Optical Spectroscopy

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Abstract:

This experiment is an exercise in the principles and practice of optical spectroscopy. The continuous emission spectrum of a tungsten halogen lamp is studied, and this is compared to the blackbody spectrum. This investigation leads to a calibration of the sensitivity of the apparatus. The emission spectrum of a mercury discharge lamp is examined, and the doublet at 576.959nm and $579.065nm^{1}$, due to the splitting of a single line (arising from spin-orbit coupling) is observed. The emission lines of mercury are found to occur at 404.21nm, 407.56nm, 435.35nm, 491.39nm and 545.78nm. The doublet lines are observed at 576.66nm and at 578.64nm. These results are accurate to within $\pm 0.4 nm$.

The transmission of light through a semiconductor film, ZnTe, is considered, and the thickness of the film is measured, and is found to be $t = 1.3 \pm 0.3 \mu m$. The dispersion relation for the index of refraction $n(\lambda)$ is observed. Further, the bandgap of the ZnTe semiconductor is measured, and this is found to be $E_g = 2.2 \pm 0.3 eV$. This compares with the actual value of $2.4 eV^2$.

The absorption and fluorescence of the laser dye rhodamine 6G is studied and the cross section for absorption is obtained. This is found to be $\sigma_{\text{max}} = 3.8 \pm 0.2 \times 10^{-20} m^2$, and this compares with the actual value of $4.0 \times 10^{-20} m^{23}$. Finally, the redshift of the fluorescence spectrum of the laser dye, relative to the absorption spectrum was measured to be $\Delta \lambda = 20 \pm 5 nm$.

¹ Jenkins, F A and White, H E, Fundamentals of Optics, 4E, McGraw-Hill, 1976.

² <u>http://www.veeco.com/learning/learning_lattice.asp</u>

³... D.A. Eastham, Taylor and Francis, London, 1986.

Theory and Equations:

1. The Blackbody emitter

The tungsten halogen lamp of experiment 1 resembles an ideal blackbody source. This radiates at all wavelengths.

The blackbody curve (Planck Distribution) gives the intensity in arbitrary units as a function of wavelength:

$$I(\lambda) = \frac{2\pi h c^2}{\lambda^5 \left[e^{\left(\frac{hc}{k_B T \lambda}\right)} - 1 \right]}$$
(1)

The characteristic spectrum is given below:



Figure 1: The blackbody spectrum at different temperatures. The y-axis gives intensity in arbitrary units.

2. The many-electron atom

In experiment 2 we study the emission spectrum of a mercury discharge lamp. Such a source emits light at discrete frequencies, and these emissions correspond to electronic transitions from states of different energy, in the mercury atom.

The electrons in mercury are strongly spin-orbit coupled. Now the general Hamiltonian for a many-electron atom is

$$\hat{H} = \hat{H}^{CF} + \hat{H}^{RC} + \hat{H}^{SO}$$
(3)

Where the first term is due to centrally symmetric potentials experienced by the electrons (the Central Field Hamiltonian), the second is due to any residual electron-electron Coulomb interactions, and the third term is the spin-orbit term, due to the interaction of the electron's spin with the nuclear magnetic field seen

by the orbiting electron. Now $\langle \hat{H}^{SO} \rangle \propto (Z\alpha)^4 = \left(\frac{80}{137}\right)^4$ for mercury, and so this term is important compared to $\langle \hat{H}^{RC} \rangle$, for heavy atoms such as mercury. The spin-orbit coupling breaks the degeneracy of spectroscopic terms with $L \neq 0$, and this leads to the doublet seen in spectrum of mercury.

3. Transmission through a ZnTe film

The film is placed on a sapphire substrate as shown in figure 2.

The condition for constructive interference (maximal reflectivity, R), is that the optical path length, δx , be an integral number of wavelengths. The optical path length takes phase shifts into account.

For *R* maximal (*T*, transmittance, minimal),

$$\left(m + \frac{1}{2}\right) = 2nt \tag{3}$$

Also, transmittance *T* is maximal when

$$m\lambda = 2nt \tag{4}$$

Where in equations (3) and (4), m is an integer and n is the index of refraction of the film.

ZnTe is a semiconductor. A semiconductor is an insulator with a small band gap. Now in solids, the allowed values of energy for the electrons cluster together in bands, and these are realized in an energy versus k plot (where k is the electron wave vector). The band gap is that region of the plot from which allowed states are absent. Electrons in states near the top of the band will not be excited by incident photons unless the photons have sufficient energy to move the electrons into allowed states in another, higher band.

The absorption spectrum of the ZnTe sample is analysed and the wavelength region in which absorption is large is noted. In this region, the photon energies are comparable to the band gap energy of the semiconductor, and so electrons are readily excited across the band gap, into the conduction band. Thus, the band gap energy is quantifiable, by a study of the wavelength-dependence of the transmission coefficient, in this wavelength region.

4. The Rhodamine Dye

Rhodamine 6G is a complex molecule used as an active medium in laser physics. This is due to the fact that the energy levels of Rhodamine approximate a fourlevel system. These are shown in figure 3. The closely spaced levels correspond to vibrational transitions (nuclear vibrations around the equilibrium bond length), and these are associated with IR photons. Thus, a series of closely spaced levels is superimposed on a ladder of electronic energy states. The separation of adjacent electron energy states is associated with photon transitions in the visible range.

Figure 3. The "band structure" of Rhodamine 6G and the sequence of transitions shown schematically.

Typically, photons are absorbed by electrons in the lower, S_0 "band" and induce transitions to the S_1 band. Thereafter, decays down the vibrational band occur, and subsequent fluorescence (emission of visible light) occurs as the electrons cascade back down to the S_0 band.

These processes are governed by the Franck-Condon principle: during electronic transitions, the nuclear coordinates are fixed. Thus, the electronic transitions of figure 3, in the energy versus nuclear separation plot, must be vertical. Consequently, fluorescence happens at lower energies (hence, higher wavelengths), compared to absorption.⁴ Consequently, the emission spectrum is shifted to higher wavelengths ("red shifted"), relative to the absorption spectrum, and this is seen in figure 4.

⁴ Where, by "fluorescence happens at lower energies", we mean that the peak fluorescence is at lower energies, relative to the peak absorption.



Figure 4. The absorption spectrum, together with the emission spectrum, as a function of wavelength. The emission spectrum is "red shifted" relative to the absorption spectrum because the Franck-Condon principle demands that nuclear coordinates must remain fixed during optical transitions. This means that the photon energy associated with emission is less than that of absorption. (After D.A. Eastham)

Experiment 1:

This experiment aims to do the following:

- To record the emission spectrum of the tungsten halogen lamp.
- To determine the sensitivity of the spectrometer system.

The spectrum of tungsten was obtained and is demonstrated in the foregoing intensity versus wavelength plots.



Figure 5. The spectrum of Tungsten. The second image has been rendered smoother by averaging adjacent values of intensity.

Wavelength / nm	Intensity (Counts)
400	37
450	255
500	1647
550	2925
600	3558
650	3489
700	2849
750	1806
800	1060
850	697
900	438
950	204
1000	68

The intensity (measured in counts) was noted for various wavelengths and the following table was obtained:

Table 1: The observed intensity as a function of wavelength.

This was compared with the blackbody model: it is assumed that tungsten is a blackbody radiating at a temperature T = 3417 K.

The intensity as a function of wavelength is then given by Planck's Law:

$$I(\lambda) = \frac{2\pi hc^2}{\lambda^5 \left[e^{\left(\frac{hc}{k_B T \lambda}\right)} - 1 \right]}$$
(1)

The values of $I(\lambda)$ for the wavelengths in the table above were obtained using this formula:

Wavelength / nm	Intensity (Arbitrary units)
400	1.01573E12
450	1.80777E12
500	2.71204E12
550	3.61169E12
600	4.41581E12
650	5.07071E12
700	5.55599E12
750	5.87489E12
800	6.04457E12
850	6.08866E12
900	6.03225E12
950	5.89896E12
1000	5.70953E12

Table 2. The theoretical intensity (in arbitrary units), as a function of wavelength.



Figure 6. The blackbody curve of Tungsten, obtained from the data in table 1.

Re-scale so that the theoretical and experimental intensity maxima are equal:

$$\begin{split} \lambda_{\max} &= .002898 / (T = 3417K) = 8.48 \times 10^{-7} \, m = 8.48 nm \dots \text{ Wien's Law} \\ \Rightarrow & (I_{\max})_{theor} = 6.09 \times 10^{12} \\ & (I_{\max})_{ex} = 3600 \\ & (I_{\max})_{ex} = (5.921 \times 10^{-10}) (I_{\max})_{theor} \end{split}$$

Now superimpose the experimental and theoretical curves:



Figure 7. The superposition of the observed and blackbody curves of Tungsten.

Finally, the sensitivity S was calculated from the following formula:

$$S = \frac{\left|I_{blackbody} - I_{observed}\right|}{I_{blackbody}}$$
, where the values of $I_{blackbody}$ have been normalized so that

the intensity maxima of the observed spectrum and the blackbody spectrum agree.

The following graph of sensitivity S against wavelength is obtained. Here, S = 0 corresponds to 100% sensitivy.



Figure 8: Sensitivity as a function of wavelength. Here, a sensitivity of zero corresponds to 100% agreement between the observed and blackbody spectra.

This calibration experiment explains the apparent "blueshift" of figure 7: it is only in the wavelength interval $\lambda \approx 500 nm$ that we can expect the observed and blackbody spectra to agree. At other wavelegnths, these differ, to the extent shown in figure 8. This difference is due to the diffraction undergone by the light in the apparatus.

Experiment 2:

This experiment aims to do the following:

- To find the wavelengths of the lines in the emission spectrum of mercury in the range $\lambda = 350 1000 nm$.
- To determine the resolving power and the resolution of the spectrometer.

The spectrum of mercury was obtained and the characteristic lines were noted at the following wavelengths:

404.21nm, 407.56nm, 435.35nm, 491.39nm (very weak), 545.78nm

Now these values for the emission lines are accurate to within ± 0.4 nm, because this is the wavelength interval at which the apparatus scans (See figure 9).

There is also a doublet (figure 9), with two distinct peaks at 576.66nm and at 578.64nm, and so the spacing between these peaks is 1.98nm.

Again, each of these is accurate to within ± 0.4 nm.



Figure 9. The Mercury doublet.

These values compare with the following, canonical values:

404.656nm, 407.781nm, 435.835nm, 491.604nm (weak), 546.074nm (green)⁵.

The doublet is found to have peaks at 576.959nm and 579.065nm (yellow-orange), giving a doublet spacing of 2.106nm.⁶

The **optical resolution** of the system at any one of the peaks is taken to be the full width at half maximum height (FWHM) at said peak. The **chromatic resolving power** is defined as $R \equiv \frac{\lambda}{\Delta \lambda}$, where $\Delta \lambda$ is the minimum wavelength difference that the spectrometer can discern – here it is taken to be the FWHM. It can be shown that *R* is also equal to *pN*, where *p* is the order of the image and *N* is the number of slits on the diffraction grating of the spectrometer.

We obtain values of optical resolution and chromatic resolving power from figures the emission lines and tabulate these data:

Wavelength /	$\Delta\lambda$ (FWHM) /	$\delta(\Delta \lambda) / nm$	R	δR
nm	nm	- ()		
404.21	1.4	0.4	288	83
407.56	1.4	0.4	291	83
435.35	1.4	0.4	310	89
491.39	1.4	0.4	350	101
545.78	1.3	0.4	419	129
576.66	1.3	0.4	443	136
578.64	1.5	0.4	386	103

Table 3.

Now the FWHM can also be calculated from the formula

FWHM = ((Spectral Range) / (Number of Pixels))×(Pixel Resolution)

Where the **spectral range** is the wavelength range recorded by the apparatus (grating and detector together). This is equal to 650nm. The number of pixels is the number of pixels in the CCD array – equal to 2048 here, while the pixel resolution can be calculated as a function of the slit width – it is found to be approximately six. This is the number of pixels that respond to a monochromatic input.

Thus, FWHM = 1.9nm, and this is comparable to the value obtained previously. It is not possible in this calculation to find the resolving power from the number of slits on the grating, N, because while the number of slits per mm is given, the width of the grating is not.

Experiment 3

⁵ Jenkins, F A and White, H E, Fundamentals of Optics, 4E, McGraw-Hill, 1976.

⁶ Ibid.

This experiment aims to do the following:

- To determine the thickness of a ZnTe film, assuming that this film is nondispersive.
- To estimate the dependence of the index of refraction of this film on wavelength.



• To determine the bandgap of ZnTe.

Figure 10. Transmission as a function of wavelength for light incident on the ZnTe sample (Interference maxima and minima).

Wavelength of Minima / nm	Wavelength of Maxima / nm
605	590
630	620
655	640
680	670
725	700
750	735
795	775
745	820
770	870
900	930
970	1000

 $\delta \lambda = \pm 5 nm$

Table 4. The wavelength at which successive maxima and minima of intensity occur.

For adjacent maxima we have that

$$2nt = m\lambda_{m}$$

$$2nt = (m+1)\lambda_{m+1}$$

$$\frac{2nt}{\lambda_{m}} = \frac{2nt}{\lambda_{m+1}} - 1$$

$$2nt\left(\frac{1}{\lambda_{m+1}} - \frac{1}{\lambda_{m}}\right) = 1$$

$$\Rightarrow 2nt(\lambda_{m} - \lambda_{m+1}) = \lambda_{m+1}\lambda_{m}$$

$$\lambda_{m} - \lambda_{m+1} = \frac{1}{2nt}\lambda_{m+1}\lambda_{m}$$
(5)

And clearly this formula holds for adjacent minima as well, where

$$2nt = \left(m + \frac{1}{2}\right)\lambda_m$$

Where n is the index of refraction of the sample – assumed constant, m is the order number (unknown) and t is the thickness of the sample.

From these formulas, it is apparent that the order number *m* must *decrease* with increasing wavelength.

From equation (5), we see to determine *t*, we must plot $\lambda_m - \lambda_{m+1}$ against $\lambda_{m+1}\lambda_m$, and this is done in the foregoing figure.





Figure 11. Plot of $\lambda_m - \lambda_{m+1}$ against $\lambda_{m+1}\lambda_m$.

Thus, we see that

 $t = \frac{1}{2n \times (m2)} = \frac{1}{2 \times 3.56 \times 0.00011...} = 1264.85...nm = (1.3 \pm 0.3) \times 10^{-6} m \cdot 10^{-6}$

The non-linearity of the graph arises from the fact that *n* is not in fact constant.

Back-substitution now yields the order-number, *m*. Thus, for $\lambda_{max} = 605nm$, m = 15. We have therefore found each of the quantities which determine *n*, the index of refraction, and can therefore plot *n* versus λ , in order to find the dispersion curve.



Figure 12. The dispersion relation: a plot of the index of refraction n, *against the wavelength, for the ZnTe sample.*

Near the bandgap of the ZnTe sample, absorption is strong, and T, the transmission coefficient, is small there. In this region, the absorption and transmittance are related by

$$T = (1 - R_1)(1 - R_2)e^{-\alpha t}$$
(6)

where R_1 and R_2 are the reflection coefficients of the air / film interface and the film / substrate interface, respectively. These coefficients are given by

$$R_{1} = \frac{(n-1)^{2}}{(n+1)^{2}} = 0.315$$
$$R_{2} = \frac{(n_{1} - n)^{2}}{(n_{1} + n)^{2}} = 0.114$$

Thus,
$$\alpha(T) = \frac{1}{t} \log \left[\frac{(1 - R_1)(1 - R_2)}{T} \right] = \frac{1}{t} \log \left(\frac{0.611}{T} \right)$$
 (7)

Furthermore, near the bandgap, we have the following equation for the dependence of the absorption coefficient α , on the photon energy $\frac{hc}{\lambda}$:

$$\alpha^{2} = B^{2} \left(\frac{hc}{\lambda} - E_{g} \right)$$
(8)

Where E_g is the energy of the bandgap.

Plotting the photon energy $\frac{hc}{\lambda}$ against the square of the absorption gives the energy of the bandgap – it is the *y* – intercept.



Figure 13. A plot of photon energy $\frac{hc}{\lambda}$ against the square of the absorption. The y-intercept gives the bandgap energy, E_g .

Thus, $E_g = 3.5 \pm 0.5 \times 10^{-19} J = 2.2 \pm 0.3 eV$

Experiment 4:

This experiment aims to do the following:

- To measure the absorbance spectrum of the 10⁻⁵ M solution of the laser dye rhodamine 6G in ethanol and to calculate the peak value of the absorption cross section of the dye molecule.
- To measure the fluorescence spectrum and calculate its red shift relative to the absorption spectrum.

Now the transmitted intensity, relative to the incident intensity, is given by the Lambert-Beer Law:

$$I(t) = I(0)e^{-\mu t}$$
(9)

Where μ is related to the absorption cross section σ (of one molecule), by $\mu = n\sigma$, where *n* is the concentration of molecules.

Now the absorbance A is defined by the formula



Figure 14. The absorption curve for the Rhodamine dye. There are discontinuities in the wavelengths in the neighbourhood of 500 nm because the apparatus had not been adjusted so as to give an everywhere non-zero value of transmission.

Thus, $\sigma = \frac{A}{nt}$ and from the figure 14, we get that

$$\sigma_{\max} = \frac{3.5}{nt} = \frac{3.5}{\left(6.02 \times 10^{21} / m^3\right) \left(1.5 \times 10^{-2} m\right)} = 3.8 \pm 0.2 \times 10^{-20} m^2$$

The red shift of the fluorescence spectrum, relative to the absorption spectrum, is the wavelength interval between the fluorescence maximum and the absorption maximum, and this is found to be $\Delta \lambda = 20 \pm 5nm$, by inspection of figures 14 and 15.



Figure 16. The transmission curve for Rhodamine.

Conclusions:

In this experiment, the sensitivity of the apparatus was investigated by studying the observed spectrum of tungsten, and by a suitable comparison with the ideal blackbody emitter. This led to the plot sensitivity as a function of wavelength given in figure 8.

The characteristic spectral lines of mercury were observed and found to lie at 404.21nm, 407.56nm, 435.35nm, 491.39nm and 545.78nm. The doublet lines were observed at 576.66nm and at 578.64nm. These results are accurate to within $\pm 0.4 nm$.

These results were used to compute the optical resolution of the apparatus, found to be 1.5 nm.

The thickness of a ZnTe sample was found by using methods of interference. This was measured to be $1.3 \pm 0.3 \mu m$. The bandgap of ZnTe was subsequently measured and was found to be $E_g = 2.2 \pm 0.3 eV$. This compares with the actual value of 2.4 eV.

Finally, the Rhodamine dye was studied and its absorption cross section was measured. The result obtained for the maximal value of cross section was $\sigma_{max} = 3.8 \pm 0.2 \times 10^{-20} m^2$. The red shift of the emission spectrum, relative to the absorption spectrum was found to be $\Delta \lambda = 20 \pm 5 nm$.