CHAPTER - 4

ERROR ANALYSIS

The errors in the experiments that measure photoabsorption, fluorescence cross sections and fluorescence quantum yield of molecules can conveniently be classified as follows: multiplicative, such as errors in pressure, temperature and absorption/fluorescence path length; additive, such as errors because of counting statistics and cross section shape errors caused by gas impurities and uncertainty in the incident photon energy. The complete description of these errors is given below in order to determine an estimate of the upper limit of actual error. The most probable estimate of the accuracy of the experiment is also given below for both SO₂ gas and CS₂ in vapour phase.

4.1 Pressure Measurement

The error in the pressure measurement could be attributed mainly to various parameters of the measuring instrument (MKS capacitance manometer), such as the instrumental calibration and drift in null reading etc. Since it is a differential gauge, the reference side has to be evacuated to pressures much better than 10⁻⁶ Torr. Hence, the order of vacuum of the reference side of the capacitance manometer may also contribute to the most probable estimate of the error, but in a small way.

The pressure of the target gas was measured absolutely
by MKS Baratron capacitance manometer (Model: 310 BH-10). This manometer was capable of measuring pressure up to 10 Torr absolutely provided the reference side of the head was evacuated to a high degree of vacuum.

In the photoabsorption experiment the SO₂ gas was introduced in the pressure ranging from 200 to 350 mTorr, whereas, the vapour pressure of CS₂ varied from 2 mTorr to 5 Torr. The systematic errors provided by the manufacturer in various pressure ranges are given in Fig. (4.1). Since the capacity of the sensor head for the measurement of pressure is up to 10 Torr, the systematic error present in lower pressure ranges is more compare to that of high pressures (Fig. 4.1). Thus, the systematic errors at the two lowest pressures used in the measurement of cross section for SO₂ and CS₂ are ±0.1% and ±1%, respectively, whereas for both the highest pressures the error is ±0.08%. As an upper limit to the actual error, the larger errors ±0.1 and ±1% were chosen as the errors due to instrument calibration for SO₂ and CS₂ gases respectively and these values were used to estimate the most probable error in photoabsorption cross section measurement.

Similarly in the fluorescence studies the pressure ranges used for SO₂ and CS₂ respectively are 2-300 mTorr and 2-850 mTorr. Again a maximum systematic error of ±1% corresponding to lowest pressures used, was considered in the measurement of fluorescence cross sections for both the gases.

Zero adjustment in the MKS capacitance manometer was possible with the help of balancing valve as described in Section (2.6.2) (Fig. (2.12)). The null reading of the MKS Baratron capacitance manometer was noted before and after the experimental scan and no drift in the null reading was observed during this period. Therefore, error due to the drift in null reading of the manometer could be ignored.
Figure 4.1 Systematical errors of MKS Baratron’s absolute pressure measurements. (for different gauge heads).
The reference side of the MKS capacitance manometer was continuously evacuated to a pressure better than $10^{-6}$ Torr. Since the pressure measured using this gauge was always greater than $10^{-3}$ Torr, which was at least three orders of magnitude larger, the errors introduced because of reference side pressure were negligible.

4.2 Thermal Transpiration Effect

The material used for the sensor of the MKS Baratron capacitance manometer is very sensitive to the thermal fluctuations. Therefore, it is operated at an elevated temperature (at 318K), while the temperature in the absorption/fluorescence chamber was around 300K. Thus we might expect the pressure in the absorption/fluorescence chamber to be slightly less than the pressure shown by the MKS unit head due to thermal transpiration effects. The thermal transpiration effects in the present work have been worked out on the lines suggested by Edmonds and Hobson (1965):

$$p_{ch} = a \sqrt{\frac{T_{ch}}{T_m}} p_m \quad \rightarrow (4.1)$$

where $p_{ch}$, $T_{ch}$ are the pressure and temperature in the absorption/fluorescence chamber, $p_m$ is the pressure indicated by the MKS sensor, $T_m$ is the temperature of the sensor head, and ‘$a$’ is a constant which depends on the geometry over which the temperature gradients occur. For an ideal aperture, $a = 1$, but in practice, it may have a value slightly greater than unity. From Eq. (4.1), it is found that the pressure in the absorption/fluorescence chamber has to be raised by 2.9%.
This pressure correction has been incorporated in the present measurements and absorption and fluorescence cross sections have been calculated accordingly. The other error which occurred was due to inaccuracy in the measurement of temperature. This could be as high as ±1 °C, which would introduce a maximum error of ±0.4%.

4.3 Uncertainty in Optical Path Lengths

The absorption path length in the present experiment is the length between the quartz plates Q₁ and Q₂ inside the absorption chamber as shown in Fig. (2.11). This was measured as 24.8 ± 0.1 cm, giving an error of ±0.4%. In case of fluorescence experiment (for \( \text{SO}_2 \)), \( \Delta l \) as defined in eqns. (3.5) and (3.8) has not been measured. Instead, the fluorescence cross sections have been normalized with some other experiment reported in literature at a certain incident photon wavelength. The maximum error in \( \Delta l \) has been estimated to be about ±2%. One point to be noted here is that the parameter \( \Delta l \) is used only in the case of fluorescence cross section measurement of \( \text{SO}_2 \), while the optical path length \( 'l' \) is used for absorption cross section measurements of both the gases, along with the fluorescence cross section measurement of \( \text{CS}_2 \).

4.4 Counting Statistics

Photon counting being a statistical process, follows Poissonian distribution. The uncertainty in 'n' number of counts is given by \( \pm \sqrt{n} \). To reduce this uncertainty it is advisable to have a large number of counts. Therefore, care was taken to give a large integration time for the collection of photons. But, the strength of the fluorescence signals was so low that, even an integration time of 20 seconds per channel was not sufficient to obtain an appreciable number of
counts. The signals measured at the end of absorption chamber in the case of photoabsorption studies were also quite weak in certain spectral regions ($\lambda < 200$ nm). Therefore a major contribution to the total estimate of error for photoabsorption and fluorescence cross sections, was due to the counting statistics.

The counting statistics in case of absorption studies for SO$_2$ has introduced an error varying from $\pm 0.4$ to $\pm 3\%$ depending upon the spectral region where the cross sections were measured, whereas for CS$_2$ vapour it varied from $\pm 0.2$ to $\pm 4\%$. The larger errors of $\pm 3$ and $\pm 4\%$ have been considered for SO$_2$ and CS$_2$ respectively for calculating the most probable estimate of accuracy. Similarly the counting statistics errors in the fluorescence studies were observed to be in the range $\pm 0.2$ to $\pm 4.0\%$ and $\pm 0.1$ to $\pm 5.0\%$ for SO$_2$ and CS$_2$ respectively depending upon the spectral region where cross sections are measured. Again, the larger errors of $\pm 4$ and $\pm 5\%$ have been considered for SO$_2$ and CS$_2$ respectively.

4.5 Gas Impurity

The research grade SO$_2$ gas was procured from L’Air Liquide, France and was 99.95% pure. Carbon disulphide vapour was obtained from an analytical-grade liquid. The vapour (CS$_2$) was purified by fractional distillation before being introduced into the absorption/fluorescence chamber. Care was taken to maintain the purity of these gases. The gas handling system was completely made of metal, and was evacuated before the experiment. Therefore, the error due to the sample gas impurity was negligible.

4.6 Conclusion

The coherent sum of the errors discussed in this
chapter, acted as an estimate of the upper limit of the actual error. In the present experiment, it has been found to be \( \pm 3.9 \), \( \pm 5.8\% \) for absorption cross section measurement, and \( \pm 7.4 \), \( \pm 6.8\% \) for fluorescence cross section measurement for \( \text{SO}_2 \) and \( \text{CS}_2 \) respectively. The incoherent sum was obtained by adding the squares of all the errors and taking the square root of the total sum. The incoherent sum represented the most probable estimate of the accuracy of the experiment. In the present experiment, the most probable error was estimated to be \( \pm 3.1 \), \( \pm 4.2\% \) for absorption cross section measurements and \( \pm 4.6 \), \( \pm 5.1\% \) for fluorescence cross section measurements for the gases \( \text{SO}_2 \) and \( \text{CS}_2 \) respectively. The most probable error for fluorescence quantum yield turned out to be \( \pm 5.5 \) and \( \pm 6.6\% \) for \( \text{SO}_2 \) and \( \text{CS}_2 \) gases.

The error budget for the measurement of photoabsorption and fluorescence cross sections for \( \text{SO}_2 \) and \( \text{CS}_2 \) has been summarized in Table (4.1).
Table 4.1 Error budget in the measurement of photoabsorption and fluorescence cross sections for \( \text{SO}_2 \) and \( \text{CS}_2 \) at room temperature.

<table>
<thead>
<tr>
<th></th>
<th>( \text{SO}_2 )</th>
<th>( \text{CS}_2 )</th>
<th>( \text{SO}_2 )</th>
<th>( \text{CS}_2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressure</td>
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<td>+1.0</td>
<td>+1.0</td>
<td>+1.0</td>
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<tr>
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<td>+0.4</td>
<td>-</td>
<td>+0.4</td>
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<td>Incoherent Sum</td>
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<td>+4.0</td>
<td>+4.0</td>
<td>+5.0</td>
</tr>
<tr>
<td>Coherent Sum</td>
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<td>+5.8</td>
<td>+7.4</td>
<td>+5.8</td>
</tr>
<tr>
<td>Incoherent Sum</td>
<td>+3.1</td>
<td>+4.2</td>
<td>+4.6</td>
<td>+5.1</td>
</tr>
</tbody>
</table>

or total r.m.s. error