

QUANTUM MECHANICS AND SPECTROSCOPY: ELECTRONIC ABSORPTION SPECTRUM OF I₂

AIMS

- (a) To record the electronic absorption spectrum of iodine vapour
- (b) To analyse the main $v'' = 0$ progression in the electronic absorption spectrum of iodine vapour.
- (c) To extend the analysis to include hot bands, and thereby to determine some vibrational properties, and the dissociation energy, of the electronic ground state of the I₂ molecule.

SKILLS USED IN THIS EXERCISE

- Measuring visible absorption spectra using an **authentic research** instrument (UV-Vis).
- Peak-picking and data modelling using **Python**.
- Interpretation of vibronic spectra.
- Preparing a captioned figure.
- Writing a critical discussion of an experimentally derived result.

INTRODUCTION

Iodine is a simple diatomic molecule which can easily be obtained in the vapour phase and which exhibits an electronic absorption spectrum in the visible region. From this spectrum, it is possible to determine several physical constants for both ground-state and excited-state molecules. It is also possible to determine quantities such as dissociation energies which are of thermodynamic importance.

The electronic spectrum of a diatomic molecule is the result of transitions between different electronic states and spectra are usually discussed with reference to the potential energy curve

(a graph of the energy of the molecule *versus* internuclear distance) for each of the electronic states involved.

Figure 1a shows potential energy curves for the two electronic states involved in the visible absorption spectrum of I₂; the electronic ground state is labeled X and the excited state is labeled B. For either electronic state, the limiting value of the potential energy as the bond length increases corresponds to dissociation of the molecule into two atoms. In the case of the excited molecular electronic state, one of those atoms is produced in an excited state.

Associated with each of these electronic states is a set of vibrational energy levels. Introducing $G(v)$, the vibrational energy in wavenumber units, the energy of these levels is approximated by:

$$G(v) = \omega_e(v + 0.5) - \omega_e x_e(v + 0.5)^2 \quad (1)$$

where $v = 0, 1, 2 \dots$ is the vibrational quantum number, ω_e is the harmonic vibrational wavenumber, and $\omega_e x_e$ is the anharmonicity constant. Note that for a given electronic state $G(v)$ is the vibrational energy measured from the minimum in the potential energy curve.

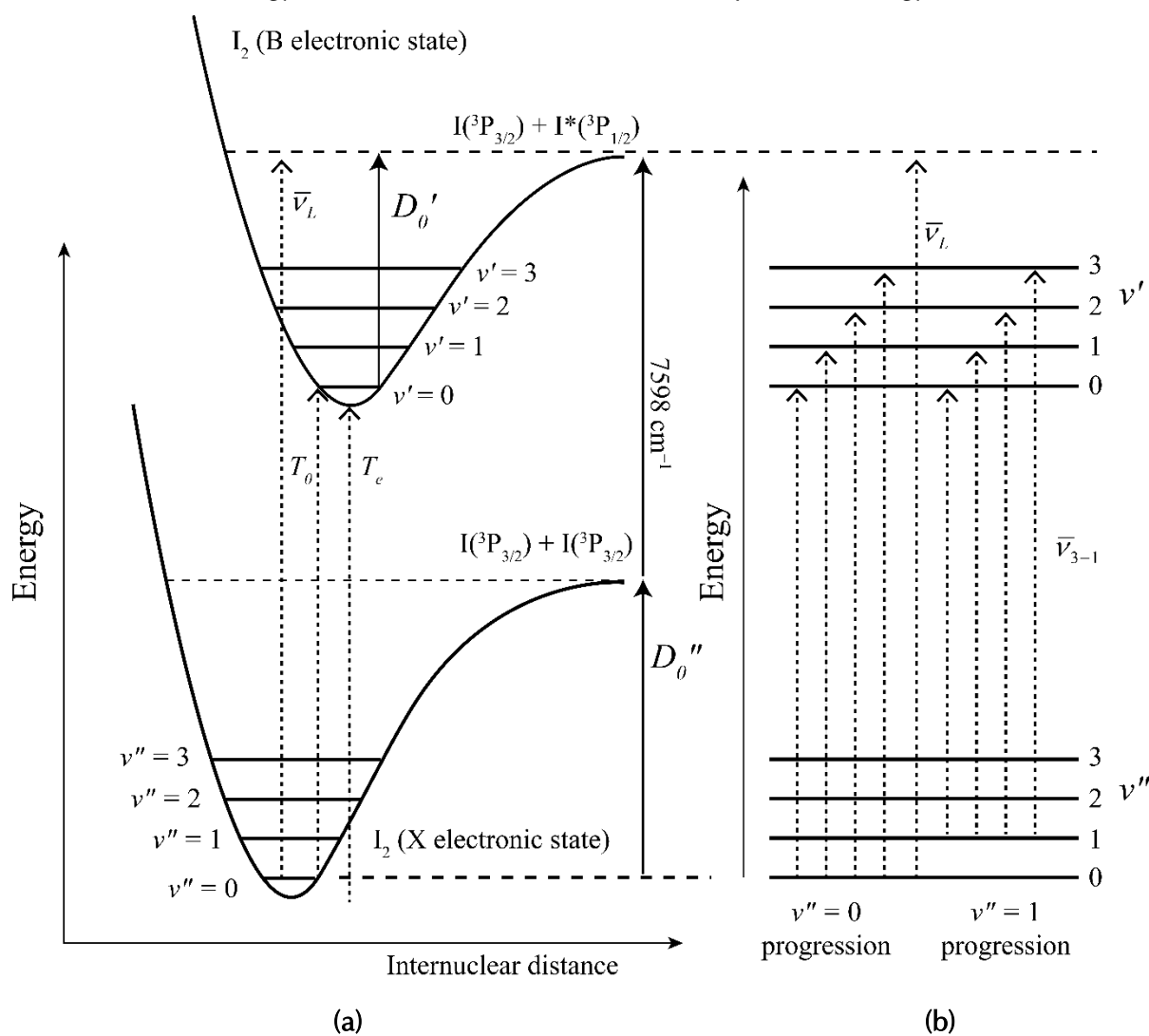


Figure 1 – (a) Potential energy curves and (b) energy levels for I₂.

Each electronic state has its own values of ω_e and $\omega_e x_e$. It is conventional to label the constants for the lower electronic state (which here is the ground state X) with double primes: v'' , ω_e'' and $\omega_e x_e''$. The constants of the upper state (B) are labeled with single primes: v' , ω_e' and $\omega_e x_e'$. Figure 1a shows some of these vibrational levels superimposed on the potential energy curves; Figure 1b shows the energy level diagram.

In the spectrum, a feature corresponding to a given vibronic (= combined *vibrational* and *electronic*) transition ($v' \leftarrow v''$) is called a *band* because at high resolution (greater resolution than employed in this experiment) it is seen to consist of a collection of rotational lines (you will analyze rotations in QS2). The transition $v' = 3 \leftarrow v'' = 1$ is shown in Figure 1b (absorptive transitions are denoted with left-arrows, emissive transitions, e.g. fluorescence, with right-arrows). The collection of all vibronic transitions between a given pair of electronic states is called a *band system*. Figure 2 shows a band system (the $B \leftarrow X$ system) for I_2 .

A sample of I_2 vapour in thermal equilibrium at room temperature has most of the molecules in the $v'' = 0$ state (in accord with the Boltzmann distribution) and the most intense transitions in the absorption spectrum start in this state.

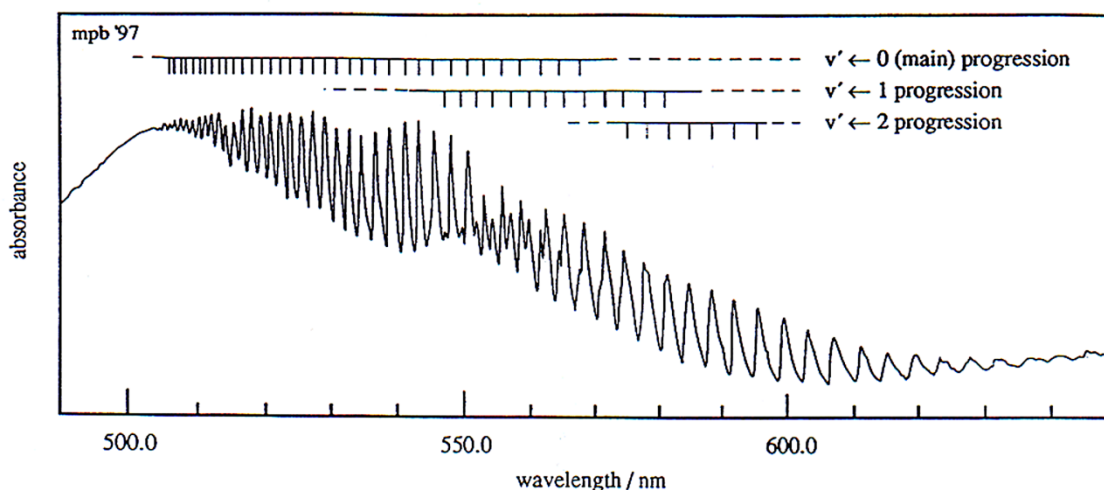


Figure 2 – The absorption spectrum of I_2 vapour in the visible region.

A series of vibronic transitions originating from a common vibrational level is called a *progression*, see Figure 1(b). The *main progression* arises from transitions originating in $v'' = 0$ level. These transitions give rise to a series of bands in the absorption spectrum, see Figure 2.

In an absorption spectrum, transitions from levels other than the $v'' = 0$ level are called *hot bands*.

Additional progressions arise from molecules occupying the $v'' = 1$ levels (indicated in Figure 1b) and from the $v'' = 2$ levels etc. Some bands belonging to these progressions have been identified in Figure 2.

Note that for a given progression the intensity of the bands varies along the progression and that the bands from different progressions may overlap in the spectrum.

If T_0 is the wavenumber for the transition $v' = 0 \leftarrow v'' = 0$, then the wavenumber for the transition $v' \leftarrow v'' = 0$, can be written as:

$$\bar{\nu}_{v'-0} = T_0 + G(v') - G(0) \quad (2)$$

Measurements of $\bar{\nu}_{v'-0}$ permit an estimation of T_0 , ω'_e , and $\omega_e x'_e$.

As a result of anharmonicity, the spacing between adjacent vibrational levels gradually decreases, and consequently the spacing between adjacent bands in the main progression gradually decreases. At the energy at which dissociation occurs the spacing between adjacent bands becomes zero and the discrete bands merge into a continuum at $\bar{\nu}_L$ (see Figure 1). Note that the dissociation leads to one iodine atom in its ground state, $I(^2P_{3/2})$, and one iodine atom in an excited electronic state, $I(^2P_{1/2})$.

If $\bar{\nu}_L$ can be estimated from the spectrum we can use it to calculate D'_0 , the energy required to dissociate molecules in the B electronic state. From D'_0 , T_0 and the energy of $I(^2P_{1/2})$ relative to $I(^2P_{3/2})$, we may calculate D''_0 , the dissociation energy of molecules in the ground electronic state of I_2 (see Figure 1a).

Although inspection of the spectrum permits a rough estimate of $\bar{\nu}_L$, a systematic approach is better. You will *globally* fit the data to the following equation, which has five free parameters:

$$\bar{\nu}_{v'-v''} = T_e + \omega'_e(v' + 0.5) - \omega_e x'_e(v' + 0.5)^2 - \omega''_e(v'' + 0.5) + \omega_e x''_e(v'' + 0.5)^2 \quad (3)$$

Where T_e is the wavenumber separation between the minimum of each of the potential energy curves. For fixed v'' , this may be plotted as a parabola in $v' + 0.5$, which has a maximum value corresponding to $\bar{\nu}_L$ at $v' + 0.5 = \omega'_e / 2\omega_e x'_e$. Substitution of this quantity into the above expression yields

$$\bar{\nu}_L = T_e + \frac{\omega_e'^2}{4\omega_e x'_e} - G(0'') \quad (4)$$

A study of the atomic spectrum of iodine shows that the $^3P_{1/2}$ excited spin-orbit state of iodine atoms is 7598 cm^{-1} above the ground state (Figure 1), and this result may be used together with $\bar{\nu}_L$ to estimate D''_0 , the dissociation energy for iodine molecules in the ground electronic state – the I-I bond energy!

$$D''_0 = \bar{\nu}_L - 7598 \quad (5)$$

This quantity can, in principle, be determined from an analysis of the ground state potential well. For instance, an analysis of the hot bands permits estimation of ω''_e and $\omega_e x''_e$, from which D''_e and therefore D''_0 may be calculated.

The electronic absorption spectrum of iodine in the visible region consists of three overlapping progressions, as illustrated above (Figure 2). All bands in the main progression originate in the $v'' = 0$ level. Each band in the first hot progression arises from the $v'' = 1$ level, and each in the second arises from $v'' = 2$. Consequently, each member of the ($v' \leftarrow 1$) progression is displaced to lower frequency (*i.e.* to longer wavelength) from its counterpart ($v' \leftarrow 0$) in the main progression, by an amount which is equal to the separation in cm^{-1} between the ground state vibrational levels $v'' = 1$ and $v'' = 0$. Similarly, each member of the second hot progression ($v' \leftarrow 2$) is displaced from its first hot progression.

The situation $\omega_e x_e = 0$ corresponds to an idealised harmonic oscillator, resulting in a potential well of simple parabolic shape. Anharmonicity (*i.e.* $\omega_e x_e > 0$) renders the potential well asymmetric, corresponding to molecular dissociation at large amplitudes of vibration, and the “height” up the potential well at which dissociation occurs depends directly upon the anharmonicity, $\omega_e x_e$. This “height” is the dissociation energy D_e , which can be evaluated by finding where the derivative of $G(v)$ with respect to v goes to zero:

$$G(v) = \omega_e(v + 0.5) - \omega_e x_e(v + 0.5)^2$$

$$\frac{dG}{d(v + 0.5)} = \omega_e - 2\omega_e x_e(v + 0.5) = 0$$

$$v_L + 0.5 = \frac{\omega_e}{2\omega_e x_e} \quad (6)$$

which is the value of the vibrational quantum number after which dissociation occurs. Substitution of this value back into the expression for $G(v)$ gives the corresponding energy, D_e , measured from the bottom of the potential well:

$$D_e = G(v_L) = \frac{\omega_e^2}{4\omega_e x_e} \quad (7)$$

Thus, an experimental determination of ω_e' and $\omega_e x_e''$ from analysis of two hot progressions is, in principle, sufficient to determine D_e'' and therefore D_0'' .

$$D_0'' = D_e - G(0) \quad (8)$$

RISK ASSESSMENT AND HEALTH AND SAFETY INFORMATION

	<i>Risk</i>	<i>Safety precautions</i>
Apparatus		
Spectrophotometer	No significant hazard.	
Glass cell	Breakages, cuts from broken glass	Broken glass to glass container
Chemicals	See MSDS.	Wear safety glasses. Do not ingest any chemical.
Iodine solid and vapour	Harmful by inhalation and in contact with skin. Very Toxic to aquatic organisms.	Avoid contact with eyes Wear safety glasses. Do not breathe gas/fumes/vapor. Avoid release to the environment.
Other hazards	None identified	
Control measures	Eye protection to be worn at all times.	
Clean up	Broken glass to 'glass only' container.	

Overall Risk assessment: Significant risk that may be effectively controlled.

Risk assessment by: Prof. Timothy Schmidt

Date: 10 March 2017

REFERENCES

- (1) Engel, T. and Reid, P., *Physical Chemistry*, Pearson New International Edition, Pearson 2014.

EXPERIMENTAL PROCEDURE

The following procedure was followed (watch the video on Moodle) to obtain the data you will use. Questions in the quiz will relate to the experimental procedure.

The instrument used for this experiment is a UV-Visible spectrometer.

If the ambient temperature in the laboratory is low the demonstrator or laboratory technician may warm the cell containing the I_2 using a heat gun to increase the vapour pressure of $I_2(g)$. This is because if there is crystalline material in the path of the instrument beam you will observe scattering and will have to repeat your measurement. Your demonstrator will provide the iodine cell and take a broad, low resolution spectra of iodine vapour over the range 400 - 800 nm (Scan controls: Ave time (s) 10, Data interval (nm): 1, Scan rate (nm/min): 300). This is the typical UV-vis spectrum of iodine. Note that the region of interest in this experiment is only a small part of this spectrum.

Your demonstrator will then hand control of the instrument over to you. Record the spectrum of iodine vapour over the range 650 – 500 nm (that is, 15 000 – 20 000 cm^{-1}), using one of the large Cary UV-Vis spectrophotometers. Detailed operating instructions for this instrument are provided below. It is very likely the instrument and its attached computer will be turned on ready for you to use. However, if this is not the case, switch on the instrument (power switch on lower left front) and ask for assistance.

We have prepared a number of spectra for you. The experimental parameters can be found in the metadata at the bottom of the files.

Cary 100 and Cary 1E Operating Instructions for QS3

Click 'Setup' button.

Click 'Cary' tab. Check 'Mode' is 'nanometers'.

Set these parameters: wavelength range 'start' 650 nm, 'stop' 500 nm

Scan controls: 'Ave time (s)': 0.2

'Data interval (nm)': 0.02

'Scan rate (nm/min)': 6

Note: these three settings are linked and changing one will change the other two.

Click 'Options' tab, change 'SBW (nm)' to 0.2 (this is the 'spectral bandwidth')

Click 'Reports' tab, turn off 'User Data Form' and 'Company Logo'; change 'Graph page height' to 100%. Click 'All Peaks'. Click OK.

Make sure your sample is ready in the instrument. Click 'Start' (the big traffic light icon).

Navigate to the directory \My Documents\CHEM2011\ (or create this directory)

Give your data file a name (*e.g.* your initials), press 'Save'.

Give the sample a name (*e.g.* iodine vapour), press 'Save'.

The instrument will now scan the spectrum of your sample. Wait for the instrument to complete the scan (about 25 min) and return to the starting wavelength.

Next smooth the spectrum to remove noise (this makes the peak detection more reliable). Choose the 'Maths' menu. Click the 'Selected trace' button. Change 'Operation' to 'Smooth' if not already set. Set 'Filter size' to 5, 'Interval' to 0.1, 'Display options' to 'New graph'. Click 'Apply', click the red '=' button. Close the Maths window and expand the new trace.

Choose 'Print setup' from the 'File' menu and choose 'Landscape' page layout.

The 4th toolbar button from the left allows you to change the axis ranges to fit your spectrum and peak data on a printout. Indicate the axis range with a dash between the two values (*e.g.* 0 – 1.6). When choosing the Y range leave some space for the labels above the spectrum. You need to print your spectrum in three parts, each covering a portion of the wavelength range you scanned with some overlap between them: 500 – 560, 550 – 610, and 600 – 650 nm. Follow ALL of the steps below for each of the three wavelength ranges.

Click the Peak labels icon (second last button on the toolbar). Tick 'X label'.

Change the Peak threshold value (*e.g.* 0.005, requires some trial and error) to label the peaks and click OK. See figure 3 for an indication of all the peaks you need to report. You must be able to see and label the small shoulders on the main bands around 570 – 580 nm. Ask the

demonstrator to check your peak labeling onscreen before you print. You may need to label some peaks manually by right clicking and selecting 'add label'.

To print your spectrum: click 'Clear Report'. Click 'Recalculate', OK. Click 'Print', choose pages 1 to 1 to print, and enough copies for your group, then click OK.

You must repeat the whole sequence of Clear Report etc. every time you print to avoid accumulating a list of reports on each printout. Your print-outs will greatly aid in the analysis. Coloured pencils are also handy for visualizing progressions.

Ensure that your spectrum is saved in a spreadsheet-readable format (e.g. **.csv**).

Tape the spectra into your lab book.

RESULTS

- In your **Python** notebook, download and plot the experimental spectra, **A.csv**, **B.csv**, **C.csv** and **D.csv**. Inspect the metadata at the tail of the files and adjust the code such that the slit bandwidth is indicated in the plot legend. Create a plot title and adjust the x- and y-ranges to best display the data. Select the highest resolution spectrum with the closest data-point spacing for further analysis.
 - In your notebook, assign **x** and **y** to the data series for your chosen dataset. E.g. if you selected **data_W**, then **x = x_W**.

Use the code in your notebook to pick the peak positions by adjusting the **prominence** (height of peak above nearest valley) and **distance** (minimum number of data points between peaks) parameters within the **find_peaks** function. Make sure that as many peaks have been picked as possible, but keep the total below 200. Extra peaks or false peaks do not matter at this stage. Figure 4 details the region where the three progressions overlap. Ensure that as many peaks as possible have been picked in this region. Each peak will now have an index displayed in parentheses which you will use to assign the peaks to progressions.

Do not continue until you have as many of the clear peaks picked as possible.

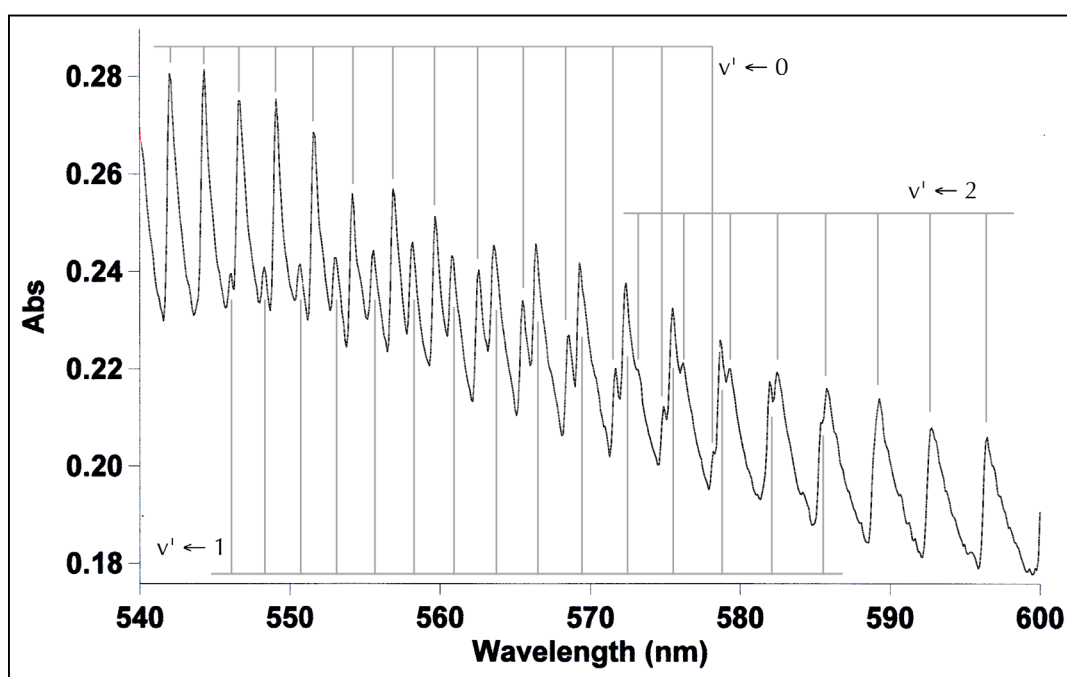


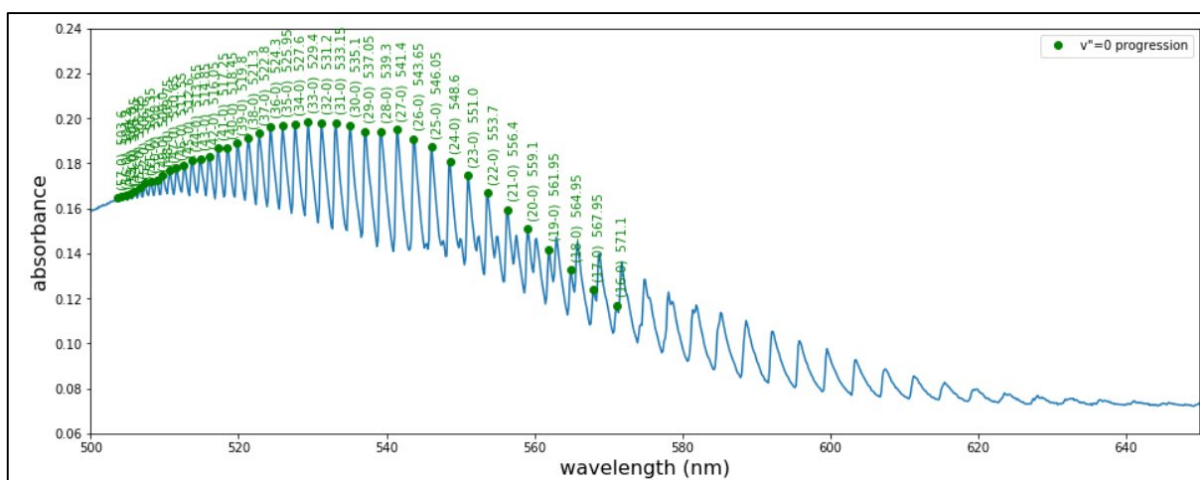
Figure 4 – Assignment of bands to progressions around 570 nm.

ANALYSIS OF THE MAIN PROGRESSION

With the aid of Figures 2 and 4, *identify* the bands which belong to the $v'' = 0$ (i.e. main) progression. Note the smooth variation of intensity for the bands within each progression. You can use this as an aid in assigning features to particular progressions.

- In your notebook, assign the main progression by listing the indices of the peaks in the array **s0**. Start by entering the index of the most intense peak. This should be an integer less than 200. Indices should be entered in numerical order.

```
##### Choose the indices of the peaks associated with the main progression (v''=0)
s0 = [126,129,131,133,135,137,139,141,143,145,147,149,151,152,153,154,155,156,157]
offset0 = 5          # Update the offset to assign the upper quantum number
#####
```



Use the code given to extract the x and y-values of the peaks from the array **peaks**. Take care in the region 550 – 580 nm in which the intensity of members of the main ($v' \leftarrow 0$) progression may be weaker than members of the $v' \leftarrow 1$ progression. Use Figure 4 to help you identify the main progression bands in this region. *Assign* upper-state quantum numbers v' to the bands in this progression using the literature data in the Table 1 for assistance. These data are provided as a guide only. Adjust **offset0** in the code so that the correct assignments appear in parentheses above the peaks. Your data must, as a minimum, include bands for $v' = 18$ through to $v' = 45$. If necessary, pick additional peaks.

Table 1 – Wavelengths of Selected $v' \leftarrow 0$, $v' \leftarrow 1$ and $v' \leftarrow 2$ Bands^a

v'	v''	λ/nm	v'	v''	λ/nm	v'	v''	λ/nm
27	0	541.2	18	1	571.6	13	2	595.7
28	0	539.0	19	1	568.6	14	2	592.0
29	0	536.9	20	1	565.6	15	2	588.5

a. from McNaught, I.J., *The Electronic Spectrum of Iodine Revisited*, J. Chem. Educ., 57, 1980, 101 – 105)

- Use your notebook to convert the wavelengths (nm) to wavenumber (cm^{-1}) and store in the array **energy**. Create arrays **vp** and **vpp** (vee-prime v' and vee-double-prime, v''). A plot of

the wavenumber of the members of the main progression against $x = v' + 0.5$ will be close to a parabola.

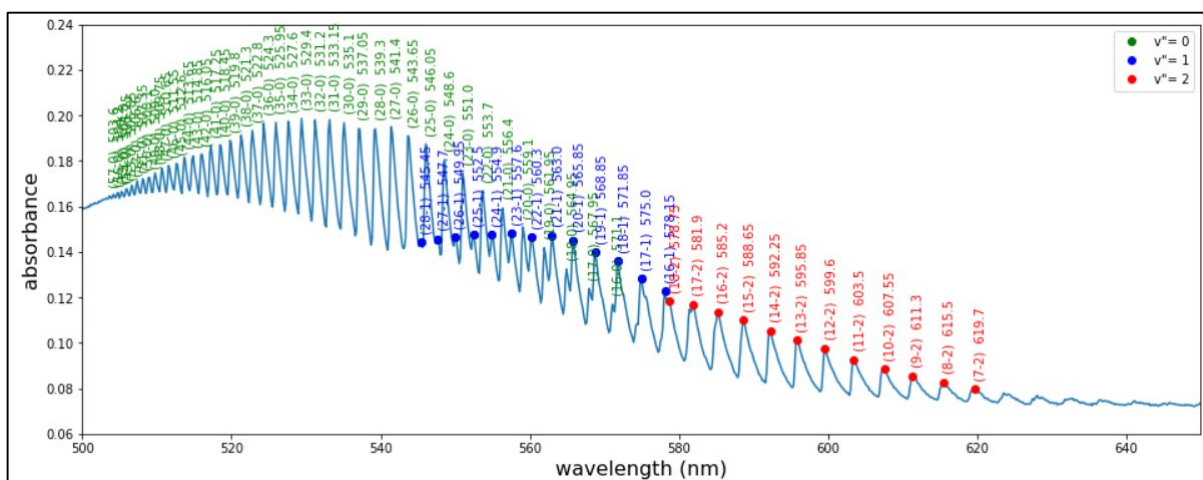
- Fit this with a quadratic curve and determine estimates for ω_e' and $\omega_e x_e'$, which will be respectively the coefficients of x and x^2 . Determine the maximum wavenumber of the parabola, which will equal $\bar{\nu}_L$. You may gauge the uncertainty in $\bar{\nu}_L$ by taking the difference in its derived value and the wavenumber of the highest energy peak you can see in the spectrum. Thus estimate D_0'' . Compare this result to that derived from the Active Thermochemical Tables (<https://atct.anl.gov/>) in Table 2.

Table 2 – Thermochemical Properties of Gaseous Iodine

Species	ΔH_f° (0K, kJ/mol)
I ₂ (g)	65.497
I(g)	107.157

ANALYSIS OF OTHER PROGRESSIONS

- Assign the members of the $v'' = 1$ and $v'' = 2$ progressions (see Table 1). Create a plot with all of your assignments. Add a caption and submit your figure. Be careful assigning peaks beyond 615 nm where the $v'' = 3$ progression may start to manifest.



- Append the arrays **energy**, **vp** and **vpp** with the new data and plot the progressions on the same graph. Ensure that each progression makes a smooth curve.
- Join the arrays **vp** and **vpp** into a $2 \times N$ array **vees**, which contains the upper and lower vibrational state quantum numbers (plus one-half). Globally fit all three progressions by defining a function of $v'' + 0.5$ and $v' + 0.5$. Determine values for ω_e' , $\omega_e x_e'$, ω_e'' , $\omega_e x_e''$, and T_e .
- To obtain reasonable values for the ground state, it is necessary to limit the upper state levels used in each progression. Edit the **s0** and **s1** arrays to limit the uppermost level to the maximum observed in the $v'' = 2$ progression and repeat the global fit. You can redefine **s0**

and **s1** after the initial declaration (remember to un-comment the code by removing the hash #).

- Determine D_0'' and its uncertainty from the determined values of ω_e'' and $\omega_e x_e''$.

The force constant, k , for stretching the iodine – iodine bond is related to ν , the vibrational frequency (in Hz), by

$$\nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$$

where μ is the reduced mass. *Convert* the ω_e' from wavenumber units to Hz and then *calculate* k' , the force constant for the stretching the iodine – iodine bond in the excited electronic state.

DISCUSSION (ANSWER IN PROSE)

1. Comment on the general appearance of your absorption spectrum. Why does the spikiness disappear?
2. What colour is the light most strongly absorbed by iodine vapour? What colour best describes the vapour? Why is it this colour?
3. Compare your determined spectroscopic constants to those listed at <http://webbook.nist.gov/cgi/cbook.cgi?Formula=I2&Nolon=on&Units=SI&cDI=on>
The ground electronic state is given the symbol X, and the excited state is B.
4. Comment on the relationship between the harmonic frequencies in the ground and excited electronic states.
5. Discuss the values of D_0'' determined in this exercise with reference to literature, how they were determined, and your experimental uncertainties.

EXTENSION

1. The individual vibronic bands are asymmetric. Why is this? (Hint: what motion of I_2 has not been accounted for yet?) Is the bond length longer or shorter in the excited state? Why? QS2 will help you answer this question.

REPORT

Answer the **online Quiz** associated with this exercise.

APPENDIX

Uncertainty propagation is important but can also be difficult. In this exercise, you must determine the uncertainty of

$$D_e = \frac{\omega_e^2}{4\omega_e x_e}$$

which is the combination of uncertainties due to both ω_e and $\omega_e x_e$,

$$\delta D_e(\omega_e) = \delta \omega_e \frac{2\omega_e}{4\omega_e x_e}$$

$$\delta D_e(\omega_e x_e) = \delta \omega_e x_e \frac{\omega_e^2}{4\omega_e x_e}$$

These should be added in quadrature.

$$\delta D_e = \sqrt{\delta D_e(\omega_e)^2 + \delta D_e(\omega_e x_e)^2}$$

The uncertainty of the observable dissociation energy, D_0 , should take into account the uncertainty of $G(0)$.

$$G(0) = \frac{\omega_e}{2} - \frac{\omega_e x_e}{4}$$

$$\delta G(0) = \sqrt{\left(\frac{\delta \omega_e}{2}\right)^2 + \left(\frac{\delta \omega_e x_e}{4}\right)^2}$$

$$\delta D_0 = \sqrt{\delta G(0)^2 + \delta D_e^2}$$