Emission spectrum of metals and Absoption spectrum of iodine vapours using constant deviation spectrometer

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In this experiment, the absorption spectrum of iodine vapour was investigated using a constant-deviation spectrometer. The recorded vibronic bands were analyzed to extract molecular parameters, yielding a dissociation energy of $D_0' = (0.2449 \pm 0.007)\,\mathrm{eV}$ and a force constant of $f = (36.88 \pm 4.50)\,\mathrm{N/m}$. These results confirm the discrete nature of vibrational energy levels and demonstrate how spectroscopic measurements can be used to test molecular models such as the Morse potential.

I. OBJECTIVE

1. Calibrate the C.D.S using a calibration source

2. Determine the weave length of the unknown spectra of the given metals in the arc lamp source.

3. 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

II. INTRODUCTION

This experiment was carried out in two parts using a constant deviation spectrometer (CDS). In the first part, mercury spectral lines of known wavelengths were used to calibrate the instrument.
In the second part, the calibrated spectrometer was employed to record the emission spectra of metals (such as copper and zinc) and to study the absorption spectrum of iodine vapour. The study of metal spectra demonstrates the characteristic line emission from excited atoms, while the iodine vapour spectrum illustrates vibronic absorption and provides information about molecular vibrational constants.

III. THEORY

Spectroscopy and Discrete Energy Levels [1]

Spectroscopy is a fundamental technique for probing the quantized structure of atoms and molecules. Each atom or molecule possesses a set of discrete energy levels, and transitions between these levels result in the absorption or emission of photons with energy

$$E = h\nu = \frac{hc}{\lambda}, \tag{1}$$

where h is Planck's constant, c the speed of light, and λ the wavelength of radiation. In atoms, transitions involve only electronic states, while in molecules they involve both electronic and vibrational levels (vibronic transitions).

Constant Deviation Spectrometer (CDS) [1]

The constant deviation spectrometer employs a Pellin–Broca prism, designed such that the emergent beam is always deviated by 90°, independent of wavelength, for a properly chosen geometry. This fixed deviation arises because one of the prism faces ensures total internal reflection at 90°, a purely geometric effect. Dispersion between different wavelengths appears as angular shifts within this 90°-deviated beam, which are measured using a calibrated drum scale.
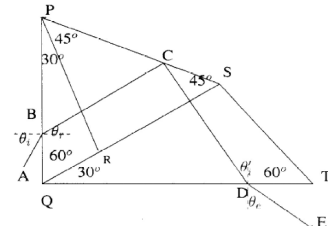

FIG. 1. Geometry of Pellin-broca prism

Calibration of the CDS is necessary because the observed drum readings are not directly equal to true wavelengths. A mercury discharge lamp, which produces sharp and well-known spectral lines across the visible range, is commonly used for this purpose. By plotting $\lambda_{\mathrm{observed}}$ against λ_{given} for Hg lines and performing a least-squares fit, a calibration equation is obtained, allowing correction of all subsequent measurements.

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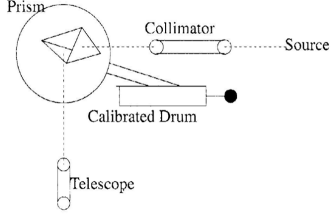
FIG. 2. Schematic of the constant deviation spectrometer experimental setup

FIG. 3. Schematic energy level diagram of iodine

Emission Spectra of Metals

When an electric arc excites metallic atoms, electrons in the atoms are promoted to higher electronic states. As these electrons relax back to lower levels, they emit photons with characteristic energies. The observed emission spectrum of a given metal therefore consists of a set of sharp lines, each corresponding to an allowed electronic transition. These line spectra serve as "fingerprints" for element identification, since each atom has a unique electronic structure. In alloys such as brass, the combined contributions of copper and zinc give rise to a richer spectrum.

Absorption Spectrum of Iodine Vapour

Molecular iodine (I_2) provides a classic example of vibronic absorption. The ground state (X) and first excited electronic state (B) each consist of vibrational sublevels. When broadband visible light passes through iodine vapour, photons matching the energy difference between $(X, \nu'') \to (B, \nu')$ are absorbed, producing dark absorption bands in the spectrum.

The potential energy of a diatomic molecule is well described by the Morse potential:

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

where D_e is the dissociation energy, r_e the equilibrium bond length, and a a molecule-dependent constant related to the vibrational frequency.

$$a = \bar{\nu}_e \sqrt{\frac{\pi c \mu}{\hbar D_e}} \qquad (3)$$

where $\bar{\nu}_e$ is the wavenumber generally in cm^{-1}, μ is the reduced mass of the system.
Solving the Schrödinger equation with this potential yields vibrational energy levels:

$$E_n = \hbar\omega\left(n + \frac{1}{2}\right) - \frac{(\hbar\omega(n+\frac{1}{2}))^2}{4D_e}$$

$$G(\nu) = \frac{E_n}{hc} = \tilde{\nu}_e\left(\nu + \frac{1}{2}\right) - \tilde{\nu}_e x_e\left(\nu + \frac{1}{2}\right)^2, \qquad (4)$$
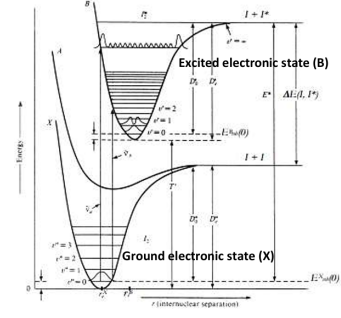
where $\tilde{\nu}_e$ is the harmonic vibrational wavenumber, $x_e = \frac{\bar{\nu}_e}{4D_e}$ the anharmonicity constant, n is order of vibrational level and ν the vibrational quantum number. The spacing between adjacent vibrational levels is

$$\Delta G_\nu = G_{n+1} - G_n = \bar{\nu}_e - 2\bar{\nu}_e x_e(n+1) \qquad (5)$$

$$\Delta\bar{\nu}_{avg} = \frac{1}{N}\sum_{n=0}^{N-1}\Delta G_n \qquad (6)$$

For iodine, x_e is small compared to $\bar{\nu}_e$, so the bands appear nearly evenly spaced. From the average spacing $\Delta\bar{\nu}$, one can determine the molecular force constant: Since

$$\bar{\nu}_e = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}}$$

$$k = 4\pi^2\mu(c\Delta\bar{\nu}_{avg})^2, \qquad (7)$$

where μ is the reduced mass of the iodine molecule and c the speed of light.

At higher energies, the vibrational levels approach a continuum, leading to dissociation of the molecule. The bond dissociation energy D_0 can be estimated from the difference between the lowest and highest observed absorption bands.

IV. OBSERVATION AND DATA ANALYSIS

In this experiment, the observations were carried out in two stages:
(i) calibration of the constant deviation spectrometer using the mercury lamp
(ii) measurement of the emission spectra of metals and the absorption spectrum of iodine vapour.

A calibration curve of λ_{given} versus λ_{obs} was plotted, and the fitted relation (which is shown in Fig.s 4 and 5) was used to determine the corrected wavelength (λ_{corr}) of any unknown spectral line.

For iodine vapour, the positions of dark absorption lines were first recorded and then corrected using the

calibration curve. These corrected wavelengths were converted into wavenumbers ($\bar{\nu} = 1/\lambda$), and successive wavenumber differences ($\Delta\bar{\nu}$) were used to determine the vibrational spacing and estimate the molecular force constant. Here polts and leastsquare fitting is done by python. the full code is available at [2].

TABLE I. Calibration data for Hg lamp

S. NO.	Color	λ_{given} (Å)	$\lambda_{observed}$(Å)
1	Green	5460	5460
2	Yellow-1	5790	5780
3	Yellow-2	5790	5810
4	Orange	5960	5970
5	Red-1	6150	6140
6	Red-2	6200	6200
7	Red-3	6230	6250
8	Red-4	6910	6950

FIG. 4. Least square fitting of $\lambda_{observed}$ vs λ_{given} plot

FIG. 5. Parameters obtained from least square fitting in fig. 4

The fitted equation obtained is

$$\lambda_{observed} = 1.025 \times \lambda_{given} + (-144.374)$$

or,

$$\lambda_{corr} = 0.9756 \times \lambda_{observed} + 140.853$$

where λ_{corr} is written in place of λ_{given}.

TABLE II. Data of emission spectrum of Brass

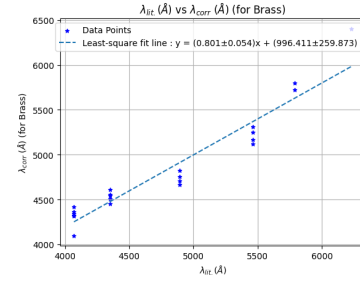| Color	λ_{obs} (Å)	λ_{corr} (Å)	$\lambda_{lit.}$(Å)
R	6420	6404.267	6230
Y-1	5800	5799.389	5790
Y-2	5720	5721.340	5790
G-1	5300	5311.584	5460
G-2	5240	5253.048	5460
G-3	5150	5165.243	5460
G-4	5100	5116.462	5460
B-1	4800	4823.780	4890
B-2	4730	4755.487	4890
B-3	4680	4706.706	4890
B-4	4640	4667.682	4890
I-1	4580	4609.145	4350
I-2	4530	4560.365	4350
I-3	4510	4540.853	4350
I-4	4480	4511.584	4350
I-5	4420	4453.048	4350
V-1	4390	4423.780	4070
V-2	4330	4365.243	4070
V-3	4310	4345.731	4070
V-4	4290	4326.219	4070
V-5	4280	4316.462	4070
V-6	4060	4101.828	4070

FIG. 6. Least square fitting curve for brass metal

TABLE III. Data of emission spectrum of Copper

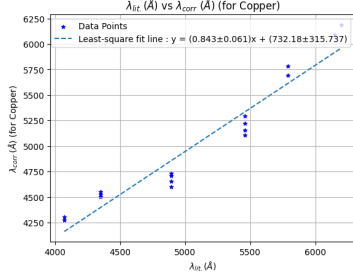| Color	λ_{obs} (Å)	λ_{corr} (Å)	$\lambda_{lit.}$(Å)
R_1	6200	6189.633	6200
R_2	6100	6092.072	6150
Y_1	5780	5779.877	5790
Y_2	5690	5692.072	5790
G_1	5280	5292.072	5460
G_2	5210	5223.780	5460
G_3	5140	5155.487	5460
G_4	5090	5106.706	5460
B_1	4710	4735.975	4890
B_2	4680	4706.706	4890
B_3	4630	4657.926	4890
B_4	4570	4599.389	4890
I_1	4520	4550.609	4350
I_2	4500	4531.097	4350
I_3	4470	4501.828	4350
V_1	4270	4306.706	4070
V_2	4240	4277.438	4070

FIG. 7. Least square fitting curve for copper metal

TABLE IV. Emission spectrum data of I-vapour with corrected wavelengths, wavenumbers, and successive differences

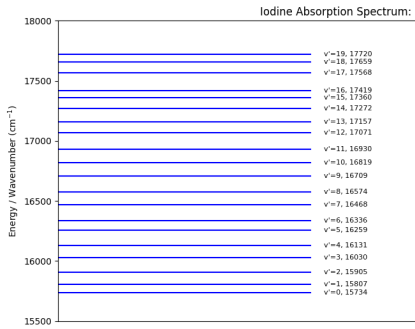| S. No.	λ_{obs} (Å)	λ_{corr} (Å)	Wavenumber $\tilde{\nu}$ (cm^{-1})	$\Delta\tilde{\nu}$ (cm^{-1})
1	5640	5643.292	17720.15	—
2	5660	5662.804	17659.10	61.05
3	5690	5692.072	17568.29	90.81
4	5740	5740.853	17419.01	149.25
5	5760	5760.365	17360.01	59
6	5790	5789.633	17272.25	87.76
7	5830	5828.658	17156.61	115.64
8	5860	5857.926	17070.89	85.72
9	5910	5906.706	16929.91	140.98
10	5950	5945.731	16818.79	111.12
11	5990	5984.755	16709.18	109.61
12	6040	6033.536	16574.03	135.15
13	6080	6072.560	16467.52	106.51
14	6130	6121.340	16336.29	131.23
15	6160	6150.609	16258.55	77.74
16	6210	6199.389	16130.62	127.93
17	6250	6238.414	16029.71	100.91
18	6300	6287.194	15905.35	124.36
19	6340	6326.219	15807.23	98.12
20	6370	6355.487	15734.43	72.80

FIG. 8. Different energy level with respect to wavenumber (Iodine)

A. Calculation of Bond Dissociation Energy and Force Constant

1. Bond Dissociation Energy in the Excited State

From the absorption series (as shown in table IV), we have
$\bar{\nu}_{\min} = 15744.43\,\text{cm}^{-1}$, and $\bar{\nu}_{\max} = 17720.15\,\text{cm}^{-1}$. The dissociation energy from the $v' = 0$ level in the excited state is

$$D_0(\text{cm}^{-1}) = \tilde{\nu}_{\max} - \tilde{\nu}_{\min} = 17720.15 - 15744.43 = 1975.72\,\text{cm}^{-1}. \tag{8}$$

In electron volts using $1\,\text{eV} = 8068\,\text{cm}^{-1}$:

$$D_0(\text{eV}) = \frac{1975.72}{8068} = 0.2449\,\text{eV}. \tag{9}$$

2. Average Vibrational Spacing and Force Constant

From the table IV, the consecutive wavenumber differences $\Delta\tilde{\nu}_i$, the mean spacing is

$$\Delta\tilde{\nu}_{\text{avg}} = 99.26\,\text{cm}^{-1}. \tag{10}$$

The reduced mass of I_2 is

$$\mu = \frac{m_I}{2} = \frac{126.90447 \times 1.660539 \times 10^{-27}}{2} = 1.05365 \times 10^{-25}\,\text{kg}. \tag{11}$$

The angular vibrational frequency is

$$\omega = 2\pi c\Delta\tilde{\nu}_{\text{avg}}, \tag{12}$$

where $c = 3 \times 10^8$ m/s and $\Delta\tilde{\nu}_{\text{avg}}$

The force constant (in standard unit) is then

$$f = \mu\omega^2 = 36.88\,\text{N/m}. \tag{13}$$

B. Error Analysis

Rather than relying on instrument resolution, we estimate the uncertainty in the vibrational spacings from the scatter of the measured $\Delta\bar{\nu}_i$ values, using the standard deviation of the data set.

The standard deviation of the set of N measurements is

$$\sigma_\Delta = \sqrt{\frac{1}{N-1}\sum_{i=1}^{N}\left(\Delta\tilde{\nu}_i - \Delta\tilde{\nu}_{\text{avg}}\right)^2}, \tag{14}$$

where $\Delta\tilde{\nu}_{\text{avg}}$ is the average spacing.

The uncertainty is the standard error of the mean (SEM), defined as

$$\sigma_{\Delta\tilde{\nu}_{\text{avg}}} = \frac{\sigma_\Delta}{\sqrt{N}}. \tag{15}$$

The values obtained from the data :

$$\Delta\bar{\nu}_{\mathrm{avg}} = 99.26\,\mathrm{cm}^{-1}, \quad \sigma_\Delta = 27.1\,\mathrm{cm}^{-1},$$

and hence

$$\sigma_{\Delta\tilde{\nu}_{\mathrm{avg}}} \approx \frac{27.1}{\sqrt{20}} \approx 6.06\,\mathrm{cm}^{-1}. \tag{16}$$

1. Uncertainty in Dissociation Energy

The dissociation energy was obtained as

$$D_0' = \bar{\nu}_{\mathrm{limit}} - \bar{\nu}_0 = 1975.72\,\mathrm{cm}^{-1}.$$

Assuming independent errors for the two limiting wavenumbers, the uncertainty is

$$\sigma_{D_0'} \approx \sqrt{2}\,\sigma_{\Delta\tilde{\nu}_{\mathrm{avg}}} \approx \sqrt{2} \times 6.06 \approx 8.57\,\mathrm{cm}^{-1}. \tag{17}$$

In electron volts,

$$D_0' = (0.2449 \pm 0.007)\,\mathrm{eV}. \tag{18}$$

2. Uncertainty in Force Constant

Error propagation for the force constant gives

$$\sigma_f = f \times \frac{2\sigma_{\Delta\tilde{\nu}_{\mathrm{avg}}}}{\Delta\tilde{\nu}_{\mathrm{avg}}}. \tag{19}$$

Substituting the values,

$$\sigma_f = 36.88 \times \frac{2 \times 6.06}{99.26} \approx 4.50\,\mathrm{N/m}.$$

Thus,

$$f = (36.88 \pm 4.50)\,\mathrm{N/m}. \tag{20}$$

V.   RESULTS AND DISCUSSION

Emission spectra of metals

The emission spectra of brass and copper electrodes were recorded using the constant-deviation spectrometer, calibrated with known mercury lines. Distinct and well-resolved spectral lines were observed across the visible region. For copper, the strongest emissions appeared near 510–528 nm (green) and 569–580 nm (yellow), in good agreement with the tabulated Cu I transitions.

In the case of brass, the spectrum displayed both copper features and additional zinc lines. Prominent Zn transitions were observed in the blue-green region around 468–472 nm and near 481 nm. The presence of these characteristic zinc lines, along with copper lines, enabled clear qualitative identification of brass as an alloy. Furthermore, the relative intensities of lines in brass compared to copper highlighted how alloying modifies the spectral fingerprint of a material. The consistency of the measured wavelengths with literature values confirms both the accuracy of calibration and the reliability of the spectrometer.

Absorption spectrum of iodine vapour

For iodine vapour, a series of dark absorption bands were recorded and analyzed. The corrected band positions were converted into vibrational term values, and successive differences provided the vibrational spacings. From the data, the average spacing was obtained as

$$\Delta\bar{\nu}_{\mathrm{avg}} = (99.26 \pm 6.06)\,\mathrm{cm}^{-1}.$$

Using the harmonic oscillator approximation, the corresponding molecular force constant was calculated as

$$f = (36.88 \pm 4.5)\,\mathrm{N/m}.$$

The bond dissociation energy in the excited state was determined from the convergence limit of the absorption series as

$$D_0 = (0.2449 \pm 0.007)\,\mathrm{eV}.$$

These values are of the correct order of magnitude compared with standard literature data. The moderate relative uncertainty in the force constant (about 12.2%) arises from scatter in the vibrational spacing values, limited resolution of absorption bands, and challenges in identifying exact band maxima. In particular, anharmonicity of the excited electronic state is expected to reduce the observed level spacings compared to a purely harmonic oscillator, explaining the systematic deviation from ground-state values.

Despite these limitations, the experiment successfully demonstrates how molecular spectroscopy can be employed to extract key molecular constants such as dissociation energy, vibrational frequency, and force constant. The results not only confirm the quantum nature of molecular vibrations but also illustrate the sensitivity of absorption spectra to electronic structure and interatomic bonding.

VI.   CONCLUSION

The experiment successfully demonstrated the use of spectroscopy to probe both atomic and molecular energy levels. The emission spectra of copper and brass showed characteristic lines consistent with literature values, confirming elemental identification. From the absorption spectrum of iodine vapour, the average vibrational spacing and molecular constants such as the force constant and dissociation energy were estimated. While deviations from theoretical values arose due to instrumental limitations and anharmonic effects, the results remained of the correct order of magnitude. Overall, the study highlights the effectiveness of emission and absorption spectroscopy in extracting fundamental physical constants and provided valuable practical experience in spectroscopic techniques.

[1] School of Physical Sciences, NISER Bhubaneswar, *Emission Spectra of Metals and Absorption Spectrum of Iodine Vapour: Laboratory Manual*, National Institute of Science Education and Research (NISER) (2024), laboratory Manual provided by the institute.

[2] A. Arya, Codify, `https://github.com/Anuj-Arya1/Codify.git` (2025).