Emission spectra of metals using constant deviation spectrometer

Introduction:

An instrument used to study the spectra with unaided eye is called spectroscope or spectrometer. When it is used to photograph, the spectrum it is called spectrograph. A constant deviation spectrometer got its name due to the fact that it uses constant deviation prism or Pellin-Broca prism.

Objective:

  (i)   Calibrate the C.D.S using a calibration source

  (ii)   Determine the weave length of the unknown spectra of the given metals in the arc lamp source.

Apparatus: The constant deviation spectrometer (C.D.S), The calibration source (mercury lamp), D.C.Power supply, the arc stand, the metals (Copper, Brass, etc.), Spirit level.

Theory:

When refraction through a prism takes place in such a manner that the angle of incidence is equal to the angle of emergence, the refracted ray will be parallel to the base of the prism (see Fig. 1). The ray is symmetrical under these conditions. It can be mathematically proved that when the above conditions are satisfied for a particular value of *i*, the deviation suffered by the light ray is minimum and the angle of deviation is known as the angle of minimum deviation δ_m. For any other value of *i*, the value of δ increases.
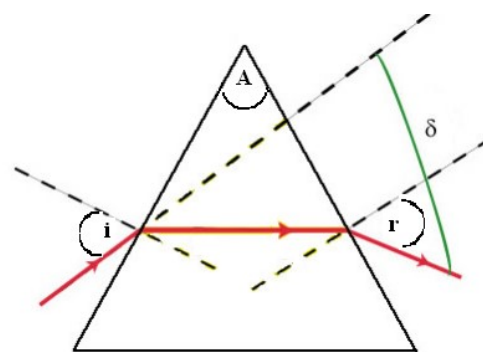

Figure 1: Angle of deviation in ordinary prism

Constant deviation prism

The construction of constant deviation prism is a single piece but can be considered as composed of two *30°* prisms, PQR and QST along with the reflecting prism PRS (see Fig. 2). AB is an incident ray and θ_i is the angle of incidence. For certain θ_i BC is normal to PR and totally reflected at PS and undergoes deviation of *90°*.

Since

$$m\angle PQT = 90º \quad \text{and} \quad m\angle\ BCD = 90º \tag{1}$$

we have, $\qquad\qquad m\angle QBC + m\angle QDC = 180°$ $\qquad\qquad$ (2)

But, since $\qquad\qquad m\angle QBC = 90° + \theta r$ and $m\angle QDC = 90° - \theta_i$, $\qquad$ (3)

Therefore, $\qquad\qquad (90° + \theta r) + (90° - \theta_i) = 180°$. $\qquad\qquad$ (4)

Thus $\theta_r = \theta_i$ and emergent ray is perpendicular to the incident ray (this can be easily proved from the geometry of the figure). Two prisms PQR and QTS can be considered as a single **prism** of *60°*. When the angle of incidence is equal to the angle of emergence and the angle of deviation is *90°*, a ray would be passing through a position of minimum deviation. This principle is used in constant deviation spectrometer.
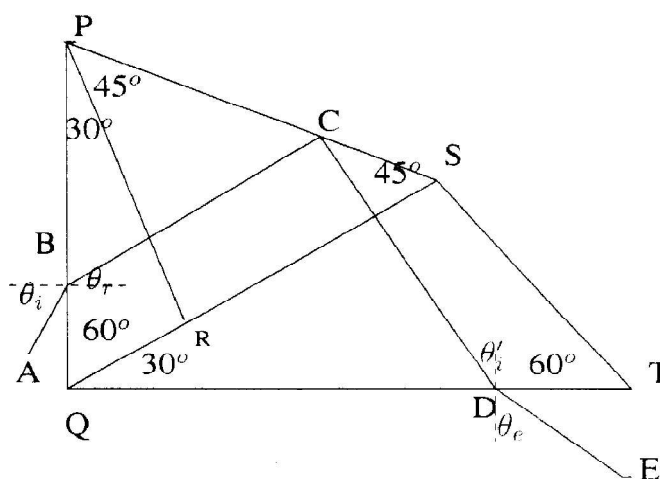

Figure 2: Constant deviation prism

Experimental set up:

The schematic of constant deviation spectrometer set up is shown in Fig.3.

The collimator and the telescope are fixed and the axes are perpendicular to each other. The prism table can be rotated about the vertical axis using a drum which is attached to the table. The head of the drum is calibrated for the wavelength and thus the wavelength can be measured directly. When the light is incident on the prism the prism table can be rotated till the angles of incidence and emergence are equal. The pointer seen in the field of view of telescope can be used for the measurement. After clamping the prism the drumhead is rotated to rotate the prism table and the desired wavelength is measured.

An ordinary prism and a spectrometer can be used for this task, but the process is time consuming. The adjustment of minimum deviation and if it is disturbed, resetting is troublesome. In case of constant deviation spectrometer, if the prism is disturbed it can easily be reset by using a source of known wavelength.
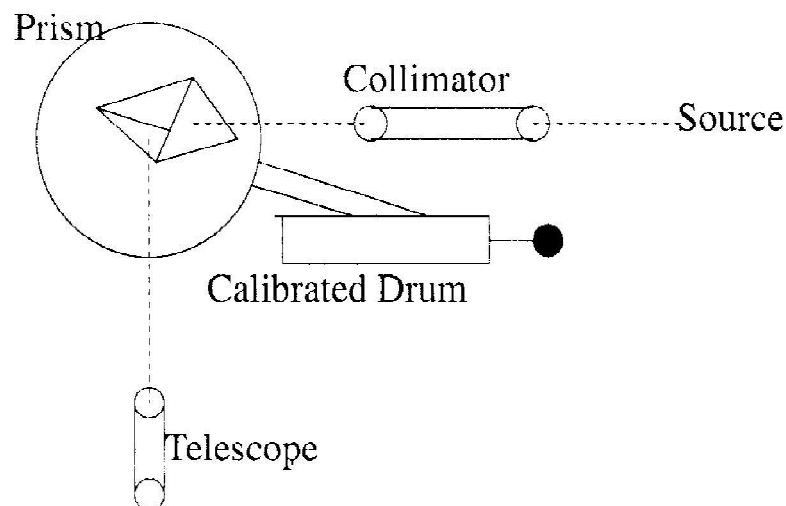
Figure 3: Experimental set up for Constant Deviation Spectrometer

PROCEDURE:

1. Level the constant deviation spectrometer by means of a sprit level and focus the telescope.

2. Place the constant deviation prism on the prism table so that its 90˚ vertex faces towards the objective of the telescope.

3. **Calibration of the spectrometer:** The drumhead is calibrated using known wavelengths of a calibration source, which is a mercury lamp in this case. The lamp is placed in front of the collimator.

4. The drum is rotated so that it reads a value closest to the value of the single and prominent green line. Now, by slightly rotating the prism and looking through the telescope, the green line is made to coincide on the pointer/crosswire.

5. Once the spectral line coincides with the pointer, clamp the prism. Now, note down the closest values read by the drum ($\lambda_{observed}$) corresponding to the given values (λ_{given}) of different wavelength of mercury. Plot $\lambda_{given} \sim \lambda_{observed}$ and fit it with a straight line to obtain the calibration parameters. Using these parameters any observed unknown wavelength can be calculated to determine the correct wavelength λ_{corr}.

6. Then replace the calibration source by the arc source using a particular metal arc of interest.

7. The D.C.power supply is connected to the arc stand holding the pointed metal arc one over

the other. Switch ON the power supply and observe the arc begins to glow.

8. The spectrum is observed in the CDS. Adjust the drum head to make the pointer/crosswire coincide on each of the spectral lines and read the characteristic wavelength of the different lines emitted by the metals directly.

9. Compare the values of spectral lines obtained for different metals with the literature values.

Observation:

(I)   Table for calibration using mercury lamp

Sl. No.	λ_{given}	$\lambda_{observed}$

(II)   Table for emission spectrum of metals

Sl. No.	$\lambda_{observed}$	λ_{corr}	λ_{lit}

PRECAUTION:

1. The arc points or the holders should not be touched as they carry high voltage.
2. To start the glow the two pointer arcs should be brought very close, nearly to touching position and after the glow a minimum gap is maintained to avoid excess load on the power supply.
3. After taking readings, allow the metal rods to cool down before changing to another pair of rods.

Absorption spectrum of Iodine vapour using constant deviation spectrometer

Introduction:

Determining the absorption spectrum of iodine is a classic experiment in Physical Chemistry. Study of this spectrum clearly shows the relationship between vibrational and electronic energy levels by introducing the concept of a vibronic transition, demonstrating the anharmonicity of vibrational energy levels, and providing the dissociative limit for the vibronic transitions.

According to Schrödinger equation every bound system of particles can have only discrete energy levels and any transition between two such levels results in absorption or emission of a photon with energy equal to energy difference of the two levels. In this experiment, a white light source with a continuous spectrum is used to excite the molecules of iodine vapour. When the spectrum of light after passing through the iodine vapour is analysed by a spectrometer, it is observed that specific wavelengths are absorbed. Each absorbed wavelength will appear as a dark line in the spectrum corresponding to the difference of different energy states of iodine molecule. The characteristics of the iodine molecule can be determined from this spectrum.

Objective:

To study the absorption spectrum of iodine vapour with Constant Deviation spectrometer and then to determine:

(a) the energy level diagram of iodine molecule

(b) the electronic energy gap and vibrational energies

(c) bond dissociation limit.

(d) force constant for the excited state

Apparatus Required: (1) Constant deviation spectrometer with the special prism (Pellin-Broca), (2) a mercury lamp for calibration, (3) an incandescent bulb of 60 to 100 watts, (4) a long glass tube with plane windows to hold the iodine vapour.

Theory:

In atoms and molecules different electronic energy levels exist corresponding to particular quantum states. The lowest energy level is called the ground state, all higher energy states are

called excited states. The potential energy experienced by the electrons in a molecule in any "bound state" is described by the anharmonic Morse potential[1]:

$$U(r) = D_e\left[1 - e^{-a(r-r_e)}\right]^2 \qquad (1)$$

where D_e is the depth of the potential well, r_e is the internuclear distance between the atoms at the energy minimum (also called the bond length), a is the constant for a particular molecule given as:

$$a = \overline{v_e}\sqrt{\left(\frac{\pi c \mu}{\hbar D_e}\right)} \qquad (2)$$
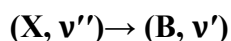
Here $\overline{v_e}$ is the wavenumber corresponding to the harmonic vibrational frequency (in cm^{-1}) in the given electronic state and μ is the reduced mass of the system. Solving the Schrodinger equation with Morse potential the vibrational energy states can be obtained as follows:

$$E(v) = \overline{v_e}\left(v + \frac{1}{2}\right) - \overline{v_e}x_e\left(v + \frac{1}{2}\right)^2 \qquad (3)$$

where v is the vibrational quantum number (=0,1,2…) and $x_e\left(= \frac{\overline{v_e}}{4D_e}\right)$ is the anharmonicity constant.

Vibronic transition in iodine:

Molecular iodine is purple in colour because it absorbs light in the visible (yellow) region of the electromagnetic spectrum. The absorption involves the following transition

$$(\mathbf{X, v''}) \rightarrow (\mathbf{B, v'})$$

where X represents the ground state and B is the first excited electronic energy state. v'' (=0, 1, 2 etc) and v' (=0,1,2, etc) represent the vibrational quantum numbers in the ground and excited electronic states, respectively.

Figure 1 shows a schematic energy level diagram of iodine with ground and first excited electronic state along with the vibrational states. At room temperature most of the molecules of iodine reside in ground state $v'' = 0$. When a beam of light having continuous spectrum is made to pass through the iodine vapour the first transition corresponds to $v'' = 0$ to $v' = 0$ which is labelled as 0←0 absorption line. The next peak corresponds to the 1←0 transition, the third, 2←0 and so on. However, according to Franck-

Condon principle[1], only those transition will be much more probable for which the wavefunctions of the two states overlap effectively. For iodine molecule the wavefunctions don't significantly overlap with the ground state wavefunction. So the transitions are usually
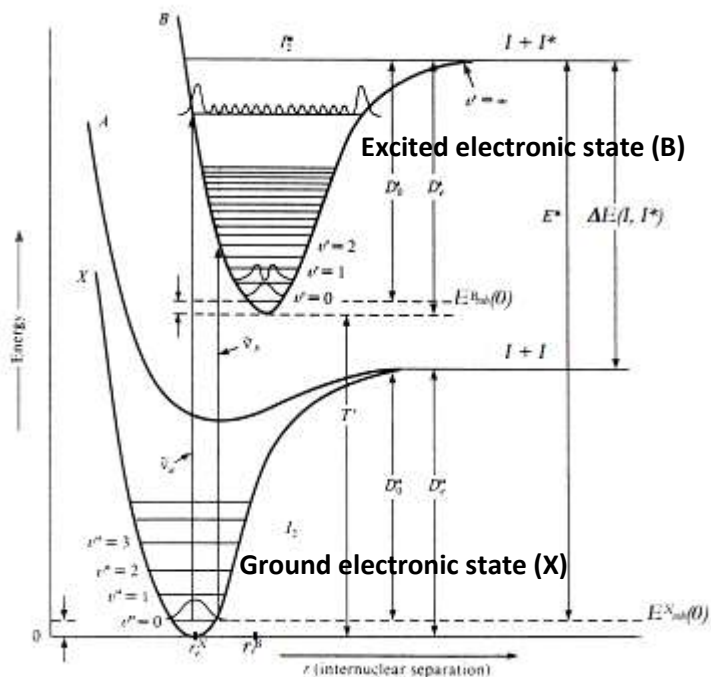

Fig. 1: Schematic energy level diagram of iodine

in the range[3] 20 to 50←0. Usually a series of narrow bands are observed in the absorption spectrum instead of sharp lines. This is due to transitions involving excited vibrational levels in the ground state (hot bands, $v'' \neq 0$) and rotational levels. At the upper edge of the well ($v' \rightarrow \infty$, let us denote it as v'_{max}) , the vibrational energy spacing decreases to 0, which means that the energies form a continuum rather than being quantized. It is at this limit where bond dissociation occurs. From Fig. 1 the bond dissociation energy in the excited state (D_0') is the difference in energy values at $v'= 0$ and v'_{max} :

$$\mathbf{D_o = E(v'= v'_{max}) - E\ (v'=0)} \qquad (4)$$

Scope of the set up:

As mentioned earlier, the absorption lines will appear as narrow bands due to superposition of hot bands and rotational bands which remain unresolved in this set up. Thus, one can estimate the approximate values of highest and lowest energy levels due to absorption. During testing of the set up it is observed that the vibronic energy levels are coarsely equispaced whereas the difference of the levels should decrease towards higher levels. This means one can safely use simple harmonic oscillator equations to

calculate the energy values (put x_e=0 in Eq. 3) and force constant etc. If $\Delta\overline{v}_{e\text{avg}}$ is the average value of change in wave number of two consecutive states, then the force constant, f, of iodine molecule in excited state is given as:
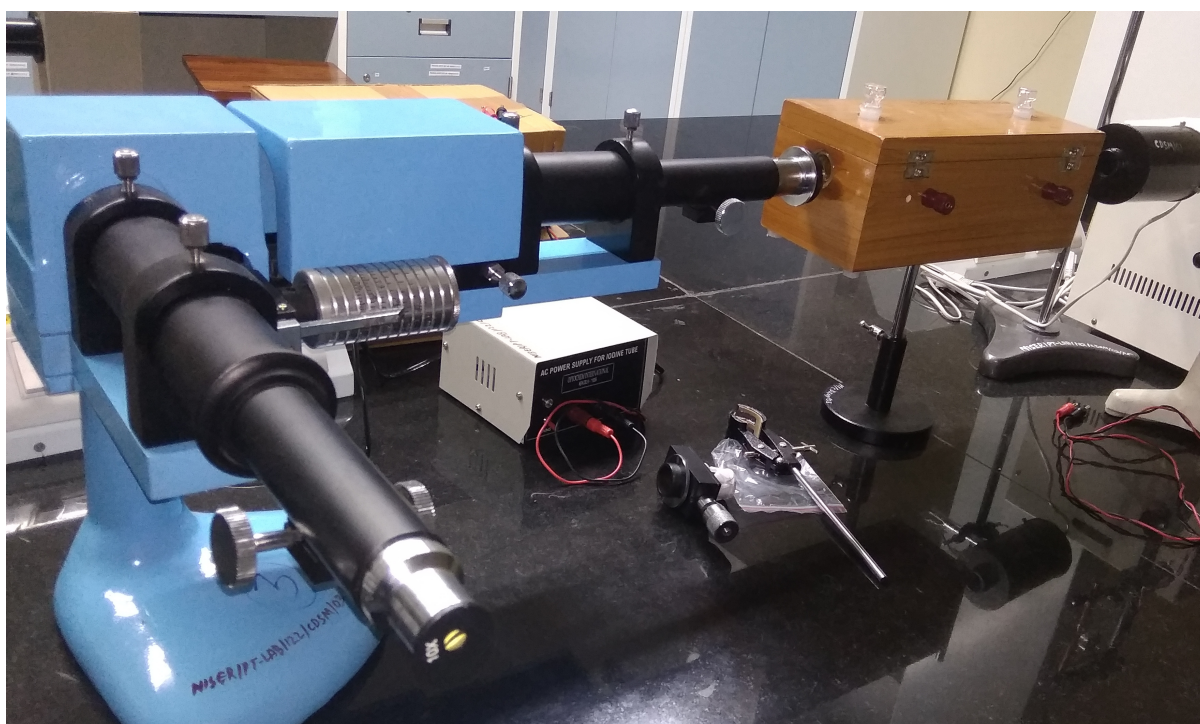
$$f = 4\pi^2\mu(c\Delta\overline{v_{eavg}})^2 \qquad\qquad (5)$$

Useful conversions/calculations:

1. Convert the wavelengths of the absorption band into the wave number by using: $\overline{v}_e(cm^{-1}) = 1/\lambda$.
2. $1eV = 8068cm^{-1}$
3. $E(eV)= hc/\lambda_{max} = hc\overline{v}_{e\,\min}$

Procedure:

Figure 2. shows the picture of the actual set up.
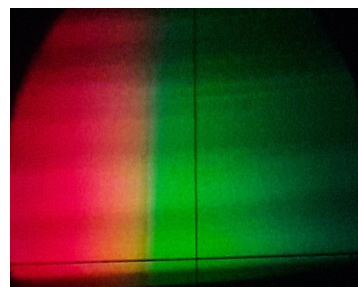

Figure 2: Set up for absorption spectrum of Iodine

(I) Calibration of constant deviation spectrometer:

Using the mercury lamp calibrate the constant deviation spectrometer as already described in the experiment "Emission spectra of metals". Obtain the calibration parameters from appropriate plot.
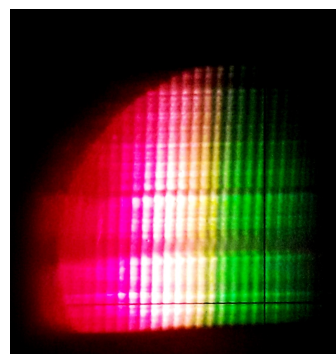
(II) Observation of Iodine spectrum

1. After calibration of spectrometer remove the mercury lamp and place the incandescent lamp (60 or 100 watts) as the source. Observe the continuous spectrum (see Fig. 3).

Fig. 3: Continuous spectrum

2. Now place the tube filled with iodine specks in between the incandescent lamp and the slit of the collimator. Wait till the tube becomes filled with iodine vapour which will look purple in colour.

3. Now observe the spectrum through the telescope adjusting the focus. You will observe narrow dark bands in the continuous spectrum as shown in Fig. 4.

Fig. 4: Absorption spectrum of Iodine

4. Note down the wavelength readings ($\lambda_{observed}$) of each dark band from the spectrometer and calculate the corrected value (λ_{corr}) using the calibration parameters.

5. Calculate the wave numbers corresponding to dark bands.

6. Draw the energy level diagram in terms of wavenumbers starting from the lowest to highest energy level.

7. The approximate energy gap is determined from the highest wavelength.

8. Determine the bond dissociation energy from Eq. 4.

9. Also calculate the difference between two consecutive vibronic levels in terms of wave number and determine the average difference in the wave number $\Delta\overline{\nu_e}_{avg.}$. Calculate the force constant using Eq. 5.

Observation:

(I)   Table for calibration using mercury lamp

Sl. No.	λ_{given}	$\lambda_{observed}$

(II)   Table for absorption spectrum of iodine

Sl. No.	$\lambda_{observed}$	λ_{corr}	Wave number $\overline{\nu_e}$ (cm^{-1})	Difference in wave number $\Delta\overline{\nu_e}$ (cm^{-1})

Graph/Calculations: Plot $\lambda_{given} \sim \lambda_{observed}$ and obtain the calibration parameters from list square fit.

Conclusions:

References:

1. Fundamentals of Molecular Spectroscopy, Text book by C. N. Banwell
2. Garland, C. W.; Nibler, J. W.; Shoemaker, D. P. *Experiments in Physical Chemistry*, 8th Ed.; McGraw-Hill: New York, 2009; pp 436-446.
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