Experiment No.8

Absorption and Fluorescence Spectrum of Iodine

AIM

1. Determine the fundamental frequency of vibration, anharmonicity constant and dissociation energy for the iodine molecule by using the absorption spectra of iodine.
2. Determine Dunham coefficient for the iodine molecule by using the Fluorescence spectra of iodine.

APPARATUS: White light source, 532 nm laser, Iodine cell, objective, Optical fibre and Spectrometer.

THEORY:

Absorption

A molecule possesses many electronic states. There are many vibrational states corresponding to each electronic state and along with these vibrational states there are many rotational states. The transitions occur according to selection rules.

Consider two electronic states: a lower (or a ground) electronic states and an upper (or first excited) electronic state. The vibrational quantum number is denoted for υ" for ground state and those in the upper state by υ'. A transition from υ' and υ" level is denoted as (υ', υ") and is called as (υ', υ") vibrational band. For example, a transition from υ'=0 to υ" =0 is called as (0,0) band. (Corresponding to these vibrational transitions, there are rotational transitions which appear as degradation to each vibrational band)
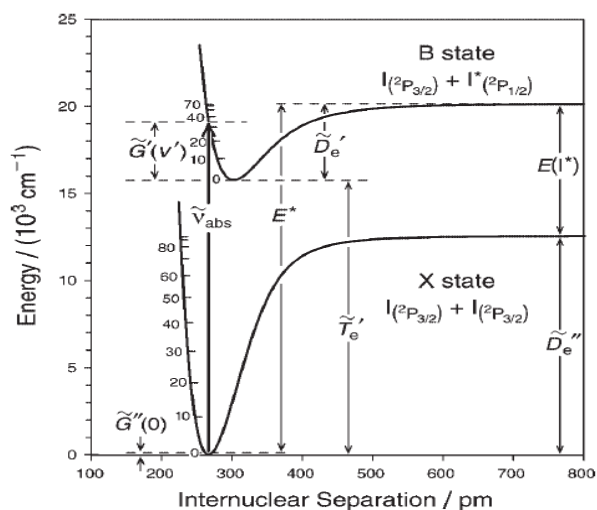

Figure 1: Potential energy curve with respect to intermolecular distance, just to show the vibration levels in the electronic state

If a continuous radiation in the visible region is passed through cell containing Iodine vapour a band spectrum can be seen through a spectrography arising from absorption by iodine molecules (I $_2$). This is an electronic transition between the ground state and the excited state as shown in the figure. The υ" = 0 to υ' = 0 known as the 0-0 transition will have the lowest frequency (highest λ) and can be located near 6200 Å. The other discrete band extend up to about 5000 Å in the place green region beyond which a continuum can be observed. Since the molecules are at room temperature, the υ" = 0 is the most populated and most of the observed bands are due to transitions for υ" = 0   to υ' = 0,1,2,3……….The wave number of these bands are denoted by " 00' " 01' " 02' "03………" 0D where D denotes the level in the upper state corresponding to dissociation (This corresponds to the onset of the continuum in the spectrum).

The total energy E of a molecules may be regarded as the sum of the individual contributions of rotational (E_r), vibrational (E_v) and electronic (E_e) energies. That is,

$$E = Ee + Ev + Er$$
(1)

[Any interaction between the above energies as well as transitional energy is neglected in Eq. (1) above]

When expressed in wave number units (cm^{-1}), Eq (1) becomes,

$$T = Te + G(v) + F(J)$$
(2)

Here, T_e , G (υ) and F(J) are the 'TERM VALUES' for electronic vibrational and rotational energies; for example, the vibrational term value is given by :

$$G(v) = Ev/hc = (v + \tfrac{1}{2})\omega e - (v + \tfrac{1}{2})2\omega e\, xe + (v + \tfrac{1}{2})3\omega e\, ye + \cdots$$
(3)

Where ω_e is the frequency for infinitesimal amplitudes of vibration and $\omega_e\ x_e$ and $\omega_e\ y_e$ are anharmonicity.

In a transition the wave-number (υ) of one of the spectral lines in by the difference between the two term values in the upper (T') and lower (T") electronics states, that is:

$$v = T' - T'' = \{(T'_e - T''_e) + (G'(v') - G''(v''))\} + \{Fv(J') - Fv(J'')\}$$
(4)

The representation of the wave-number (υ) of one of the spectral lines in an electronic transition by means of the value difference is represented in Fig.(1) and given by Equation (4) has the form:

$$v = v_e + v_v + v_r$$
(5)

Where the emitted or absorbed wave-number may be regarded as the sum of the electronic, vibrational and rotational part v_v and v_r are the wave numbers corresponding to the vibrational and rotational energy changes, respectively, and

$$ve = \frac{E'_e - E''_e}{hc}$$

v_e is the energy difference in cm^{-1} units between the minima of the upper and lower electronic states.
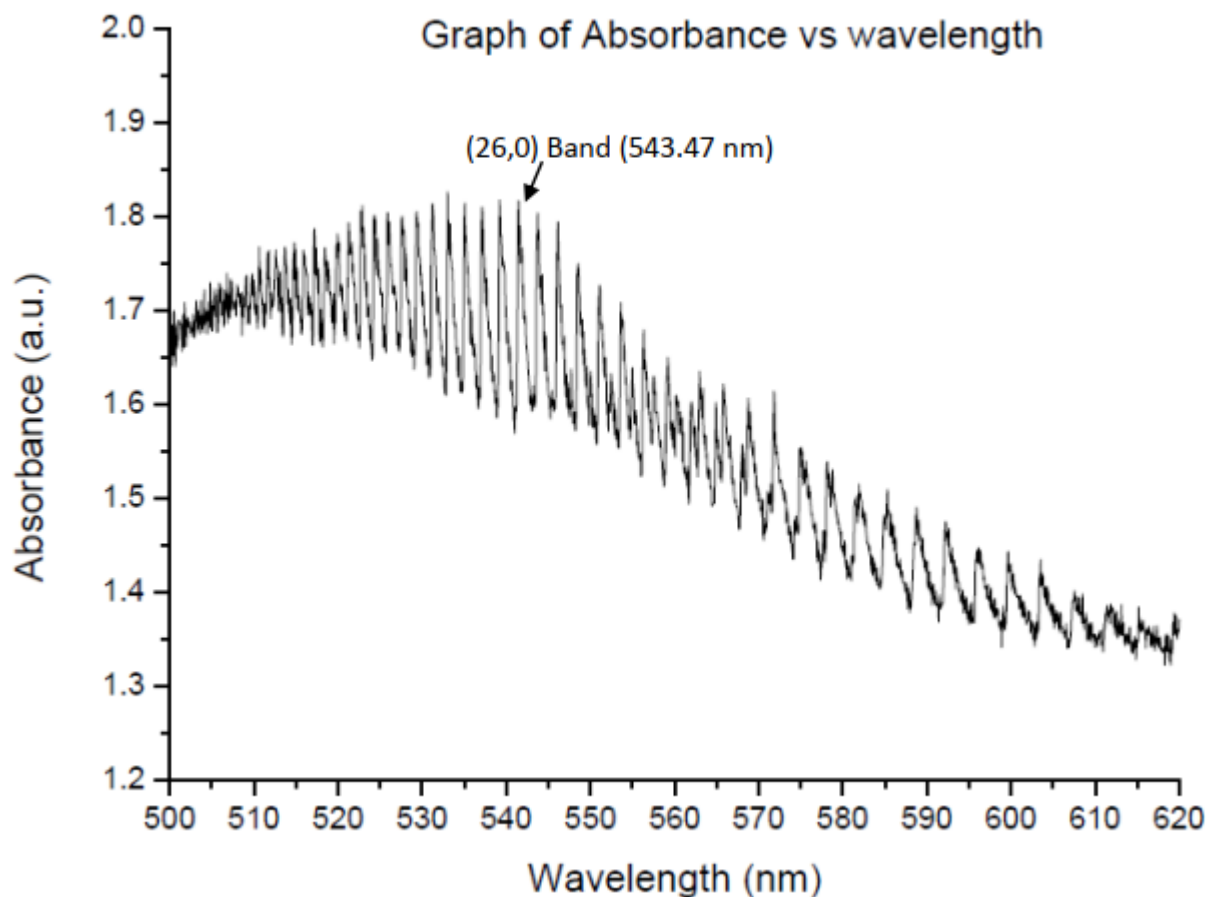

Figure 2:Absorption spectra of iodine molecule

The spectrum appears due to the absorbance of visible photons by iodine molecules, and hence electrons are promoted from the ground electronic state to the upper excited state. In the wavelength region of 500-545 nm, the nature of the spectrum is simple, and the lines originate from $v'' = 0$ vibrational level in the ground electronic state to all values of v' in the upper excited electronic state. But as we go beyond the region of 545nm wavelength, the spectrum becomes complicated due to the other bands originating from $v'' = 1$ and $v'' = 2$ in the ground electronic state.

Each small hump, or peak, such as the (26,0) band labeled on the spectrum, corresponds to a transition between two vibrational levels and is called a band. Each band is comprised of several hundred lines, each of which involves different upper and lower rotational quantum numbers as mentioned, these lines are not resolved in the present experiment. The region of maximum absorption in each band is caused by many of these lines falling together; it is called the band head.

The set of all of these bands is referred to as the visible band system of Iodine.

Find accurately the λ and $1/\lambda$ ($=\upsilon$) for the bands.

The vibrational energy terms not to the minimum of the potential energy curve where $G(\upsilon) = 0$ but to the $\upsilon = 0$ vibrational level where from equation (3) it follows that this vibrational term $G(0)$ is given by:

$$G(0) = \frac{1}{2}\omega_e - \frac{1}{4}x_e\,\omega_e + \frac{1}{8}y_e\,\omega_e + \dots \tag{6}$$

The vibrational energy term values are then measured from this $G(0)$ value, which is chosen as the new zero, and the vibrational term values are represented by the symbol $G_0(\upsilon)$ where:

$$G_0(\upsilon) = \omega_0\upsilon - x_0\omega_0\upsilon^2 + y_0\omega_0\upsilon^3 \tag{7}$$

and

$$G(\upsilon) = G_0(\upsilon) + G(0) \tag{8}$$

From figure 3 it can be seen that the wave number for transition is given by:

$$\upsilon = \upsilon_{00} + G_0'(\upsilon') - G_0''(\upsilon'') \tag{9}$$

The difference between successive levels in the excited state is given by

$G(\upsilon+1) - G(\upsilon)$, which is the wave-number separation of two successive vibrational levels in one electronic state, is represented by $\Delta G(\upsilon)$ where:

$$\Delta G(\upsilon) = G(\upsilon+1) - G(\upsilon) = \{G(0) + G_0(\upsilon+1)\} - \{G(0) + G_0(\upsilon)\} \tag{10}$$

$$\Delta G(\upsilon) = G_0(\upsilon+1) - G_0(\upsilon) = \{\omega_0(\upsilon+1) - x_0\omega_0(\upsilon+1)^2\} - \{\omega_0\upsilon - x_0\omega_0\upsilon^2\}$$

$$= \omega_0 - \omega_0x_0 - 2\,\omega_0x_0\upsilon \tag{11}$$

and $\Delta G(\upsilon)$ is known as the ***first difference.***

One can plot a graph between $\Delta G (\upsilon)$ and υ. As seen from eqn. (11), the slope of this graph gives **- 2 $\omega_0 x_0$** and intercept on y axis gives **ω_0 - $\omega_0 x_0$**.

When the quadratic expression $\omega_0\upsilon – x_0\omega_0\upsilon^2$ represents all the vibrational levels correctly.

The energy required to break the molecule into atoms is called the dissociation energy, D_0 (in cm^{-1}) is given by

$$D_0 = \frac{\omega_0^2}{4\omega_0 x_0} \tag{12}$$

Check the second difference $\Delta^2 G (\upsilon)$ is defined by

$$\Delta^2 G (\upsilon) = \Delta G(\upsilon+1) - \Delta G(\upsilon) = -2 \omega_0 x_0 \tag{13}$$

$\Delta^2 G (\upsilon)$ is known as the **_second difference._**

Thus, if the analysis is correct the second difference values for both the upper and lower electronic states have to give constant values of -2 $x_0' \omega_0'$ and -2 $x_0'' \omega_0''$ respectively. If values are not roughly constant, then the analysis is unsatisfactory.
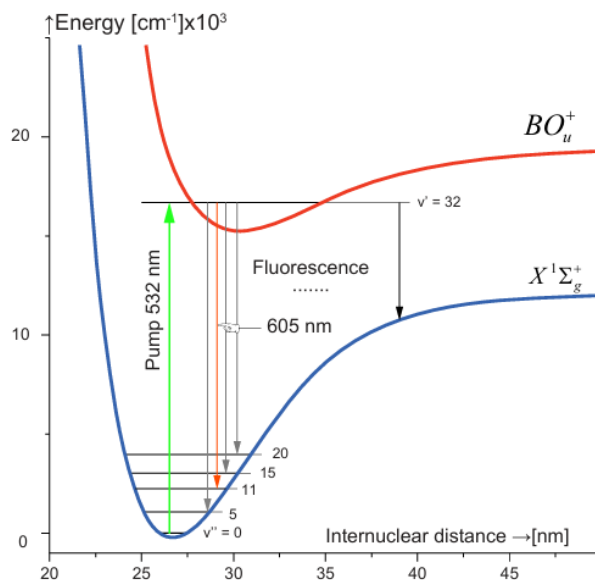
Fluorescence

Figure 3:Radiative transitions in a homonuclear diatomic

The iodine fluorescence experiment provides insights into the electronic, vibrational, and rotational energy levels of iodine molecules. By analyzing the emitted fluorescence spectrum, one can determine important molecular constants such as Dunham coefficients.

Most of the precise potential curves have been derived from experimental data with the aid of different computational schemes. They rely on semi-empirical methods like the WKB procedure, an approximation method for the solution of the one-dimensional Schrödinger equation named after the initials of the inventors Wentzel, Kramers, and Brillouin. It would be out of the frame of this introduction to explain the method. Thus, we refer to [5] for further details.

Dunham expansion which is a very common expression to calculate the rotational-vibrational energy levels of a diatomic molecule.

$$E_{vJ} = \sum_{j=0}^{\infty} \sum_{k=0}^{\infty} Y_{jk} \left(v + \frac{1}{2}\right)^j j^k (j+1)^k \tag{14}$$

Whereby v and j are the vibrational and rotational quantum numbers. The constant coefficients Y_{jk}, are called Dunham coefficients with Y_{00} representing the electronic energy. The Dunham expansion is a valuable and practical tool to calculate and identify observed transitions inside molecular energy levels.

A specific feature of homonuclear diatomic molecules is that optical (dipole) transitions are only allowed between rotational-vibrational levels of different electronic states but not within one electronic state. A further selection rule for iodine is $\Delta J = \pm 1$ for the rotational levels, while for the vibrational levels all transitions with $\Delta v = 0, 1, \cdots n$ are possible. However, the strength of the transitions depends on the Franck-Condon coefficient $q(v', v'')$, which are a measure for the overlap integral of the square of the vibrational wave functions $p(v, r)$ for some vibrational levels.

Let us now consider the situation, when green laser light at $532\ nm$ from the laser pointer is directed into the iodine cell. The wavelength of $532\ nm$ corresponds to an energy of $18797\ cm^{-1}$, which allows to shift the molecule from $v'' = 0$ of the electronic ground state to the vibrational level $v' = 32$ in the excited electronic state, as shown in Fig. 03.
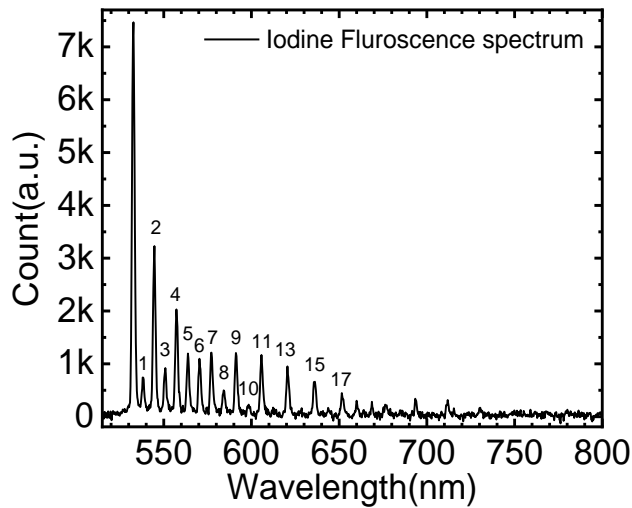

Figure 4 Measured fluorescence spectrum

After excitation, the molecules emit fluorescence lines, corresponding to transitions from the excited level $v' = 32$ to many vibrational levels of the electronic ground state, resulting in a fluorescence

progression as measured in Fig. 05. The progression may extend up to $v" = 72$, far into the infrared, but ends here at $v" = 35$, due to the sensitivity limit of the used spectrometer.

From the progression data (vibrational numbers and transition wavelengths (energies) we may determine the Dunham expansion coefficients for the electronic ground state, according to the equation

$$E = Y_{00} + Y_{10}\left(v" + \frac{1}{2}\right) + Y_{20}\left(v" + \frac{1}{2}\right)^2 + Y_{30}\left(v" + \frac{1}{2}\right)^3 + \cdots \tag{15}$$

We ignore the rotational level in this simple approximation for the moment. The value for $E(v' \rightarrow v")$ we take from the measured spectrum by converting the peak wavelength λ into energy in cm^{-1} using the relation $E(cm^{-1}) = \frac{1}{\lambda}\ (cm^{-1})$. The wavelength of $532\ nm$ for instance is related to an energy of $18797\ cm^{-1}$
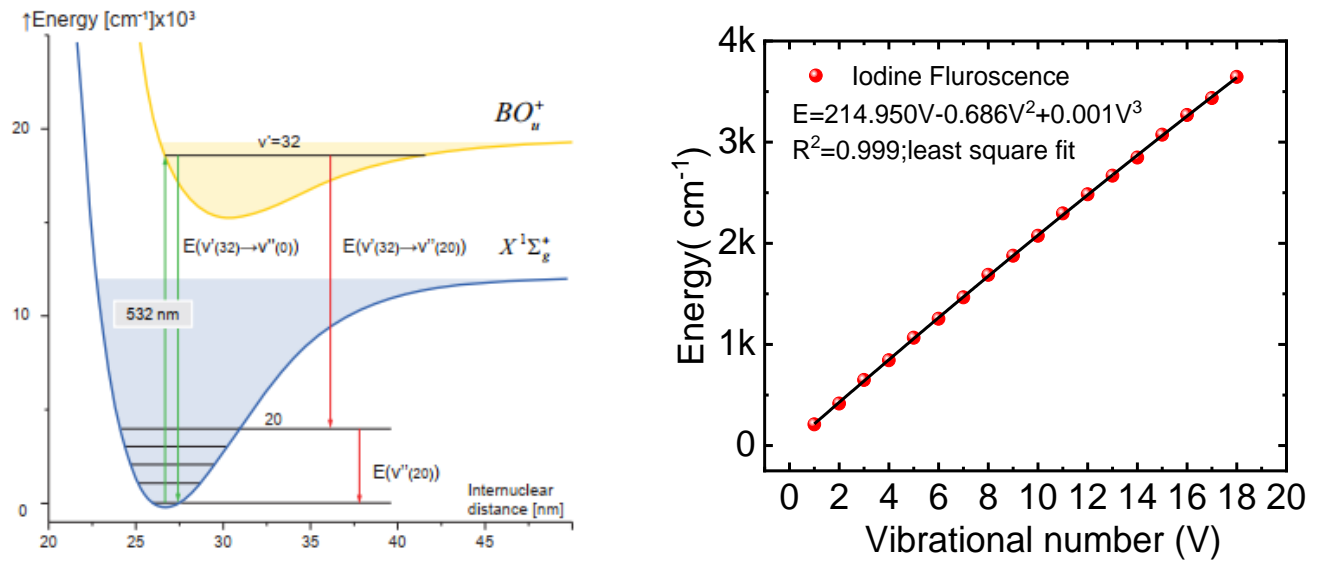

Figure 5:(a) Determine the energy E(v), (b) Ground state Energy E(v'') for the Iodine molecule

To determine the energy $E(v")$ from the measured spectrum, we need to calculate (see also Fig.5a):

$$E(v") = E_{532\ nm} - E(v' \rightarrow v") \tag{16}$$

with all energies given in cm^{-1} (1/λ). We may then create a plot of the energy values versus the vibrational number v" given in Fig. 5(b)

A least square fit of the measured energies (wavelengths) yields good parameters for the Dunham expansion
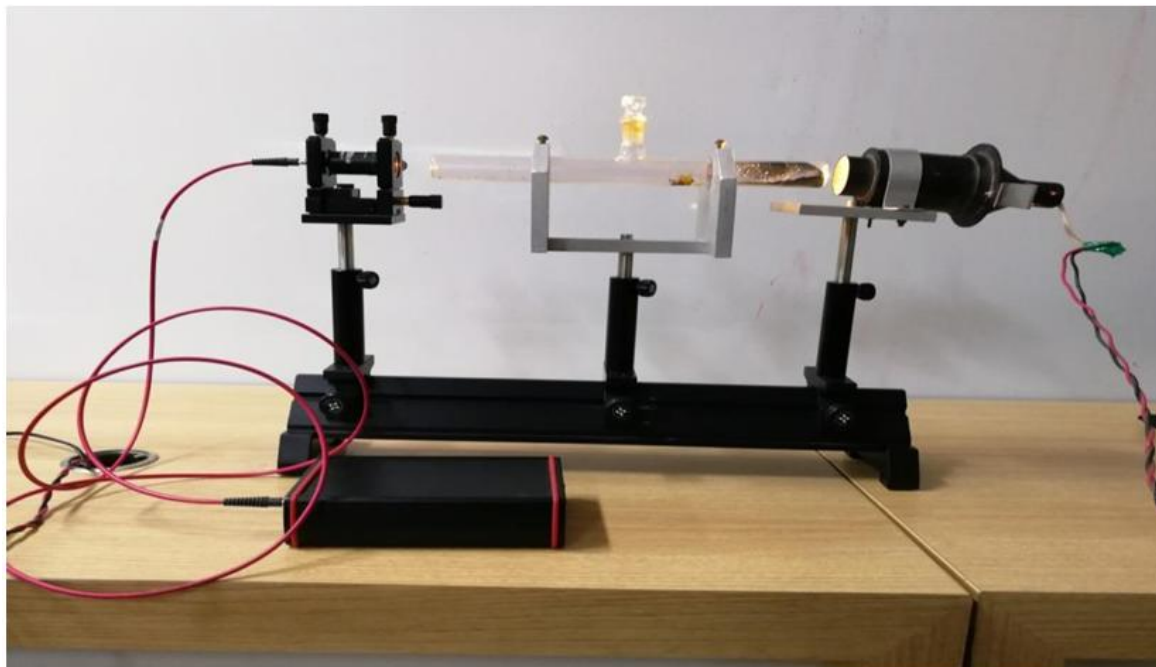
PROCEDURE:

Absorption

Figure 6.Setup for the iodine absorption spectra.

To Obtain the visible absorption spectrum of I_2 from 500-650 nm using Avantes high resolution spectrometer that has a resolution of at least 0.2 nm.

1. Place a few crystals of iodine in one of the 10 cm cells, and cap the cell. The vapour pressure of iodine is sufficient at room temperature to obtain a usable spectrum.

2. Place sample cell in the broad band light path.

3. Put the objective in front of sample cell and make sure that that the objective is aligned to the transmitted light.

4. Collect the light through multimode fibre.

5. One end of fibre connects to SMA and other end is connected to spectrometer as shown in figure 6. Heating the cell by wrapping it with heating coil will increase the intensity of the transitions.
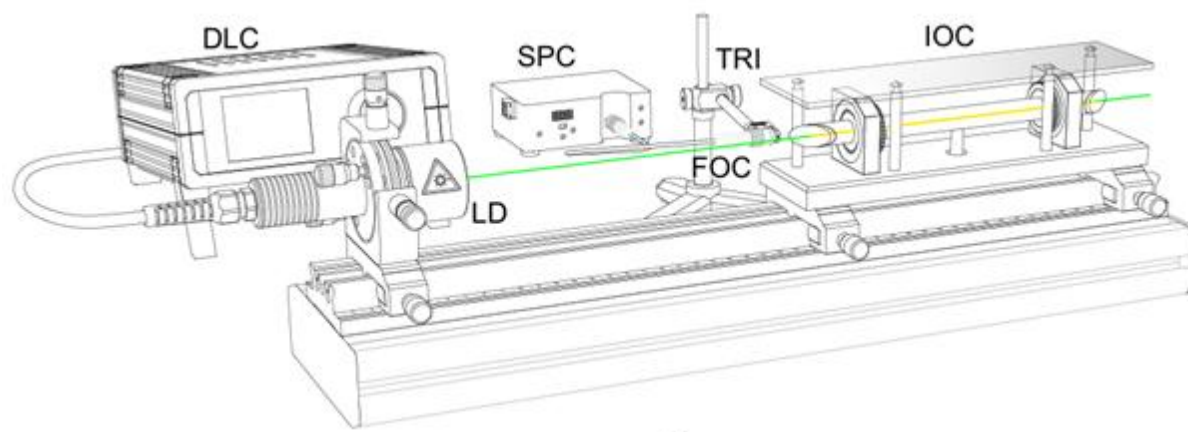
Fluorescence

Figure 7. Schematic experimental setup for Iodine Fluorescence spectrum

To obtain the fluorescence spectrum here we use 532 nm diode pump laser to excite the iodine molecules.

1. Use only one rail for the experiment.
2. Place the laser at the utmost left of the rail.
3. Position the iodine cell (IOC) at the utmost right of the rail.
4. Align the holder, which holds the glass fiber ferrule, to face the fluorescence track and adjust its position for maximum fluorescence signal.
5. Set the pump laser (LD) power around 320 mA.
6. Set the temperature to achieve maximum fluorescence, exploring a typical range of 25 – 27 °C.
7. Determine the optimal temperature experimentally, as it cannot be predicted beforehand.
8. Observe whether the fluorescence becomes stronger or weaker.
9. Continue adjustments within the specified temperature range until the strongest fluorescence is achieved.
10. The process should take approximately 15–20 minutes to identify the optimal temperature for best absorption and fluorescence.

Data Reduction and Analysis:

From absorption spectra:

Figure 2 shows a sample absorption spectrum for iodine. Assign each peak in the visible absorption spectrum of iodine to the $v'' = 0$ vibrational quantum number labelling the vibrational state in the ground electronic state in which the transition originated and the $v' = 55, 54, …15$ vibrational quantum number in the excited electronic state. Note that we also see transition originating from $v' = 1$ level of the ground state, as well as transition originating $v'' = 2$. As can

be seen from the spectrum, the intensity of these 'hot bands' swamps the intensity of the transition originating from the $v'' = 0$ state. Note that the assignment of these transitions is complicated by the fact that transitions originating from the $v'' = 0,1,2$ overlap strongly in portions of the spectrum.

From Fluorescence spectra:

Figure 4 shows a sample fluorescence spectrum for iodine. Assign each peak in the visible fluorescence spectrum of iodine. Then labelling the vibrational state in the ground electronic state $v'' = 1,2,3,4 ... ...$in which the transition occurred from $v' = 32$ vibrational quantum number in the first excited electronic state. Then determine the $E(v'')$ and calculate coefficient of Dunham expansion.

CALCULATION:

1. Draw the Birge-Sponer plot ΔG vs v. Determine the fundamental frequency of vibration (ω_0) and anharmonicity constant (χ_0).
2. Determine the dissociation energy (D_0) of iodine molecule.
3. Determine coefficient of Dunham expansion

PRECAUTIONS:

1. If the fibre is not in use than keep the fibre end closed.

2. While taking the reference spectrum, keep the fibre end sufficient away from the lamp so that spectrometer count won't get saturate.

3. Fibre, collimator and spectrometer keep back into the plastic box, once the measurement is done.

QUESTIONS:

1. What does the area under the Birge-Sponer plot suggest?
2. What is zero point energy of Morse oscillator?
3. What does integration time of spectrometer signify?
4. How accurate a result is possible using the spectrometer?
5. How would increase the temperature affect the spectrum?
6. Why you can't distinguish the peaks before 500nm in absorption spectra?
7. How many bands did you observe in your experiment?

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