

Lab 2 - Molecular Spectroscopy

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November 2020

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1 Abstract

This experiment involved the use of many spectroscopic measurement techniques to determine properties of molecular spectra in both absorbtion and emission cases.

The first part of this experiment involved gaining familiarity with the equipment (flame s, flame t spectrometers), calibrating the flame spectrometers to a suitable range and measuring quantities such as FWHM and resolving power which agreed with literature. It was also found that both spectrometers were 16 bit as they did not reach saturation till 66000 counts. Their respective pixel ranges were 2048 and 3648.

The second part of this experiment involved constructing a deslandres table from an obtained nitrogen emission spectrum line, and after producing relevant constants, plotting a mose potential. It was found that at low energy levels, the mose potential is similar to the harmonic oscillator, but at higher energy levels it is far more accurate due to how well it traces the curvature or change of steepness of the potential.

The third part of this experiment involved measuring the relative irradiance of

the spectrometer for white light emanating from a tungsten halogen lamp. It was found that max sensitivity occurred at a wavelength of 530nm.
The fourth experiment was to analyse an absorption spectrum of iodine for the tungsten halogen lamp. The beer lambert law was verified i.e (Absorbance) \propto (Temperature).
The convergence limit of the wavenumber was also extrapolated from a quadratic fit using a deslandres table to be 21000 which agreed to a 6% error with the literature value specified.

2 Theory

The peaks in an emission spectrum are caused by the movement of an electron from a higher energy level in an excited state to a lower energy level, expelling energy($h\nu$) in the process. However, for molecules, the respective motion of the particles is important and as such vibrational energy levels exist. In quantum terms energy can be thought of as

$$\frac{E_J}{hc} = BJ(J + 1)$$

As a sum of rotational and vibrational energies in units of cm^{-1} conventionally. A crude approximation of this potential can be taken to be the simple harmonic oscillator in the form

$$\frac{1}{2}kx^2$$

This is inaccurate for higher energy levels as shall be demonstrated in the experiment but quite adequate for lower energy levels. The energy can be then expressed as

$$E = (v + 1/2)\hbar\omega$$

This can be further extrapolated upon to obtain by use of a taylor series to obtain

$$G(v) = V_B(v + 1/2) - V_B X_B(v + 1/2)^2 v$$

. Solving this and tidying up terms leaves

$$\Delta V = V_B - 2V_B X_B(v + 1)$$

This is useful the birge sponer plots used extensively for analysing data in the field of spectroscopy.

The dissociation energy(D_e) is the energy required to break a bond. The zero point energy(D_0) is the energy of the ground state of the atom.

Further theoretical material such as some derivations or further explanations were included in the appendix(Figures 7 and 8).

3 experimental procedure

experiment 1:

The aims of this experiment were to calibrate the flame spectrometer and the

flame t spectrometer(appendix - figure 1) for appropriate ranges(350-1000nm and 300-510nm respectively) using the mercury lamp, and to measure properties such as resolution. The mercury lamp was aligned with each of the respective spectrometers one at a time and a reading was taken using the oceansoftware, taking care to adjust the integration time and boxcar width to suitable values. The integration time was experimented with until the saturation limit was reached for both spectrometers. Using this the number of bits of each spectrometer's respective adc was determined. i.e $16\text{ bit} = 2^{16} = 65536$ counts and $12\text{ bit} = 2^{12} = 4096$ counts.

The number of pixels that each flame spectrometer could respectively measure over was also respectively noted.

The optical resolution and resolving power were measured through use of the FWHM of a number of peaks for each distribution. Unfortunately, this process could not be totally automated in python as I did not know how to code an appropriate polyfit. As such an interactive plot was constructed and FWHM values were measured by tedious evaluation of each peak by zooming in x amount of times and taking the appropriate measurements from each axis, hence there may be an element of human error that could have been avoided here. Source (4) in the bibliography was used for comparison of a lot of values here.

experiment 2(Nitrogen emission spectrum):

The nitrogen lamp(appendix- figure 2) was brought in line with the flame T spectrometer and an emission spectrum for the N₂ molecule was created. To label each peak appropriately before inserting it into a deslandres table it was necessary to use Franck Condon factors to compare the relative heights of peaks to each other in order to identify them. These relative factors are denoted in the table below with source (3) from the bibliography.

$v' \setminus v''$	0	1	2	3	4	5	6	7
0	4527	3291	1462	517.2	158.8	45.4	12.2	3.2
1	3949	215.7	2033	1989	1097	466.3	171	56.8
2	1330	3413	238.4	634.4	1605	1393	791	362
3	202	2530	2110	890	50	936	1310	987
4	9	537	3300	1160	1160	34.8	402	1010

Table 1: Table of Franck-Condon factors ($\times 10^4$) for N₂. Rows are v' , columns are v'' .

It was possible to return the values of the fundamental frequency and anharmonicity analytically by solving the following set of simultaneous equations for corresponding values in the deslandres table. Note that to use wavelength values in the deslandres table, it was necessary to take their reciprocal in order to obtain the wavenumber.

$$v_{00} - v_{01} = V_B - 2V_B X_B$$

$$v_{00} - v_{02} = 2V_B - 6V_B X_B$$

Birge sponer analysis was conducted using the resulting table. This involves creating graphs with $v+1$ vs Δv (wavenumber). This was performed for each set of transitions, i.e 0-x, 1-x, and 2-x. An approximate straight line estimation was used for each of these values with the line relating to the equation

$$\Delta v = V_B - 2V_B X_B(v + 1)$$

in the form $y=mx+c$, where the intercept is the value of the fundamental frequency and the slope is the fundamental frequency multiplied by twice the anharmonicity constant. Simple calculations return these values.

Using these values it was possible to calculate some constants which would be useful for plotting the morse potential.

$$u = \frac{m_1 m_2}{m_1 + m_2}$$

$$\frac{D_0}{hc} = \frac{V_B^2}{4V_B X_0}$$

$$\frac{D_e}{hc} = 0.5V_B - 0.25V_B X_B + \frac{V_B^2}{4V_B X_0}$$

To convert each of these energies from cm^{-1} to eV they are simply multiplied by hc where $hc = 1.2398 \times 10^{-4} ev.cm$.

$$k = u(2\pi c)^2$$

$$B = \sqrt{\frac{k}{2D_e}}$$

Finally, a morse potential was plotted in python utilising the obtained values

$$V(r) = D_e(1 - e^{-B(r-r_0)})^2$$

taking $D_e = 5.4\text{eV}$, $r_0 = 1.2\text{\AA}$, $B = 2.64\text{\AA}^{-1}$.

Experiment 3: Emission spectrum of a tungsten halogen lamp

The aim of this experiment was to establish a comparison between the obtained irradiance of a light source and the expected irradiance. The tungsten halogen lamp can be observed in figure 3 of the appendix. The expected irradiance was obtained using Planck's radiation law

$$I(\lambda) = \frac{2\pi hc^2}{(\lambda^5)(e^{\frac{hc}{\lambda kT}})}$$

The expected value and obtained value graphs were both plotted. Relative sensitivity as a function of wavelength was found by taking the obtained values for every wavelength value and dividing them by the expected value to gain a relative intensity. The wavelength of max sensitivity was also noted. Experiment 4: The absorption spectrum of Iodine The apparatus in figure 4 was setup. A heater and thermometer in figures 5 and 6 respectively were also utilised. A vial of iodine was placed between the spectrometer and the tungsten halogen lamp and an absorption spectrum was measured using the ocean software. Absorption spectra at multiple temperatures were taken and overlaid on top of each other to prove the relationship between absorption and temperature i.e the beer lambert law.

$$I = I_0 e^{-ux}$$

One of these spectra was then taken and analysed in more detail, labelling wavenumbers and forming a deslandres table.

A sample graph of the way in which analysis is performed is included below, taken directly from the lab manual.

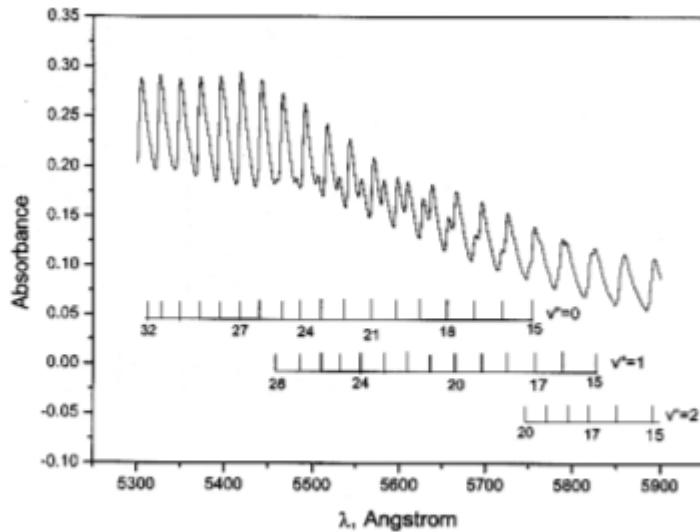


Figure 6: Example absorption spectrum of I_2 . Numbered scales represent vibrational level assignments.

Once a deslandres table is made using the above labelling system, a plot of v vs $v+1/2$ was created to which was fitted a quadratic. The a value of this quadratic (in the form $ax^2 + bx + c$) was taken to be $V_B X_B$ while the b value was V_B . The maximum point of this quadratic fit was also taken to be the convergence limit (E^*) of the wavenumber.

4 experimental results + discussion

Experiment 1: Emission spectrum of a mercury discharge lamp. Spectrometer resolution and resolving power.

Flame T data

FWHM position height(counts)	wavelength(nm)	max height(counts)	FWHM(nm)	Resolving power($\frac{\lambda}{\Delta\lambda}$)
1122	365.3	2244	1.875	194.29
1087	403	4173	2.0625	195
697	406	754	1.16	351
10107	434	14542	0.7813	556
20236	544	40469	1	544
3000	576	4642	0.9375	614.4

From these values it can be seen that the resolution(FWHM) is from 0.8nm which agrees with the ocean spectrometer hardware specifications which states this to be 0.1nm-1nm.

The max number of pixels obtained using this spectrometer was 3648 pixels. This agrees with the specifications which(all of which is all show below) but also makes alot of sense. Since the flame T spectrometer is used in the range 350-510nm, a smaller range than the flame S one, it requires greater sensitivity to preserve the accuracy of the data.

It was also found that the maximum number of counts before saturation was reached was 65500. This allows us to determine the number of bits the adc has. 2^{16} is 65536, therefore the flame T spectrometer has an adc of 16 bits.

Flame S data

FWHM position height(counts)	wavelength(nm)	max height(counts)	FWHM(nm)	Resolving power($\frac{\lambda}{\Delta\lambda}$)
1800	313	1924	0.167	1874
2343	314	3070	0.367	856
429	335	858	0.52	642
24129	366	44259	0.52	704
4393	367	6408	0.41	895.12
17847	405	35693	0.53	764.15
1738	408	3475	0.54	755
30813	436	61626	0.55	792.7
321	493	642	0.415	1187.95

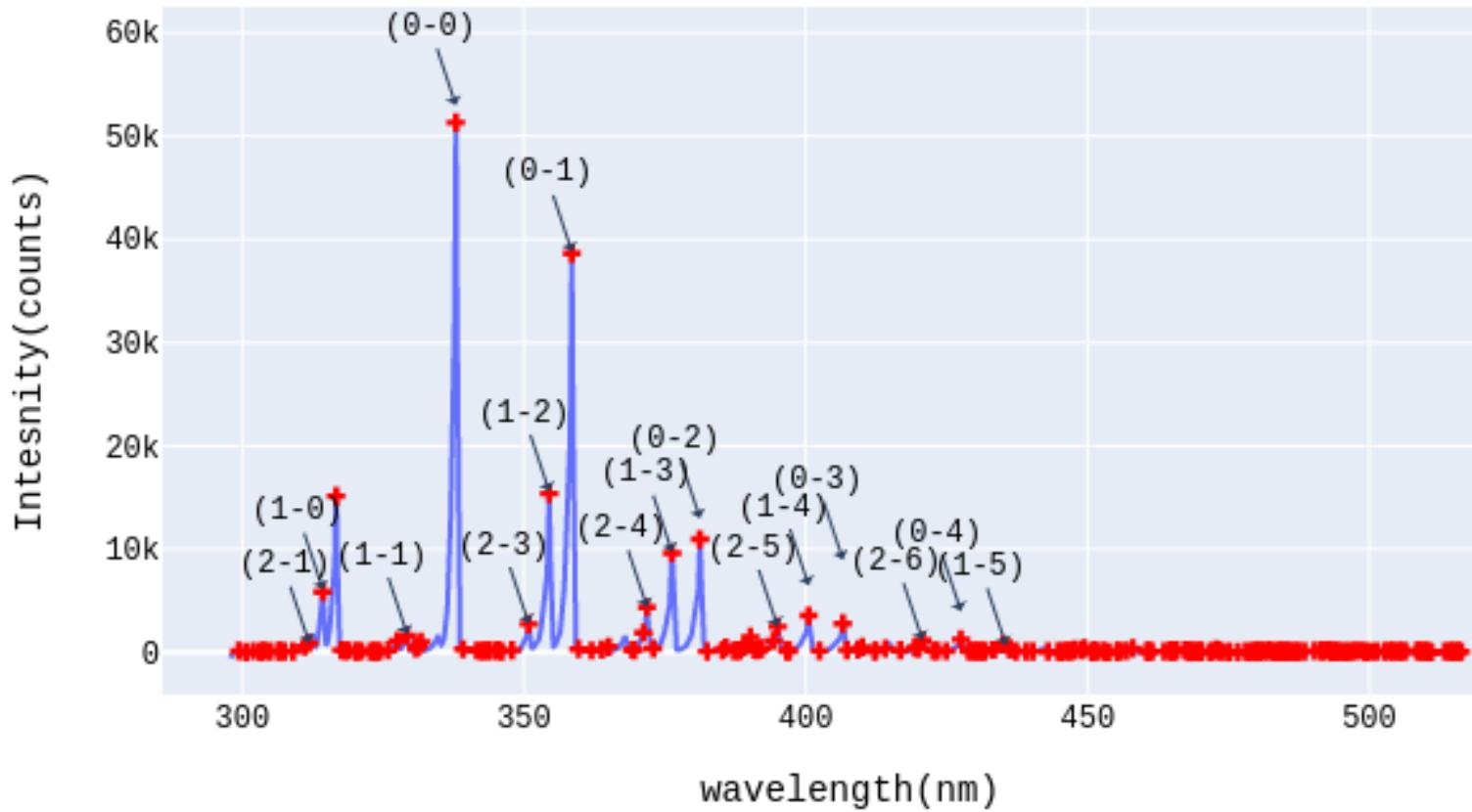
The resolution(FWHM) is 0.2nm from this table of values. Given that the flame S spectrometer normally has a resolution of 0.1nm- 1nm this is within expectations.

The max number of pixels obtained was 2048. This agrees with the specifications in the manual and also makes sense like the flame T. The flame s deals with a larger range of values (510-1000)nm and therefore, less precision is needed to gain meaningful values.

Contrary to what was said in the lab manual, the flame S spectrometer was also found to be 16 bit(i.e saturation beyond 65500). This is probably simply due to the age of the lab manuals and new models of spectrometers being brought in. It was noted in one of the relevant documents for this experiment on the desktop of the lab pc that there were slight errors in the manual so this is not unexpected.

Experiment 2: Emission Spectrum of N_2

Emission spectrum of N₂



The peaks of the nitrogen emission spectrum were analysed and labelled according to the Franck-Condon factors detailed in the experimental procedure. Using the wavenumbers found by taking the inverse of the wavelength at each spectral line, a deslandres table was constructed.

$v \backslash v''$	$0(\text{cm}^{-1})$	$\Delta v(\text{cm}^{-1})$	$1(\text{cm}^{-1})$	$\Delta v(\text{cm}^{-1})$	$2(\text{cm}^{-1})$	$\Delta v(\text{cm}^{-1})$	$3(\text{cm}^{-1})$	$\Delta v(\text{cm}^{-1})$	$4(\text{cm}^{-1})$	$\Delta v(\text{cm}^{-1})$	$5(\text{cm}^{-1})$	$\Delta v(\text{cm}^{-1})$	$6(\text{cm}^{-1})$
0	29594	1699	27895	1664	26231	1636	24595	1205	23390				
1	31816	1447	30369	2158	28211	1635	26576	1608	24968	1578	23390		
2			32065				28504	1610	26894	1578	25316	1547	23769

Using these values in the deslandres table and the simultaneous equation detailed in the experimental procedure, values of V_B and $V_B X_B$ were found. These were returned as

$$V_B = 1734.02 \text{ cm}^{-1} \text{ and } V_B X_B = 17.47 \text{ cm}^{-1}$$

$X_B = 1 \times 10^{-2}$ Further analysis, using the formulae detailed in the experimental procedure yielded the following values

$$\frac{D_0}{hc} \text{ cm}^{-1} = 43019 \text{ cm}^{-1}$$

$$D_0(\text{eV}) = 5.33 \text{ eV}$$

$$\frac{D_e}{hc} \text{ cm}^{-1} = 43882 \text{ cm}^{-1}$$

$$D_e(\text{eV}) = 5.44 \text{ eV}$$

$$k(N/m) = 1214.68 \text{ N/m}$$

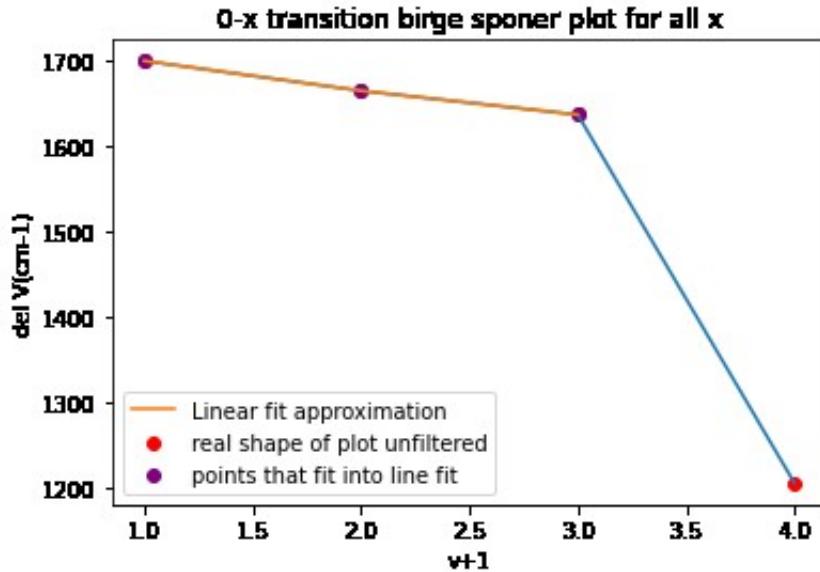
$$u = 1.16 \times 10^{-26} \text{ kg}$$

B (morse potential constant) = 2.64 \AA^{-1} Before making a morse potential using these values, it was necessary to confirm them experimentally using birge sponer plots for each i-x set of transitions. Note that while doing the birge sponer analysis I used approximately linear plots which may cause some slight overestimation of values.

The birge sponer plot is a model of the equation

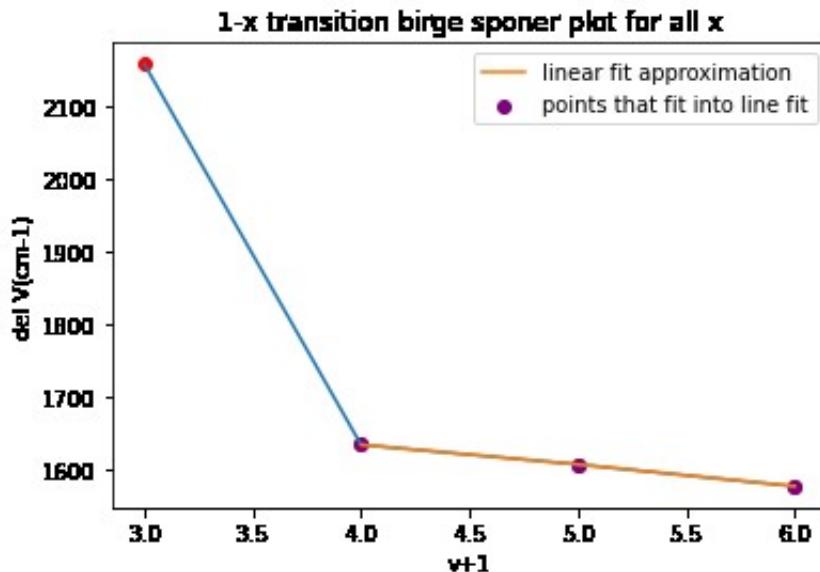
$$V_{obs} = V_B - 2X_e V_e$$

The slope should be twice by the anharmonicity correction and the intercept should equal the fundamental frequency derived from the simultaneous equation.



slope=-31.465798442777665, intercept=1729.3750977418433

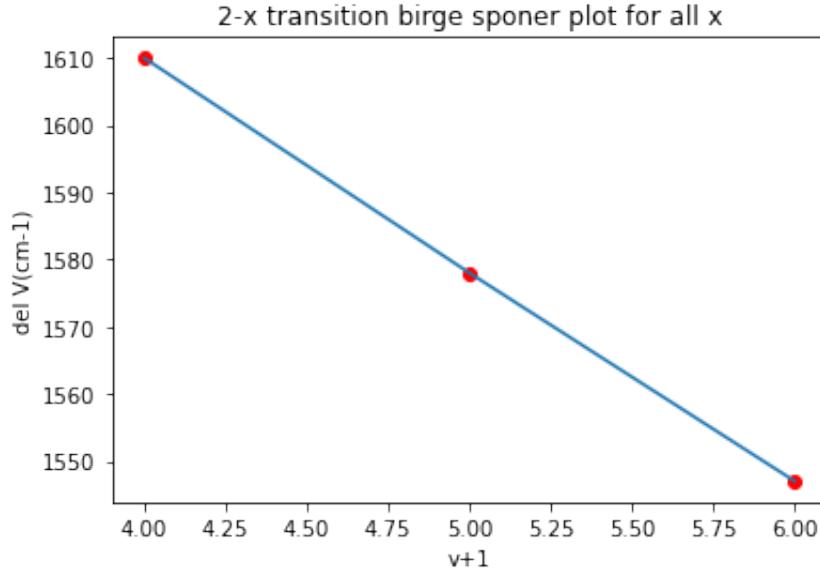
Therefore $V_B = 1729 \text{ cm}^{-1}$ (only 5 less than the analytical value) and $V_B X_B = 31.46/2 = 15.73 \text{ cm}^{-1}$ (only slightly smaller than the analytical value), $X_B = 0.909 \times 10^{-2}$. The integral of this fit yielded a dissociation value of 5.921 eV, an overestimation of the analytical value as expected.



slope=-28.5, intercept=1749.5

Therefore $V_B = 1749.5 \text{ cm}^{-1}$ and $V_B X_B = 28.5/2 = 14.25 \text{ cm}^{-1}$, $X_B = 0.81 \times 10^{-2}$. These values are also in line with the analytical values though there is some slight

error in in the anharmonicity which is likely just due to the approximation. The integral of this fit yielded a dissociation value of 6.43eV, an overapproximation somewhat but quite close to the literature value of 7eV.

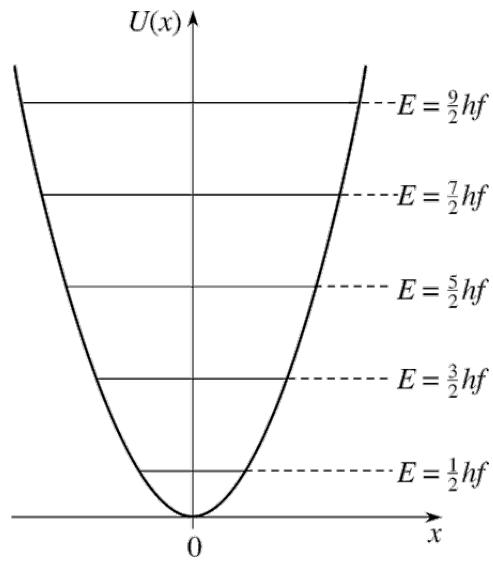
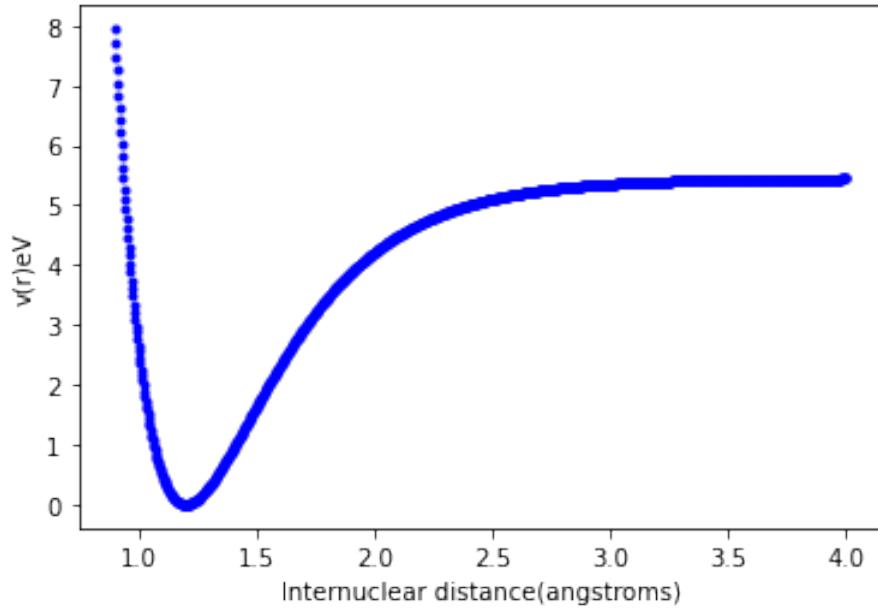


slope=-31.5, intercept=1735.833

Therefore $V_B = 1735\text{cm}^{-1}$ and $V_B X_B = 31.5/2 = 15.75\text{cm}^{-1}$, $X_B = 0.9 \times 10^{-2}$. The integral of this fit yielded a dissociation energy of 5.87eV.

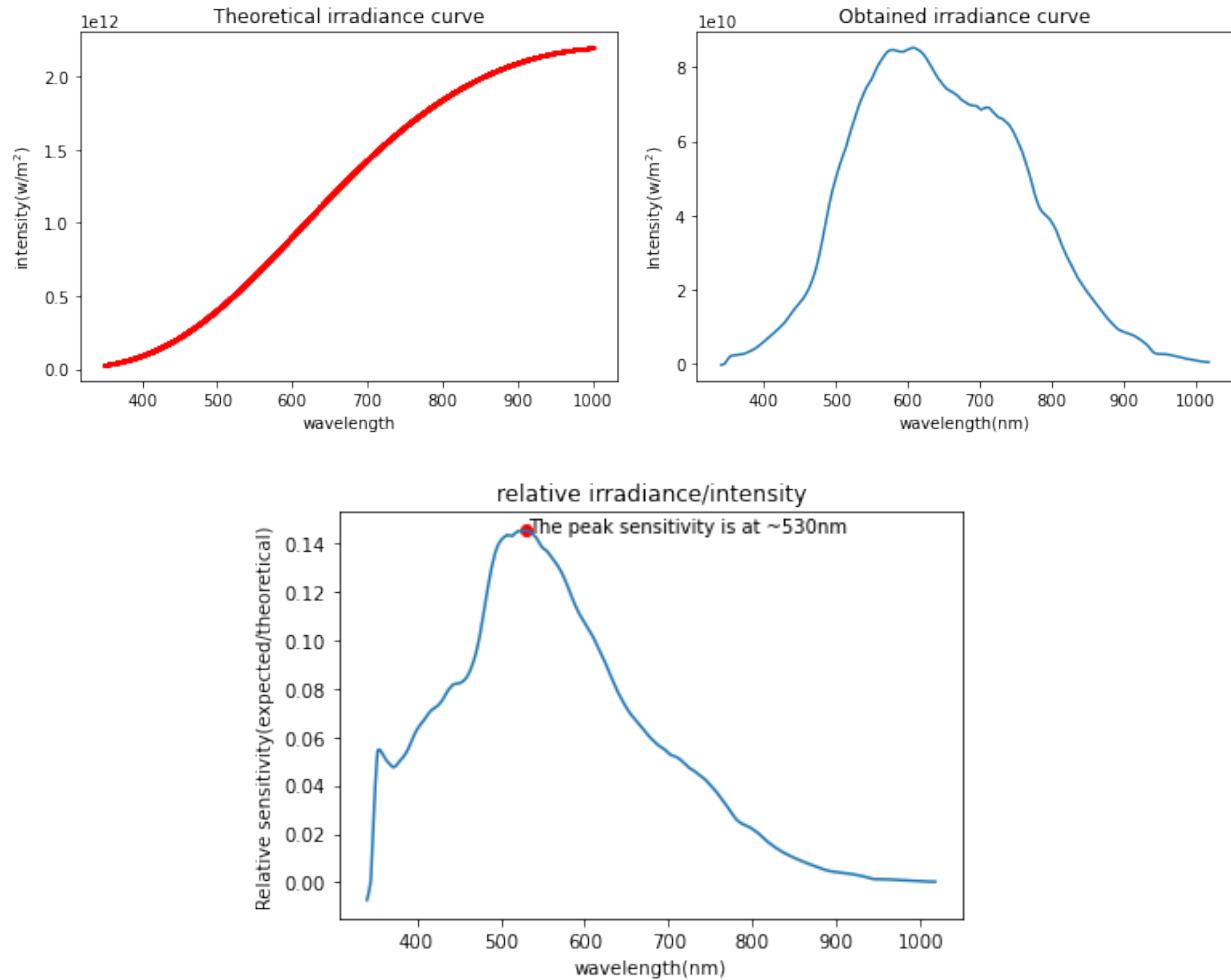
Now that the analytical values have been correlated with the analytical values, these can be used to plot an approximate morse potential. This, along with a sample of the harmonic oscillator potential approximation are included below and shall be compared. Most of these values compare quite well with literature(1). The literature values of some of these are

$k=1235\text{N/m}$ $V_B = 1730 \text{ cm}^{-1}$ $V_B X_B = 14.1 \text{ cm}^{-1}$ $\text{De} = 7.45 \text{ eV}$. The notable difference here is in the expected value of De and the obtained one. This is a difference of 2 eV which is reasonably large considering how small these values are, coming out as an error from the expected value of 26percent. The average of the 4 dissociation values however is reasonably closer 5.9eV with an error of 20. The other values obtained seem reasonable so this may have been a calculation error or alignment error.



The top image is the modelled solution obtained using python and the constants for the Morse potential and below it is the shape of the harmonic oscillator. As can be observed with these images alongside each other, as r increases, the harmonic oscillator becomes less accurate as it does not account for the change in steepness of the potential energy curve since it is uniform and homogeneous. Indeed, at the dissociation point the harmonic oscillator will prove to be completely off.

Experiment 3: Emission spectrum of a continuum white light source. This part of the experiment involved determining the sensitivity of the instrument for irradiance measurements relative to wavelength. To compute this, a theoretical mapping of expected results is compared to the obtained value. This process is detailed in the experimental procedure.

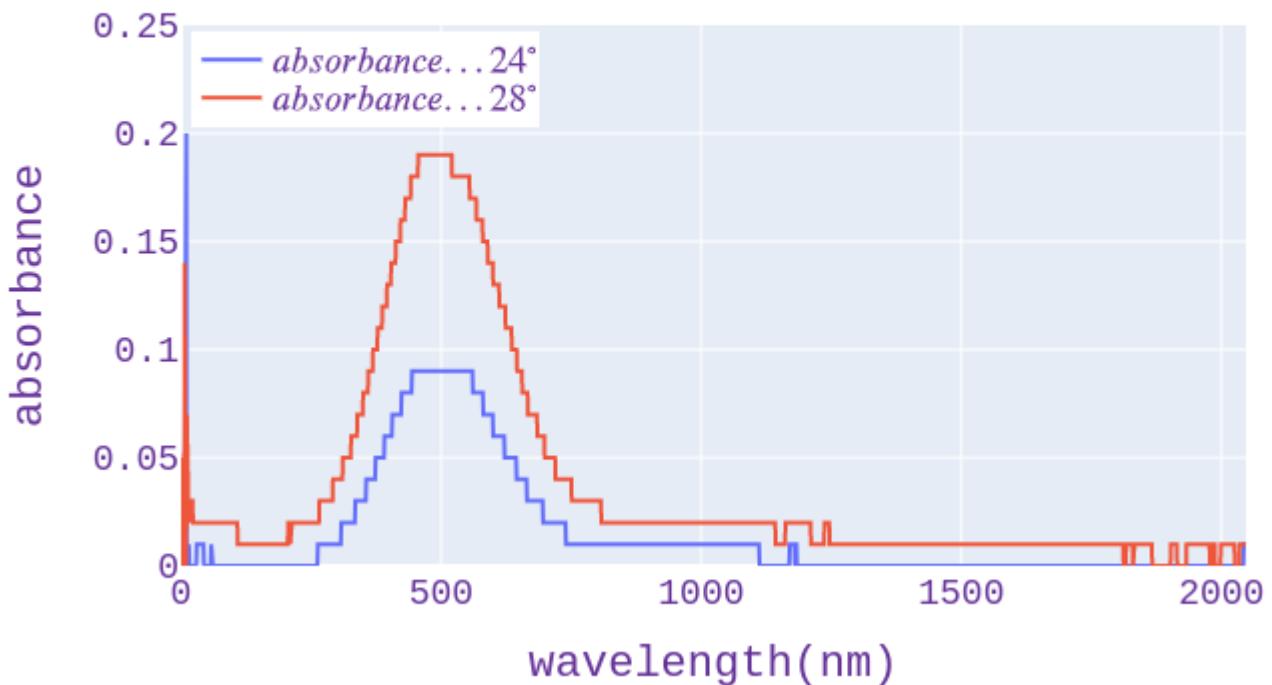


The peak sensitivity for the irradiance was located at 530nm.

Experiment 4: Absorption spectrum of I_2

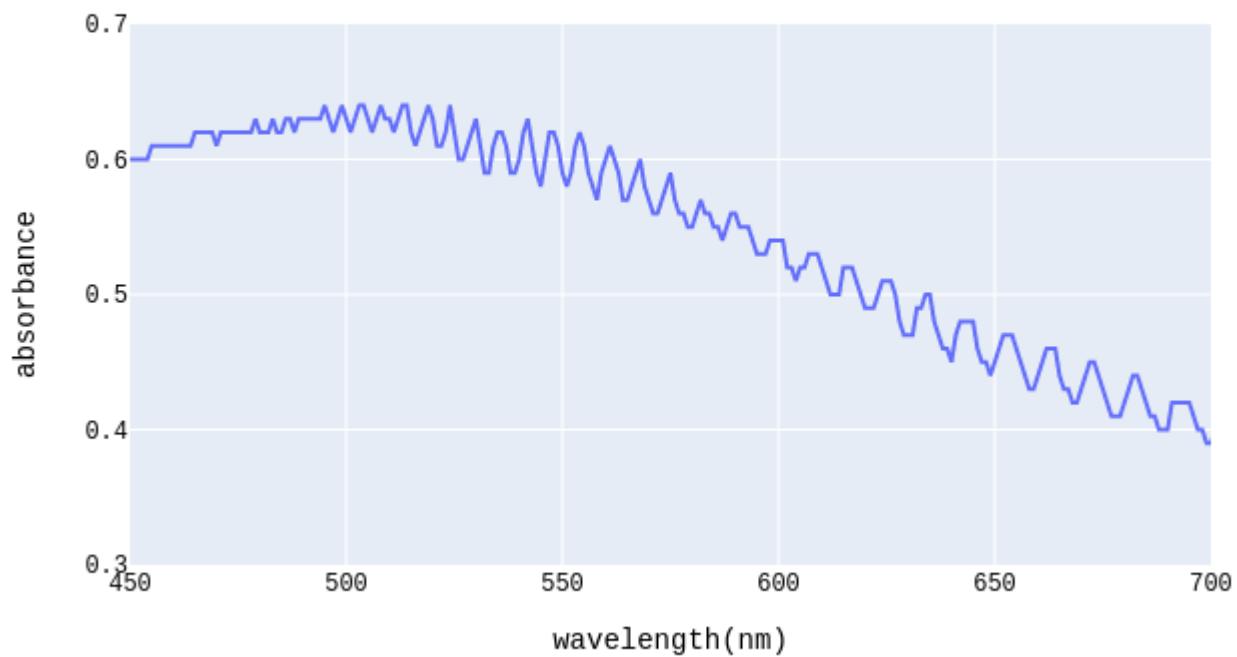
Before we get into the more complicated data analysis, it is necessary to analyse the relationship between absorbance and temperature. While the boxcar width on the graphs below is quite large (and hence not useful for later stages of data analysis) they still demonstrate this useful relationship.

absorbance spectrums for varying temperatures:



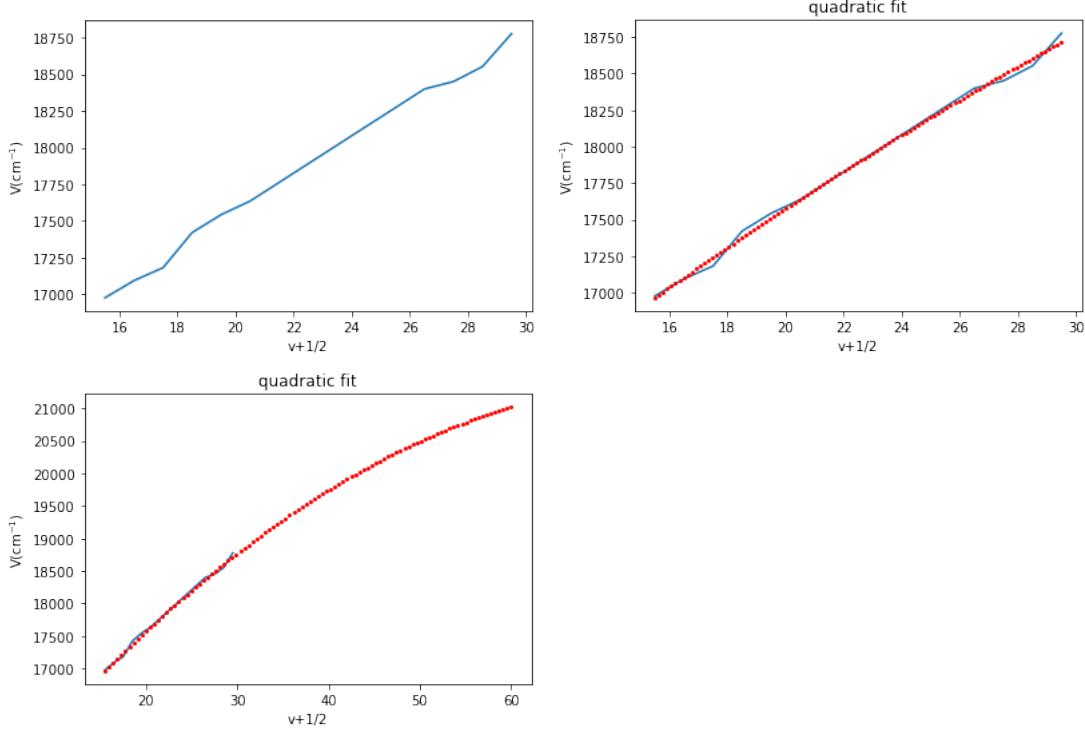
As can be seen from the above image, as temperature increases, the absorbance increases (intensity decreases), hence verifying the beer lambert law. The dataset on the next page taken with a boxcar width of 0 was used for the data analysis from which was constructed a deslandres table and birge sponer plot.

absorbance spectrums iodine(used for analysing energy transitions



v'	v''	$\lambda(nm)$	v'	v''	$\lambda(nm)$	v'	v''	$\lambda(nm)$
26	0	543.5	18	1	574	15	2	589
27	0	542	19	1	570	16	2	585
28	0	539	20	1	567	17	2	582

A plot of the wavenumber(cm^{-1}) vs $(v+1/2)$ was constructed, and a quadratic was overlaid onto it like such.



If this quadratic function is allowed to extend, V_{max} occurs at $v=21019cm^{-1}$ which equals E^* , known as the convergence limit. The fundamental frequency and anharmonicity constant were able to be determined from the fit parameters of this quadratic function. The function was of the form $ax^2 + bx + c$. $a = V_B X_B$ and $b = V_B$. $b = 175cm^{-1}$ and $a = 1.1cm^{-1}$. This means that the anharmonicity constant = $a/v_B = 0.63 \times 10^{-2}$. The literature values for these (ref(2)) were taken as anharmonicity = 0.67 and $v_B = 132cm^{-1}$. While the anharmonicity value seems to be reasonably close, the fundamental frequency is somewhat divergent with a deviation from the expected value of 32%. The convergence limit E^* found in literature was 19735 which isn't too far off what was obtained, with an error of 6%.

5 error analysis

experiment 1: In experiment 1 the main source of error would have been human, since the FWHM was measured manually by zooming in and using appropriate axes ticks. Granted this does remove rounding error of a looping algorithm for this, it could account for any discrepancy in the resolution obtained which seemed to agree very well with the values specified.

experiment 2: The error in part 2 cannot be quantified reliably as any error in this part of the experiment is error in determining by eye and by correlation with the franck condon table where respective peaks produced by energy level transitions are located. These peaks

were used to construct a deslandres table which was used throughout the experiment.
experiment 3: With this experiment there is not really any way to obtain an error other than at the point where the spectrometer is aligned with the tungsten lamp in a non optimal position. It is simply overlaying an easily plotted theoretical formula with an expected value and comparing these.

experiment 4:

Here any error that arose was likely due to a poor understanding of how to construct a deslandres table in a useful way like shown in the experimental procedure to form a quadratic. This error is also one of understanding and is somewhat difficult to quantify other than by comparison to literature values.

6 Conclusion

In conclusion, the aims of this experiment were largely fulfilled. The resolution, pixel number and bit number of each spectrometer was measured, a sufficient morse potential was created using the relevant calculations but with some slight discrepancy in De noted. The values obtained in the final part were also quite close to literature values but with some variation. The experiment was largely a success but numerical inaccuracy and deviating results may have been caused by poor execution of molecular spectroscopy methods in certain areas.

7 bibliography

- (1):Citation: Am. J. Phys. 80, 664 (2012); doi: 10.1119/1.4722793 View online:
<http://dx.doi.org/10.1119/1.4722793>
- (2)The electronic spectrum of iodine
<https://pubs.acs.org/doi/pdf/10.1021/ed057p101>
- (3) TCD lab manual - junior sophister - molecular spectroscopy
- (4) Ocean software flame specs/ located on desktop of relevant pc used for this experiment.
- (5) Harmonic oscillator expected graph (phys 11.2 the quantum harmonic oscillator /www.met.reading.ac.uk)

8 appendix

Experimental code:

```
1 #import relevant libraries and datafile
2 import numpy as np
3 import matplotlib.pyplot as plt
4 position,intensity=np.loadtxt('/home/Benjamin/Desktop/lab 2
      relevant files/3.1 experiment1.csv', delimiter=',', skiprows=1,
      unpack=True )
5 import plotly.graph_objects as go
6 import pandas as pd
```

```

7  from scipy.signal import find_peaks
8  x=position
9  y=intensity
10 fig1 = go.Figure(data=go.Scatter(x=x,y = y,mode = 'lines'))
11 intensities_peaks= find_peaks(y,threshold=15)[0]
12 #locates intensities and organises them into an array
13
14 fig = go.Figure()
15
16 fig.add_trace(go.Scatter(x=x,
17     y=y,
18
19     mode='lines',
20     name='Original Plot',
21 ))
22
23
24 fig.add_trace(go.Scatter(x=x[intensities_peaks],y=[y[j] for j in
25     intensities_peaks]
26
27         ,mode='markers',
28         ,marker=dict(size=0,color='red',symbol='
29             cross' ),
30             name='Detected Peaks'))
31
32
33
34 # EXPERIMENT 2
35
36 #import relevant libraries and datafile
37 import numpy as np
38 import matplotlib.pyplot as plt
39 position,intensity=np.loadtxt('/home/Benjamin/Desktop/lab 2
40     relevant files/3.2 nitrogen spectrum.csv', delimiter=',',
41     skiprows=1, unpack=True )
42
43 fig = go.Figure()
44
45 #creates figure
46 fig.add_trace(go.Scatter(x=x,
47     y=y,
48
49     mode='lines',
50     name='Original Plot',
51 ))
52 #adds trace of original points
53
54 fig.add_trace(go.Scatter(x=x[intensities_peaks],y=[y[j] for j in
55     intensities_peaks]
56
57         ,mode='markers',
58         ,marker=dict(size=0,color='red',symbol='
59             cross' ),
60             name='Detected Peaks'))
61 #adds peaks indicated with a cross symbol

```

```

58 fig.add_annotation(x=337.9, y=53000,
59             text="(0-0)",
60             showarrow=True,
61             arrowhead=1)
62 #labels each energy transition peak with an arrow
63 #this is repeated for the number of energy transitions found
64 fig.add_annotation(x=358.481, y=38830,
65             text="(0-1)",
66             showarrow=True,
67             arrowhead=1)
68 #etc etc..... for all other points labelled
69
70 vnum_0= [1,2,3,4]
71 #creates x axis values for part 2
72 from sklearn import metrics
73 wavelength_0_nm
    =[337.9*10**-7,358.481*10**-7,381.223*10**-7,406.583*10**-7,427.53*10**-7]

74 #values ready to be converted to cm^-1 when flipped
75 wavenumber_0= np.reciprocal(wavelength_0_nm)
76 #wavenumber is simply the reciprocal of wavelength
77 del_wavenumber_0= np.abs([x - wavenumber_0[i - 1] for i, x in
    enumerate(wavenumber_0) if i > 0])
78 #creates difference in wavenumber for 0-x transitions
79 #print(wavenumber_0)
80 #print(del_wavenumber_0)
81 plt.plot(vnum_0,del_wavenumber_0)
82 #plots number+1 vs wavenumber for 0-x transitions
83 plt.scatter(vnum_0,del_wavenumber_0,marker='o',color='red',label='
    real shape of plot unfiltered')
84 plt.title('0-x transition birge sponer plot for all x')
85 plt.xlabel('v+1')
86 plt.ylabel('del V(cm-1)')
87 #adds labels to plot
88 plt.plot(vnum_0[:-1],del_wavenumber_0[:-1],label='Linear fit
    approximation')
89 plt.scatter(vnum_0[:-1],del_wavenumber_0[:-1],marker='o',color='
    purple',label='points that fit into line fit')
90 plt.legend(loc='best')
91
92 wavelength_1_nm
    =[314.307*10**-7,329.273*10**-7,354.464*10**-7,376.248*10**-7,400.506*10**-7,435*10**-7]

93 wavenumber_1= np.reciprocal(wavelength_1_nm)
94 del_wavenumber_1= np.abs([x - wavenumber_1[i - 1] for i, x in
    enumerate(wavenumber_1) if i > 0])
95 #creates difference in wavenumber for 1-x transitions
96 del_wave1_nooutlier= [2158,1635,1608,1578]
97 #print(wavenumber_1)
98 #print(del_wavenumber_1)
99
100 plt.figure(2)
101 #creates a figure
102 vnum_1= [3,4,5,6]
103 #indicates x values of figure
104 plt.plot(vnum_1,del_wave1_nooutlier)
105 #plots number vs difference in wavenumber

```

```

106 plt.scatter(vnum_1,del_wave1_nooutlier,marker='o',color='red')
107 #adds these datapoints as discrete scatterpoints for better
108     observation
109 plt.title('1-x transition birge sponer plot for all x')
110 plt.xlabel('v+1')
111 plt.ylabel('del V(cm-1)')
112 #creates plot
113 plt.plot(vnum_1[1:],del_wave1_nooutlier[1:],label='linear fit
114     approximation')
115 #creates plot where a linear fit can be observed
116 plt.scatter(vnum_1[1:],del_wave1_nooutlier[1:],marker='o',color='
117     purple',label='points that fit into line fit')
118 #adds these as scatter points
119 plt.legend(loc='best')
120
121 vnum_2=[0,1,2,3,4]
122 wavelength_2_nm
123     =[350.823*10**-7,371.817*10**-7,394.993*10**-7,420.709*10**-7]
124 wavenumber_2= np.reciprocal(wavelength_2_nm)
125 del_wavenumber_2= [1610,1578,1547]
126 #print(wavenumber_2)
127 print(del_wavenumber_2)
128 #plt.figure(3)
129 #vnum_2= [0.1,100]
130 #lt.plot(vnum_2,del_wavenumber_2)
131 #lt.scatter(vnum_2,del_wavenumber_2,marker='o',color='red')
132 #plt.title('2-x transition birge sponer plot for all x')
133 #plt.xlabel('v+1')
134 #plt.ylabel('del V(cm-1)')
135 #area_2=np.trapz(vnum_2,(del_wavenumber_2))
136 #print(area_2)
137
138 #this is the code for a quadratic fit, ran through each set of
139     transitions
140 #was unable to properly interpret these, so I stuck with using
141     linear approximations even though they are overestimations of
142     the true value
143
144 fitparameter=optimization.curve_fit(func,vnum_1[1:],
145     del_wave1_nooutlier[1:],x0)[0]
146 print(fitparameter[0],'is a')
147 print(fitparameter[1],'is b')
148 print(fitparameter[2],'is c for 1-x transitions')
149 def integrand(x, a, b,c):
150     return a*(x**2) + b*x + c
151 a=fitparameter[0]
152 b=fitparameter[1]
153 c=fitparameter[2]
154 I = quad(integrand, vnum_1[0], vnum_1[-1], args=(a,b,c))
155 print(I,'is the integral for the 1-x transitions')
156
157 import math as math
158 w_0= (1734.02*(10**2))
159 c= (3*(10**8))
160 u=( 1.16*10**-26)
161 De= 5.4488*(1.6*10**-19)
162 k=1214.68

```

```

155 r_0= 1.20
156 #defines set of constants obtained from calculations for use in the
    morse potential
157 B=((k/(2*De))**((1/2)))*(10**-10)
158 # the value for B is obtained
159 print(B)
160 morse=[]
161 V=0
162 #while i<2:
163 #    r= i/100
164 De_=5.4488
165 #defines dissociation energy in units of electron volts
166 def Morse_v(r):
167     v=((1-((math.exp((-B*(r-r_0))))))**2))
168     return v
169 #defines a function for the morse potential
170 r=np.linspace(0.9,(4),1000)
171 #plotting range
172 for i in r:
173     plt.figure(1)
174     plt.plot(i,Morse_v(i),marker='.',color='blue')
175 plt.xlabel('Internuclear distance(angstroms)')
176 plt.ylabel('v(r)eV')
177 #plots the morse potential with the values derived in a range where
    the features can be suitably observed
178
179 # EXPERIMENT 3
180 plt.plot(position,intensity)
181 plt.xlabel('wavelength(nm)')
182 plt.ylabel('counts(w/m$^2$/nm)')
183 plt.title('Tungsten halogen lamp irradiance')
184 #rough plot off tungsten halogen lamp irradiance with labels and
    axes
185 T=2800
186 h= 6.626*(10**-34)
187 c=3*(10**8)
188 k= 1.380*(10**-23)
189 lambda_= np.linspace(350*(10**-9),1000*(10**-9),2048)
190 #suitable constants and linspace created before plotting planck
    intensity distribution
191 def intensity_(y):
192     a= (2*(math.pi)*h*(c**2))/((y**5)*(math.exp((h*c)/(y*k*T))-1))
193     return a
194 #planck intensity distribution function is made
195 real=[]
196 for i in lambda_:
197     real.append(intensity_(i))
198     plt.plot(i*(10**9),intensity_(i),marker='o',color='red',ms='2')
199 #creates a plot of the theoretical intensity while adding y values
    to a list for further evaluation later
200 scaled_intensity=[]
201 #creates empty list where real intensity values converted from w/m
    ^2/nm will be converted too w/m^2
202 plt.title('Theoretical irradiance curve')
203 plt.xlabel('wavelength')
204 plt.ylabel('intensity(w/m$^2$)')
205 #adds labels to theoretical plot

```

```

206 for i in range(0,2048):
207     scaled_intensity.append(intensity[i]/lambda_[i])
208 #the device returns units of w/m^2/nm. we obtain w/m^2 by dividing
209 #the counts by each wavelength value
210 plt.figure(2)
211 plt.plot(position,scaled_intensity)
212 plt.xlabel('wavelength(nm)')
213 plt.ylabel('Intensity(w/m$^2$)')
214 plt.title('Obtained irradiance curve')
215 #plots the new scaled intensity vs wavelength
216 #print(scaled_intensity)
217 relative_y=[]
218 #makes empty list which will house the relative intensity obtained
219 #at each point
220 for i in range(0,2048):
221     relative_y.append(scaled_intensity[i]/real[i])
222 #relative intensity is simply the ratio of the scaled intensity to
223 #the real intensity
224 plt.figure(3)
225 plt.plot(position,relative_y)
226 plt.xlabel('wavelength(nm)')
227 plt.ylabel('Relative sensitivity(expected/theoretical)')
228 plt.title('relative irradiance/intensity')
229 #graphs relative intensity as a function of wavelength
230 max=np.where(relative_y == np.amax(relative_y))
231 print(position[max], np.amax(relative_y))
232 plt.scatter(position[max],np.amax(relative_y),marker='o',color='red')
233 plt.annotate('The peak sensitivity is at ~530nm',(533,0.145))
234 #finds the max intensity on this graph and labels its position
235 #while indicating its wavelength
236 #EXPERIMENT 4
237 plt.figure(4)
238 vnumI=[15.5,16.5,17.5,18.5,19.5,20.5,26.5,27.5,28.5,29.5]
239 wavenumberI
240     =[16977,17094,17182,17421,17543,17636,18399,18450,18552,18776]
241 del_wavenumber_I= np.abs([x - wavenumberI[i - 1] for i, x in
242     enumerate(wavenumberI) if i > 0])
243 #del_num_new= [0, del_wavenumber_1[0],del_wavenumber_1[1]]
244 plt.plot(vnumI, wavenumberI)
245 plt.xlabel('v+1/2')
246 plt.ylabel('V(cm$^{-1}$)')
247 plt.title('quadratic fit')
248 #a=np.polyfit(vnumI,del_num_new,2)
249 #print(a)
250 import scipy.optimize as optimization
251 print(wavenumberI)
252 x0= [0.1,123,1]
253 def func(x,a,b,c):
254     return a*(x**2) +b*x+ c
255 fitparameter=optimization.curve_fit(func,vnumI,wavenumberI,x0)[0]
256 print(fitparameter[0])
257 print(fitparameter[1])
258 print(fitparameter[2])
259 r=np.linspace(15.5,60,100)

```

```

256 fit=[]
257 for i in r:
258     plt.figure(4)
259     fit.append(func(i,fitparameter[0],fitparameter[1],fitparameter
260 [2]))
261     plt.plot(i,func(i,fitparameter[0],fitparameter[1],fitparameter
262 [2]),marker='o',color='red',ms=2)
261 print(np.amax(fit))

```

Listing 1: Code for graphing and processing of experiments

Figure 1: flame s and flame t spectrometers



Figure 2: nitrogen lamp



Figure 3: tungsten halogen lamp

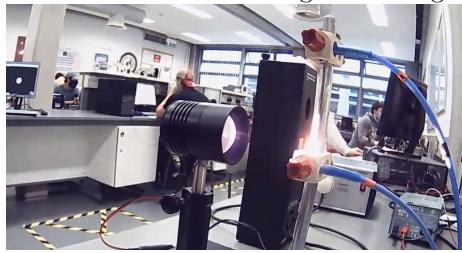


Figure 4: iodine experiment setup

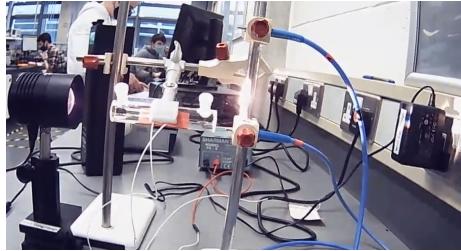


Figure 5: heater

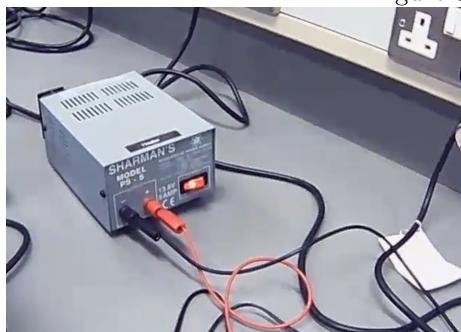


Figure 6: thermometer



Figure 7: Theory 1

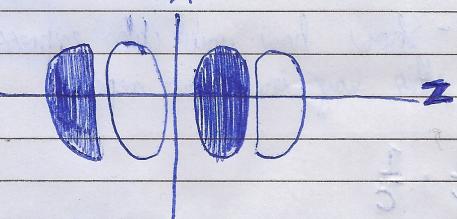
	Molecular spectroscopy: Theoretical derivations
-	Explain why one must consider the system in terms of reduced mass.
	Reduced mass $\mu = \frac{m_1 m_2}{m_1 + m_2}$
	Taking the reduced mass allows us to represent a 2-body system as a single body, making subsequent analysis much easier.
-	$v = \frac{\omega}{2\pi c}$ - Show how you can express ν in this way in your report.
	$\tilde{v} = \frac{v}{c} = \frac{\omega}{2\pi} \cdot \frac{1}{c}$
	$v = \frac{\omega}{2\pi}$ ← angular frequency $\frac{1}{c}$ ← total wavenum / cycle
-	Explain with reference to the potential well of a harmonic and anharmonic oscillator why the approximation is not not appropriate for high energy levels.
	 <ul style="list-style-type: none"> - = True energy -- = harmonic oscillator • The true potential energy is more spread out at high energies. • As we reach dissociation the harmonic oscillator is totally off.

Figure 8: Theory 2

- Explain the key differences between bonding and antibonding orbitals. Hint: Consider the graphs for charge density $P = \psi^{\pm 2}$.

- Antibonding:

A molecular orbital becomes antibonding when there is less electron density between the two nuclei than there would be if there were no bonding interactions. Destructive interference of waves occurs.



- Bonding:

A molecular orbital is bonding if there exists an attractive interaction between the orbitals of the ~~not~~ constituent atoms, i.e. they overlap. This constructive interference of waves creates a stable bond between the atoms in the molecule.

