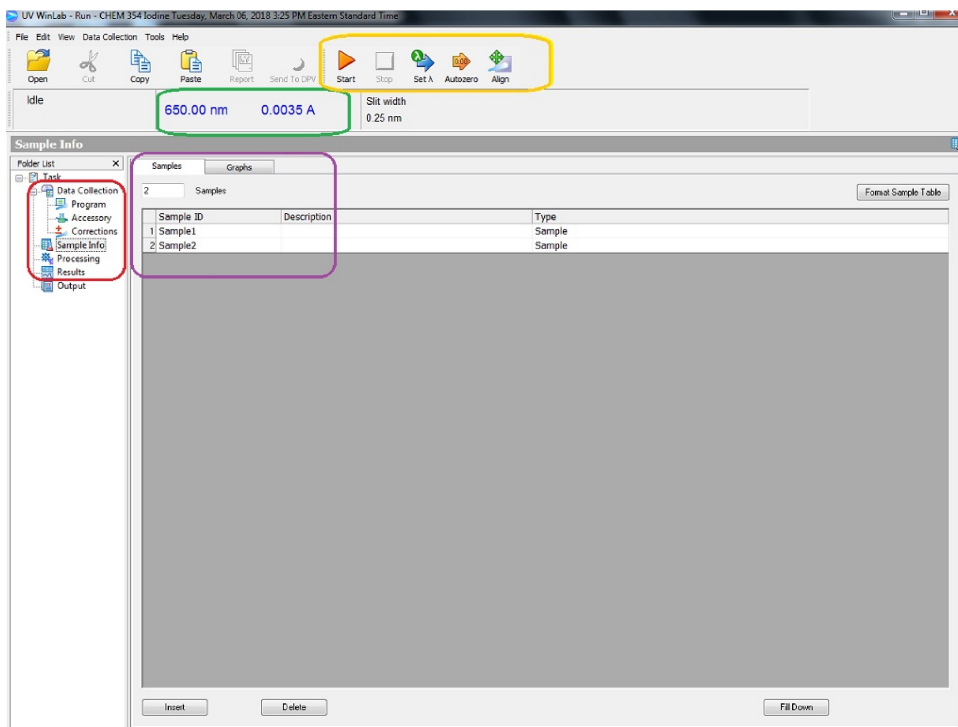


Figure 3: The main screen of the program is shown here. The colored boxes represent the following; **Red:** The various aspects of the method. Clicking on data collection will show the parameters the instrument is set to use, results and sample info are as named, **Orange:** the action buttons to start the instrument and adjust other miscellaneous hardware settings, **Purple:** when sample info is highlighted this tab will show the samples the method is loaded to run, they can only be renamed before they are run but more sample slots can be added as needed using the insert button below, **Green:** where the instrument is currently measuring followed by the resolution.

6. The method will have two sample files ready to go by default. Rename these with the lab group initials or a similarly descriptive name. If more sample files are needed because

10. When the instrument is done taking its 100%T/0A correction, a prompt should appear:

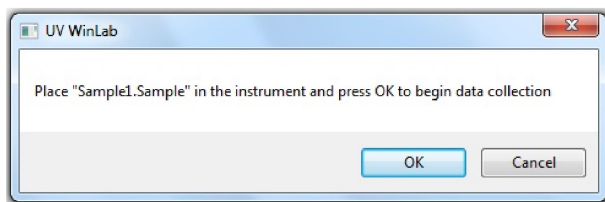


Figure 6: This dialog box should appear after the instrument is done running its background. The 'Sample1' would be replaced with the name of the first sample file.

11. Follow the prompts and place the 50.0 mm cuvette in the sample holder⁷, close the spectrometer with the iodine filled cuvette inside, and hit "OK".
12. The instrument will now begin taking its spectra. The software should automatically switch to observing the graph of the spectra being taken as it runs. If this does not happen on its own, simply click on the "Results" task found in the red box of Figure 3.
13. If the absorbance values are greater than one, then the results will not be meaningful⁸. If this happens, stop the instrument (Orange box Figure 3), remove the cuvette, and restart the procedure using a 10.0 mm cuvette instead. This will also require the sample holder to be switched from the 50.0 mm one to the 10.0 mm one. The shorter path length should lower the absorbance values to an acceptable range.
14. Once the resolution of one of the spectra is acceptable, move on to step 15. Until then, take more spectra until the individual peaks are clear⁹.
15. Export the best spectra out of the program and onto a USB drive. Click on "File" → "Export" → In the upper portion designate where the file will be saved on the PC, and in the bottom portion click on "XY Data(raw)" and leave the default "Samples by Columns" selected. Clicking on "Export" in the dialog box will complete the process.
16. The rest of the lab will consist of making the spectra presentable and running calculations. An example spectra is provided on the next page:

⁷Make sure the correct sample holder is installed in the spectrometer, if not, ask the lab instructor to switch it for the right one

⁸Recall from previous General Chemistry courses that if this happens, then the Beer's Law plot is no longer linear.

⁹NOTE: This step is important! The majority of the calculations are assigning quantum numbers to peaks, make sure they are easily distinguished on the spectra before moving on.

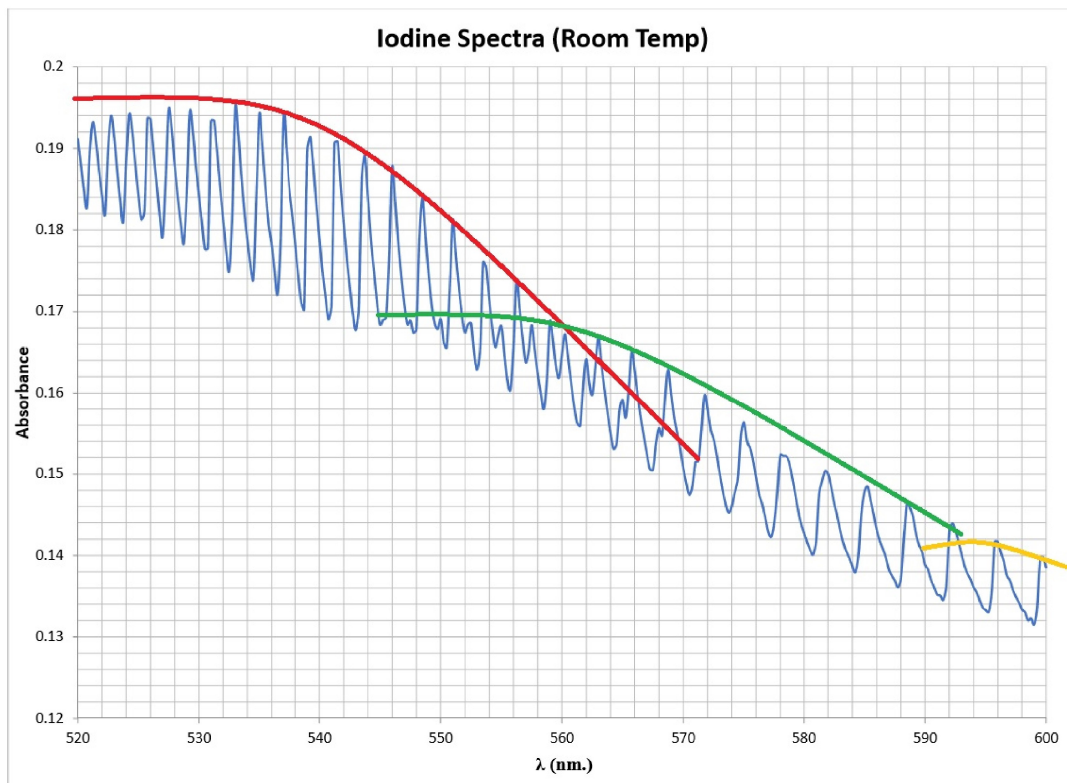


Figure 7: Shown above is an example of what the spectrum should look like with the "hot bands" labeled. The peaks marked in red are from transitions originating at $v'' = 0$, the green at $v'' = 1$ and orange at $v'' = 2$. The $v'' = 1$, and 2 transitions might become hard to distinguish.

3 Calculations

Recall from the end of section 1.2 the crucial equation for this experiment was:

$$\tilde{\nu}_{transition} = \tilde{\nu}_e + \omega'_e(v' + 1/2) - \omega'_e\chi'_e(v' + 1/2)^2 - \omega''_e(v'' + 1/2) + \omega''_e\chi''_e(v'' + 1/2)^2$$

In the spectrum, each and every single peak, represents a transition, $\tilde{\nu}_{transition}$. Every peak on the graph corresponds to an I_2 molecule absorbing a photon and promoting an electron from $v'' \rightarrow v'$. According to this equation, the transition wavenumber is a function of two variables, v' and v'' . However, if it is thought of in that way, the equation is quadratic in those variables. On the other hand, the function can be thought of as a function of four variables x_1, x_2, x_3 , and x_4 where $x_1 = (v' + 1/2)$, $x_2 = (v' + 1/2)^2$, $x_3 = (v'' + 1/2)$, and $x_4 = (v'' + 1/2)^2$. Notice that the transition wavenumber, as a function of these variables, is linear. Assign each transition wavenumber a x_1, x_2, x_3 and x_4 'coordinate'. Running a multiple linear regression in a data analysis software package should yield values for the coefficients of each x_i , these coefficients will be $\omega'_e, \omega'_e\chi'_e, \omega''_e$, and $\omega''_e\chi''_e$. The constant term in the regression will analogously be $\tilde{\nu}_e$. The quantum numbers will increase by 1 as the wavelength decreases, the hard part is assigning the first numbers. This is an extremely difficult task, and outside the scope of this experiment, so here are some literature values to begin with.

v'	v''	λ	v'	v''	λ	v'	v''	λ
27	0	541.2	18	1	571.6	13	2	595.7
28	0	539	19	1	568.6	14	2	592
29	0	536.9	20	1	565.6	15	2	588.5

Figure 8: The above table gives the quantum number designations to certain known transitions and their accompanying wavelength in nm. These assignments were proposed in [7] by intensity distributions and proven in [1] based on isotopic effects.

After assigning numbers to a few transitions originating at all three ground state vibrational numbers, a Deslandres table should be made to check that the numbering is consistent. To do this, list a few wavenumbers that are to the same excited state between the three ground state levels, (i.e. $\tilde{\nu}_{0 \rightarrow 16}$, $\tilde{\nu}_{1 \rightarrow 16}$, $\tilde{\nu}_{2 \rightarrow 16}$) The table consists of the wavenumbers arranged by v' along the rows and v'' along the columns. Calculate the differences in the wavenumbers between each pair of row entries and column entries. If the numbering is consistent, the differences by row should all be equal and the differences by column should all be equal. After reviewing the initial numbering with such a table, move on to assigning quantum numbers to the rest of the peaks and running the regression¹⁰. The hard part of the calculations is now over, the formulas for the rest of the parameters are straightforward once values for both ω_e 's, $\omega_e \chi_e$'s and $\tilde{\nu}_e$ are obtained. The other equations needed were derived in the Background section, here they are again arranged in a logical order of calculating them.

3.1 Summary

- $\tilde{\nu}_e$, ω'_e , $\omega'_e \chi'_e$, ω''_e , $\omega''_e \chi''_e$ are all from the multivariate linear regression.
- $v_{max} = \frac{\omega'_e}{2\omega'_e \chi'_e} - 1$
- $E^* = \tilde{\nu}_{transition}(v) + 1/2[\omega'_e - 2\omega'_e \chi'_e(v + 1)][v_{max} - v]$ calculate an E^* for each transition originating at $v'' = 0$, report a mean and standard deviation
- $D''_o = E^* - E(I^*)$ where $E(I^*) = 7589\text{cm}^{-1}$ [6]
- $D''_e = D''_o + \frac{\omega''_e}{2} - \frac{\omega''_e \chi''_e}{4}$
- $D'_e = E^* - \tilde{\nu}_e + \frac{\omega'_e}{2} - \frac{\omega'_e \chi'_e}{4}$
- $D'_o = D'_e - \frac{\omega'_e}{2} + \frac{\omega'_e \chi'_e}{4}$
- $k = \frac{4D_e}{\omega_e}$ calculate the force constant for the both states by using the appropriate D_e and ω_e
- $\beta' = \pi\omega'_e \sqrt{\frac{2c\mu}{D'_e h}}$
- $U(r''_e) = \tilde{\nu}(v'' = 0 \rightarrow v_m) + \frac{\omega''_e}{2} - \tilde{\nu}_e$ See the background section for definition of v_m
- $r'_e = 2.666 + \frac{1}{\beta'} [\ln(1 + \sqrt{\frac{U(r''_e)}{D'_e}})]$ be careful with units, the value of β' calculated above is in m^{-1} , for this equation it is needed in reciprocal angstroms.

¹⁰Most data analysis software packages allow for multivariate linear regressions. Find supplemental information as necessary to learn how to run one in the chosen package.

4 Post-Lab

1. The basis for most of the calculations in this laboratory is the Morse potential. Using the experimental values, plot the Morse and harmonic potential for the excited state B , how quickly does this model deviate significantly ($>5\%$) from the harmonic potential?
2. Assess the two predictions made in the Pre-Lab. Do the results support the hypotheses?
3. As a thought exercise, examine the values of the anharmonicity constants χ_e' and χ_e'' . Other literature methods suggest adding in a third order constant, Υ_e . Given the magnitude of the second order constants, χ_e , and the strength of your regression, why might we be justified in excluding these third order constants?

References

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