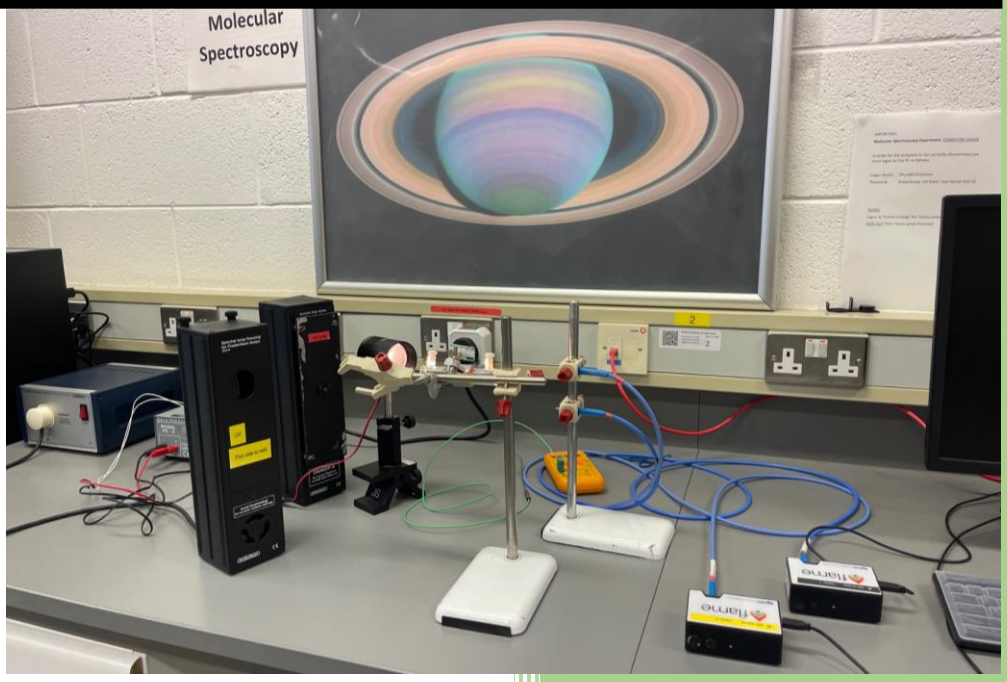
Junior Sophister Laboratory

Molecular Spectroscopy



Molecular Spectroscopy

This experiment introduces students to the principles of optical emission and absorption spectroscopy with an emphasis on molecular spectroscopy, containing information on not only the transitions between the electronic energy levels but between rotational and vibrational energy levels.

A student completing this experiment should achieve the following experimental learning outcomes:

1. Understand how to take spectroscopic measurements
2. Measure and interpret spectra of molecular systems
3. Work with literature resources and scientific papers

Students must read the background materials in advanced of attending the laboratory.

Molecular Spectroscopy

Note: While the data collection for this experiment is relatively straight forward, the data analysis is quite involved. You should attempt to complete as much of this data analysis as possible within the lab, or between laboratory sessions, so that you allow yourself the possibility of repeating parts of the experiment if you find issues with your results.

1 Introduction

The overall aim of this experiment is to introduce you to the principles of optical emission and absorption spectroscopy with an emphasis on molecular spectroscopy and what one can then learn about the molecules in question. The experiment uses two small, computerised diffraction grating spectrometers that allow a rapid acquisition of a spectrum. The spectrometer is a crossed Czerny-Turner type and uses a $50\ \mu m$ diameter optical fibre to input the light. The small size of this fibre makes it unnecessary to use an input slit on the spectrometer. The spectrum is read out in parallel using a charge-coupled device (CCD) array and fed to the computer via an analogue-to-digital converter (ADC); further details are given in the appendix and in the Software Manual. Any spectroscopy experiment requires a well characterised and calibrated spectrometer and before the experimental spectra are recorded an intensity and wavelength calibration is necessary and will be discussed.

Spectroscopy is used in many aspects of science from analysing stellar atmospheres to identifying contaminants in food samples. While Fraunhofer took the spectrum of the sun before its formulation, the major triumph of quantum mechanics is in its ability to explain such spectra.

Like atoms, a molecule has a unique spectrum associated with it containing information on not only the transitions between the electronic energy levels but between rotational and vibrational energy levels as well. This experiment looks at both the emission spectrum of nitrogen gas and the absorption spectrum of iodine gas in order to classify the types of transitions occurring and determine various constants that govern the shape of the potential well of the molecule's ground state and one of its excited states. Once the observed peaks corresponding to either specific absorption or emission transitions have been labelled and the wavenumbers of the transitions calculated it will be possible to calculate the fundamental frequency of vibrations in this anharmonic oscillator, the anharmonicity constant and force constant of the bond and plot the potential energy curve of the bond.

2 Background and Theory

As you are probably aware by now, the peaks in an atomic emission spectrum are due to electrons in a high energy level transitioning to a lower energy level emitting photons of a specific frequency given by $\Delta E = h\nu$ where ν is the frequency of the photon and ΔE is the energy difference between the upper and lower levels. This is a transition between two *electronic energy levels*. Molecules are unlike atoms in a major way in that they *vibrate* and *rotate* in different directions which give rise to *vibrational* and *rotational* energy levels respectively (Figure 1). A number of vibrational energy levels will fit within an electronic energy level and a number of rotational energy levels will subsequently fit within a vibrational energy level.

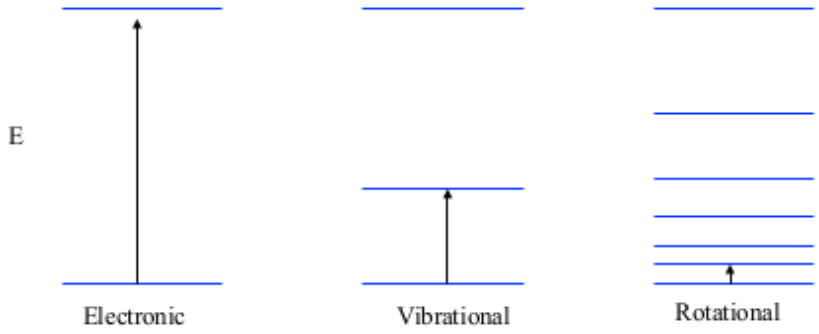


Figure 1*: Typical spacings of electronic, vibrational, and rotational energy levels.*

2.1 Molecular Vibration

Molecules vibrate similarly to a mass on a spring that is a simplest model conceivable. In this case it is two masses coupled by a spring that is almost entirely equivalent. Consider said mass and spring where its restoring force is proportional to displacement, $F = -kx$. This gives an energy potential

$$V(x) = \frac{1}{2} k\, x^2 \tag{1}$$

Solving the Schrödinger equation for a potential of this sort yields

$$E_\nu = \left(\nu + \frac{1}{2}\right)\hbar\omega \tag{2}$$

where, traditionally, ν is now and for the remainder of this script, the principle quantum number. $\omega = \sqrt{\frac{k}{\mu}}$ is the fundamental frequency of the oscillation, $\mu = \frac{m_1 m_2}{m_1 + m_2}$ is the reduced mass and k is the force constant or spring constant. *Explain why one must consider the system in terms of reduced mass.*

Again, similarly to *F(J)* in (4) expressing the system as the vibrational term we get

$$G(\nu) = (\nu + \tfrac{1}{2})\tilde{\nu} \tag{3}$$

where

$$\tilde{\nu} = \frac{\omega}{2\pi c} \tag{4}$$

is the wavenumber of the fundamental frequency of the vibration. *Show how you can express $\tilde{\nu}$ in this way in your report. What are the dimensions of wavenumbers? How does one convert wavenumbers to energy?*

Unfortunately, as is often the case, the simple harmonic oscillator is too simple an approximation to make. Although it holds well for low energy levels, the approximation is not accurate at high energy levels.

Explain with reference to the potential well of a harmonic and anharmonic oscillator why

the approximation is not appropriate for high energy levels.

To correct for this, we must consider an anharmonic oscillator with an asymmetric potential, which is called the Morse potential

$$V(r) = D_e\left(1 - e^{-\beta(r-r_0)}\right)^2 \tag{5}$$

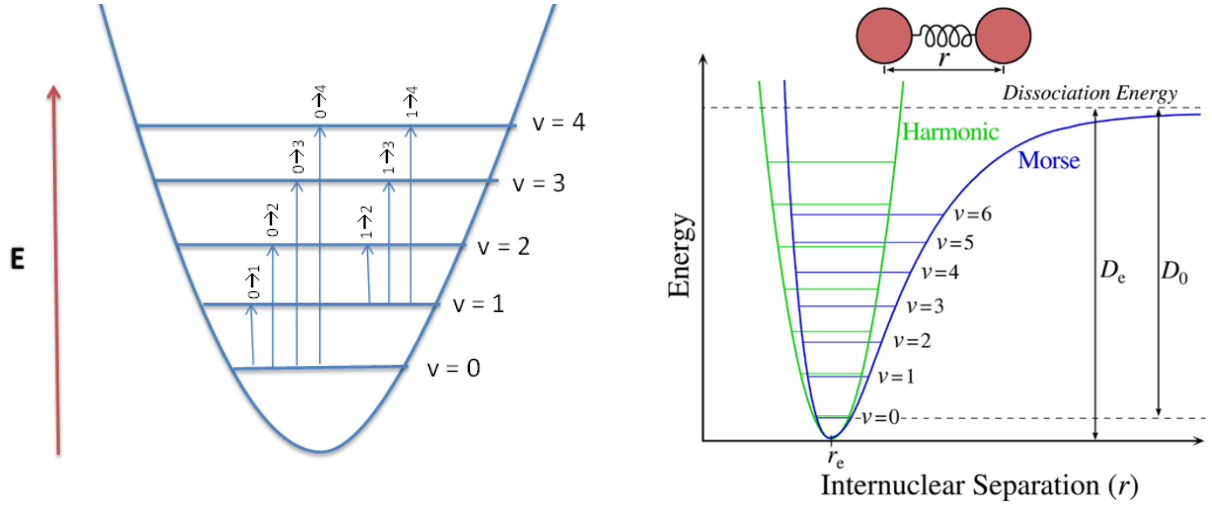
where D_e is the depth of the potential well, r is the internuclear distance, r_0 is the equilibrium distance between the two nuclei and β is related to $\tilde{\nu}$ by

$$\tilde{\nu} = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}} = \frac{\beta}{c}\sqrt{\frac{D_e}{2\,\pi^2\mu}} \tag{6}$$

Solving the Schrödinger equation for the Morse potential results in a vibrational term of

$$G(v) = \left(v + \tfrac{1}{2}\right)\tilde{\nu} - \left(v + \tfrac{1}{2}\right)^2 x_e\tilde{\nu} \tag{7}$$

where x_e is the anharmonicity constant.



(a) *(b)*

***Figure 2**: (a) Potential energy diagram for a vibrating diatomic molecule, (b) harmonic oscillator (green parabola) superimposed on the anharmonic oscillator (blue curve) on a potential energy diagram. V(R) is the potential energy of a diatomic molecule and r is the radius between the centers of the two atoms (towards the left is compression of the bond, towards the right it is the extension).*

2.2 Molecular Rotation

Not only do molecules vibrate but they also rotate. Nitrogen and iodine are both homonuclear diatomic molecules, i.e. a molecule that consists of two of the same atom joined by a bond, making them one of the simpler molecules to analyse and understand. Both are linear molecules, which also means that the moment of inertia of the rotation along the axis of the two

atoms is equal to zero. In other words, the molecule only rotates around two orthogonal axes. The energy of rotation about one axis is given by

$$E = \frac{J^2}{2I} \tag{8}$$

where J is the angular momentum and I is the moment of inertia.

$$I = \sum_i m_i r_i^2 \tag{9}$$

Quantum mechanics tells us that angular momentum is quantised and so

$$E_J = \frac{J(J+1)\hbar^2}{2I} \tag{10}$$

with $J = 0,1,2, ...$

Energies in rotational and vibrational spectroscopy are usually expressed as a rotational or vibrational term measured in cm^{-1} (inverse centimeters or wavenumbers)

$$\frac{E_J}{hc} = F(J) = BJ(J+1) \tag{11}$$

where B, the rotational constant, satisfies:

$$hcB = \frac{\hbar^2}{2I} \tag{12}$$

Equation (10) (and 11) gives rise to a ladder of energy levels where the separation between adjacent levels increases with J (see Figure 3 below).

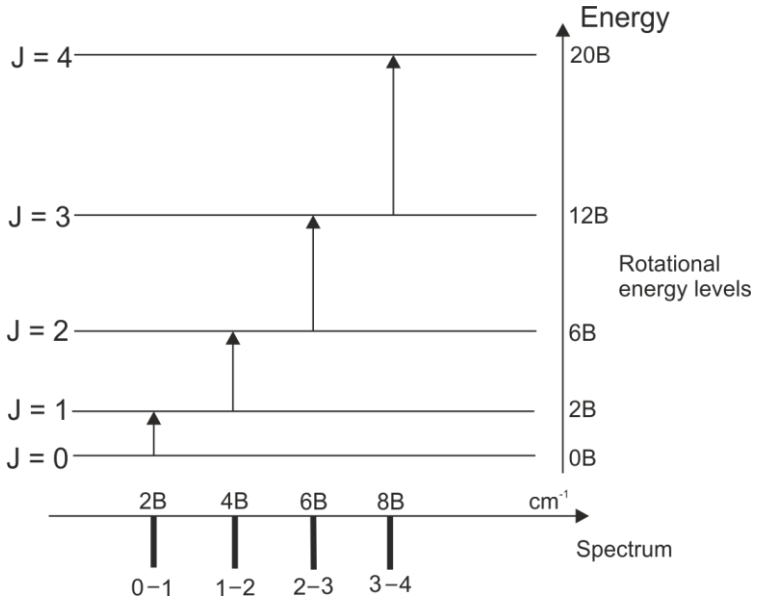


Figure 3*: Rotational energy levels of a molecule. A rotational spectrum would have the appearance as it is shown on the bottom of the image. Each line corresponds to a transition between energy levels, as shown. Notice that there are no lines for transitions (as an example) from J = 0 to J = ,2 etc. This is because the pure rotation spectrum obeys the selection rule ΔJ = ±1. The energy gap between each level increases by 2B as the energy levels we consider increase by J = 1. This leads to the line spacing of 2B in the spectrum. Each transition has an energy value of 2B more than the previous transition.*

NB! In this experiment you will not be able to observe rotational component in the resulting spectra as it would require spectrometers of much higher resolution. Instead only a combination of electronic and vibrational transitions will be seen that are called vibronic transitions.

2.3 Molecular Bonding

When the atomic orbitals of each atom combine with each other to form a molecule their wavefunctions are superimposed either constructively (bonding orbitals) or destructively (anti-bonding orbitals) depending on the symmetry of the combined wavefunction (Figure 4).

Explain the key differences between bonding and antibonding orbitals. Hint: consider the graphs for charge density $\rho = |\psi_{\pm}|^2$.

This gives rise to a splitting in energy levels with the bonding orbital having a lower potential energy than the corresponding atomic orbital and conversely the anti-bonding orbital having a higher potential energy. In the case where the atomic orbitals have a head on overlap these bonds are called σ and σ^* bonds respectively while a sideways overlap, not oriented along the internuclear bond axis, are called π and π^* bonds respectively (Figure 3).

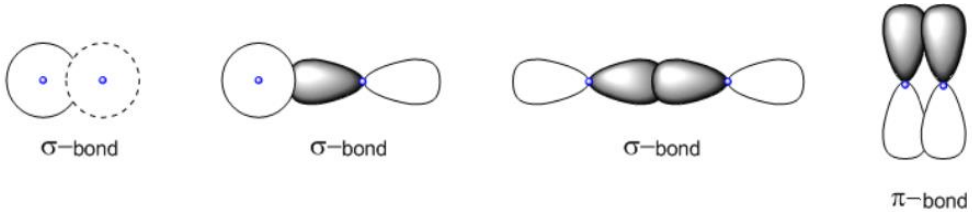


***Figure 3**: Types of bonds.*

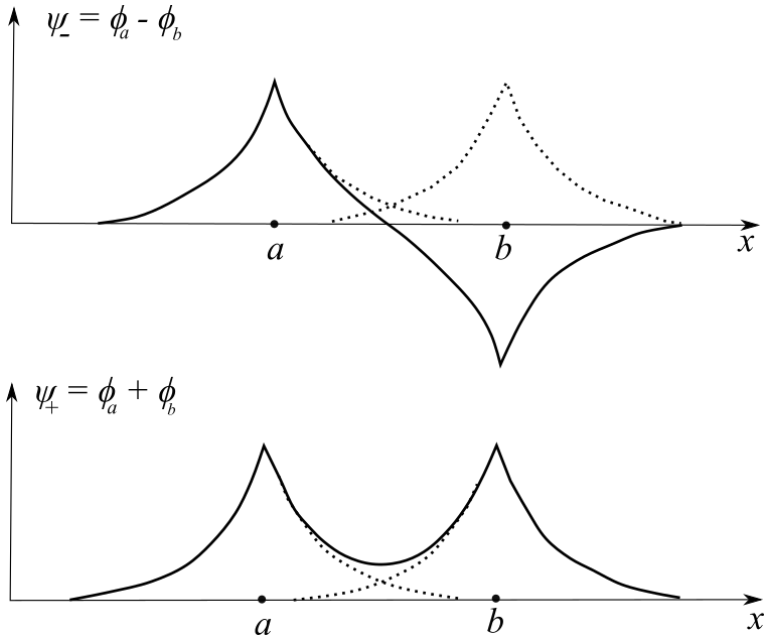


***Figure 4**: Wavefunctions for an anti-bonding orbital (top) and bonding orbital (bottom) in the simplest case of a hydrogen molecule showing atomic 1s orbitals in each case.*

The energy scales for vibrational excitations in many molecules are very low energies which correspond to wavelengths in the mid-infrared region. Instead, electronic excitations which now involve excited molecular states where one of the adjacent electrons in the neighbouring atoms may be in a higher energy atomic orbital and no longer in the ground state. The energy scale for such electronic excitations may be of the orders of several electron volts, and thus correspond to photon energies whose wavelengths fall within the visible range. This experiment will look at electronic de-excitations from high energy excited molecular states to lower energy molecular state in the case of the nitrogen molecule where the molecular emission spectrum is observed. The second part of this experiment will then look at electronic excitations from the ground to excited electronic states in the case of the iodine molecule where molecular absorption spectra will be observed.

This experiment looks at the emission spectrum of a nitrogen molecule between the $C^3\Pi_u$ and $B^3\Pi_g$ where C and B refer to the 3rd and 2nd excited electronic states for N_2 respectively and the subscripts u and g denote whether molecular orbitals are symmetric (g or gerade) or asymmetric (u or ungerade) under inversions about the centre of mass of the molecule. The labelling is a consistent way of describing the molecular states. In general, the molecular orbitals of nitrogen are formed from the overlap of the 2s and 2p atomic orbitals which can be seen in the molecular orbital diagram of N_2 on Figure 5. The potential wells and the shape and asymmetry or anharmonicity of the upper and lower potential wells against the internuclear distance coordinate are determined by the energies and interactions of the electronic states and atomic orbitals that form the bonds and states in question.

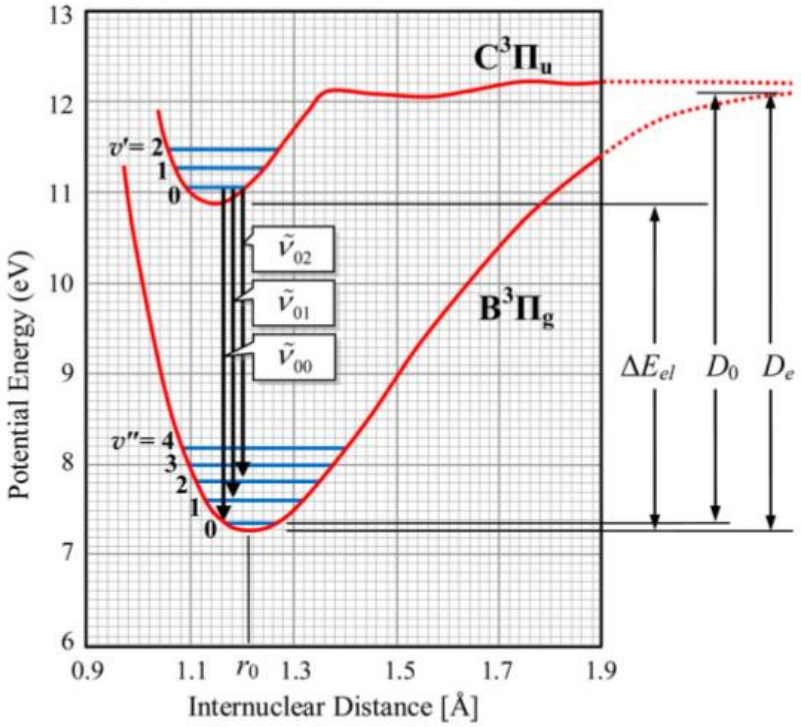


***Figure 5**: Potential energy diagram of $C^3\Pi_u$ and $B^3\Pi_u$ molecular levels with vibrational levels v' and v'' respectively. Note, the excitation energy for the $C^3\Pi_u$ state is* 11.1 eV.

2.3. Vibronic Transitions and Franck-Condon Factors

While transitions between vibrational levels within the same electronic energy levels are decided only by the selection rule of $\Delta v = \pm 1$, transitions between vibrational levels from one electronic level to another have more quantum mechanical subtleties associated with them, and are of course of higher energy, given the vertical energy scale. These vibrational-electronic (vibronic) transitions are governed by the overlap of the wavefunctions of the vibrational levels between which the transition occurs. The relation is that the transition probability is proportional to the square of the overlap integrals between the initial and final vibrational level wavefunctions, also known as the Franck-Condon factor:

$$P_{mn} \propto \left(\int \psi_{xm}^{*}(r) \psi_{yn}(r) dr \right)^{2} \tag{13}$$

where ψ_{xm} is the wavefunction of the m^{th} vibrational level in the x^{th} electronic level, ψ_{yn} is the wavefunction of the n^{th} vibrational level in the y^{th} electronic level $(y > x)$ and r is the nuclear coordinate or distance. This can be visualised in Figure 6, where portions of the wavefunctions of the vibrational level v' in the excited state and the vibrational level v'' in the ground state have the strongest degree of overlap if there is to be a minimal change in nuclear coordinates in the transition. This is expected as due to the fact that electronic transitions happen very fast compared to the timescale needed for nuclear motions, vertical electronic and vibrational transition, or vibronic transition, like the ones in Figure 6 are favored.

How do the timescales of nuclear motion and electronic motion compare to make this assumption accurate? Relate frequencies of motion of molecules, atoms, and electrons to the frequencies of the electromagnetic spectrum.

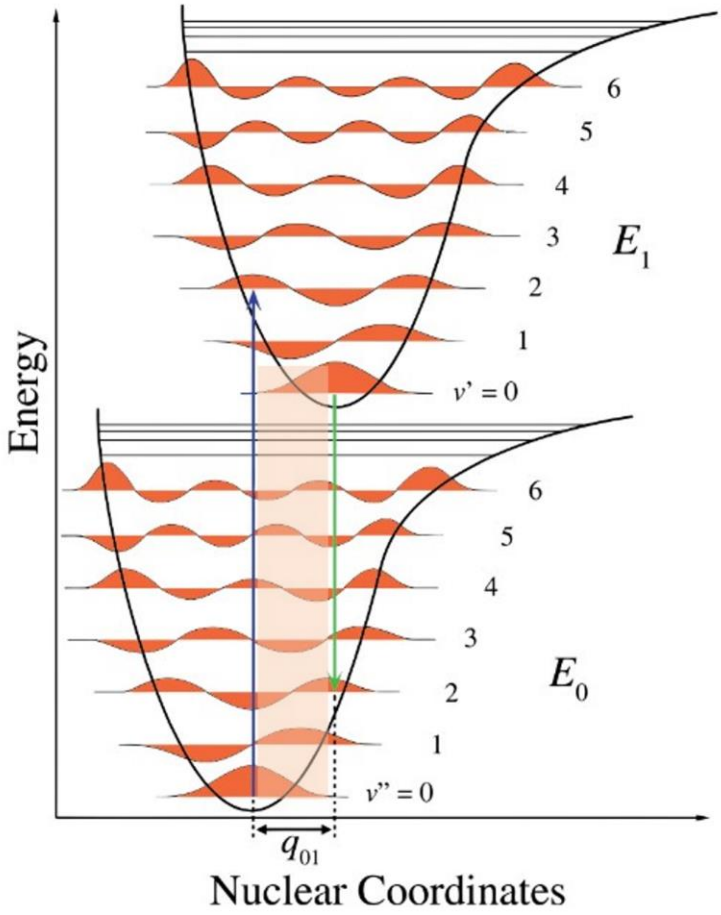


Figure 6*: Diagram demonstrating the Franck-Condon principle. The two coloured lines indicate an excitation or absorption of a photon (in blue) and a de-excitation or emission of a photon (in green). These transitions would be labelled according to the vibrational quantum numbers in the upper and lower levels. For the emission line shown in green this has an initial state where* $v' = 0$ *and* $v'' = 2$ *which is then labelled as* $\tilde{\nu}_{02}$ *as shown earlier in Figure 5. The transparent orange column demonstrates the area with large wavefunctions overlap for 0 – 0 transition.*

Following from this, a vibronic transition with a large overlap of wavefunctions (high Franck-Condon factor) has a higher probability of occurring, thus will have a larger intensity in the spectrum of the molecule. An example would be the $0 - 0$ transition in the visible emission spectrum of N_2 which has the highest Franck-Condon factor and similarly the highest intensity in the visible spectrum of N_2. A number of Franck-Condon factors are given in Table 1 to be used to help recognise and label the peaks of the N_2 spectrum. Note that some peaks with very different Franck-Condon factors are similar in intensity, why might this be?

$\nu' \setminus \nu''$	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* N_2*. Rows are* ν'*, and colums are* ν''*.*

To explain Table 1 further, the rows correspond to progressions of higher *initial* vibrational states ν'in the upper electronic state $C^3\Pi_u$ to the same *final* vibrational level in the lower electronic state. The columns are ν'' and correspond to progressions of differing *final* vibrational states in the lower electronic state $B^3\Pi_u$, arising from de-excitation from the same *initial* vibrational level in the upper electronic state. The values are in proportion to the expected intensity arising from the quantum-mechanical overlap as from Equation 13.

2.4. Energy of Vibronic Transitions

Vibronic transitions are a combination of electronic and vibrational transitions occurring at the same time, thus the energy of a vibronic transition can be found from the energies of the vibrational and electronic transitions involved. The labelling is by convention according to the vibrational quantum numbers in the upper and lower electronic states respectively as illustrated in Figures 5 and 6. This can be written in terms of the change in energy where we use wavenumbers

$$\begin{aligned}\tilde{\nu}_{\nu'\nu''} &= \frac{\Delta E}{hc} = \frac{\Delta E_{el}}{hc} + \left(\frac{E_{\nu'}}{hc} - \frac{E_{\nu''}}{hc}\right) \\ &= \tilde{\nu}_{el} + \tilde{\nu}_C\left[\left(\nu' + \frac{1}{2}\right) - x_C\left(\nu' + \frac{1}{2}\right)^2\right] \\ &\quad -\tilde{\nu}_B\left[\left(\nu'' + \tfrac{1}{2}\right) - x_B\left(\nu'' + \tfrac{1}{2}\right)^2\right] \end{aligned} \quad (14)$$

In the case of the purely electronic $0-0$ transition, for example, this gives

$$\tilde{\nu}_{00} = \tilde{\nu}_{el} + \tfrac{1}{2}(\tilde{\nu}_C - \tilde{\nu}_B) - \tfrac{1}{4}(x_B\tilde{\nu}_B - x_C\tilde{\nu}_C) \quad (15)$$

where the subscript *C* and subscript *B* refer to the 3rd and 2nd excited electronic states in nitrogen which are the upper and lower electronic states of the emitted photon in the 0 – 0 transition in the above equation.

It is convenient to combine and rearrange Eq. (14) and (15) so that the $\tilde{\nu}_{el}$ term drops out

$$\tilde{\nu}_{\nu'\nu''} = \tilde{\nu}_{00} + \tilde{\nu}_C\,\nu' - \tilde{\nu}_B\,\nu'' - \tilde{\nu}_C\,x_C(\nu' + 1)\nu' + \tilde{\nu}_B\,x_B(\nu'' + 1)\nu'' \quad (16)$$

Note that this equation now details the energy difference between the upper and lower electronic states, as being the sum of the energy between the 0 – 0 transition and two corrections for the energy above the lowest vibrational level in the upper electronic state (increasing the total transition energy) and the energy above the lowest vibrational level in the lower electronic state, decreasing the total transition energy.

The observed emission lines will all correspond to differing $\tilde{\nu}_{\nu'\nu''}$ each with distinct differing upper and lower vibrational quantum numbers. However, energetic coincidences might occur where two differing transitions are close in energy and overlap or coincide in the emission spectrum.

Evaluating $\tilde{\nu}_{01}$ and $\tilde{\nu}_{02}$ and substituting them into Eq. (16) results in two equations with two unknowns that can be solved simultaneously or via matrix multiplication depending on one's proficiency in mathematics.

$$\begin{cases} \tilde{\nu}_B - 2\,\tilde{\nu}_B x_B = \tilde{\nu}_{00} - \tilde{\nu}_{01} \\ 2\tilde{\nu}_B - 6\,\tilde{\nu}_B x_B = \tilde{\nu}_{00} - \tilde{\nu}_{02} \end{cases} \tag{17}$$

What would the simultaneous equation for finding $\tilde{\nu}_C$ and $\tilde{\nu}_c x_C$ look like?

Once the values for $\tilde{\nu}$ and $\tilde{\nu} x_B$ have been found it is possible to calculate the dissociation energy of the molecule given by

$$\frac{D_0}{hc} = \frac{\tilde{\nu}^2}{4\tilde{\nu}\, x_B} \tag{18}$$

This value can be obtained by plotting the difference in wavenumbers between two levels against $(\nu + 1)$ and calculating the area under the curve.

What sort of curve would you expect to get? If it's a straight line, what is its slope/intercept? If it's a quadratic, what are the roots, etc.?

The depth of the potential well, as seen in Figure 5, can then be found by adding the dissociation energy to the zero-point energy E_0.

$$\frac{D_e}{hc} = \frac{E_0}{hc} + \frac{D_0}{hc} = \frac{1}{2}\tilde{\nu} - \frac{1}{4}\tilde{\nu} x_B + \frac{\tilde{\nu}^2}{4\tilde{\nu} x_B} \tag{19}$$

This represents an overview of the minimum information that can be obtained from the observed spectrum of a diatomic molecule and students should consult the available literature – students **must consult** the references from the literature for more details.

3 Experiment Setup and Procedure

You will be using two different spectrometers for different parts of the experiment - the Flame T and the Flame S spectrometer. Each spectrometer is designed to have an optical fibre connected to serve as the input to the spectrometer comprised of a dispersing element i.e. the diffraction grating, and the detector. See Appendix A for the different characteristics of the two different spectrometers. The spectrometers are connected to the PC by USB, and both can use the same OceanView software to record spectra. Both of the spectrometers should be connected to the PC via USB **before** opening the OceanView software. A tab on the left-hand side of the screen allows you to switch between the spectrometer you wish to adjust the settings of (FLMS04364_1 for Flame S and FLMT01605_2 for Flame T).

With the spectrometers connected, open the OceanView software. Familiarise yourself with the operation of the software. You can look up the details of any particular aspect by clicking on its help menu or by referring to the pdf of the software manual which you will find on the PC desktop.

You should see a clear real-time spectrum from whatever the open end of the fibre is pointing at. Emission spectra can be recorded immediately with some small optimisation of intensities (positioning of fibre and coupling of light into the fibre) and of acquisition parameters (accumulation times). The transmission spectrum of a sample can be measured by placing an absorption cell in the optical path between a continuum source and the spectrometer and then recording the spectrum of the source with, and without, the sample in the cell. The absorption can then be calculated from the ratio of the spectra with and without the sample in the cell.

The OceanView software makes it possible to acquire, save and display background spectra (source blocked), set this as electronic dark noise spectra, acquire and label reference spectra (without sample) and sample spectra, whether for absorption or for emission spectra. Detailed operation of the software is as described in the software manual or help files (examine contents or search index for these topics). It is then possible to calculate and plot transmission or absorbance spectra.

At the start of the experiment, the open ends of the fibre optic cable of both spectrometers should be attached to the retort stand, with cable A on the top and cable B on the bottom. **If this is not the case, consult the lab technician.**

Always have any lamp in use facing the wall as UV rays from both lamps can damage skin. Never look directly into the lamps as this can damage your eyes.

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

Aims:

1. To determine the wavelengths of the lines in the emission spectrum of mercury in the range $300 - 510\ nm$ to calibrate the USB Flame T spectrometer, followed by the lines in the $350 - 850\ nm$ to calibrate the USB Flame S spectrometer;
2. To become familiar with the operation of the spectrometers;
3. To determine the wavelength calibration, resolving power, and resolution of the differing spectrometers.

Procedure: This calibration procedure should first be carried out for the USB Flame T spectrometer with spectral range of $300 - 510\ nm$.

1. Ensure both spectrometers are connected to the PC before opening the OceanView software. As you will be recording the spectra from the mercury discharge lamp, the open end of the fibre optic cable from the Flame T spectrometer will need to be positioned to receive light from the mercury lamp.

Ask the technician to connect up the open end of the fibre from the flame spectrometer to the optical post for viewing the mercury lamp. Do not connect or disconnect either of the fibre optical cables yourself as they can easily be damaged.

2. To login use Login/Password from a printout on the wall behind the experimental station.
3. Click on the OceanView software and view the spectrum in continuous acquisition mode (blue curve) and the spectral intensities of the light being collected by the fibre optic cable will be displayed by the software on the screen, i.e. the emission spectrum of the mercury discharge lamp. You may ignore the data from the other spectrometer (red curve) for the time being.
4. Record and explain the effect of changing the values of:
    - integration time,
    - average (number of scans over which to average),
    - boxcar setting
    - selecting "correct for electrical dark" in order to obtain a suitable spectrum (the boxcar setting must be set at 0; experiment with this and explain why?).
5. Familiarise yourself with the use of the cursor. Find the maximum number of counts before "saturation" is reached and explain why it occurs at this value (Hint: the ADC likely has 12 bits, 14 bits or 16 bits). In general, you should try to have a large count (why?), but saturation must be avoided. Examine and record the effect on the spectrum of changing the position of the lamp or of the fibre. Does the shape of the spectrum remain unchanged? If not, why not? Is the "noise" in the spectrum really noise or has it some other cause – if so, what is it?
6. Record the mercury emission spectrum and measure as accurately as possible the wavelengths of the lines according to the spectrometer and its software. Compare this data for the mercury emission spectrum to known or literature values [4] and determine any necessary offset. Determine the doublet spacing near $313\ nm$ (or near $577\ nm$

when you repeat the calibration for the Flame S spectrometer). Having measured a calibration spectrum and compared to standard values, how should one then treat subsequent recorded emission or absorption spectra?

7. Measure the optical resolution and resolving power at wavelengths corresponding to a couple of the single lines within the spectral range. Compare the optical resolution to the doublet spacing. Calculate the resolution and resolving power expected for the spectrometer using both the Rayleigh criterion and also the known width of the entrance aperture and wavelength range per pixel. Compare your theoretical values with the measured value and hence find what factors determine the resolution in this spectrometer. The definition of optical resolution and resolving power and guidelines on how to calculate them are given in the **Appendix A** or you may consult an appropriate optics textbook. You may find commercial information on the available spectrometers on the manufacturer's website, but you should also perform your own calculations.
8. Once the calibration procedure has been completed for the Flame T spectrometer (blue curve), repeat the procedure for the Flame S spectrometer (red curve).

Ask the technician to now connect the optical fibre (A) from the Flame T spectrometer to the nitrogen lamp for use in the next experiment, and to connect the optical fibre (B) from the Flame S spectrometer to the mercury lamp for calibration. Do not connect or disconnect the fibre optical cables yourself as they have a minimum bend radius, and the end of the fibre is very fragile therefore they are easily damaged. What is an optical fibre cable? Why is it so fragile?

3.2 Experiment 2: Emission Spectrum of N_2

Aims: To record, interpret and analyse the molecular emission spectrum of N_2.

1. Open the OceanView software on the computer and turn on the N_2 discharge lamp and with the fibre mounted on the panel in front of the bulb one should immediately see a clear spectrum with the maximum intensity of the $0-0$ transition at ~ 50000 counts.

Note, the N_2 discharge lamp emits a certain amount of radiation in the UV part of the spectrum. Be careful not to stare at the lamp or expose it to your skin for longer than necessary.

In all cases the lamp should NOT be turned on for longer than 15 minutes!

Also note, when turning off the lamp allow the lamp to cool down before turning back on. If there is no light being emitted when the lamp is on, turn it off, wait ~ 2 minutes and turn it back on again. If this fails, make sure the lamp is plugged in.

2. The spectrum can be observed and optimised while being acquired in continuous acquisition mode while appropriate software settings are adjusted. Note, it is possible to pause the data acquisition and save the spectrum. After an appropriate spectrum has been obtained and saved you can turn off the nitrogen discharge lamp.
3. In order to get the position and wavelength of the low intensity features in the nitrogen molecular emission spectrum take two successive spectra from the Ocean Optics spectrometer without adjustment in position, but increasing the integration time to

accumulate the low intensity features nearer to the maximum counts - yes the intense features saturate, but the position (and shape) of the low intensity features is now much clearer.

Once again: remember to turn off the N_2 lamp. Set the timer attached to the lamps plug by pressing the green button once, it should not be on longer than 15 minutes at a time.

4. Using the Franck-Condon factors in Table 1, label each of the peaks in the spectrum as $\tilde{\nu}_{\nu'\nu''}$ with differing upper ν' and lower ν'' vibrational quantum numbers from the initial and final vibrational levels. In each case calculate and tabulate the wavenumber of each peak. Click the columns button, the third button from the right that says '*View results in table* form' when you hover over it with the mouse, to get the data in a table which can be copied into a spreadsheet of your choice. You can use an example layout shown in Table 2.

$\tilde{\nu}_{\nu'\nu''}$	λ(nm)	$\tilde{\nu}$(cm^{-1})	
$\tilde{\nu}_{00}$			*the 0 – 0 transition,*
$\tilde{\nu}_{01}$			*the 0 – 1 transition,*
$\tilde{\nu}_{02}$			*the 0 – 2 transition,*
…			*etc;*
$\tilde{\nu}_{10}$			*the 1 – 0 transition,*
$\tilde{\nu}_{11}$			*the 1 – 1 transition,*
$\tilde{\nu}_{12}$			*the 1 – 2 transition,*
…			*etc;*
$\tilde{\nu}_{21}$			*the 2 – 1 transition,*
$\tilde{\nu}_{22}$			*the 2 – 2 transition,*
$\tilde{\nu}_{23}$			*the 2 – 3 transition,*
…			*etc.*

***Table 2**: N_2 emission peaks assigned using Frank-Condon factors.*

5. Include this plot in your report with labelled peaks. Ensure that the positions of the principal emission spectral lines from which you derive your quantum number assignments are clearly indicated and labelled. Make sure this plot is legible, suggest using a full-page landscape format and/or inset graphs and the most appropriate spectral ranges.
6. From the wavenumbers you found above, create a Deslandres table. An example of a Deslandres table is shown in Table 3 below, where ν'' values label the columns, ν' values label the rows, while the cells are filled with the values of the differences between them. The cell marked $\Delta\tilde{\nu}(0-1)$ is the difference in wavenumbers between the wavenumber values of the $\tilde{\nu}_{00}$ transition and the wavenumber value of the $\tilde{\nu}_{01}$ transition and may be written as. This difference is an energy interval between successive vibrational levels. Why is this the case? Explain.
   If a mistake in peak labelling is made it should become obvious from the Deslandres table that this is the case by examining the numerical progression of the intervals. Explain why. If so then ***iterate*** and trial a new peak labelling by firstly working out which emitted line has been misidentified.

Hint: what would you expect the difference in subsequent wavenumber intervals or energy separations between successive vibrational levels to be? Should the intervals be constant, should they monotonically increase, or monotonically decrease?

$v'\backslash v''$	0	$\Delta\tilde{\nu}(0-1)$	1	$\Delta\tilde{\nu}(1-2)$	2	$\Delta\tilde{\nu}(2-3)$	3
0	$\tilde{\nu}_{00}$	$\tilde{\nu}_{00}-\tilde{\nu}_{01}$	$\tilde{\nu}_{01}$	$\tilde{\nu}_{01}-\tilde{\nu}_{02}$	$\tilde{\nu}_{02}$	$\tilde{\nu}_{02}-\tilde{\nu}_{03}$	$\tilde{\nu}_{03}$
1	…	…	…	…	…	…	…

Table 3*: Example of a Deslandres table.*

7. Using Eq. (17) find values for the fundamental frequency and anharmonicity correction ($\tilde{\nu}$ and $x_B\tilde{\nu}$).

3.2.1 Birge-Sponer Data Analysis

1. Plot $\Delta\tilde{\nu}$ (e.g.$\tilde{\nu}_{00}-\tilde{\nu}_{01}$, $\tilde{\nu}_{01}-\tilde{\nu}_{02}$, etc) vs. $\nu+1$ (e.g. 1, 2, 3…) for the $0-\nu''$ transitions and determine $\tilde{\nu}$ and $x_e\tilde{\nu}$ from the slope and the intercept of the linear fit.

2. Compare the values found from the graph to those found from the Equation (17).

3. Repeat for the $1-\nu''$ and $2-\nu''$ transitions.

4. Include these graphs in your report.

3.2.2 Plotting the Morse Potential

1. Using the values for $\tilde{\nu}$ you have found from above and the depth of the potential wall D_e from Eq. (18-19), find the value of β using Eq. (6).
2. Using Python, Origin or similar, plot the Morse potential using (5) with a value of r_0 taken from Figure 5 i.e. $r_0 \approx 1.2$ Å.
3. Overlay your plot with a number of energy levels, particularly at low energies and high energies, showing the similarities and differences of the potential to that of a harmonic oscillator and include it in your report.

3.3 Experiment 3: Emission spectrum of a continuum white light source.

Aims: To evaluate the wavelength sensitivity of a spectrometer. The aim before using any spectrometer is to calibrate or know either the absolute sensitivity with wavelength of the spectrometer or, at least, the relative sensitivity with wavelength of the spectrometer. To this end the initial experiment has the objectives:

1. To record the emission spectrum of the tungsten halogen lamp.

2. To determine and account for the spectrometer system sensitivity as a function of wavelength.

Due to the spectral range this section of the experiment and that of the iodine absorption

measurement (Experiment 4) will need the USB Flame S spectrometer.

As before with the nitrogen lamp, the halogen lamp emits UV radiation. Point the lamp away from you while the lamp is turned on. Avoid unnecessary exposure to the light and do not look directly into the light source.

If not already in place, ask the technician to connect up the USB Flame S optical fibre (B) to the post on the retort stand – do not connect up the fibre yourself as you may damage the fibre.

Procedure:

1. View the spectrum of the halogen lamp in quick view or continuous acquisition mode. Again as in the Experiment 1 record and explain the effect of changing the values of:
    - integration time,
    - averaging parameter,
    - boxcar setting,
    - selecting "correct for electrical dark".
2. Familiarise yourself with the use of the cursor. Find the maximum number of counts before "saturation" is reached and explain why it occurs at this value. Similarly, you should try to have a large count but saturation must be avoided. Examine and record the effect on the spectrum of changing the position of the lamp or of the fibre.

To a good approximation the emission of this tungsten halogen lamp is that of a black body radiator with a temperature of $2800\ K$. However, your recorded spectrum will not correspond to this because the sensitivity of the spectrometer varies with wavelength. The **Appendix A** lists some of the reasons for this. The aim of this part of the experiment is to determine the sensitivity as a function of wavelength.

3. Adjust the lamp position for a "smooth" spectrum and save a copy of this spectrum.
4. Adjust the boxcar setting to smooth out the rapid variations in count and save another copy. You may assume that the emission is from a black body radiator with temperature of $2800\ K$. Planck's radiation law gives the intensity $I(\lambda)$ of a black body radiator as

$$I(\lambda) = \frac{2\pi hc^2}{\lambda^5(\exp\left(\frac{hc}{\lambda kT}\right)-1)} \tag{20}$$

5. Use this to calculate and plot a simulated black body emission spectrum over the same spectral range as the spectrometer. By comparing this simulated blackbody emission spectrum with the recorded spectrum calculate and plot the spectrometer system sensitivity (in arbitrary units) as a function of wavelength. State what you think are the main reasons for the variation of sensitivity with wavelength.

3.4 Experiment 4: Absorption spectrum of I_2

Aims: To record, interpret and analyse the molecular absorption spectrum of I_2.

This section of the experiment, that of the measurement of the absorption spectrum of molecular iodine, will require the USB Flame S spectrometer due to the spectral range it can measure.

A simple iodine vapour cell with a heater is available for this experiment. By heating the cell, (even in principle with the heat from your hand, but this is not what we will do), the solid iodine will sublimate producing within the vapour cell a column of I_2 vapour even while well below its melting point (113.6^oC)[4]. With increasing temperature, the density of the column of iodine vapour increases and hence the absorption from the Lambert-Beer law

$$I = I_0 e^{-\mu x} \tag{21}$$

will increase where $\mu = n\sigma$ is the linear absorption coefficient i.e. product of the number density, n, and cross section for absorption, σ and where x is the length of the column. As temperature increases more solid iodine is sublimated to I_2 vapour increasing its number density n and hence the total absorption. At room temperature (with no heating), the I_2 vapour pressure is minimal.

The objective of this experiment is to get an appropriate temperature where a measurable absorption occurs, allowing clear observation and identification of the I_2 molecular spectrum, but obtaining a spectrum which is neither saturated nor occurring from anything other than the molecular ground state, i.e. the absorption transitions in I_2 occur from $v'' = 0$ to values of v'. To heat the iodine vapour cell a low power heating mat is in place around the iodine cell.

Before you start the experiment with iodine, you will need to measure the I_0 spectrum without I_2 in iodine cell.

Procedure:

1. Ensure the power supply to the heating mat is switched off. Check that the heating mat is wrapped around the outer circumference of the iodine cell and connect to the power supply**. If the heating mat is not in place, then please ask the technician to help put it in place.**
2. The empty iodine cell and heating mat in the clamp should be positioned in front of the white light source and the white light source can be switched on.
3. Adjust the position of the optical fibre so that the intensity plot on the screen is at a maximum but not saturated (near the edge of the iodine cell) or if saturated adjust the integration time of the spectrometer.
4. Set up the OceanView software to take an absorption spectrum using the following steps:
    a) Click the OceanView logo under ‘File’.
    b) Click ‘Absorbance’ (top left) and then ‘Absorbance only’.
    c) Follow the wizard adjusting parameters as needed.
    d) Pay particular attention to integration time, what is the effect of changing this and what is a suitable value?
5. Measure the I_0 spectrum or spectral intensity distribution of the white light source used in this experiment. Obtain this spectrum through the cell to be used but without any iodine in the cell. Copy the intensity data into Origin or similar as this I_0 is required and will be used later to find the absorption peaks.
6. **Only then ask the technician to place a sample of iodine in the cell.**
7. Produce a column of iodine vapour within the cell. Turn on the power supply to the heater and allow the iodine cell to heat up to equilibrium ≈ 10 mins.

The cell temperature should not exceed 30^oC – if necessary, the cell temperature can be measured by placing a thermocouple on the outside of the cell wall away from the heater. (Figure A3 (**Appendix B**) shows portions of intensity spectra recorded at 18° C and 25° C illustrating the effects of heating the sample).

8. Measure the I spectrum or the spectral intensity distribution of the white light source following attenuation through the iodine vapour which will show a series of absorption features due to the possible electronic or vibronic excitations in the molecular spectrum of I_2. Again, copy the recorded intensity data into a spreadsheet for use as I. The absorption graph that was set up earlier should result in a graph similar to Figure 7 below. *Plot I_0 and I on the same graph. What kind of normalization procedure, if any, should one use in the next step?*
9. Plot wavelength vs. $-\frac{I}{I_0}$ (the minus sign is to make labelling the peaks using a "peak find" function easier) and label the absorption peaks.
10. Include this plot in your report with labelled peaks. Ensure that the positions of the principal absorption spectral lines from which you derive your quantum number assignments are clearly indicated and labelled. Make sure this plot is legible, suggest using a full-page landscape format and/or inset graphs and the most appropriate spectral ranges. Explain, with reference to the Lambert-Beer law, why one might plot in this fashion.
11. As can be seen from the guide in Figure 7, the absorption peaks between $\approx 530\,nm$ and $\approx 540\,nm$ are almost exclusively from the $v'' = 0$ level where the $0 - 26$ absorption band is at $\approx 543.5\,nm$, the exact wavelengths corresponding to this and assignments of transitions to other energy levels can be found in the literature[6,7]. Consult the literature, find the wavenumbers of these peaks.

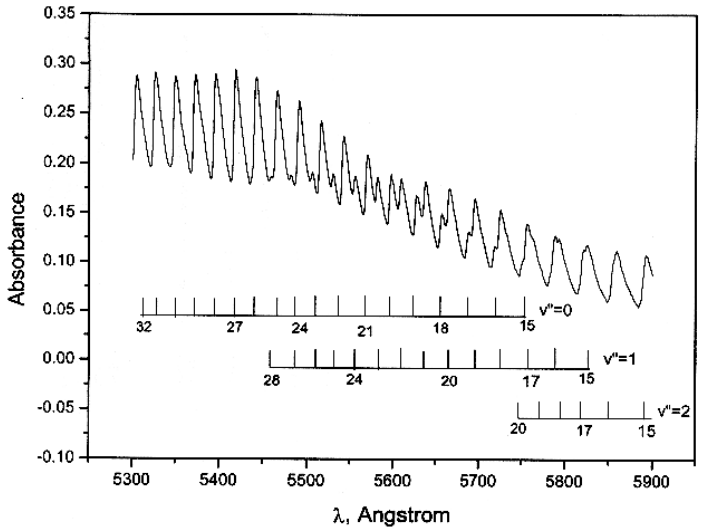


***Figure 7**: Example absorption spectrum of I_2. Numbered scales represent vibrational level assignments.*

3.4.1 Data Analysis

1. Plot $\Delta\tilde{\nu}$ vs $v+\frac{1}{2}$ and fit a quadratic function to this curve. Find the fundamental frequency and anharmonicity constant from the appropriate parameters of the curve. Refer to literature [5] and Eq. 12 for the meaning of the parameters of the quadratic function. *Include this graph in your report*. (Hint: Eq. (7) gives you the energy at a particular level) *How (and why) does this analysis differ from the analysis suggested for N_2?*

2. *Extrapolate from the graph to find E^*, the convergence limit (absorption from $v''=0$ to $v'=v'_{max}$) and include it in your report.* Hint: Both E^* and $\tilde{\nu}$ are measured in wavenumbers (cm^{-1}) meaning $\tilde{\nu}_{max}=E^*$.

3. What other data analysis, derived quantities or inferences are appropriate to calculate from the iodine spectrum bearing in mind that already undertaken for the nitrogen spectrum and the detailed suggestions in the literature? *Complete as much further analysis as is possible.*

4 Conclusions

In your conclusions compare to literature values all of the quantities derived from your diatomic molecular spectroscopy measurements of nitrogen and iodine. Further, contrast what you have learned about the relevant excited or ground state potentials and anharmonicities in the cases of both iodine and nitrogen. How do these differ and how are they similar? Is there a noticeable influence on the spectra observed from the masses of the relevant constituents?

5 References

1. Atkins, Physical Chemistry 9^{th} edition, Chapter 12

2. Herzberg, Molecular Spectra and Molecular Structure Volume 1, Chapter 3

3. Wright, J.C. ; Zielinski, T.J, "Franck-Condon Factors and Their Use in Under-graduate Quantum Mechanics," J. Chem. Educ. 1999, 76, 1367-1373. http: //dx.doi.org/10.1021/ed076p1367

4. Kaye & Laby, Tables of Physical and Chemical Constants, 16th edition, page 213; [A hardcopy of this reference book can be found on the shelf in the Junior Sophister physics laboratory.]

5. Pursell, C. J. ; Doezema, L. "The Electronic Absorption Spectrum of Molecular Iodine: A New Fitting Procedure for the Physical Chemistry Laboratory," J. Chem. Educ., 1999, 76, 839-841. http://dx.doi.org/10.1021/ed076p839

6. McNaught, I.J, "The Electronic Spectrum of Iodine Revisited," J. Chem. Educ., 1980, 57, 101-105. http://dx.doi.org/10.1021/ed057p101

7. George, S. ; Krishnamurthy N, "Absorption spectrum of iodine vapor - An experiment," Am. J. Phys., 1989, 57, 850-853. http://dx.doi.org/10.1119/1.15914

6 Image Sources

Fig. 1: Lecture 14 (2016), slide 4 from Module PY3PO5 Prof. Peter Gallagher's Atomic Spectroscopy course.

Fig. 2: Atkins, Physical Chemistry 9^{th} edition, Chapter 12

Fig. 4: Lecture 13 (2016), slide 5 from Module PY3PO5 Prof. Peter Gallagher's Atomic Spectroscopy course.

Fig. 5: S.B. Bayram ; M. V. Freamat, "Vibrational spectra of N_2: An advanced undergraduate laboratory in atomic and molecular spectroscopy," Am. J. Phys., 2012, 80, 664-669. [http://dx.doi.org/10.1119/1.4722793]

Fig. 6: https://en.wikipedia.org/wiki/File:Franck_Condon_Diagram.svg

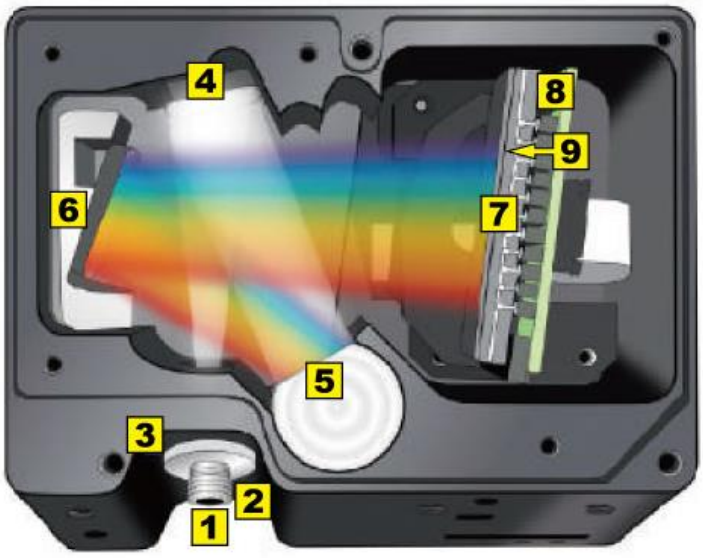
Fig. 7: http://webpages.sou.edu/~chapman/ch445/fig2.htm

Web links correct as of August 22 2016.

Appendix A. The Spectrometer

For further details see USB Flame T and S Specs located in the Spectrometer Information folder on the desktop and Optical Resolution Calculations $p(I)$ to $p(VI)$.

The OceanOptics USB Flame whether mounted on the optical rail or otherwise is plugged into the PC via a standard USB connector. The spectrometer, as illustrated in Figure A1, is a crossed Czerny-Turner type and uses a $50\mu m$ diameter optical fibre to input the light. The small size of this fibre in principal makes it unnecessary to use an input slit, but a narrower slit can be placed in front of the optical fibre to give higher spectral resolution if the customer desires. The spectrum is read out in parallel using a charge-coupled device (CCD) array and fed to the computer via an analogue-to-digital converter (ADC). The detector is a 2048 element (pixel) for Flame S and 3648 element for Flame T linear CCD array with a responsive range for photons between $190 - 1100\,nm$. However, depending on the spectrometer used the grating and spectrometer configuration only covers the range $300 - 510\,nm$ (Flame T) or $350 - 850\,nm$ (Flame S). The diffraction gratings have line densities of $1800\,lines/mm$ (Flame T) and $600\,lines/mm$ (Flame S) respectively. The efficiency of any mechanically ruled diffraction grating varies with wavelength as shown in Figure A2 and is chosen to have a maximum efficiency at a specific wavelength (the blaze wavelength), which for the holographically ruled grating in the USB Flame has an efficiency response between $200 - 635\,nm$. For the USB Flame T and the grating specifically chosen in this configuration and for this experiment, only light of wavelengths in the range $300 - 510\,nm$ is recorded by the detector so that the spectral range is $210\,nm$. Alternatively, for the USB Flame S spectrometer and the grating mounted in that spectrometer only light of wavelengths in the range $350 - 850\,nm$ is recorded by the detector so that the spectral range is $500\,nm$.



1. SMA/FC connector (optical fiber attachment position, light input port)
2. entrance slit
3. long pass filter
4. collimating mirror
5. grating
6. focus mirror
7. detector condenser lens
8. CMOS detector
9. OFLV filter (suppression of 2nd order light and 3rd order light)

Figure A1*: Internal sketch of fibre optic grating based spectrometer showing imaging onto the CCD of differing wavelengths following their diffraction from the diffraction grating.*

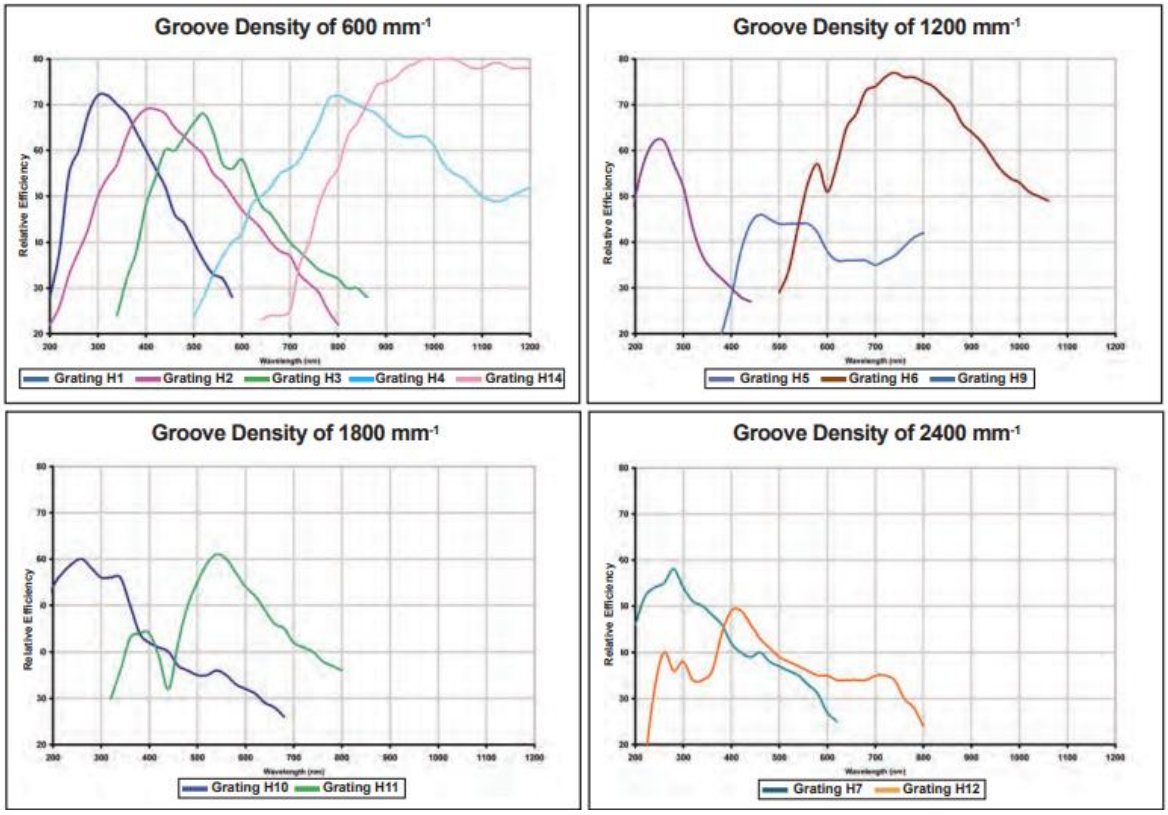


***Figure A2**: Sketch of grating efficiency versus wavelength for a blazed mechanically ruled grating (Flame S grating: H3 – 600 mm^{-1}, Flame T grating: H10 – 1800 mm^{-1}).*

A.1. Optical resolution and resolving power

The *optical resolution* is taken as the full width at half-maximum height (FWHM) of the line due to a monochromatic source.

The *chromatic resolving power*, R, is defined as $R = \lambda/\Delta\lambda$ where $\Delta\lambda$ is the minimum wavelength difference that can be distinguished by the spectrometer; in these experiments you may take $\Delta\lambda$ = FWHM.

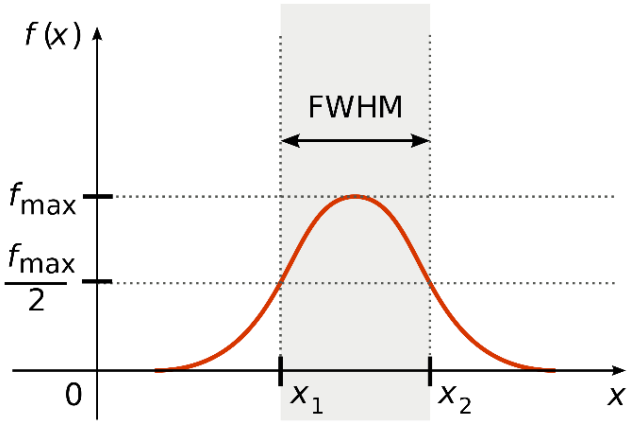


***Figure A3**: Visualization of the FWHM*

The three parameters that are most important in determining the resolution are:

1. The total number of lines on the grating.
2. The wavelength range per pixel.
3. The width of the entrance aperture.

For a grating the Rayleigh criterion gives $R = \frac{\lambda}{\Delta\lambda} = p \cdot N$ where p is the order number and N is the total number of lines on the grating. Obviously, for a grating of fixed width increasing the line density (i.e. lines per *mm*) will increase N. However, this will also reduce the spectral range (why?).

For these spectrometers Flame T and Flame S take $p = 1$ and $N = 21600$ or $N = 7200$ respectively – in each case the total number of illuminated lines on the grating that contribute to the diffracted spectrum.

The resolving power is increased by reducing the aperture width (why?). Figure A3 shows how, for this spectrometer, the *pixel resolution* varies with the slit width/fiber diameter; in this instrument of fiber diameter is 50 μm. The pixel resolution is the number of pixels that will respond for a monochromatic input; the FWHM can be calculated from this, knowing the wavelength range per pixel (this in turn can be found from the spectral range and total number of pixels).

The **sensitivity** of the instrument varies with wavelength. Many factors affect the wavelength dependence of the sensitivity including CCD response, fiber attenuation, grating efficiency and collection optics. The only practical way to account for all these factors is to do a calibration experiment.

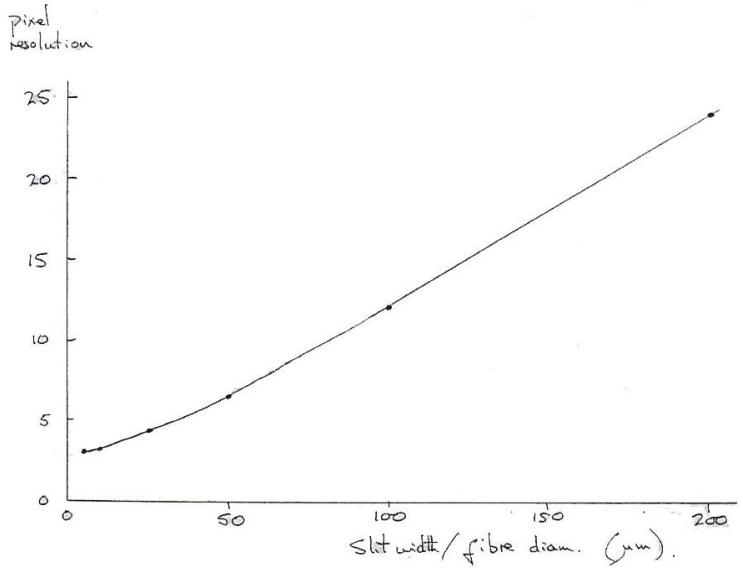


***Figure A4**: Pixel resolution versus slit width / fibre diameter. Spectral resolution takes into account the number of pixels across the spectral range of the detector.*

Appendix B.

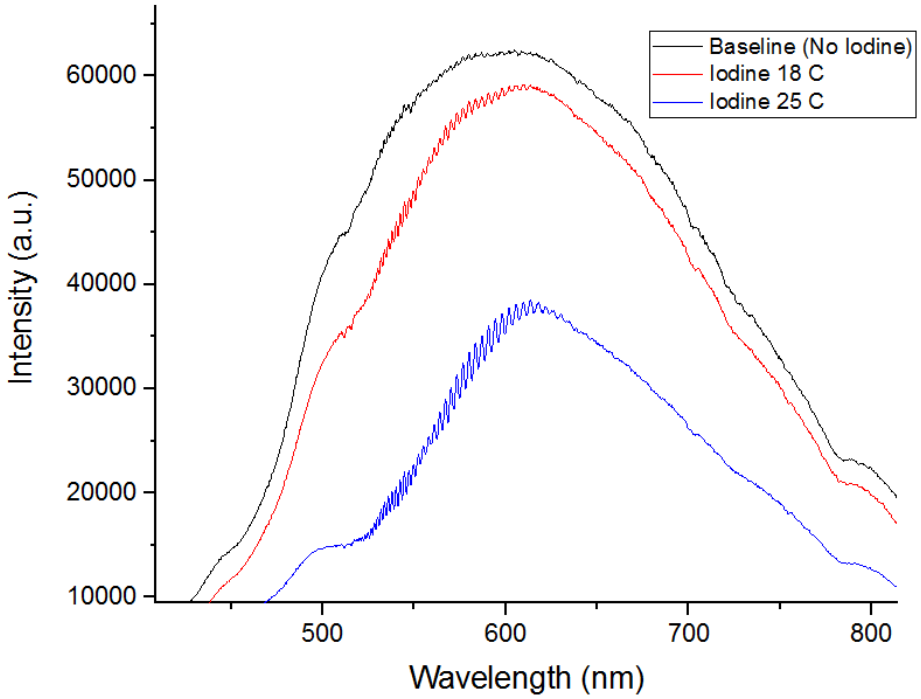


Figure A5. *Comparison of spectra recorded with no iodine present, iodine with no additional heating (18° C) and iodine after heating for 15 minutes (25° C). Note the absorption peaks are stronger for the heated sample, and that the overall intensity is lower due to the increased density of iodine in the column.*