

Dissociation energy of Iodine molecule using a constant deviation spectrometer

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Aim: To verify the Hartmann Dispersion Formula and to determine the dissociation energy of I_2 molecule using a constant deviation spectrometer

Apparatus

Constant deviation spectrometer, travelling microscope, polarimeter tube, iodine crystals, candle, mercury vapour lamp.

Principle of the experiment

Absorption spectrum of I_2 molecule

One of the most readily observed band spectrum of I_2 is the visible absorption band system which is responsible for the violet color of the iodine vapour. The system can be obtained by passing continuous spectrum light through iodine vapour and then admitting it into a spectrograph. It is found to be composed of a very large number of narrow bands extending from the far red to the absorption limit at about 5000 Å. The electronic transition involved is $^1\Sigma_g^+$ (ground state) $\rightarrow O_u^+$.

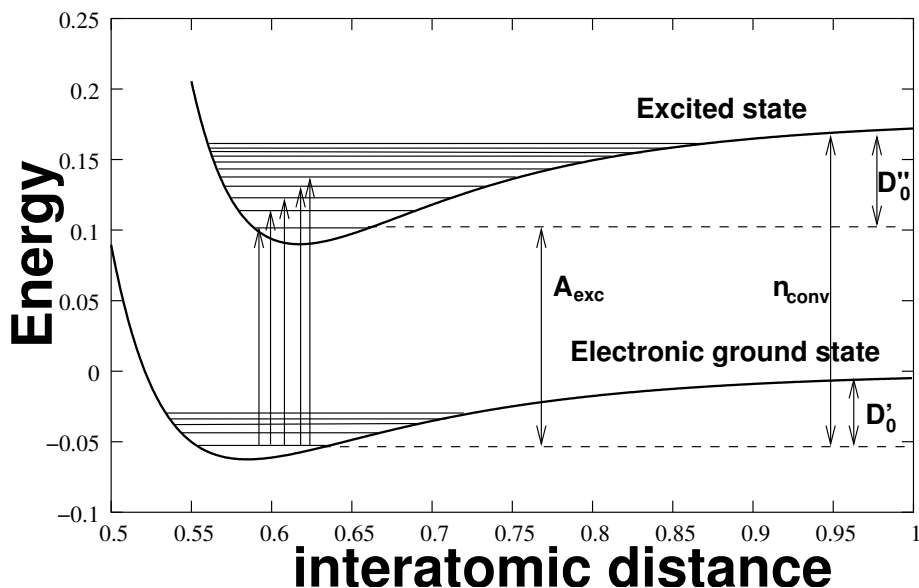


Figure 1: Energy diagram for transition between the ground state and excited state of the I_2 molecule. Each electronic state consists of many vibrational levels.

Dissociation energy of I_2 molecule

D'_0 = Dissociation energy of the ground state = 1.5422 eV D''_0 = Dissociation energy of the O_u^+ state = 0.5502 eV

Excitation energy of transition is 7598 cm^{-1} .

$$1eV = 8068cm^{-1}$$

Wavenumber $n = 1/\lambda$. In our case

$$n = \frac{10^8}{\lambda(\text{in } \text{\AA} \text{ units})} cm^{-1}.$$

Dissociation energy of the ground state

$$D''_0 = (n_{conv} - A_{exc})cm^{-1}$$

$$D''_0 = \frac{1}{8068}(n_{conv} - 7598)eV.$$

Dissociation energy of the excited state

$$D'_0 = (n_{conv} - n_{oo})cm^{-1}$$

$$D'_0 = \frac{1}{8068}(n_{conv} - 15598.3)eV.$$

n_{conv} = convergence limit = $20399.8 cm^{-1}$ (for example) This is obtained from the experimental graph.

Constant Deviation Spectrometer

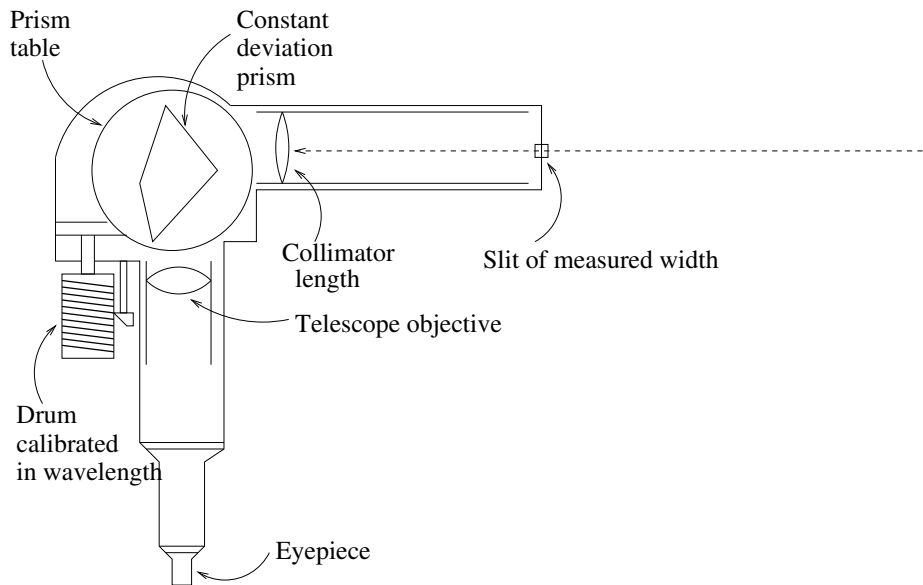


Figure 2: Constant deviation spectrometer.

A constant deviation spectrometer is shown in the figure. It consists of a Hartmann slit diaphragm, a collimator tube, a specially shaped constant deviation prism, and a microscope to view the spectrum.

The prism table can be rotated using a drum which is calibrated. By rotating the drum a particular line of the spectrum can be brought at the pointer, and then the wavelength of the line can be read out from the drum (provided the drum has been appropriately calibrated). In this manner, the wavelength of all the lines of a spectrum can be found out.

Hartmann Dispersion Formula

When a narrow beam of white light passes through a prism, it gets refracted and thus changes direction when it comes out. More importantly, the extent of refraction depends on the wavelength of light.

When this emerging refracted light is made to fall on a flat screen, it forms various narrow spots corresponding to different wavelength. Now it turns out that even if the wavelengths present in the incident light are uniformly separated from each other, the resultant spots on the screen are not uniformly separated. In other words, *dispersion does not follow a linear relationship with the wavelength.*

In fact, dispersion follows a relationship with the wavelength which is given by the *Hartmann Dispersion Formula*, which goes as

$$x = x_0 + \frac{a}{\lambda - \lambda_0}, \quad (1)$$

where x is the position of the line with wavelength λ , on the linear scale, and x_0 , a and λ_0 are undetermined constants.

This relation can be verified by using a modified setup by putting a travelling microscope in place of the eyepiece of the spectrometer.

Determination of unknown constants

Hartmann dispersion formula contains three unknown constants, so we would need three independent equations to determine them.

Suppose we have made three observations by measuring the positions of the resultant lines of three *known* wavelengths:

Wavelength λ (Å)	Line position x (cm)
λ_1	x_1
λ_2	x_2
λ_3	x_3

Putting them in the Hartmann formula (1), we get

$$\begin{aligned} x_1 &= x_0 + \frac{a}{\lambda_1 - \lambda_0}, \\ x_2 &= x_0 + \frac{a}{\lambda_2 - \lambda_0}, \\ x_3 &= x_0 + \frac{a}{\lambda_3 - \lambda_0}. \end{aligned} \quad (2)$$

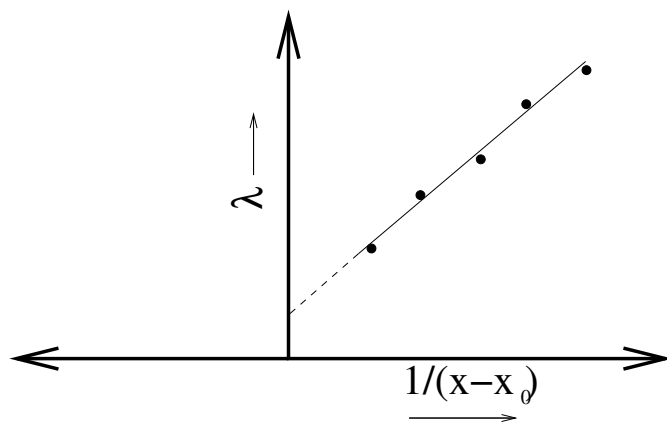
Solving these, one obtains:

$$x_0 = \frac{x_3(\lambda_3 - \lambda_2)(x_1 - x_2) - x_1(\lambda_2 - \lambda_1)(x_2 - x_3)}{(\lambda_3 - \lambda_2)(x_1 - x_2) - (\lambda_2 - \lambda_1)(x_2 - x_3)} \quad (3)$$

The other two constants λ_0 and a can also be calculated, but we will be satisfied with one constant for the time being. Now, equation (1) can also be cast in the form:

$$\lambda = \lambda_0 + \frac{a}{x - x_0}, \quad (4)$$

Equation (4) tells us that if we plot λ versus $\frac{1}{x - x_0}$, we should get a straight line. The slope of this line would be equal to a , and the intercept on the y-axis would give you λ_0 . Thus, the other two constants can be determined from the graph.



Procedure

Part 1

- Setup the CD spectrometer in front of the **mercury lamp**.
- Fix the drum at 5000 \AA and *it should not be disturbed after that*.
- adjust the travelling microscope so that you can go from one end of the spectrum to the other, using just the horizontal motion screw of the microscope.
- Once this is achieved, adjust the travelling microscope so that cross-wires lie on the violet line of the spectrum. Note the horizontal scale reading of the travelling microscope.
- Turn the horizontal motion screw until the next line comes on the cross-wires. Note the horizontal scale reading.
- Repeat this procedure for all the lines, until you reach the end of the spectrum.
- Once this is done, the calibration of the spectrometer is possible.

Part 2

Next, replace the mercury lamp by an ordinary lamp. Put the tube containing iodine crystals between the light source and the slit, so that the light passing through the tube falls on the slit. This might require a bit of alignment. The result will be a continuous spectrum ranging from red to violet.

Heat the tube uniformly using a candle or better, a spirit lamp. At this stage the absorption spectrum should be viewable through the microscope in its full glory. Study the spectrum carefully and adjust the slit width so as to increase the contrast of the dark bands, and to make them sharp. Note the position of as many bands as possible, using the horizontal motion screw of the travelling microscope. *Care should be taken to get as many values as possible in the region where the bands come closer to each other.* This region is crucial for getting the value of the dissociation energy. The region where the bands come very close to each other is the region of that wavelength of light which, if absorbed, dissociates the I_2 molecule.

Observations and calculation

Hartmann Dispersion Formula

λ (Å)	Line position x (cm)	$\frac{1}{x-x_0}$ (cm^{-1})(after calculating x_0)
Violet1 (4046.56)	2.888	0.221061
Violet2 (4077.83)	2.822	0.224334
Indigo (4358.33)	2.215	0.259698
Blue (4916)	1.402	0.329204
Green (5460.74)	0.885	0.396727
Yellow1(5769.60)	0.660	0.435611
Yellow2(5790.66)	0.647	0.438092

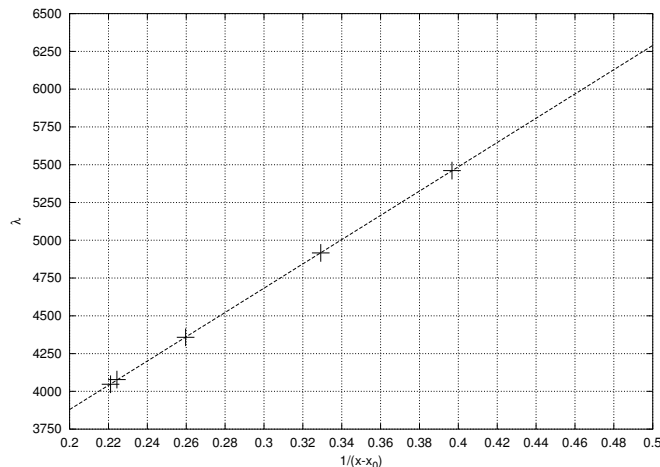
The constant x_0 can be calculated using the formula

$$x_0 = \frac{x_3(\lambda_3 - \lambda_2)(x_1 - x_2) - x_1(\lambda_2 - \lambda_1)(x_2 - x_3)}{(\lambda_3 - \lambda_2)(x_1 - x_2) - (\lambda_2 - \lambda_1)(x_2 - x_3)} \quad (5)$$

Using the *three* lines with wavelengths 4047, 4358 and 5461 we calculate x_0 :

$$x_0 = -1.63562$$

Calculate $1/(x - x_0)$ for all the lines. Plot λ versus $1/(x - x_0)$ for all the points except the two yellow lines. Draw a visual best fit line through these points, so that the line intersects the y-axis.



Calculate the slope of the line, which will give you a . You can use the values of x_0 , a and any one reading to calculate λ_0 . Alternately it can also be read out as the intercept of the line.

$$\begin{aligned} \lambda_0 &= 2272 \text{Å} \\ a &= 8034 \text{Åcm} \end{aligned}$$

Read out the wavelengths of other known lines from the graph and note what is the error.

Iodine absorption spectrum

Band no.	x (cm)	Wavelength (calculated from x) λ (Å)	n (cm^{-1})
1	..	5750	1.739×10^4
2	..	5730	1.745×10^4
3	..	5700	1.754×10^4
4	..	5670	1.764×10^4
5	..	5640	1.773×10^4
6	..	5620	1.779×10^4
7	..	5580	1.792×10^4
8	..	5550	1.802×10^4
9	..	5520	1.812×10^4
10	..	5490	1.821×10^4
11	..	5470	1.828×10^4
12	..	5450	1.835×10^4
13	..	5430	1.842×10^4
14	..	5410	1.848×10^4
15	..	5390	1.855×10^4
16	..	5370	1.862×10^4
17	..	5350	1.869×10^4
18	..	5330	1.876×10^4
19	..	5320	1.880×10^4
20	..	5310	1.883×10^4
21	..	5300	1.887×10^4
22	..	5290	1.890×10^4
23	..	5280	1.894×10^4
24	..	5270	1.898×10^4

Now plot a graph between the band number (on the x-axis) and the wave-number n (on the y-axis) and extrapolate the curve till the point where it becomes completely flat. This will give you the convergence limit n_{conv} .

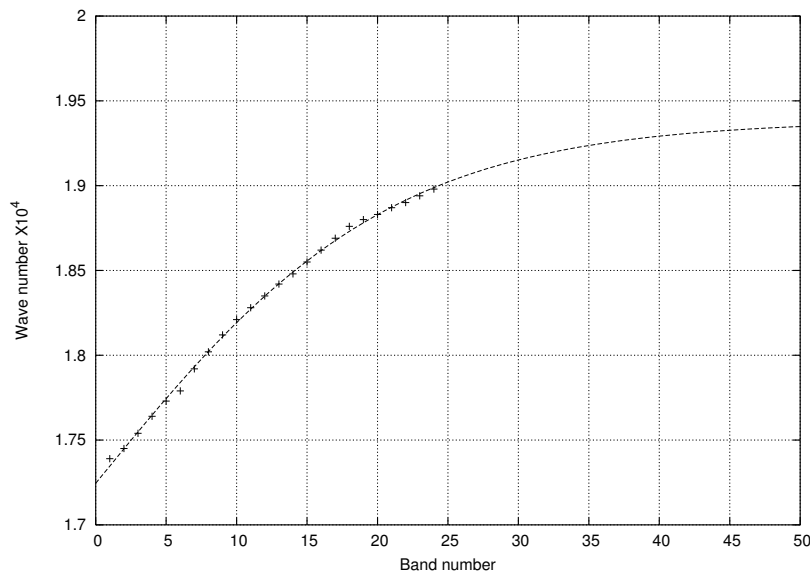


Figure 3: Plot between the band number and its wavenumber.