# PHOTOABSORPTION STUDIES OF MOLECULES AT DIFFERENT TEMPERATURES

# V. PRAHLAD Ph.D. THESIS



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## PHOTOABSORPTION STUDIES OF MOLECULES AT DIFFERENT TEMPERATURES

by

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A THESIS SUBMITTED FOR THE DEGREE OF DOCTOR OF PHILOSOPHY OF THE GUJARAT UNIVERSITY

FEBRUARY 1996

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## TO MY PARENTS

## CERTIFICATE

I hereby declare that the work presented in this thesis is original and has not formed the basis for the award of any Degree or Diploma by any University or Institution.

Certified by :-

Prof. Vijay Kumar Ahmedabad

# CERTIFICATE

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Prof. Vijay Kumar Ahmedabad February, 1996

## STATEMENT

Photoabsorption cross sections for atoms and molecules are essential input parameters for modeling the atmospheres of planets. They are used for estimating the attenuation in the incident solar flux caused by the constituent gases of different layers in the atmospheres. Also these cross sections are used in estimating the various photochemical reactions occurring at different altitudes in the atmospheres.

In general, photoabsorption cross sections depend on the temperature of the absorbing gas, primarily due to the thermal distribution of its molecules in their various vibrational and rotational levels given by the Maxwell-Boltzmann distribution. Also, the transition probabilities for transitions from different vibrational states of the ground electronic state to the same vibrational level in the higher excited state are drastically different. The temperature dependence of the photoabsorption cross sections for polyatomic molecules is remarkably appreciable. This is due to the fact that their vibrational and rotational levels are closely spaced and hence it is easier to either populate or depopulate these levels even with a moderate change in temperature.

It is also known that the temperature of atmospheres of planets vary with altitude. Therefore, it becomes necessary to know the temperature dependence of photoabsorption cross sections in the relevant temperature and wavelength regions for those molecules which are present in the atmospheres of planets. In view of the above, laboratory measurements of temperature dependence of photoabsorption cross sections for polyatomic molecules becomes extremely important.

The basic aim of the present work is to study the photoabsorption of molecules at different temperatures. For this purpose, an experimental system was designed and fabricated in the laboratory and the cross sections of some of the molecular gases at temperatures ranging from 220-300 K and in the wavelength region 180-340 nm were measured. The experimental set-up consists of an argon mini-arc source capable of producing a continuum in the UV region from 110 nm to wavelengths longer than 330 nm, a 1-meter near normal incidence monochromator, a beam splitter to monitor the intensity of the photon beam during the experiment, an evacuable photoabsorption chamber, two cooled photomultipliers and a fast data acquisition system. The instrumental resolution was fixed at 0.1 nm.

The UV continuum produced by the argon mini-arc source was monochromatized by the 1-meter monochromator. A portion of the monochromatic radiation was reflected into a photomultiplier tube by using a beam splitter arrangement, which helped in monitoring the intensity variations of the light source. The transmitted monochromatic radiation was allowed to pass through a long absorption chamber. The intensity of the transmitted radiation at the end of the absorption chamber was measured using a cooled photomultiplier tube. The two photomultiplier tubes cooled thermoelectrically were operated in the counting mode and after proper amplification, the signals were stored in a microprocessor-controlled 1024 channel dual multichannel analyzer. The desired low temperatures for the photoabsorption chamber could be achieved by immersing it in the coolant contained in a cold bath. The cold bath was externally cooled by a servo-controlled two stage mechanical refrigeration system. There would be large temperature gradients at the edges of the cell and therefore the entire optical path length cannot be brought under a uniform temperature. In order to avoid these temperature gradients, two quartz tubes sealed on one side with quartz windows were used. These tubes could be moved in and out of the chamber until the whole optical path length can be brought under uniform temperature. The optical path length of the photoabsorption chamber was measured to be 76.1 cm. The number density of the absorbing molecules was determined by knowing the pressure and temperature of the absorbing gas. The pressure inside the absorption chamber was measured absolutely by using an MKS Baratron capacitance manometer. The temperature of the absorbing gas was taken to be same as that of the temperature

of the walls of the absorption chamber. The temperature of the walls of the chamber and the cold bath was measured using a thermocouple. The monochromator and the absorption chamber were evacuated to pressures of  $10^{-5}$  and  $10^{-6}$  torr respectively.

Photoabsorption cross sections for  $CCl_4$  and  $SO_2$  were measured at different temperatures ranging from 220 to 300 K at an interval of 20 K. For  $CCl_4$ , such measurements were made in the spectral region 186-240 nm whereas for  $SO_2$ , cross sections were measured in two spectral regions, 188-220 nm and 280-320 nm with an instrumental resolution of 0.1 nm.

The photoabsorption cross sections for the above two gases at room temperature were measured without any unforeseen problem. But in the case of similar measurements at low temperatures, three problems were identified. These are the thermal transpiration effect, the vapour pressure of the target gas and the large adsorption of molecular gases on the quartz windows.

The MKS Baratron capacitance manometer used for absolute measurement of target gas pressure is always held at an elevated temperature of 318 K whereas the temperature of the absorption chamber could be as low as 220 K. Due to this large temperature difference, there would be a thermomolecular flow from the chamber to the manometer. This effect is known as thermal transpiration effect. Due to this effect, the manometer always overestimates the target gas pressure. The necessary correction to the measured pressure was made by adopting the method suggested by Poulter et al (Poulter et al, 1983)

The absorbance due to a target gas can be increased by increasing its pressure. However, the target gas pressure cannot exceed the vapour pressure at that particular temperature otherwise the gas will condense into its liquid phase in the photoabsorption chamber. Hence, the vapour pressure of the target gas restricts the application of higher pressure in the experiments. Also this vapour pressure data was used to estimate the actual temperature of the target gas. It was found that the actual temperature of the gas was in agreement with the measured temperature of the walls of the chamber.

It was observed that at low temperatures, the transmission of the photoabsorption spectrometer changed with time after the introduction of target gas. This effect was attributed to the adsorption of the target gas on the quartz windows used in the experimental chamber. A separate experiment was conducted to determine the change in transmission as a function of time elapsed after introducing the gas. This change in transmission was used to correct the measured absorbance during the actual experiment. It was observed that the change in transmission due to adsorption was relatively independent of pressures used in the experiment for the two gases, but was found to depend on the temperature of the gas.

The error analysis has been carried out systematically. Apart from the three systematic errors described above, there are errors introduced in the measured cross section. These include the errors in the measurement of pressure and temperature, the uncertainty in the path length, uncertainty in incident photon energies and the error in the measured absorbance due to photon counting statistics. The most probable error in the case of CCl<sub>4</sub> and SO<sub>2</sub> was estimated to be about  $\pm 4\%$ 

The photoabsorption spectrum of  $CCl_4$  at 300 K is continuous in the wavelength region 186-240 nm. The absorption cross sections measured in the present experiment show a sharp decline in value with increasing wavelength. This decline is almost exponential excepting for a broad negative shoulder peaking around the wavelength 194 nm. $CCl_4$  is known to photodissociate in this spectral region due to the breaking of C-Cl bond. Photoabsorption cross sections were also measured at four other temperatures from 220-280 K at an interval of 20 K. For 260 and 240 K, cross sections could not be measured beyond 235 nm and at 220 K, it was not possible to measure beyond 223 nm, since the pressures required to measure the cross sections in this wavelength region were larger than the vapour pressure of the target gas at that particular temperature. The photoabsorption cross sections for the longer wavelengths decreased with a decrease in temperature. Temperature effect was found to vanish for shorter wavelengths. The observed feature in the temperature dependence of photoabsorption for CCl<sub>4</sub> could be attributed the decreasing population density in the higher vibrational states (of the ground electronic state) with a decrease in temperature. To put it quantitatively, the cross sections did not show any temperature dependence up to 206 nm. At 206.5 nm, such dependence could be observed for temperatures 220, 240 and 260 K whereas for 280 K, the threshold wavelength showing change in cross section was found to be 209 nm.

The photoabsorption cross section for SO<sub>2</sub> were measured in the two spectral regions 188-220 nm and 280-320 nm at temperatures from 220-300 K at an interval of 20 K. SO<sub>2</sub> has discrete band structure in the first spectral region; this is due to the transition  $\tilde{C}^1B_2 \leftarrow \tilde{X}^1A_1$ . The second spectral region consists of discrete bands  $(\tilde{A}^1A_2 \leftarrow \tilde{A}^1A_1)$  superimposed on an apparent continuum  $(\tilde{B}^1B_1 \leftarrow \tilde{X}^1A_1)$ . In both the spectral regions, the photoabsorption cross sections obtained at 300 K were compared with the existing data in the literature at the same instrumental resolution (0.1 nm). It was observed that the values of photoabsorption cross sections measured in continuously flowing systems were on the lower side compared to those measured in the closed cell experiments. The present experimental set-up is a continuously flowing system.

In both the spectral regions of  $SO_2$ , the cross section values at the peaks of the absorption bands were found to increase with the decrease in temperature. In the first spectral region (188-220 nm), the cross sections measured at different temperatures could not be compared with other data as no other measurements at different temperatures have been reported so far. In the second spectral region (280-320 nm), a comparison, however has been possible as the cross sections at different temperatures reported by other researchers though only at a few selected wavelengths are available. The discrepancies in the results wherever found have been explained at only a few wavelengths both quantitatively and qualitatively. The fact that there does not emerge a definite pattern in the study of temperature dependence of photoabsorption cross sections at different temperatures has at least been qualitatively explained by introducing two types of temperature dependence and their added effect.

conneally going through the manuscript of the thesis and making valuable suggestions at several places.

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# Chapter 1

# INTRODUCTION

## 1.1 Photoabsorption Cross Section of Gases

When a parallel beam of monochromatic radiation of certain incident intensity passes through a column of gaseous medium, a fraction of this intensity is absorbed by the gaseous medium. This process is known as photoabsorption. The difference between the incident and the transmitted intensity is called the absorbed intensity whereas the species constituting the gaseous medium which absorbs the radiation are called the absorbing species or the the target gas species.

#### 1.1.1 Beer-Lambert Law

Photoabsorption is characteristic of the target gas and also the wavelength of the incident monochromatic radiation. The extent of photoabsorption at a particular wavelength in any gaseous medium can be estimated by the applying the Beer-Lambert law. The Beer-Lambert law may be applied to study the photoabsorption in any gas provided the following conditions are satisfied :

• The incident radiation should be parallel beam and also must be monochromatic.



Figure 1.1: The process of photoabsorption.  $I_0$  is the incident intensity of the monochromatic radiation.  $-\frac{\Delta I}{I}$  is the fractional intensity absorbed by the gaseous medium in an element of path length  $\Delta l$ .

• The absorbing gas medium should be homogeneously mixed.

• The photon intensity is such that the absorption is a single photon process

Then according to Lambert (1760), if a monochromatic radiation of wavelength  $\lambda$  and incident intensity  $I_o$ , passes through a column of gaseous medium (Figure 1.1), the fractional intensity  $-\frac{\Delta I}{I}$  absorbed by the gaseous medium remains the same for each element of path length  $\Delta l$  traversed. Therefore

$$-\frac{\Delta I}{I} = \mathcal{K}(\lambda) \,\Delta l \tag{1.1}$$

 $\mathcal{K}(\lambda)$  is called the linear absorption co-efficient; it is a characteristic of the properties of the absorbing medium and the wavelength of the incident monochromatic radiation. If the incident intensity (at l = 0) is  $I_o$ , then the intensity I of the radiation after traversing a length l through the gaseous medium may be obtained by integrating Equation 1.1

$$I = I_o \exp\left[-\mathcal{K}(\lambda)\,l\right] \tag{1.2}$$

Beer (1852) found that the absorption co-efficient was always proportional to the concentration of the absorbing medium.

$$\mathcal{K}(\lambda) = \sigma(\lambda) \, n \tag{1.3}$$

where n is the concentration of the absorbing medium and  $\sigma(\lambda)$  is the proportionality factor. If n is expressed as the number density of molecules in units of number of molecules/c.c, then  $\sigma(\lambda)$  has the dimensions of cross section and is called the photoabsorption cross section.  $\sigma(\lambda)$  can be conveniently expressed in units of cm<sup>2</sup> or Megarbarn (1 Megabarn =  $10^6$  barn =  $10^{-18}$  cm<sup>2</sup>). Hence the Beer-Lambert law equation for photoabsorption becomes.

$$I = I_o \exp\left(-\sigma(\lambda) n l\right) \tag{1.4}$$

 $\sigma(\lambda)$  is characteristic only of the absorbing species and the wavelength of incident radiation. The quantity  $\ln\left(\frac{I_0}{I}\right)$  is called the absorbance of the target gas species. At any wavelength  $\lambda$  the graph between  $\ln\left(\frac{I_0}{I}\right)$  and n would always follow a straight line provided Beer-Lambert law is valid. For any absorbing species, the photoabsorption cross section  $\sigma(\lambda)$  can be measured as a function of incident photon wavelength. The resultant spectrum obtained by plotting the absorption cross sections against wavelength is called the photoabsorption spectrum. The photoabsorption spectrum is characteristic of the absorbing species.

#### 1.1.2 Semi-classical Description of Photoabsorption

When a monochromatic photon is absorbed by the target species (atom or molecule) in some particular quantum state (not necessarily the ground state), it may acquire any of the higher energy states. The process of absorption for a two level system is described by Einstein's semi classical theory of radiation. The absorbed intensity (Herzberg, 1950) is given by

$$I_{abs} = -\Delta I = \rho n_m B_m^n \left(\frac{hc}{\lambda}\right) \Delta l$$
(1.5)

where the co-efficient  $B_{mn}$  is called the Einstein's transition probability for a transition from a lower state m to an upper state n,  $\lambda$  is the wavelength of the incident radiation,  $\rho$  is the energy density of the radiation and  $\Delta l$  is the path length traversed. The intensity in terms of energy density of radiation is given by

$$I = \rho c \tag{1.6}$$

Substituting this value of  $\rho$  in Equation 1.5,

$$I_{abs} = -\Delta I = n_m B_m^n \left(\frac{h}{\lambda}\right) I \Delta l \tag{1.7}$$

Therefore, the extent of photoabsorption for any atom or molecule is directly proportional to the transition probability.

$$B_m^n = \frac{8\pi^3}{3h^2c} |R_{mn}|^2 \tag{1.8}$$

where,

$$R_{mn} = \int \psi_m^* \mathbf{M} \, \psi_n \, d\tau_e \tag{1.9}$$

 $R_{mn}$  is the transition matrix element,  $\psi_m$  and  $\psi_n$  are the wave functions for lower and upper electronic states respectively. **M** is the dipole moment operator representing the oscillating electric dipole induced by the incident monochromatic radiation. In case of atoms, the transition is a simple resonant excitation of its energy state whereas for molecules, the transition involves excitation of its electronic states. Also, associated with the excitation of the electronic states are vibrational and rotational transitions. The contribution of vibrational and rotational transition moments to the transition probability for a molecule, would be discussed in Section 1.5.

## **1.2 Electronic States of Molecules**

In general, for molecules, the photoabsorption in the UV is due to the excitation from their ground electronic state to the excited electronic states. The nature of the photoabsorption spectrum, to a large extent, depends on the type of the electronic states involved in the transition. In this section, the origin of the electronic states and also certain properties relevant to the photoabsorption process would be discussed.

## 1.2.1 Schrödinger Equation for a Molecule

The electronic states of a molecule are the quantized states of the energy of the system describing the motion of electrons and their coulombic interaction with the constituent nuclei. The total energy of the molecule is the kinetic energy of the electrons and nuclei plus the potential energy V(R,r). V(R,r) is a sum total of the potential due to the coulombic interaction of electrons-nuclei,  $V_e(r)$  and nuclei-nuclei,  $V_n(R)$ . Considering the total energy to be constant, the Schrödinger equation for the molecule (Herzberg, 1966) may be written as

$$\left[-\sum_{n} \frac{\hbar^{2}}{2M_{n}} \nabla_{n}^{2} + \sum_{e} \frac{\hbar^{2}}{2m} \nabla_{e}^{2} + V(R,r)\right] \Psi(R,r) = E\Psi(R,r)$$
(1.10)

where  $\nabla_n^2$  and  $\nabla_e^2$  operate on the nuclear and electronic co-ordinates respectively. R and r are the nuclear and electronic coordinates respectively, V(R,r) is the total potential energy, E is the total energy and  $\Psi(R,r)$  is the total wave function.

Even for the simplest molecular system, it is extremely difficult to solve this Schrödinger equation for exact solutions. The problem may be simplified by decoupling the electronic and nuclear motions. This can be achieved by adopting the Born-Oppenheimer approximation.

## 1.2.2 Born-Oppenheimer Approximation

In a molecule, since the mass of the electrons is much smaller than that of the nuclei, the electrons can follow the motion of the nuclei almost instantaneously. If this condition is valid in a molecule, then, according to Born-Oppenheimer (1927), Equation 1.10 can be decoupled into two equations; one which describes the motion of electrons in the potential provided by the fixed nuclei and the other which describes the motion of the nuclei in the potential provided by the sum total of electronic energy  $E_{el}$  and the potential due to the repulsion of nuclei  $V_n(R)$ . This decoupling can be achieved by expressing the total wave function  $\Psi(R, r)$  as a product of the electronic wave function  $\psi_e(r)$  and the wave function for nuclear motion  $\psi_{\nu}(R)$  (Herzberg, 1966). The Schrödinger equation for electronic motion is

$$\left[-\sum_{e} \frac{\hbar^{2}}{2m} \nabla_{e}^{2} + V_{e}(r)\right] \psi_{e}(r) = E_{el} \psi_{e}(r) \qquad (1.11)$$

The Schrödinger equation for nuclear motion is

$$\left[-\sum_{n} \frac{\hbar^{2}}{2M_{n}} \nabla_{n}^{2} + (E_{el} + V_{n}(r))\right] \psi_{v}(r) = E \psi_{v}(r) \qquad (1.12)$$

The eigen functions  $\psi_e(r)$  and the eigen values  $E_{el}$  of Equation 1.11 describe the electronic states and the corresponding energies (for a fixed nuclei conformation).

#### **1.2.3 Potential Energy Diagram of Electronic States**

For any particular electronic state of the molecule, the eigen state energy  $E_{el}$  described by Equation 1.11 and the coulombic repulsive potential due to nuclei  $V_n(R)$ , constitute the potential energy  $U(R-R_e)$  which is a function of the internuclear distance  $(R-R_e)$ where  $R_e$  is the equilibrium position of nuclei. The potential energy diagram or curve for the corresponding electronic state can therefore be constructed by determining the potential  $U(R-R_e)$  as a function of  $(R-R_e)$ . The nuclei of the constituent atoms perform vibrational motion under the influence of this potential.

In the case of diatomic molecule, the potential energy diagram for any particular electronic state is a simple two dimensional curve of potential energy  $U(R - R_e)$ versus the internuclear distance  $(R - R_e)$ . But in the case of polyatomic molecules, the potential energy diagram for electronic state consists of 3N - 6 (3N - 5 for linear molecules) hyper surfaces in a 3N - 5 (3N - 4 for linear molecules) dimensional space (Herzberg, 1966). Here, N denote the number of atoms in the molecule. Therefore the potential energy diagram even for a simplest polyatomic molecule (i.e. a triatomic molecule) is very complicated. The nature of potential energy diagram may be understood qualitatively by considering a diatomic molecule for the sake of convenience. Based on their shapes, the potential energy curves may be broadly classified into two types; one is the bound state curve and the other the repulsive





state curve. Figure 1.2(a) shows the potential energy curve for the ground state of a diatomic molecule. The curve shows a well defined minimum in its potential energy; this potential is attractive and the atoms are bound together in such a potential. Therefore, the electronic state corresponding to such a potential is called a bound state. The height of the asymptote on the right side of the potential energy curve gives the dissociation energy  $D_e$  of the molecule. Above this dissociation limit, the atoms are no longer bound in a molecule. This potential can be represented by the Morse function

$$U(R - R_e) = D_e \left[ 1 - e^{-\beta (R - R_e)} \right]^2$$
(1.13)

where  $\beta$  is a constant for a particular molecule. The constituent atoms in the molecule perform their vibrations in the potential defined by the Morse function. Figure 1.2 (b) shows the potential energy curve for one of the electronic states of a diatomic molecule. The curve has no minimum; therefore the potential in such a state is repulsive. The electronic state corresponding to such a potential is called a repulsive state. In a repulsive state, the atoms can never be bound together as a molecule; in other words, the molecule dissociates.

#### 1.2.4 The Notation of Electronic States

The notation followed for denoting electronic states of a molecule, in general, consists of two terms. The first term describes the excitation level of the electronic state and the second term describes the symmetry properties of the of the wave function representing the electronic state.

In case of atoms the ground state and the successive excited states are denoted by the principal quantum numbers n = 0, 1, 2, 3... In case of molecules, the notation used to denote the electronic states is as follows. According to convention, the ground electronic state is always denoted by X. The excited states of same multiplicity are denoted by A, B, C, ... and those of different multiplicity by small letters a, b, c, ... The notation followed for describing the electronic states of the molecules differ in the case of diatomic and polyatomic molecules. The electronic states of a diatomic molecule are characterized by the following quantum numbers; the total orbital angular momentum  $\Lambda$ , the total spin S and the total angular momentum  $\Omega = |\Lambda + S|$ . The spectroscopic terms for the electronic states are represented by the general notation

## $^{2S+1}\Lambda_{\Omega}$

where 2S + 1 is the spin multiplicity and  $\Lambda$  can take values  $\Lambda = 0, \pm 1, \pm 2, \ldots$  and are denoted by  $\Sigma, \Pi, \Delta, \ldots$ 

For polyatomic molecules the notation for describing the electronic state is as follows. The structure of any molecule remains unchanged under certain symmetry operations. Based on these symmetry operations, the molecules can be said to belong to a particular point group. There are five kinds of symmetry operations which are necessary for classifying a point group. They are, the rotation about an axis of symmetry  $\mathbf{c}_{\mathbf{p}}$ , the reflection in a plane of symmetry  $\sigma$ , the inversion through a centre of symmetry i, the rotation about an axis followed by reflection in plane perpendicular to it and the identity operation I. The electronic wave function changes sign or remains unchanged by the symmetry operations allowed by the point group to which the molecule belongs. In case of polyatomic molecules, the electronic states are classified according to these symmetry properties. Each such electronic state belongs to one of the so called irreducible representation of the point group. For example, in case of  $SO_2$  which was a target gas in the present experiment, the ground state belongs to the irreducible representation  ${}^{1}A_{1}$ . Hence the ground electronic state of SO<sub>2</sub> is denoted as  $\tilde{X}^1A_1$ . A detailed description for the notation for the symmetry of the electronic states of molecules based on the point groups is given by Herzberg (1966)

## 1.3 Vibrations and Rotations of Molecules

The nuclei of the atoms that are bound in a molecule can perform vibrational motion along their bond axis. The vibrations along the bond axis is similar to a spring - mass system, which vibrates under the influence of a stretching force and a restoring force. In a molecule the electrostatic repulsive forces between the nuclei play the role of stretching force. The electrostatic attraction of the electron cloud around the nucleus of an atom in a molecule with the nuclei of its surrounding atoms plays the role of a restoring force. The effective potential that can describe both the stretching and restoring forces for a molecule in a particular electronic state is its Morse potential. Under the influence of this potential the nuclei vibrate about their equilibrium position. Apart from the vibrational motion, the molecule can perform rotational motion also. The rotation could be along any preferred axis. The energies associated with the vibrational and rotational motion of a molecule are called the the vibrational and rotational energies. These energies are quantized and the respective quanta of energy are called vibrational and rotational levels.

## 1.3.1 Vibrational Levels of a Molecule

In case of a diatomic molecule, there is only a single mode of vibration where the nuclei of the atoms vibrate along their bond axis whereas in case of a polyatomic molecule, there are more than one mode of vibration. In general, these vibrational modes are coupled; they can exchange the vibrational energy freely. Therefore the vibrations in a polyatomic molecule are complicated. However, by a suitable linear transformation, a new co-ordinate system may be defined (Atkins, 1969) which reduces these coupled modes into independent modes of vibration called the normal modes. The co-ordinate system which describes the motion in normal modes is called the system of normal co-ordinates. For a better understanding of the nature of vibration of a normal mode in a molecule, it would be more convenient to consider the vibrations of a diatomic molecule as an example. As mentioned in Section 1.2.3, the nuclei perform vibration in the Morse potential. These vibrations are equivalent to that of a quantum mechanical anharmonic oscillator. The vibrational energy of such an oscillator is quantized and the vibrational energy is given by

$$G(v) = \omega_e \left(v + \frac{1}{2}\right) - \omega_e x_e \left(v + \frac{1}{2}\right)^2 + \omega_e y_e \left(v + \frac{1}{2}\right)^3$$
(1.14)

Here,  $\omega_e$  is called the vibrational constant and v is the vibrational quantum number. $\omega_e$  is generally expressed in cm<sup>-1</sup> and is given by

$$\omega_e = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}} \tag{1.15}$$

where  $\mu$  is the reduced mass, k is the force constant. The first term is Equation 1.14 corresponds to a quantum mechanical simple harmonic oscillator. The second and third terms include constants  $\omega_e x_e$ ,  $\omega_e y_e$  which account for the anharmonicity in the oscillator. The energy difference between the successive vibrational levels decreases with an increasing quantum number, and finally merges into a continuum. The threshold of the continuum is called the dissociation limit. The vibrational energy for a polyatomic molecule is given by

$$G(\omega_1, \omega_2 \dots) = \sum_{i} \omega_i \left( v + \frac{1}{2} \right) - \sum_{i} \sum_{k>i} x_{ik} \left( v_i + \frac{1}{2} \right) \left( v_k + \frac{1}{2} \right)$$
(1.16)

where  $\omega_i$  is the frequency corresponding to the  $i_{th}$  mode and  $x_{ik}$  is its respective anharmonicity constant.

## 1.3.2 Rotational Levels of a Molecule

In the case of diatomic molecules, the molecule can rotate about an axis perpendicular to the internuclear axis. The rotation of a diatomic molecule is equivalent to that of a non-rigid rotor. The energy eigen values for such a rotor are given by

$$F_{\nu}(J) = B_{\nu}J(J+1) - D_{\nu}J^{2}(J+1)^{2}$$
(1.17)

 $B_v$  is called the rotational constant and J is the rotational quantum number.  $B_v$  is expressed in units of cm<sup>-1</sup>.

The first term in Equation 1.17 corresponds to the energy of a rigid rotor and the second term takes care of the non-rigidity.  $D_v$  is called the centrifugal stretching term. In any molecule there, is always a small interaction of its rotations with the vibrations. The subscript v in the constants indicate that they have been corrected for this interaction of vibration with the rotation The corrected constants may be expressed in terms of their known values at the equilibrium position as follows.

$$B_{v} = B_{e} - \alpha_{e}(v + \frac{1}{2})$$
(1.18)

$$D_{v} = D_{e} - \beta_{e}(v + \frac{1}{2}) \tag{1.19}$$

here,  $B_e$ ,  $D_e$  are the constants defined at equilibrium position and  $\alpha_e$ ,  $\beta_e$  are constants describing the interaction of vibration with rotation. v is the quantum number of the vibrational level, whose interaction with the given rotation is needed to be known. The values of the rotational constants defined at the equilibrium position are given by

$$B_e = \frac{\hbar}{4\pi \, c \, I} \tag{1.20}$$

$$D_e = \frac{4B^3}{\omega^2} \tag{1.21}$$

where I is the moment of inertia about the axis of rotation and  $\omega$  is the vibrational constant. For polyatomic molecules (except for linear molecules), there are three perpendicular rotational axes. These axes are called the principal axes and the moments of inertia about these axes are called principal moments of inertia. The rotational constants corresponding to these principal axes are designated as  $A_e$ ,  $B_e$ ,  $C_e$ , whereas the corresponding axes are designated as a, b, c. According to international nomenclature,  $A_e > B_e > C_e$ . Based on the relation between these principal moments of inertia, the polyatomic molecules may be broadly classified into three types. They are the prolate symmetric top, the oblate symmetric top and the linear type rotor.

Table 1.1: The three types of symmetric tops and their respective rotational energy formulae. Here K is the projection of the total angular momentum J on the top axis.

Relation	Туре	Rotational
between rotational	of	energy
constants	molecule	formula
$B_e = C_e$	Prolate symmetric top	$F(J,K) = B_v J(J+1) + (A_v - B_v) K^2$
$A_e = B_e$	Oblate symmetric top	$F(J, K) = B_{v}J(J+1) + (B_{v} - C_{v})K^{2}$
$B_e = A_e = C_e$	Linear	$F(J) = B_v J(J+1)$

The relation between the moments of inertia, the corresponding types of the molecule and their respective formulae for rotational energy are listed in Table 1.1

A general rotational energy formula for any type of molecule is given by

$$F_{\nu}(J_{\tau}) = \frac{1}{2}(B_{\nu} + C_{\nu})J(J+1) \left[A_{\nu} - \frac{1}{2}(B_{\nu} + C_{\nu})\right]W_{\tau_{J}}$$
(1.22)

where  $\tau = J, J-1, \ldots - J$  is the (2J+1) degenerate states of a given J. The quantity  $W_{\tau_J}$  is tabulated in terms of asymmetry parameter b up to J = 6 by Herzberg (1945) The rotational constants  $A_v$ ,  $B_v$ ,  $C_v$  are corrected for centrifugal stretching and also for the interaction of vibration with rotation.

#### **1.3.3** Vibrational and Rotational Constants

proportional to

As seen in section 1.3.2, the vibrational constants are inversely proportional to reduced mass and the rotational constants are inversely proportional to their respective moments of Inertia. This implies that for heavy and polyatomic molecules which have larger mass and also large moments of inertia, the values of their vibrational and rotational constants are smaller when compared to those of light diatomic molecules. Table 1.2 compares the masses, vibrational and rotational constants of some of the molecules.

Heavy diatomic and most of the polyatomic molecules possess vibrational constants which are smaller in value when compared to those of light diatomic molecules (see

Table 1.2: A comparison of molecular weights and vibrational and rotational constants for a few known molecules.

Molecule	State	Mass	Vibrational constants (cm <sup>-1</sup> )			Rotational constants (cm <sup>-1</sup> )		
		(a.m.u)	$\omega_1$	$\omega_2$	$\omega_3$	А	В	С
H <sub>2</sub>	$X^{1}\Sigma_{q}^{+}$	2.0158	4395.3	-		-	60.80	- internal
02	$X^{3}\Sigma_{q}^{-}$	31.998	1580.361		-	-	1.44566	-
SO <sub>2</sub>	$\tilde{X}^1 A_1$	64.06	1151.3	517.6	1361.7	2.02736	0.34417	0.293525
I <sub>2</sub>	$X^{1}\Sigma_{g}^{+}$	253.809	214.57		-	-	0.03735	-

## 1.3.4 Thermal Distribution of Vibrational levels

According to Maxwell-Boltzmann distribution law, the number of molecules in thermodynamic equilibrium, possessing an energy E at an absolute temperature T is proportional to the factor  $e^{-E/KT}$ . Therefore, the number of molecules in a vibrational state v possessing an energy G(v), at an absolute temperature T, is given by

$$\mathbf{V}_{v} = \frac{N}{Q_{vib}} \exp\left(-\frac{G(v)}{KT}\right) \tag{1.23}$$

where, N is the total number of molecules and  $Q_{vib}$  is the partition function. The partition function is given by,

$$Q_{vib} = \sum_{v} \exp\left(-\frac{G(v)}{KT}\right)$$
(1.24)

where the summation is over all possible vibrational levels. The ratio of the number of molecules in a vibrational state v to the number of molecules,  $N_0$ , in the zeroth vibrational level is given by

$$\frac{N_{\nu}}{N_0} = \exp\left(-\frac{G_0(\nu)}{KT}\right) \tag{1.25}$$

where  $G_0(v)$  is the energy difference between the vibrational level v and the zeroth vibrational level (v = 0) i.e

$$G_0(v) = G(v) - G(0)$$

Heavy diatomic and most of the polyatomic molecules possess vibrational constants which are smaller in value when compared to those of light diatomic molecules (see

Table 1.2: A comparison of molecular weights and vibrational and rotational constants for a few known molecules.

Molecule	State	Mass	Vibrational constants (cm <sup>-1</sup> )			Rotational constants (cm <sup>-1</sup> )		
+ Atro	om temp	(a.m.u)	$\omega_1$	$\omega_2$	$\omega_3$	A	В	С
H <sub>2</sub>	$X^{1}\Sigma_{a}^{+}$	2.0158	4395.3	-	-	-	60.80	-
02	$X^{3}\Sigma_{q}^{-}$	31.998	1580.361	nolecul	a are for	nd in the	1.44566	rational
SO <sub>2</sub>	$\tilde{X}^1 A_1$	64.06	1151.3	517.6	1361.7	2.02736	0.34417	0.293525
I <sub>2</sub>	$X^{1}\Sigma_{g}^{+}$	253.809	214.57	-	-	-	0.03735	-

## 1.3.4 Thermal Distribution of Vibrational levels

According to Maxwell-Boltzmann distribution law, the number of molecules in thermodynamic equilibrium, possessing an energy E at an absolute temperature T is proportional to the factor  $e^{-E/KT}$ . Therefore, the number of molecules in a vibrational state v possessing an energy G(v), at an absolute temperature T, is given by

$$N_{v} = \frac{N}{Q_{vib}} \exp\left(-\frac{G(v)}{KT}\right)$$
(1.23)

where, N is the total number of molecules and  $Q_{vib}$  is the partition function. The partition function is given by,

$$Q_{vib} = \sum_{v} \exp\left(-\frac{G(v)}{KT}\right)$$
(1.24)

where the summation is over all possible vibrational levels. The ratio of the number of molecules in a vibrational state v to the number of molecules,  $N_0$ , in the zeroth vibrational level is given by

$$\frac{N_v}{N_0} = \exp\left(-\frac{G_0(v)}{KT}\right) \tag{1.25}$$

where  $G_0(v)$  is the energy difference between the vibrational level v and the zeroth vibrational level (v = 0) i.e

 $G_0(v) = G(v) - G(0)$ 

Heavy diatomic and most of the polyatomic molecules possess vibrational constants which are smaller in value when compared to those of light diatomic molecules (see section 1.3.3.). The nature of the vibrational distribution of molecules depend on their respective vibrational constants.

- At room temperature (300 K) in case of light diatomic molecules, only a negligible fraction of the total number of molecules are found in the higher vibrational states, whereas in case of heavy diatomic and polyatomic molecules, an appreciable fraction of molecules can be found in their higher vibrational levels.
- In the case of heavy diatomic molecules and polyatomic molecules, an appreciable change in the distribution can be brought about by a moderate change in the temperature. In comparison, such distributions for light diatomic molecules do not get affected (except for very large changes in temperature).

The above points are being clearly illustrated in Figure 1.3 (a) and 1.3 (b) where the thermal distributions of vibrational levels for molecular hydrogen and Iodine have been presented at three temperatures of 300, 260 and 220 K respectively. For the calculation of these distributions, the vibrational constants have been taken from table 1.1. The points made above for heavier diatomic molecules like iodine are conspicuously clear as seen in Figure 1.3 (b).

#### **1.3.5 Thermal Distribution of Rotational Levels**

The Maxwell-Boltzmann distribution can be applied even for the case of rotations. However, the degeneracy in the rotational level has to be considered ( $M_J$  can take values from -J to J; hence there is degeneracy 2J + 1). The number of molecules in a rotational state J, belonging to the lowest vibrational level v = 0 and possessing a rotational energy F(J) at an absolute temperature T is given by

$$N_J = \frac{N}{Q_{rot}} \left(2J+1\right) \exp\left(-\frac{F(J)}{KT}\right)$$
(1.26)

where N is the total number of molecules,  $Q_J$  is the partition function. The partition function is given by:



Figure 1.3: Thermal distribution of vibrational levels of (a)  $H_2$  and (b)  $I_2$ .

where N is the total number of molecules,  $Q_J$  is the partition function. The partition function is given by,

$$Q_{rot} = \sum_{J} \left(2J+1\right) \exp\left(-\frac{F(J)}{KT}\right)$$
(1.27)

where the summation is over all the possible rotational levels, J. The ratio of number of molecules in a rotational state J to the number of molecules  $N_0$  in rotational state (J = 0) is given by

$$\frac{N_J}{N_0} = (2J+1) \exp\left(-\frac{F(J)}{KT}\right)$$
(1.28)

Rotational constants in the case of heavy diatomic and most of polyatomic molecules are smaller in value when compared to those for light molecules (section 1.3.3). The nature of the rotational distribution of molecules primarily depends on their rotational constants.

- In case of normal diatomic molecules, at room temperature, 300 K, only a small fraction of the number of molecules are found in the higher rotational levels. However, a large fraction of molecules can be found in their higher rotational levels for heavy diatomic and most of the polyatomic molecules.
- In case of heavy diatomic and polyatomic molecules, large changes in rotational distribution can be brought about by a moderate change in temperature. In comparison, the light diatomic molecules change in temperature has negligible effect on the rotational distribution.

The thermal distributions of rotational levels for molecular hydrogen and iodine have been shown in Figures 1.4(a) and 1.4(b) respectively at three temperatures of 300, 260 and 220 K. For the calculation of these distributions, the rotational constants have been taken from Table 1.2. The points made above for heavier diatomic molecules like lodine are conspicuously clear as seen in Figure 1.4 (b).







Figure 1.4: Thermal distribution of Rotational levels of (a)  $H_2$  and (b)  $I_2$ .

## 1.4 Electronic Transitions

If  $\psi_m$  and  $\psi_n$  are the total wave functions describing the lower electronic state m and the upper electronic state n respectively then as described in Section 1.1.2, the total transition moment  $|R_{mn}|^2$  for the transition can be calculated using Equation 1.9. When the molecule undergoes such a transition then associated with the electronic excitation there are vibrational and rotational transitions. All these transitions and their individual contribution to total transition moment are described in this Section.

Under the Born-Oppenheimer approximation (assuming no interaction of vibration and rotation for first approximation), the total wave function  $\Psi$  may be decoupled (Herzberg, 1966) as

$$\Psi = \psi_e \,\psi_v \,\frac{\psi_r}{r} \tag{1.29}$$

 $\psi_e$  is the electronic wave function,  $\psi_v$  is the wave function for vibration,  $\psi_r$  is the wave function for rotation. The dipole moment operator **M** may be written as

$$\mathbf{M} = \mathbf{M}_{\mathbf{e}} + \mathbf{M}_{\mathbf{n}}$$

 $(M_e \text{ is for the electrons, } M_n \text{ is for nuclei})$ . Under the above approximation the matrix element  $R_{mn}$  may be decoupled in terms of the individual contributions due to electronic, vibrational and rotational transitions.

$$R_{mn} = R_e^{mn} R_{vib}^{\nu_m \nu_n} R_{rot}^{J_m J_n}$$
(1.30)

where  $R_e^{mn}$  is the matrix element for electronic excitation and is given by

$$R_e^{mn} = \int \psi_m^* \mathbf{M}_{\mathbf{e}} \,\psi_n \, d\tau_e \tag{1.31}$$

 $R_{vib}^{v_m v_n}$  is called the Franck-Condon factor, which describes the transition from a vibrational level  $v_m$  in the ground electronic state m to a vibrational level  $v_n$  in the excited electronic state n. Similarly  $R_{rot}^{J_m J_n}$  is the transition matrix element for rotation, which describes the transition from a rotational level  $J_m$  belonging to a vibrational level  $v_m$
in the ground electronic state m to a rotational level  $J_n$  belonging to a vibrational level  $v_n$  in the excited electronic state n.

In case of a molecule, for a transition from an electronic state m to n, involving transitions of vibrational levels from  $v_m$  to  $v_n$  and rotational levels  $J_m$  to  $J_n$ , the Einstein's co-efficient for transition probability is  $B_{v_m}^{v_n J_m}$ . In terms of the transition matrix elements mentioned above, the co-efficient is given by,

$$B_{\nu_m J_m}^{\nu_n J_n} = \frac{8\pi^3}{3h^2c} \mid R_e^{mn} \mid^2 \mid R_{\nu i b}^{\nu_m \nu_n} \mid^2 \frac{\sum \mid R_{rot}^{J_m J_n} \mid^2}{g_J}$$
(1.32)

where  $g_J$  stands for the degeneracy in state  $J_m$  ( $g_J = 2J_m + 1$ ); the summation is over all the degenerate levels in  $J_m$  and  $J_n$ .

The intensity of radiation absorbed upon traveling a distance of  $\Delta l$  in a medium of molecular gas may be obtained by summing over all the possible vibrational and rotational transitions (see Section 1.1.2). In a particular electronic transition, it is given by

$$-\Delta I = \sum_{\nu_m \nu_n J_m J_n} B^{\nu_n J_n}_{\nu_m J_m} n_{\nu_m J_m} I\left(\frac{h}{\lambda}\right) \Delta l \qquad (1.33)$$

where  $n_{v_m J_m}$  is the number density of the molecules in an electronic state m and vibrational state  $v_m$  and rotational state  $J_m$ . This number density may be determined from the thermal distribution of molecules in their various vibrational and rotational levels (section 1.3.4, 1.3.5). The effect of thermal distribution on the photoabsorption is discussed in Section 1.6. The significance of each of the transition moments contributing to the photoabsorption is discussed in the following sections.

#### 1.4.1 Selection Rules

The strength of electronic transitions is characterized by the magnitude of their transition moments (the value is always less than one). The transition is called an allowed transition if the transition moment has a non-zero value. Since the extent of photoabsorption depends directly on the value of the electronic transition moments, allowed transitions can cause strong photoabsorption. For diatomic molecules, from the symmetry properties of the electronic states and that of the electric dipole (induced by the incident radiation), the following rules which govern the strength of the electronic transitions may be derived. These rules are called the dipole selection rules For a very weak coupling between  $\Lambda$  and S, we have  $\Delta \Lambda = 0, \pm 1$  ( $\Lambda = 0$  to  $\Lambda = 0$ is not allowed) and  $\Delta S = 0$  (No change in spin multiplicity).

Irrespective of the kind of coupling between  $\Lambda$  and  $S \Delta \Omega = 0, \pm 1$  ( $\Omega = 0$  to  $\Omega = 0$  is not allowed).

The first two dipole selection rules may be broken if there is a finite interaction between  $\Lambda$  and S.

For polyatomic molecules the general selection rule is as follows,

$$R_e^{mn} = \int \psi_m^* \mathbf{M}_{\mathbf{e}} \psi_n \ d\tau_e$$

is different from zero for allowed transitions. where,  $\psi_m^*$  and  $\psi_n$  are the wave functions for the electronic states. The nature of the transition, whether allowed or not can be predicted from the symmetry properties of the wave function and  $\mathbf{M}_{e}$ . However, the selection rule for spin multiplicity described above for the diatomic molecules is true for polyatomic molecules. The selection rules in general may be broken if there is a finite interaction between vibration and electronic motion. The corresponding transition moments are small and are called Forbidden transitions.

#### 1.4.2 Franck-Condon Principle

The Franck-Condon principle describes the probability for transitions in the molecules from a vibrational level  $v_m$  in ground electronic state, to a vibrational level  $v_n$  in the upper excited electronic state. This principle assumes that the electronic transition in a molecule occurs so rapidly in comparison to the nuclear motion that immediately after the electronic excitation, the nuclei still have nearly the same relative position and velocity, as that before the transition. After the transition has occurred, the nuclei are located in a new potential energy conformation corresponding to that of the excited electronic state. Due to the effect of the new potential energy the nuclei would now start vibrating with a characteristic frequency (corresponding to vibrational level  $v_n$ ) which is different from the vibrational frequency before the transition (corresponding to vibrational level  $v_m$ ). The molecule is then said to have undergone a vibrational transition (i.e. from a vibration level  $v_m$  to vibrational level  $v_n$ ). According to Franck-Condon (Franck, 1925, Condon, 1928), during an electronic transition, the transition probability from any vibrational level in the ground electronic state to any of the vibrational levels in the excited electronic state is maximum for vibrational transitions which involve very small or negligible change in internuclear distance. The Franck-Condon principle is illustrated in Figure 1.5(a). Quantum mechanically the principle may be expressed as follows. The transition from a vibrational level  $v_m$  to  $v_n$ is maximum, when  $R_{vib}^{v_m v_n}$ , the Franck-Condon (overlap integral), is maximum. The Franck-Condon factor is given by

$$R_{vib}^{\upsilon_m\upsilon_n} = \int \psi_{\upsilon_m}\psi_{\upsilon_n} \, d\tau_{\upsilon} \tag{1.34}$$

where  $\psi_{v_m}$  and  $\psi_{v_n}$  are the wave functions describing the vibrational levels  $v_m$  and  $v_n$  respectively.

The Franck-Condon factor is the primary factor which is responsible for producing the observed structures in the photoabsorption spectrum. The structures observed in the photoabsorption spectrum due to vibrational transitions are called vibrational band structures.

#### 1.4.3 Hönl-London Formulae

The quantity  $\sum |R_{rot}^{J_m J_n}|^2$  appearing in the Equation 1.32 for transition probability, is called the line strength. The line strength is denoted by the symbol  $S_{J_m J_n}$ ; the values of these line strengths can be obtained from a set of formulae known as the Hönl-London formulae (Kovacs, 1962). The Hönl-London formulae  $S_{J_m J_n}$  give the probability for a transition from a rotational state  $J_m$  belonging to a particular vibrational level  $v_m$  in the ground electronic state m to a rotational state  $J_n$ , belonging to a particular vibrational level  $v_n$  in the excited electronic state n. The magnitude of the transition probabilities defined by these formulae depend upon the symmetry of the rotational levels involved in the transition. These formulae are also called 'line strengths'. The vibrational band structures described in section 1.5 comprises of 'rotational structures' arising due to these line strengths. However the rotational structures are very narrow and need high resolution (< 0.01 nm) to be observed in the photoabsorption spectrum.

#### 1.4.4 Photoabsorption for Polyatomic Molecules

After substituting for the Einstein's coefficient from Equation 1.32 the absorbed intensity given by Equation 1.33 may be written as

$$-\Delta I = \sum_{v_m v_n J_m J_n} \frac{8\pi^3}{3h^2 c} |R_e^{mn}|^2 |R_{vib}^{v_m v_n}|^2 \frac{S_{J_m J_n}}{2J_m + 1} n_{v_m J_m} \frac{h}{\lambda} I \Delta l$$
(1.35)

The absorbance is obtained by integrating the Equation 1.35

num in its potential, f

$$\ln\left(\frac{I_0}{I}\right) = \sum_{\nu_m\nu_n J_m J_n} \frac{8\pi^3}{3h^2c} |R_e^{mn}|^2 |R_{\nu ib}^{\nu_m\nu_n}|^2 \frac{S_{J_mJ_n}}{2J_m+1} n_{\nu_m J_m} \frac{h}{\lambda} l$$
(1.36)

The number density of molecules in a rotational state  $J_m$  belonging to a vibrational level  $v_m$  may be obtained from the thermal distribution of vibrational and rotational levels and is given by

$$n_{v_m J_m} = \frac{n_m}{Q(T)} \left(2J+1\right) \exp\left(-\left[G(v_m) + F_{v_m}(J_m)\right]/KT\right)$$
(1.37)

where  $n_m$  is the number density of molecules in the ground electronic state Q(T)is the partition function which may be decoupled into its vibrational and rotational contributions and can be expressed as,

$$Q(T) = Q_{vib}(T) \times Q_{rot}(T)$$
(1.38)

where  $Q_{vib}(T)$  and  $Q_{rot}(T)$  are the individual partition functions for thermal distributions in vibration and rotational levels.

$$Q(T) = \sum_{v_m} \exp\left[-G(v_m)/KT\right] \times \sum_{J_m} (2J_m + 1) \exp\left[-F_{v_m}(J_m)/KT\right]$$
(1.39)

The absorption cross section is given by

$$\sigma_{\lambda}(T) = \frac{1}{n_m l} \ln\left(\frac{I_0}{I}\right) \tag{1.40}$$

From Equations 1.40,1.37 and 1.36,

$$\sigma_{\lambda}(T) = \sum_{v_m v_n J_m J_n} \frac{8\pi^3}{3h^2 c} \frac{h}{\lambda} |R_e^{mn}|^2 |R_{vib}^{v_m v_n}|^2 \frac{S_{J_m J_n}}{Q(T)} \\ \times \exp\left(-\left[G(v_m) + F_{v_m}(J_m)\right]/KT\right)$$
(1.41)

Hence the cross section, apart from the transition moment, also depends on the thermal distribution of vibrational and rotational levels. Thus the measured photoabsorption cross section has a dependence on temperature due to the thermal distribution. The rate of change of photoabsorption cross sections with temperature depends on the extent of variation in the thermal distributions brought about by the change in temperature. The temperature dependence is discussed in detail in Section 1.6.

## 1.5 Nature of Photoabsorption Spectrum

The observed band structure in the photoabsorption spectrum owes its origin to the respective Franck-Condon factors. The Franck-Condon factors depend on the shapes and position of their potential energy surfaces (the ground electronic state always being a bound state). Since for polyatomic molecules, the potential energy diagrams are complicated hypersurfaces, the process may be understood by considering the diatomic molecule for sake of convenience. If the ground electronic state is a bound state (Figure 1.5(a)) and the excited state is also a bound state with a well defined minimum in its potential, then the photoabsorption, spectrum would have a band

structure comprising of peaks and valleys. The peak of each of such bands corresponds to one of the vibrational transitions which has a maximum transition probability for the particular wave length at which the peak occurs. The height of the peak represents the strength of the particular vibrational transition given by Franck-Condon factor and also the number density of molecules in the particular vibrational level (of the ground electronic state). In this case, the molecule is said to have undergone photo excitation.

If the ground electronic state is a bound state and the excited state is also a bound state but with a shallow minimum in its potential, then the photoabsorption spectrum would have a band structure converging onto a continuum. The band convergence originates because of transitions occurring from the vibrational levels of the ground electronic state to the dissociation limit of the upper electronic state (see Figure 1.5(b)). At the dissociation limit of the upper electronic state, the energy spacing between the vibrational levels becomes progressively smaller and the higher levels merge into a continuum. In this case, the molecule is said to have undergone a photo-dissociation at the convergence limit of the upper electronic state. If the ground electronic state is a bound state but the excited state is a repulsive state, (Figure 1.5(c)) then the photoabsorption would be a continuum. Since the upper electronic state is not a bound state, there is a continuum of states describing the motion of nuclei instead of the discrete vibrational levels. Once the molecule reaches such a repulsive state, the photo dissociated products of the molecule fly apart with some relative kinetic energy. This process is called direct photo-dissociation. The photon energy corresponding to the long wavelength limit of the absorption spectrum for direct dissociation exceeds the bond dissociation energy  $D_e$  of the ground electronic state.

It is well known that potential energy curves possessing the same multiplicity cannot cross whereas curves possessing different multiplicity can do the same. Figure1.5(d) illustrates a case in which the molecule has a ground state which is a singlet



Figure 1.5: The process of; (a) Photoexcitation (b) The Band convergence (c) The direct Photodissociation (d) The predissociation.

state. It has two excited states a singlet and a triplet. The potential energy curves of the excited singlet and triplet states cross each other. If the molecule is excited to a vibrational state which lies just above the point of curve crossing, the molecule can jump into the triplet state due to a finite perturbation occurring at the point of curve crossing. If the vibrational energy in the excited singlet state is larger than the dissociation limit of the triplet state, the molecule dissociates. Hence a photon which had an energy less than the energy required to directly photodissociate, could also dissociate the molecule. This type of dissociation is called the predissociation. The process is illustrated in Figure 1.5(d). Predissociation manifests itself as a sudden weakening in the fluorescence spectrum which has been observed for SO<sub>2</sub> by Okabe (1974) and NO<sub>2</sub> by Douglas and Huber (1965).

## 1.6 Effect of Temperature on Photoabsorption Spectrum

The effect of temperature on the photoabsorption spectrum of a molecule differs according to the nature of the absorption spectrum, namely either continuous absorption spectrum or structured absorption spectrum. The origin of these types of spectra has been discussed in section 1.5. The variation in photoabsorption spectrum brought about by the change in temperature is primarily due to the thermal distribution of molecules in the rotational and vibrational levels of the ground electronic state. As mentioned in sections 1.3.4 and 1.3.5, the thermal distribution of vibrational and rotational levels in the case of polyatomic molecules has a strong dependence on temperature. Since the photoabsorption depends on the thermal distributions (see Equation 1.41), it exhibits a strong temperature dependence. It may be pointed out here that the transition probabilities also play a significant role in deciding the temperature dependence of photoabsorption cross section of molecules. The transition probabilities of transitions from different vibrational levels of the ground electronic state to the same vibrational level in the excited state are drastically different.

#### 1.6.1 Temperature Dependence in Continuous Spectrum

The photoabsorption spectrum is continuous if the electronic transition is from a lower bound state to an upper repulsive electronic tate. It involves transitions from the vibrational levels of the lower bound electronic state to the continuum of vibrational levels in the upper repulsive electronic state. These transitions also follow the Franck-Condon principle. According to Franck-Condon principle, the contribution to the absorbance from the higher vibrational levels of the ground electronic state progressively increases with wavelength in a continuous absorption spectrum and reaches its maximum at the longer wavelength end of the spectrum. In other words, the contribution to absorbance on the longer wavelength side of the spectrum is predominantly due to the transitions from the higher vibrational levels of the ground electronic state to the continuum of vibrational levels in the upper electronic state, whereas the contribution to absorbance on the shorter wavelength end of the absorption spectrum could be due to transitions from any of the vibrational levels (either lower or higher) of the ground electronic state . This kind of behavior is due to the decrease in energy of the photons on the longer wavelength side. The energy available with a longer wavelength photon may not be sufficient to induce transitions from the lower most vibrational levels of the ground electronic state, but may be sufficient enough to cause transitions from the higher vibrational levels. When the temperature of the target gas is reduced, the number density of molecules in their higher vibrational levels of the ground electronic state which were contributing to the absorbance on the longer wavelength side, reduces. Therefore, the measured absorbance and hence the photoabsorption cross section values decrease with a decrease in temperature on the longer wavelength side of the absorption spectrum. However, on the shorter wavelength side, the reduction in the number density of molecules in their higher vibrational levels, has got no effect on the absorbance and therefore their cross sections do not show any temperature dependence.

#### 1.6.2 Temperature Dependence in Structured Absorption

In the case of structured absorption, the decrease in temperature leads to cooling of the hot bands in the measured absorption spectrum. The distribution of the rotational manifold becomes sharper and also more number of molecules get populated in the lower vibrational levels. Due to a combination of these effects, the peaks appearing in the structured absorption become sharper and the cross section values increase with a decrease in temperature. The values of Franck-Condon factors are not the same for all the vibrational levels involved in the transition and hence the effect of temperature may not be similar on all the vibrational bands appearing in the spectrum.

## 1.7 Importance of Photoabsorption Cross section in Planetary Atmospheres

The solar radiation gets progressively attenuated as it penetrates through the atmosphere of the planets. The attenuation of solar radiation by the atmospheres is primarily due to the photoabsorption by its constituent atoms and molecules. The intensity of the solar radiation of particular wavelength  $\lambda$  reaching a particular altitude Z, is a function of the distance the radiation has penetrated through the atmosphere, the number density  $n_i(Z)$  of the absorbing species and their corresponding photoabsorption cross sections  $\sigma_i$ . The intensity at a particular altitude Z is given by

$$I(Z) = I(\infty) \exp\left(-\sec(\chi) \int_{z}^{\infty} \sum_{i} \sigma_{i} n_{i}(Z) dz\right)$$
(1.42)

 $I(\infty)$  is the solar intensity outside the atmosphere. The number density of any absorbing species is assumed to vary exponentially with height and is given by,

$$n_i(Z) = n_i(0) \exp(-Z/H)$$
(1.43)

H is called the scale height,  $\chi$  is the solar zenith angle. The summation in the integral is over all the absorbing species. Photo-dissociation co-efficient  $J(Z, \chi)$  of a molecule is an important input parameter for studying the photochemistry of atmosphere. It is given by (see Brasseur and Solomon, 1984),

$$J(Z,\chi) = \int_{\lambda_x}^{\lambda_y} \epsilon(\lambda) \,\sigma(\lambda) \,I_\lambda(Z,\chi) \,d\lambda \tag{1.44}$$

where  $\sigma(\lambda)$  is the photoabsorption cross section of the molecule.  $\epsilon(\lambda)$  is the quantum efficiency (or quantum yield) of photo dissociation of the molecule at wavelength  $\lambda$ .  $I_{\lambda}(Z,\chi)$  is the intensity of solar radiation of wavelength  $\lambda$  at a height Z and  $\chi$  is the solar zenith angle. The integration is carried out over the spectral region  $\lambda_x$  to  $\lambda_y$  From the above discussion it is clear that photoabsorption cross section play a key role in determining the attenuation of solar intensity in atmospheric and also in studying the photo chemistry of atmospheres. Hence photoabsorption cross sections of gases which are of interest in the photo chemistry of atmospheres of planets are measured in the laboratory.

#### 1.7.1 Thermal Structure of Planetary Atmospheres

The atmosphere of planets show large variations in temperature as a function of their altitude. The variation in temperature with altitude in a particular region of the atmosphere of a planet depends upon the effective heating mechanism operating in that particular region. The variation of temperature with altitude in case of earth's atmosphere is shown in Figure 1.6(a). Depending upon the trend in variation of temperature with altitude, the earth's atmosphere may be classified into different regions. In each such region, the variation in temperature with altitude follows a single trend throughout the particular region. These regions are also indicated in Figure 1.6(a). For the present work, the region of interest was the stratosphere, where the temperature decreased from 300 K to 200 K with an increase in the altitude. The variation of altitude in the atmosphere of venus is shown in Figure 1.6(b). The surface temperature of venus is about 750 K. The temperature declines steadily with altitude to about 430 K at the base of the clouds, which are



#### 1.8.1 Techniques of Photoabsorption



Figure 1.6: Thermal structure of planetary atmosphere of (a) Earth and (b) Venus

present at an altitude of about 40 km. These clouds are believed to have constituents like  $H_2SO_4$  droplets. Above these clouds, the temperature declines rapidly to about 100 K at an altitude of 100 km.

## 1.8 Survey of Experimental Methods

The importance of photoabsorption cross section and the need for measuring their temperature dependence was discussed in section 1.7. In this section, the experimental methods for measuring the photoabsorption cross section and the methods adopted by various workers for studying the temperature dependence of photoabsorption are discussed.

#### 1.8.1 Techniques of Photoabsorption

Photoabsorption for many polyatomic molecule can be studied by passing monochromatic UV radiation through a cell containing the target gas molecules at a known pressure. By measuring the attenuation of the intensity by the gas column, estimating the number density of target gas molecules (from pressure) and knowing the optical path length, the photoabsorption cross sections can be determined. However this method requires that the light source be extremely stable during the experiment in order to maintain the incident intensity constant. The other methods, namely the double beam, split beam and double-ion chamber methods are capable of correcting for any variations in the incident intensity. In dual beam experiments, a wedge shaped oscillating mirror is used to reflect the monochromatic light into two separate cells alternately; one is a reference cell which is always empty and in the other the target gas is filled at a known pressure. Initially, the target gas cell is held empty and the ratio of transmitted intensity of the reference cell to the target gas cell is measured. Then the target gas cell is filled with a target gas at a known pressure and the ratio of transmitted intensities is determined. From the ratio of intensities so measured in both the cases, the absorbance  $\ln(I_0/I)$  of the target gas can easily be determined. In the split-beam technique, a wire mesh coated with sodium salicylate or a window may be used to split the incident monochromatic radiation to monitor the variations in incident intensity. The choice of the coated wire mesh or window material depends upon the spectral region where photoabsorption studies have to be carried out. Below 100 nm, the coated wire mesh is used whereas above 105 nm, different window materials could be used. The double-ion chamber is used for measuring the photoabsorption cross section in the vacuum ultra violet region. In a double-ion chamber, the ratio of ion currents produced at two parallel electrodes due to the photo ionization caused by the energetic vacuum ultra violet radiation is used to determine the absorbance. All the above techniques have been discussed in detail by Samson (1967) and Samson(1982).

#### 1.8.2 Types of Photoabsorption Chambers

As discussed above, it is essential to build photoabsorption chamber for carrying out photoabsorption studies of molecules. The design of the photoabsorption chamber depends upon the wavelength region of interest and the nature of the target gas. The basic parameter for any photoabsorption chamber is the optical path length of the cell. Photoabsorption chambers with long optical path length are desirable for gases which possess low absorption cross section. With respect to the type of optical path, the photoabsorption cells may be classified into two types namely the single pass cell and multipass cell. The multipass cell is also called White cell (White, 1942). In the case of single pass cell, the photon beam passes only once through the gas column in the cell and emerges out whereas in the multipass cells, the photon beam can be made to pass through the same gas column several times before it comes out of the cell. This is achieved by using highly reflecting concave mirrors at both ends of the cell. The optical path length of the multipass cell is large (Number of passes  $\times$  length of gas column traversed for single pass) hence it is suitable for measuring cross sections which are very low in value (of the order of  $10^{-21}$  to  $10^{-24}$  cm<sup>2</sup>).

#### 1.8.3 Temperature Variable Photoabsorption Chambers

To measure the temperature dependence in photoabsorption cross section for polyatomic molecules, it is necessary to build photo absorption chambers having hot/cold baths. The basic design of the photoabsorption chamber remains the same, but a provision is made for either heating or cooling their walls to a desired temperature. These chambers could be either a single pass type or a multipass type. Temperature variable photoabsorption chambers were built by a few researchers and their design varied according to the temperature region of interest and the method adopted to avoid the temperature gradients along the optical path length. The basic designs of some of the temperature variable photoabsorption chambers are discussed below. Hudson et al (1966) constructed a photoabsorption cell of 96.7 cm path length. The cell was made of suprasil quartz sealed on both the ends with quartz windows. The cell was introduced into a furnace whose temperature could be varied from 300 to 900 K. They used the cell to study the temperature dependence of photo absorption for  $O_2$  (Schumann Runge continuum) at a resolution of 0.075 nm. Molina et al (1981) used a double beam spectrometer with two quartz cells, one of 10 cm optical path length cooled by an insulated glass jacket and the other of 180 cm path length. The 180 cm long cell was wrapped with a copper coil which circulated methanol. They measured the temperature dependence of photoabsorption for OCS at 295 and 225 K. Lux and Coquart (1989) built a multipass cell of 5.7 m optical path length. The cell had a double walled stainless-steel jacket and cold freon could be circulated through the inter-wall spacing. Wu et al. (1989) constructed a two temperature photoabsorption cell made of brass and the refrigerant was circulated in a closed loop around the cell to study the temperature dependence of photolysis rate co-efficient of  $NO_2$ . Shetter et al (1987) constructed a photoabsorption cell whose temperature could be varied from -70° to -30°C. The photoabsorption cell was a triple walled quartz cell.

The temperature controlling fluid was flown through the innermost inter wall spacing; the outer most wall spacing was evacuated to prevent fogging and also to provide thermal insulation. McGee and Burris (1987) built an absorption cell of length 50.5 cm and sealed with double walled window to prevent fogging. They used ethanol/dry ice slurry to cool the cell to 210 K. Gillotay and Simon (1988) constructed a double jacketed photoabsorption cell of 2 m optical path length to measure the temperature dependence of photoabsorption for methyl bromide.

#### 1.8.4 Merits of the Present Photoabsorption Chamber

Cooling a photoabsorption chamber by immersing it in the coolant of a cold bath is a much simpler and a more efficient method as compared to the one where the coolant is circulated through a coil wrapped around the walls of the chamber. But the former method has a draw back. Since the cell cannot be cooled flush right up to its edges, there would be large temperature gradients at the edges (edge effect). Insulated glass jackets may be used to take care of this effect but it may be difficult to fabricate specially in case of cell having large path length. However these (glass jackets) are more suitable for measurements at higher temperatures. In the present experiment, the photoabsorption chamber was kept immersed in the coolant of a cold bath. Hence there were large temperature gradients at the edges. Two quartz tubes with quartz windows sealed at one end were used to take care of this effect. These tubes could be moved in and out at the ends of the absorption camber. The actual method is described in detail in section 2.3.2. The present experimental set-up was operated in the wavelength region from 180 nm onwards in the temperature region from 300 K to 220 K. The detailed description of the experimental set-up is given in Chapter 2.

#### 1.9 Choice of Target Gases

The ozone depletion in the earth's stratosphere is caused by active chlorine which is liberated as a photodissociated product when the halocarbons present in the stratosphere interact with the ultra-violet light [Molina and Rowland, (1974); Stolarski and Cicerone, (1974)]. Carbon tetrachloride is one such halo carbon which gets transported from troposphere to the stratosphere. There, it gets photodissociated and liberates the free chlorine. Carbon tetrachloride is estimated to contribute 5-10 % of the total ozone depletion caused by halocarbons. The concentration of CCl4 in the stratosphere have been measured by Borchers et al (1983) and Fabian and Goemer (1984) by balloon borne cryogenic sampling techniques. Zander et al (1987) made concentration measurement using ATMOS (Atmospheric Trace Gas Molecular Spectroscopy) instrument. Also, CCl4 is estimated to have a life time of 40-60 years (Fisher et al, 1990). Sulphur dioxide is also an important constituent in the stratosphere and troposphere of earth's atmosphere (Frenzy et al, 1983) and also in the atmospheres of Venus (Conway et al, 1979; Stewart et al, 1979; Barker et al, 1979) and Io (Bertaux and Betton, 1979; Smythe et al, 1979). The El chichon volcanic eruption in 1982 (Krueger, 1983) and the Mount Pinatubo eruption in 1991 (Goldman et al, 1992) have deposited  $SO_2$  into the atmosphere in the form of solid and gaseous materials. The role of  $SO_2$  as an aerosol precursor and its effect on the climate have been emphasized by Bluth et al (1992). In view of the above it becomes necessary to measure the photo absorption cross sections and in particular, their temperature dependence for  $CCl_4$  and  $SO_2$  at temperatures prevailing in the stratosphere (300 to 210 K) and in the wavelength region from 180 to 320 nm. In the present work, the photoabsorption cross section for  $CCl_4$  were measured in the spectral region 186-240 nm and for  $SO_2$ in the spectral regions 188-220 nm and 280-320 nm at temperatures ranging from 220 to 300 K at an interval of 20 K.

# Chapter 2

# EXPERIMENTAL SET-UP

The necessity for studying the temperature dependence of photoabsorption for polyatomic molecules quantitatively has been discussed in the preceding chapter. In this chapter, the experimental set-up and its various components are discussed in detail.

The experimental system was designed and fabricated to measure the photoabsorption cross sections for polyatomic molecules at different temperatures ranging from 300 K to 220 K in the wavelength region 180-330 nm at an instrumental resolution of 0.1 nm. The experimental set up includes an argon mini-arc intense light source giving a continuum in the extended spectral region from extreme ultraviolet to visible, an evacuable one-meter near normal incidence monochromator, a beam splitter to monitor any change in intensity of the monochromatic radiation, an evacuable long absorption cell with a cold bath, a two-stage refrigeration system to cool the coolant in the jacket, two thermoelectrically cooled photomultipliers and a fast data acquisition system. The block diagram explaining the whole experimental set up has been shown in Figure 2.1. The details regarding the various subsystems their individual performance and performance of the integrated system are presented in the following sections.



## 2.1 The Ultraviolet Continuum Source

#### 2.1.1 Choice of Light Source

Out of all the light sources available in the vacuum ultra-violet and UV region, only continuum sources could be used meaningfully in the measurement of photoabsorption cross sections of polyatomic molecules. There are a few continuum sources which find applicability depending upon the wavelength region of study. Some such sources are the Hydrogen glow discharge (160-230 nm), the rare gas continua (60-100 nm for helium continuum, 105-155 nm for argon continuum, 125-180 nm for krypton continuum, 148-200 nm for xenon continuum), the Lyman continuum (90 nm-visible), the Deuterium lamp and the argon mini-arc source. Lyman continuum in the modified form can be used conveniently in the spectral region ranging from 50 to 200 nm. It requires an external spark gap to trigger the discharge; therefore it is a difficult light source to work with. The rare gas continua and hydrogen glow discharge do not cover the full wavelength range required in the present experiment. The Deuterium lamp is widely used as a continuum source for photoabsorption studies in the wavelength region 175 to 330 nm. Although the Deuterium lamp has certain advantages such as low power requirement and small size, it has some limitations. The lamp shows variability depending upon how the discharge positions itself on the electrodes; therefore it needs frequent recalibration and realignment. The realignment is a time consuming procedure.

In view of the above arguments, it is clear that another continuum light source is required which covers the desired spectral region and takes care of the short comings and disadvantages associated with the Deuterium light source. A new continuum source called the argon mini-arc source was therefore designed and constructed by Bridges and Ott (1977).

The argon mini-arc can produce a continuum from 110 nm to wavelengths



ARGON GAS INPUTS

Figure 2.2: The schematic diagram of the argon mini-arc source.

larger than 330 nm and has the following salient features:

- Intense nearly line free continuum only a few lines corresponding to some elements are found to be superimposed on the continuum.
- Stability and reproducibility over many hours of operation.
- Uniform output over a large solid angle.
- Simple alignment and operation.

Considering the above mentioned advantages the argon mini-arc was chosen as a continuum source for the present work.

#### 2.1.2 Description of the Source

The source developed by Bridges and Ott (1977) is shown in Figure 2.2. It essentially consists of three plates made of copper and are separated by insulating silicone rubber rings. These three plates are clamped together to form a gas tight enclosure. The

central plate guides and constricts the discharge. One of the outer plates is the anode T of solid copper and the other is the cathode C consisting of a 3.2 mm thoriated tungsten rod pressed into it. All the plates are water cooled; the water flows through the holes drilled in the sides of the plates.

Argon gas was chosen as the source gas because it gives a stable discharge and line free continuum and also, its power requirement is minimal. Argon gas is admitted into the source input through a high grade plastic tubing connected to a calibrated manometer. The pressure inside the source chamber could be adjusted by regulating the flow of argon. The argon flows out through the exhaust ports.

The radiation from the arc axis emerges through the  $MgF_2$  window W on the cathode side. The arc plasma could be observed end on through a hole drilled in the electrodes. The arc source is always mounted on an insulating platform. The arc discharge in the source was driven by a home made low voltage, current regulated DC power supply which is described in the following section.

#### 2.1.3 DC Power Supply

A low voltage, high current DC power supply is needed to operate the source. A minimum of 40 amperes at 40 Volts is necessary to initiate the discharge. A steady intensity from the source is desirable for photoabsorption studies. In order to maintain a steady intensity, a stable discharge is necessary in the source. Instabilities in the discharge current of argon mini-arc can occur due to fluctuations in the line voltage or due to changes in the positioning of the arc on the electrodes. Therefore current regulation becomes necessary for the power supply in order to sustain a stable discharge. To meet the above requirements, a power supply was designed and fabricated in the laboratory (Kriplani and Misra, 1988). The schematic diagram of the DC power supply is shown in Figure 2.3. In order to extract currents up to 45 amperes, an air-cooled three-phase step-down transformer, with the primary of 440 Volts and



Fig.2.3. The schematic diagram of the DC current regulated power supply.

1

secondary of 40 Volts was used. Voltage rectification was achieved by a full wave rectifier which delivered a DC voltage of 56 Volts having a ripple factor up to 4.5 %. This voltage was fed to the positive end of the light source through a 0.6 ohm (200 W) resistance. This resistance limits the overall circuit current to 100 amperes. A voltage regulator IC-723, featuring high ripple rejection and excellent temperature stability is used. The output voltage of the IC could be varied from 2 to 12 Volts by means of a 10 kilo-ohm potentiometer (not shown in the Figure); this corresponds to a variation of 30 - 50 amperes current across the discharge.

#### 2.1.4 Operation of the Source

The operation of the argon mini-arc source requires a continuous flow of pure argon in order to maintain high degree of purity of the source gas. The gas purity is necessary in order to maintain arc stability and reproducibility in the continuum emission. The gas purity also helps in reducing the radiant power of the atomic resonant lines in the spectrum which arise from small ppm concentrations of oxygen, nitrogen, carbon and water vapour. In the present work 99.9 % pure argon was used for producing the continuum.

A voltage of at least 40 volts is applied between the electrodes. To initiate the discharge, a tungsten rod which is externally connected to the anode potential is inserted into the source until it touches the cathode. The discharge is transferred from the tip of the tungsten rod to the anode as the rod is withdrawn. The arc current can then be set at the desired value by adjusting the potentiometer of the power supply. A current of at least 40 amperes is needed to initiate the discharge. The normal operating conditions for the present experiment were a current of 35 amperes at 56 volts.



Figure 2.4: A part of the continuum produced by the argon mini-arc source.

#### 2.1.5 Performance of the Source

The continuum of the argon arc arises mainly from the atomic recombination radiation. At short wavelength end (120-130 nm), it is due to the molecular continuum. Bridges and Ott (1977) compared the spectral radiance of the argon mini-arc with NBS wall stabilized hydrogen arc. The temperature of the black body line radiator was 11800 K with hydrogen arc as the primary standard.

The effect of varying the arc current and pressure of argon gas is discussed below. The intensity of the continuum radiation is directly proportional to the square of the electron density in the arc discharge. Hence the argon mini-arc radiance decreases when the arc current decreases. When the argon gas pressure is varied, two parameters of the arc discharge get affected namely, the electron density and the ionization fraction of argon ions in the discharge. When the argon gas pressure is reduced, the electron density decreases and hence (as mentioned above) the spectral radiance tends to decrease. However the ionization fraction tends to compensate this effect; the electron temperature in the discharge increases when the source gas pressure is reduced. The increase in electron temperature can cause an increase in the ionization fraction, which in turn tends to increase the spectral radiance. Hence in the case of argon gas pressure variation, the electron density and the ionization fraction tend to compete with each other in bringing about a net change in the spectral radiance. The source when operated at the conditions as mentioned in the previous section, had good stability and reproducibility over many hours of operation. A part of the continuum produced from the combination of the argon mini-arc source and a monochromator is shown in Figure 2.4. A few atomic resonant lines always appeared in the continuum due to small quantities of impurities like carbon, nitrogen and hydrogen present in the discharge. The effect of impurities is discussed in detail in the following section.

## 2.1.6 Effect of Contamination

The performance of the source can deteriorate if there are contaminants in the source. The major contaminants are carbon and tungsten powder. The small quantities of hydrocarbons present in the source gas produce carbon during the discharge. The carbon so produced, gets deposited as a thin layer on the electrodes. The presence of carbon in the source causes difficulties in initiating the discharge and also reduces the spectral radiance. Small quantities of tungsten powder is produced while initiating the discharge. This tungsten powder settles inside the source chamber. The presence of tungsten powder causes instability in the discharge, which in turn produces fluctuations in the output intensity.

The transmission of  $MgF_2$  can go down, due to the formation of colour centres after several hours of exposure to ultraviolet light.

#### 2.1.7 Cleaning Procedure

The following procedure was adopted for cleaning the source. The electrodes and tungsten rods were first cleaned by gently removing the carbon and tungsten powder and were then rinsed in absolute alcohol. This was done after every twenty hours of operation of the source.

The  $MgF_2$  window was removed and was baked at 400° C for 48 hours in an oven to reduce the effect of colour centre formation. This helped in improving the window transmission.

## 2.2 VUV Monochromator

#### 2.2.1 Description of the Monochromator

1-meter normal incidence asymmetric monochromator (ASM - 100 Jobin Yvon, France) has been used to disperse the UV continuum radiation produced by the argon miniarc light source. The special holographic concave grating (Jobin - Yvon, France) used in the monochromator had a ruling of 1200 lines/mm and was blazed at 200 nm to have maximum reflection in the wavelength region ranging from 100 to 300 nm. This type of asymmetrical near normal incidence monochromator has distinct advantage over the conventional normal-incidence monochromator. In case of conventional type, the focusing and monochromatization is achieved by rotating the grating as well as moving the grating mount translationally whereas in the case of asymmetric mounting, both actions could be achieved by rotation of the grating alone. This is achieved by keeping the entrance slit arm from the entrance slit to the centre of the concave grating 73 cm long whereas the exit slit arm has a length of 127 cm. The entrance and exit slits are fixed with bilateral slit assemblies. In the present ASM - 100 monochromator, sine-drive mechanism has been used for the rotation of the grating. Several scanning speeds from 0.1 nm/min to 10 nm/min have been provided to suit



Figure 2.5: The C-I impurity line. The FWHM was measured for this line at 193.1nm.

the convenience. The monochromator has been well corrected for astigmatism over the spectral range extending from 30 to 300 nm. The monochromator is evacuated to a pressure of better than  $10^{-5}$  torr.

#### 2.2.2 Resolution of the Monochromator

Limiting resolution of 0.01 nm has been claimed by the manufacturers whereas highest luminosity condition can only be achieved at a resolution equal to or poorer than 0.04 nm. In practice, the instrumental resolution is taken as full width at half maximum (FWHM) of any resonant line present in the spectral region of interest. In the present experiment, the entrance and exit slits have been kept 100 micron wide and the instrumental resolution has been calculated using the line profile obtained from C-I resonant line at 193.1 nm. This line is the carbon impurity line superimposed on the UV continuum obtained by argon mini-arc source. The FWHM for this line under the present experimental conditions was found to be 0.1 nm (see Figure 2.5). This would give a resolving power of 1931 at 193.1 nm.

#### 2.2.3 Wavelength Calibration of the Monochromator

The wavelength counter of the monochromator had zero offset. Due to this offset, there always existed a difference in the wavelength as read on the counter of the monochromator and the actual value. Therefore, it was necessary to perform the wavelength calibration. The offset can be determined by taking the zero order produced by the grating of the monochromator as reference. But the offset so determined may not be uniform throughout the entire spectral region. Hence in the spectral region of interest a known standard resonant line, either from a line source or an impurity line from the continuum source can be taken as the reference for wavelength calibration. In the present experiment, the C-I line at 193.1 nm was chosen as the reference for wavelength calibration.

## 2.3 Beam Splitter

For the photoabsorption cross section measurement, it is necessary to monitor the incident intensity during the experiment. Any change in the incident intensity during the experiment can be accounted for while estimating the absorbance. For this purpose a beam splitter was introduced into the experimental system. The beam splitter reflects a small fraction of the incident monochromatic radiation still allowing the transmitted part of the photon beam to enter the experimental chamber. The intensity of the reflected beam is linearly proportional to the incident intensity; hence any change in the incident intensity can be monitored.



(9558 QB)

Figure 2.6: The schematic diagram of the beam splitter.

Beam splitter essentially consist of a reflecting surface held at  $45^{\circ}$  to the direction of incident radiation. Two types of beam splitters can be used for absorption spectroscopy. The major difference between the two types is the surface which is used to split the beam. The first type uses a wire mesh to reflect the light. The reflected light is made to fall on a perspex light pipe whose front end is coated with sodium salicylate scintillator. The scintillator converts the UV light to visible, and is detected by a suitable photomultiplier tube. The second type uses either a quartz or MgF<sub>2</sub> window to split the beam. It does not need a scintillator and a light pipe. The first type is normally used for radiations below 105 nm because in this spectral region ,no window materials are available. For the present work, the second type was chosen primarily because it has relatively more reflectivity in the wavelength region 180 nm and above.

The beam splitter used in the present work is shown in Figure 2.6. It consists of a 1-inch diameter quartz window held at 45° to the incident photon beam. About 10% of the total intensity of monochromatic radiation from the exit slit of the monochromator was reflected by the window and was detected by the photomultiplier tube (Thorn EMI 9558 QB). The rest of the intensity was transmitted through the window to the photoabsorption chamber. The photomultiplier was thermoelectrically cooled in order to reduce the dark current and have large output pulses. The beam splitter chamber was evacuated to a pressure  $10^{-5}$  torr through the exit slit of the monochromator. The beam splitter chamber was isolated vacuum wise from the absorption chamber using appropriate window materials

## 2.4 Photoabsorption Chamber

The monochromatic photon beam transmitted from the beam splitter enters the absorption chamber which is used to measure the absorption cross section for the target gas. The photoabsorption chamber is a stainless steel chamber with a cold bath fabricated around it. The chamber could be evacuated to a pressure of  $10^{-6}$  torr and could be cooled down to 200 K.

The target gas introduced in the chamber equilibrates to the temperature of the cold bath within a few hours. The target gas molecules in the absorption chamber absorb the incoming monochromatic photons. The photoabsorption cross sections for the target gas at a given temperature could be measured using the transmission technique.

#### 2.4.1 Construction of the Chamber

The photoabsorption chamber and the cold bath were designed and fabricated in the laboratory. The chamber was one meter long and was machined out of a circular pipe of non-magnetic stainless steel 304. The outer diameter of the pipe was 2 inch whereas the wall thickness was 2 mm. Different parts of the absorption chamber are shown in Figure 2.7. Also the different parts in the chamber, their physical dimensions and function are described below.

A pumping port of 1.5 inch diameter was used in the centre of the absorption

chamber. The pumping port was perpendicular to the chamber axis, in the downward direction and is indicated by the dotted circle in Figure 2.7. The pumping port was used for evacuating the absorption chamber. There are three ports each less than one inch diameter yielded to the chamber, one for introducing the target gas, the abcord for measuring the pressure of the target absolutely and the third an addition port which could be used as and when required.



Figure 2.7: The schematic diagram of the coolable photoabsorption chamber.

In the present work, a new method was used to take core of the temperatu

chamber. The pumping port was perpendicular to the chamber axis, in the downward direction and is indicated by the dotted circle in Figure 2.7. The pumping port was used for evacuating the absorption chamber. There are three ports each less than one inch diameter welded to the chamber, one for introducing the target gas, the second for measuring the pressure of the target absolutely and the third an auxiliary port which could be used as and when required.

The photoabsorption chamber used a coolant in the cold bath, which was cooled by a two stage mechanical refrigeration system (cooling unit). The construction of the cold bath and the function of the cooling unit are discussed in the following sections.

### 2.4.2 The Temperature Gradient and Optical Path Length

The photoabsorption chamber was evacuated to a pressure of  $10^{-6}$  torr. Also, the chamber had to be vacuum-isolated from the beam splitter at the entrance port and the photomultiplier tube assembly at the exit port. This isolation is essential, since it prevents the target gas from flowing either into the beam splitter at the entrance port or into the photomultiplier tube assembly at the exit port. The widely adopted method is to seal both the entrance and exit port with either quartz or MgF<sub>2</sub> windows. The optical path length for such an arrangement is just the geometrical distance between these two windows. But this arrangement has a draw back when used in a cooled photoabsorption chamber. Since the chamber cannot be cooled flush right up to its edges, there would be large temperature gradients near the ends of the chamber. As a result, the chamber cannot be maintained at a uniform fixed temperature throughout its entire length. Therefore, the optical path length used for cross section measurement would not be the same as the geometric length between the two quartz windows at the ends of the chamber.

In the present work, a new method was used to take care of the temperature

gradients at the ends of the absorption chamber. Two quartz tubes each of one inch diameter and 20 cm length were taken and one side of each of these tubes were fused with high grade suprasil quartz windows. These quartz tubes were then introduced into the chamber; one at the entrance port and the other at the exit port, with their fused quartz windows facing each other inside the chamber (Figure 2.7). Each of the two quartz tubes were held vacuum tight at their respective positions by the combination of a O-ring and a brass nut. The brass nuts were used to tighten and loosen the tubes.

As can be seen in Figure 2.7, the optical path length in this arrangement is the distance between the two fused quartz windows. The quartz tubes could be moved in and out by loosening the brass nuts. This way, the optical path length in the chamber could be varied. The quartz tubes were sufficiently pushed into the photoabsorption chamber, thereby avoiding the region of temperature gradients which are present at the edges. Thus the entire optical path length was brought into a region of uniform temperature. The optical path length of the chamber was measured to be 76.13 cm.

#### 2.4.3 Beam Alignment Assembly

Two sets of beam alignment assemblies were placed inside each of the two quartz tubes. Each alignment assembly consisted of three light baffles. The small apertures drilled at the centre of these rings prevent the light scattered at the edges of both the quartz tubes from reentering into the photoabsorption chamber. These rings having an outer diameter of 24 mm, were machined out of 0.5 mm thick aluminium plate. A circular aperture of 3 mm diameter was drilled at the centre of all the rings which were held by brass struts so as to give perfect optical alignment. The beam alignment rings and the brass struts were blackened by coating them with aquadag in order to avoid scattering of light at the edges. The beam alignment assembly at the exit end of photoabsorption chamber has another distinct advantage. It restricts the solid angle subtended by the target gas molecules along the photon beam axis at the photon detector. It may be pointed out that the molecules after absorption of monochromatic photons may fluoresce, depending upon the quantum yield of the molecule. The fluorescent radiation if considered isotropic would also be reaching the photon detector on the exit side of the absorption chamber. This way, the the detector signal would have an additional contribution due to fluorescence. In other words, the measured transmitted intensity would be larger and this would not give the true photoabsorption cross sections. Hence for photoabsorption experiments, it is desirable to have small solid angles subtended at the detector. The small apertures (3 mm diameter as mentioned above) used in the present experiment reduced the solid angle significantly.

#### 2.4.4 Optical Alignment

The quartz tubes along with the beam alignment assemblies are properly aligned along the incoming photon beam axis. This is carried out first using a helium-neon laser and then with the argon mini-arc lamp while the monochromator was set in the zero order. The photoabsorption along with the cold bath and vacuum systems were supported firmly by sturdy steel jacks. The steel jacks were thermally insulated so as to curtail heat leaks to the cooling systems. Care was also taken to prevent mechanical vibration from the rotary mechanical pumps getting transferred to the absorption chamber.

#### 2.5 Cold Bath

The photoabsorption chamber could be cooled by immersing it in the coolant of the cold bath. The cold bath is a stainless steel jacket fabricated around the photoabsorption chamber as shown in Figure 2.7. The outer walls of the jacket were thermally insulated by sticking thermocole sheets with the help of silicone rubber solution. The temperature of the coolant in the cold bath could be brought down by immersing in it the cooling probe of the cooling unit. The cooling unit was a servo controlled two stage mechanical refrigeration system with a built in temperature controller. The actual mechanism of cooling unit and the function of the cooling probe is described in Section 2.6.

The coolant in the cold bath acts as a medium in efficiently conducting the heat from the walls of the photoabsorption chamber to the cooling probe. The coolant must be a fluid possessing the following properties.

- The coolant must have a low freezing point so that the bath can be operated at temperatures much lower than the room temperature.
- It should have low viscosity even at low temperatures so that the temperature uniformity could be easily attained in the bath.
- It should not be chemically reactive to the cooling probe which is made of soft monel metal.

In principle, any alcohol can be used as a coolant since this would satisfy all the above conditions. For the present work, methanol was chosen because it is available easily commercially. The freezing point of methanol is -93.9° C. About ten liters of methanol was filled in the cold bath in order to immerse the whole length of the photoabsorption chamber. Therefore it was required to use a refrigeration system which could cool their volume to about 200 K within a short time

### 2.6 Cooling Unit

The cold bath was cooled by means of a cooling unit which actually was a servocontrolled two-stage mechanical refrigeration system. The refrigerator was procured from Messrs FTS Cooling System Inc, NY (Flexi cool temperature system model MFC 100DII). The refrigerator's compressor was hermetically sealed to a cooling
probe through a rugged stainless steel flexible tube. The cooling probe is a co-axial cartridge made of monel metal. The refrigerator is air cooled and it used propane and ethylene for the two different stages of cooling. The stainless steel tube is co-axial so as to allow the liquid refrigerant to be pumped through the central capillary tube. The cooling probe is kept immersed in methanol contained in the cold bath. The liquid refrigerant removes the heat from the cold bath and returns back to the compressor through the outer tube. The outer wall of the co-axial stainless steel tube is thermally insulated so as to prevent heat leak.

The cooling unit has a built in temperature controller to regulate the cooling process and thereby maintain the desired low temperature in the cold bath. The temperature controller of the cooling unit comprises of a thermal sensor and a microprocessor-based servo controller mechanism. The thermal sensor is a calibrated copper-constantan thermocouple supplied by FTS systems. The thermal sensor is also kept immersed in the cold bath. The thermocouple senses the temperature of the cold bath and displays it on a digital display. The desired low temperature could be preselected on the temperature controller. The cooling unit pumps the refrigerant to the cooling probe until the desired low temperature is achieved.

The microprocessor based servo control mechanism uses the thermal sensor in controlling the flow of liquid refrigerant to the cooling probe. Thus by controlling the flow of refrigerant, the temperature controller regulates the cooling process, thereby maintaining the temperature of the cold bath at the preselected value.

The servo-control mechanism was capable of controlling the low temperature to an accuracy of  $\pm 0.5^{\circ}$  C. As quoted by the manufacturer, the FTS system has the capability to cool 8 liters of methanol to -80° C in 35 minutes. However for any cooling system, the ultimate minimum temperature that can be attained and also the rate of cooling depends on;

• the heat load available in the cold bath to the cooling unit and

• the finite heat leaks present in the system.

In the present experimental set-up an ultimate temperature of  $-70^{\circ}$  C could be achieved for 10 liters of methanol in about 70 minutes.

## 2.7 The Vacuum System

The entire experimental system has to be evacuated to reduce the absorption of the ultra-violet radiation by molecular oxygen present in the atmosphere. The one-meter monochromator was evacuated to a pressure lower than  $10^{-5}$  torr by means of a 500 lit/sec oil diffusion pump (Model OD 114, Messrs Hind High Vac, India) backed by a 400 lit/mini rotary pump (Model ED-18, Hind High Vacuum Co. Ltd., India). The beam splitter was also evacuated through the exit slit of the monochromator. The photoabsorption chamber was evacuated to  $10^{-6}$  torr by a 300 lit/sec diffstak pump (Model MK2 Series, 300 Edwards, UK) backed by 750 lit/min rotary pump (Model CD-45, Hind High Vacuum Co. Ltd., India). The reference side of the MKS differential capacitance manometer was evacuated to a pressure of  $10^{-6}$  torr so as to make the measured pressure absolute (see Section 2.8). An oil diffusion pump of 300 lit/sec (Model 0-120, BARC, India) backed by 250 lit/mini rotary pump (Model VT-2012, Vacuum Techniques Pvt. Ltd., India) was used to produce the reference vacuum. Also, the space (for accommodating the quartz tube) in between the photomultiplier tube and the exit port was evacuated through the reference side of the capacitance manometer.

The ultimate vacuum in the absorption chamber, monochromator and the reference side of the differential manometer were measured using Penning ionization gauges. The pressure in all the backing lines of the vacuum systems were monitored using thermocouple gauges.

### 2.8 Pressure Measurement System

For the photoabsorption cross section measurement, it is necessary to know the number density of the absorbing species inside the photoabsorption cell. The number density of the absorbing species can be determined by using the ideal gas law, if the absolute pressure and temperature of the target gas are known. The MKS Baratron capacitance manometer is one such device which has a very high accuracy and precision in measuring low pressures. This consists of a metal membrane held between the two plates of a capacitor which is enclosed in a metal casing. One side of the membrane is called the pressure sensing side and the other side is called the reference side. If the reference side is maintained at a pressure  $P_R$  and a pressure  $P_S$  is applied to the pressure sensing side, the differential pressure  $P_S - P_R$  between the sensing and the reference side produces a deflection in the membrane; the deflection produces a change in the capacitance. The change in the capacitance is calibrated against the applied differential pressure; therefore the manometer always measures the differential pressure  $P_{brt} = P_S - P_R$ . An absolute pressure measurement can be made by evacuating the reference side to a pressure at least three orders of magnitude lower than the applied pressure i.e.  $P_R \ll P_S$  Hence, in such a case,  $P_R$  can be neglected and  $P_{brt} = P_S.$ 

For the present work, an MKS differential capacitance manometer was used to measure the pressure. The gauge head used was of the type BH 310 (10 torr head). The gauge head was factory calibrated. The reference side of the Baratron head was maintained at a pressure of  $10^{-6}$  torr so as to make the pressure measurement absolute. The arrangement of the head is shown in Figure 2.8. The pressure sensing side of the manometer was connected to the photoabsorption chamber by a 6mm inner diameter copper pipe and greaseless KONTES valve V1. A balancing valve (greaseless KONTES valve) V2 is connected to the differential manometer head. When no pressure measurement is being done by the differential manometer valve V1



Figure 2.8: The Arrangement of differential capacitance manometer for absolute pressure measurement.

is kept closed and the balance valve V2 is kept open. In this case, the pressure on both the reference and the sensing side is the same  $(10^{-6} \text{ torr})$  and the manometer reads zero pressure. Whenever the pressure in the photoabsorption chamber was to be measured, the valve V1 was opened and the balancing valve V2 was closed. Then the manometer sensed the differential pressure. This pressure was taken to be the absolute pressure of the target gas in the photoabsorption chamber since the pressure in the reference side was  $10^{-6}$  torr.

The material used in the capacitance manometer for sensing the pressure is very sensitive to ambient temperature. Any change in the ambient temperature can affect the pressure measurement. Hence the manometer head is always maintained at a constant elevated temperature of 318 K.

The vapour extraction system essentially consisted of a horosilicate glass flask F1 of one juch inner diameter with a side stem: The glass flask is inserted in a thermas firsk which contained ethanol and liquid nitrogen mixture. The glass flask F1 was connected to a greaseless KONTES Valve V1. The other casi of the KONTES valve



Figure 2.9: The schematic diagram of the vapour extraction system.

### 2.9 Vapour Extraction and Gas Handling System

In the case of the target gases which exist in liquid phase at room temperature, the photoabsorption experiment is performed by extracting their vapors. carbon tetrachloride exists as a liquid at room temperature. The freezing point for  $CCl_4$ is  $-23.0^{\circ}C$  and hence it can conveniently frozen by using a mixture of ethanol and liquid nitrogen which maintain a temperature of  $-88^{\circ}$  C. The impurity gases above the solid carbon tetrachloride could then be pumped out. The solid carbon tetrachloride is liquefied again at room temperature where it has a large vapour pressure. The carbon tetrachloride vapors are then extracted. The vapour extraction system used for the present study is detailed below.

The schematic diagram of the vapour extraction system is shown in Figure 2.9. The vapour extraction system essentially consisted of a borosilicate glass flask F1 of one inch inner diameter with a side stem. The glass flask is inserted in a thermos flask which contained ethanol and liquid nitrogen mixture. The glass flask F1 was connected to a greaseless KONTES Valve V1. The other end of the KONTES valve was connected to an empty glass flask F2 which served as a buffer volume. The glass flask F2 was connected to the input of a leak valve V2, through a stainless steel bellow. Using the fine control of the leak valve (Granville Philips Model No.203), the vapour pressure of the target gas inside the cell could be maintained at desired value of pressure during the experiment.

For the present experiment, spectroscopic grade  $CCl_4$  was procured from Messrs Spectrochem, India. The purity of the spectroscopic grade  $CCl_4$  liquid (as quoted by the supplier) was 99.9 %. Sulphur dioxide which is a gas at room temperature could be extracted directly from the cylinder.  $SO_2$  used in the present experiment was of research grade quality (Messrs Grisheim, Germany) and was used without further purification. The pressure of  $SO_2$  gas in the photoabsorption chamber could be maintained constant at a desired value by means of Granville Philips leak valve mentioned above.

## 2.10 Photon Detectors

Two photon detectors are required in the present experiment; one at the beam splitter end to measure the intensity of the incident photon beam and the other at the end of the absorption chamber to measure the transmitted intensity. The two photon detectors should be similar in spectral response, quantum efficiency, signal-to-noise ratio. Also, the two detectors should be placed as close as possible to the beam splitter port and the exit port of the absorption chamber. In case they are not flush with the ports and there is some volume of air present between the ports and the detectors, the ultra-violet signals may get absorbed. In that case, such a space should be continuously evacuated during the experiment. In the present experiment the photon detector is flush with beam splitter port but it is not the same in case of the exit port. Therefore, the space between the second photon detector and the exit port of the photoabsorption chamber is evacuated to a pressure of  $10^{-6}$  torr (see sec.2.8). In the present experiment, photomultiplier tubes were used as photon detectors.

Photomultiplier tubes are extremely sensitive photon detectors which can convert the light intensity into an electrical output. They can be used for detecting ultraviolet, visible and near Infra-red radiations depending upon the type of photocathode used. Because of their high gain and extreme sensitivity, they find application in the measurement of low intensity radiations.

### 2.10.1 Description

The photomultiplier tube essentially works on the principle of photoelectric effect and subsequent amplification of the photoelectric signal. It consists of three components : the photo cathode, the electron multiplier and the anode. The photocathode and the electron multiplier along with the anode are held in an evacuated glass casing. The inner surface of the photocathode is coated with a photo sensitive material. A photon incident on the photocathode produces a photoelectron, provided the energy of the photon is sufficient enough to pull out the electron. The gain in a photomultiplier tube is due to its electron multiplier which essentially consists of a set of dynodes. A high voltage is applied to supply the necessary inner electrode voltages. The photoelectrons produced at the cathode are focused and they get accelerated towards the first dynode; each electron produces two or more secondary electrons. The process continues with the subsequent dynodes and this results in a huge multiplication in the number of electrons. The gain achieved in this process is typically of the order of  $10^5$  to  $10^7$ .

The output of the photomultiplier tube is obtained in terms of electrical pulses. The number of such pulses produced per unit time depends linearly on the incident intensity. The principle and functioning of the photomultiplier tubes is described in detail by Andrew (1976).



Figure 2.10: (a) The spectral response of S-20 type photocathode (b) The temperature dependence of dark current for S-20 photocathode.

### 2.10.2 Choice of Photomultiplier Tube

oice of the photomultiplier tube primarily depends on the spectral response of the otocathode. The photocathode is chosen so as to have maximum quantum effincy in the wavelength region of interest. For the present work, the photomultiplier bes used were of 9558QB type (Thorn EMI,UK). The photocathode material is e trialkali Na-K-Sb-Cs and had the S-20 type of spectral response (Figure 2.10(a)). he front end window of the photomultiplier tube was made of high grade quartz and nce the photocathode had an 'extended spectral response' in the UV region down 170nm. The extended spectral response has a maximum around 270nm, in case of 58QB photomultiplier tube.

### 10.3 High Voltage Units

negative voltage is applied to the photocathode with respect to the anode load sistor. The anode is kept grounded. The first dynode is kept at a positive potential th respect to the photocathode in order to accelerate the emitted photoelectrons. he subsequent dynodes are supplied with a successively increasing positive voltage order to produce the electron multiplication. A single source of high voltage in mbination with a resistive voltage divider network was used to supply the necessary oftage differences between the dynodes. The gain of the photomultiplier is very sentive to changes in the applied voltage, hence there should be no ripple in the output the high voltage units. For the present work, two DC high voltage units (Model V 1008E, Electronics Corporation of India Ltd., India) were used for supplying the scessary high voltage for the two photomultipliers. The high voltage units had the llowing features :

- Variable voltage ranging from 0 to -3000V
- Good voltage stability and very low ripple factor

### 2.10.4 Photon Counting

The photomultiplier tube can be operated either in the current mode or in the photon counting mode. The photon counting mode is generally preferred for systems involving low intensity measurements or when better signal-to-noise ratio is desired. The entire photon counting system was built in our laboratory. The output pulses from the anode of the photomultiplier tube are fed to a fast charge sensitive preamplifier having a decay constant of about 330 nano second. The output from the preamplifier is fed to an amplifier for sufficient amplification. The output pulses from the amplifier are fed to a variable threshold discriminator; the pulses whose height is below the threshold level are rejected. The clean and uniform pulses from the output of the discriminator are fed to the counter, which is interfaced to a dual multi channel analyzer as described in Section 2.11. The schematic diagram of the photon counting system is shown in Figure 2.12 along with the data acquisition system.

### 2.10.5 Dark Count

Even with no light incident on the photocathode, the photomultiplier tube produces an output current. This is called the dark current. When operated in the counting mode, this is called the 'Dark count'.

At room temperature, the photocathode material and the dynodes emit thermal electrons. The multiplication of these thermal electrons in the photomultiplier tube constitutes a major part of the dark current. Apart from this, cosmic radiation, thermionic emission and traces of radioactive impurities also contribute, to some extent, to the dark current. The emission of thermal electrons can be reduced by cooling the photocathode. Cooling the photocathode helps in drastically reducing the dark current. However, for the S-20 type photocathode, cooling below a temperature of  $-25^{\circ}$  C has little or no effect in reducing the dark current of the photomultiplier. The effect of cooling on photocathode having S-20 spectral response is shown in Figure 2.10(b).

The dark current due to the thermal electrons emitted by the dynodes can be suppressed by operating the photomultiplier in the counting mode. The output electric pulses produced by the thermal electrons from the dynodes are smaller in amplitude, than those due to either photoelectrons or thermal electrons, produced at the photocathode. By suitably setting the threshold level of the pulse height discriminator at a value higher than their amplitudes, output electric pulses due to the thermal electrons emitted at the dynodes could be easily rejected.

In the present experiment, the photocathodes of the two photomultipliers were cooled by using commercially available, thermoelectrically cooled 'Photomultiplier Housings' (FACT MK III type Thorn EMI, UK). The two photocathodes were thermo electrically cooled by peltier elements and the temperature of the photocathodes was brought down to -25° C. The temperature was monitored by an in-built temperature-controlling circuit. The front end of the housings were sealed by doublewalled Suprasil quartz window which has a UV cut off at 170 nm.

### 2.10.6 Signal-to- Noise Ratio

Optimization of signal-to-noise ratio (SNR) was carried out for both the photomultipliers used at the beam splitter and the exit port of the absorption chamber. By alternately closing and opening the shutter at the output of the argon mini-arc light source, the ratio of the measured intensity to the dark current could be obtained. This ratio was taken as the SNR value of the photomultiplier tube. The SNR was measured for each photomultiplier as a function of voltage applied across the photocathode and anode of the photomultiplier. The voltage at which SNR value was found to be maximum was chosen as the operating voltage during the experiment for the respective photo multipliers. The SNR versus applied voltage curve is shown in



Figure 2.11: The signal to noise ratio optimization for photomultipliers.

Figure 2.11. As seen from the figure, the two photomultipliers were operated at 1130 and 1210 volts for optimum results.

## 2.11 Data Acquisition System

Data acquisition system includes pre-amplifier, amplifier, discriminator units for the photomultipliers and a microprocessor controlled 1024-channel dual multichannel analyzer. The pre-amplifier, amplifier and discriminator unit have already been discussed in section 2.10.4. The dual multichannel analyzer which was designed and fabricated in the laboratory to suit the requirements of the experiment would now be discussed. The data acquisition system is schematically shown in Figure 2.12.

The multichannel analyzer consisted of two main units : the interface and the micro-computer. The micro-computer was programmed, so as to function as a Dual multi channel analyzer operating in the scalar mode. The MCA had two sets of 1024



channels for data storage. Each channel had a storage capacity of  $2^{20}$ -1 counts per channel.

The interface consisted of two 20-bit counters, two 8-bit digital-to-analog converters and a timer. the timer had the capability to generate gate pulses of width ranging from 0.1 to 100 sec.

The micro-computer used a video terminal as its console for accepting various commands. To start with, the various acquisition parameters like the number of scans and time duration of gate pulse were fed to the multichannel analyzer through the video terminal. The micro computer triggered the timer to generate the gate pulses of the preselected value. During this time interval, the pulses coming from the discriminator of the two photomultipliers were counted in the two separate counters. At the end of the gate pulse, both the sets of counts from the counters were retrieved by the micro-computer and stored in the respective channel memory. Then the channel number is advanced, the counters are reset and a fresh trigger is given to the timer to start the acquisition.

A very fast scan of channel numbers and corresponding data are fed to two D/A converters to produce X and Y sweep voltages to produce visual display of the data profile during the experiment. The multichannel analyzer was also interfaced to an IBM compatible PC-AT 386 personal computer. After the completion of data acquisition, the raw data could be transferred for off line processing.

# 2.12 Operation and Performance of the System

The operation of the experimental system primarily involved the measurement of intensities at the beam splitter end and the exit port of the absorption chamber at any particular wavelength. This is done while keeping the various other parameters like target gas and temperature of the bath constant. The instrument was operated in sets of scans of wavelength typically 100  $A^0$  in range; these scans were called *spectral* scans. The actual operation of the instrument was done in steps as described below.

- To start with, the monochromator, the photoabsorption chamber, the reference side of the differential capacitance manometer, the vapour extraction system and the various gas introduction lines were thoroughly pumped down to a pressure of  $10^{-6}$  torr.
- The photocathode cooling, the photomultiplier high voltages and amplifiers were put on 5 to 6 hours prior to the starting of the experiment.
- CCl<sub>4</sub>: In the case of carbon tetrachloride, about 25 ml of spectroscopic grade CCl<sub>4</sub> was filled in the glass flask F1 of the vapour extraction system. Methanol and liquid nitrogen.Slurry was filled in a thermos flask. The glass flask containing the CCl<sub>4</sub> liquid was immersed in the slurry. After CCl<sub>4</sub> was completely solidified, the impurity gases above the surface of the solid CCl<sub>4</sub> were pumped out until a background pressure of better than 10<sup>-4</sup> torr was reached. Then all the valves to the vacuum lines pumping the vapour extraction system are closed. The slurry was removed and carbon tetrachloride was allowed to be liquefied.
- SO<sub>2</sub> : In the case of sulphur dioxide, it was directly extracted from the cylinder without further purification.
- The two stage mechanical refrigeration system was switched on only after a back ground pressure of 10<sup>-6</sup> torr was reached in the absorption chamber and most of the degassing of the chamber had taken place. The compressor of the cooling unit was turned on and the desired low-temperature was set on the temperature controller. The electro-mechanical stirrer in the cold bath was turned on. The temperature of the cold bath was monitored by the thermal sensor of the cooling unit. After the cold bath reached the desired low temperature, it was allowed to stabilize for about 2 hours before starting the experiment.

• The argon mini-arc source was switched on and the arc current was set at 35 amps. The source was allowed to stabilize for 20 minutes.

The measurement of absorbance was done in sets of spectral scans typically covering a wavelength range of 100 A° per scan. The monochromator was set at the scanning speed of 5 A° per minute and a gate pulse of width 10 seconds was set in the dual multichannel analyzer. This gave a wavelength step of  $0.83A^\circ$  per channel. In the spectral regions where absorbance of the target molecules was low, a lower scanning speed of 2 A° per minute and a larger gate width of 20 seconds was used so as to increase the integration time for data acquisition. The wavelength step in this case was  $0.66 A^\circ$  per channel.

After fixing the various parameters like wavelength region, temperature, target gas pressure and data acquisition parameters, a spectral scan with no target gas in the photoabsorption chamber was taken; this was called the *no-gas scan*. Then the target gas at a known pressure was introduced into the chamber and the wavelength scan was taken. This was called the *gas-scan*. From the intensity data obtained from the photomultipliers at beam splitter and the transmission port for the gas and no-gas scans, it was possible to determine the absorbance. The actual method adopted for determining the absorbance is described in Chapter III.

At least three gas scans were taken at different target gas pressures for each wavelength region. At a given temperature, the target gas pressures in case of carbon tetrachloride were chosen such that they do not exceed the vapour pressure of carbon tetrachloride at that particular temperature. Otherwise the vapour of the target gas would condense into its liquid phase inside the chamber. This aspect is discussed in detail in Chapter 3 The target gas pressure chosen in the case of  $SO_2$  should be within the limits of 'validity of Beer-Lambert law'. The validity of Beer-Lambert law is discussed in detail in Chapter 3.

At temperatures below 280 K, it was found that the transmission of the spectrometer changed with time after the introduction of gas or vapour. This was due to the 'adsorption' of gas molecules on the quartz windows. A separate experiment was conducted at all the low temperatures at which the instrument was operated for photoabsorption cross section measurement. This experiment was conducted for carbon tetrachloride and sulphur dioxide. The experiment measured the change in the transmission with time after the introduction of the target gas in the photoabsorption chamber. This change in transmission with time was incorporated while calculating the photoabsorption cross sections from observables. This correction is discussed in detail in Chapter 3.

The quartz windows used in the experimental system allowed the instrument to operate at wavelengths 180 nm and above. With the slit widths at 100 microns each, the resolution of the monochromator was 0.1 nm. Hence the photoabsorption cross section measurements could be carried out at an instrumental resolution of 0.1 nm. The temperature range over which the instrument could be operated was 300 K to 220 K. Temperature stability in the cold bath was about  $\pm 0.5$  K. Temperature stability in the cold bath was about  $\pm 0.5$  K. Temperature of 220 K. All the Viton O-rings used for coupling different parts of the system could function trouble free even when the temperature of the cold bath was 200 K.

The pressures used in the measurement of the photoabsorption cross sections for CCl<sub>4</sub> ranged from 300 mtorr to 3 torr. The pressures were chosen so that the absorbance varied from 0.15 to 0.8 in different wavelength regions. The minimum absorption cross section that could be measured with the present system was  $10^{-21}$  cm<sup>2</sup>.

In the case of SO<sub>2</sub>, pressures of 10-18 mtorr were used for the spectral region 180-220 nm and the minimum cross-section that could be measured was  $10^{-19}$  cm<sup>2</sup>. For the second spectral region 280-320 nm, pressures of 130-150 mtorr were used and the minimum cross section that could be measured was  $10^{-20}$  cm<sup>2</sup>.

Pressure stabilities during experiments could be achieved up to a reasonable accuracy by using the leak valve and also by controlling the flow of gas in the absorption chamber, by means of the baffle valve in the diffstak pump.

# Chapter 3

# METHOD

The importance of studying the photoabsorption of molecules and the accessity for measuring their photoabsorption cross sections as a function of temperature below 200 K has been discussed in Section 1.7. The methods available, in general for measuring the photoabsorption cross sections of molecular gases, their metrics and demarits have also been discussed in Section 1.8.4. In this chapter, the experimental method used in the present work for measuring the photoabsorption cross sections at low temperatures is discussed in detail. The basic technique for measuring the photoabsorption cross section at low temperatures remains almost the same as that used for measurements at 300 K. However, in the present work at low temperatures, three unforeneon problems were identified; these are the thermal transpiration effect, the vapour pressure related problems of the target gas at low temperatures and the adsorption of the target gas molecules on the quartz windows of the photoabsorption chamber. The thermal transpiration is in general applicable for measurements at temperatures different from the ambient temperature (300 K). The problems due to the vapour pressure and adsorption of target gas could be exceptional for the photoabsorption experiment at low temperatures. All the above mentioned problems, and the mathods adopted to make the necessary corrections are described in detail in this chapter.

# Chapter 3

# METHOD

The importance of studying the photoabsorption of molecules and the necessity for measuring their photoabsorption cross sections as a function of temperature below 300 K has been discussed in Section 1.7. The methods available, in general for measuring the photoabsorption cross sections of molecular gases, their merits and demerits have also been discussed in Section 1.8.4. In this chapter, the experimental method used in the present work for measuring the photoabsorption cross sections at low temperatures is discussed in detail. The basic technique for measuring the photoabsorption cross section at low temperatures remains almost the same as that used for measurements at 300 K. However, in the present work at low temperatures, three unforeseen problems were identified; these are the thermal transpiration effect, the vapour pressure related problems of the target gas at low temperatures and the adsorption of the target gas molecules on the quartz windows of the photoabsorption chamber. The thermal transpiration is in general applicable for measurements at temperatures different from the ambient temperature (300 K). The problems due to the vapour pressure and adsorption of target gas could be exceptional for the photoabsorption experiment at low temperatures. All the above mentioned problems, and the methods adopted to make the necessary corrections are described in detail in this chapter.

### **Photoabsorption Cross Section Measurement**

ssed in Section 1.1, photoabsorption cross sections of molecules can be meang the Beer-Lambert law, The photoabsorption cross section at a temperar a wavelength  $\lambda$  is determined by

$$\sigma_{\lambda}(T) = \frac{1}{nl} \ln \left[ \frac{I_0(\lambda)}{I(\lambda, T)} \right]$$
(3.1)

s the optical path length for the experimental set-up. In the present set-up, cm, n is the number density of the target gas molecules and the quantity  $\frac{1}{D}$  is the absorbance. The number density of the target gas molecules is

$$n = n_0 \times \frac{P}{760} \times \frac{273}{T}$$
 (3.2)

, is the Loschmidt number and is equal to  $2.69 \times 10^{19}$  molecules/cc, P is the e) pressure of the target gas expressed in torr and T is the temperature of the us is kelvin. As described in Section 2.9, the absolute pressure of the target easured by the MKS Baratron capacitance manometer. The temperature of et gas is assumed to be same as that of the walls of the absorption chamber.

bsorbance at any given wavelength is estimated from the ratio of the meacident intensity  $I_o(\lambda)$  to the transmitted intensity  $I(\lambda, T)$ . The technique he present work for estimating this ratio, required the intensity measured by omultiplier at the beam splitter and the transmitted intensity measured by omultiplier at the exit port of the photoabsorption chamber. This technique ibed by Ahmed (1990) has the advantage of monitoring the fluctuations in intensity and also measuring the absolute photoabsorption cross sections of ar gases. The technique is described below.

is mentioned in Section 2.13, the photoabsorption experiment was carried ets of wavelength scans called spectral scans. Initially the photoabsorption chamber is evacuated to a pressure of  $10^{-6}$  torr and is cooled to the desired low temperature. Then, the wavelength is scanned by the monochromator. The intensity  $I_{NGA}(\lambda, T)$  measured by the photo multiplier at the exit port of the photoabsorption chamber and intensity  $I_{NGB}(\lambda)$  measured by the photomultiplier at the beam splitter are recorded as a function of wavelength when there was no target gas in the absorption chamber. This spectral scan is called the no gas scan. Next, the target gas is introduced at a known pressure P and a gas scan is performed. During the gas scan, the intensities  $I_{GA}(\lambda, T)$  and  $I_{GB}(\lambda)$  are measured as a function of wavelength by the photo multipliers respectively, at the exit port of the absorption chamber and the beam splitter.

During the gas scan, at any wavelength the measured intensity at the exit port of the absorption chamber is proportional to the measured intensity at the beam splitter i.e.

$$I_{NGA}(\lambda, T) = F I_{NGB}(\lambda) \tag{3.3}$$

Here, F is a geometrical factor. During the gas scan, the measured intensity at the exit port of the absorption chamber is proportional to the incident intensity at beam splitter but reduced by a factor  $\left[\frac{I(\lambda,T)}{I_0(\lambda)}\right]$ . The factor  $\left[\frac{I(\lambda,T)}{I_0(\lambda)}\right]$  is due to the photoabsorption of gaseous column (of length l). This may be expressed as,

$$I_{GA}(\lambda,T) = F I_{GB}(\lambda) \left[ \frac{I(\lambda,T)}{I_0(\lambda)} \right]$$
(3.4)

where  $I(\lambda, T)$  and  $I_0(\lambda)$  are the actual transmitted and incident intensities respectively.

The quantity  $\left[\frac{I(\lambda,T)}{I_0(\lambda)}\right]$  can be determined from equations 3.3 and 3.4, by eliminating the geometrical factor F. The absorbance is given by

$$\ln\left[\frac{I_0(\lambda)}{I(\lambda,T)}\right] = \ln\left[\frac{I_{GB}(\lambda)}{I_{GA}(\lambda,T)} \times \frac{I_{NGA}(\lambda,T)}{I_{NGB}(\lambda)}\right]$$
(3.5)

Hence, by knowing the absorbance, number density and path length, the photoabsorption cross sections of molecules can be measured at any desired temperature of the target gas (Equation 3.1).

# 3.2 The Validity of Beer-Lambert Law

For photoabsorption of molecules, the Beer-Lambert law is valid so long as the absorbance varies linearly with the target gas pressure. In other words, the measured photoabsorption cross section is independent of pressure. It is well known that in the case of molecules having structured absorption spectrum, the Beer-Lambert law remains valid only up to a certain 'limiting pressure'. Beyond this limiting pressure, photoabsorption deviates from the Beer-Lambert law. The range of pressures in which the Beer-Lambert law is valid is used for measuring the photoabsorption cross sections. Beyond the region of validity, the curve has a decreasing slope with an increase in the applied pressure. The cross section values determined at pressures outside the region of validity do not represent the true photoabsorption cross sections. It is also known that in case of molecules having continuous photoabsorption spectrum, the curve of absorbance versus applied pressure remains a straight line with no limiting value on the range of pressures which may be used for measuring the photoabsorption cross sections.

In view of the above, it becomes essential to study the validity of Beer-Lambert law for any absorbing species before measuring their photoabsorption cross sections. For structured photoabsorption spectrum, a convenient absorption band appearing at the centre of the spectral region is chosen. The validity of Beer-Lambert law is studied at the wavelength corresponding to the peak of the absorption band. For continuous photoabsorption, a convenient wavelength at the centre of the spectral region is chosen for studying the validity of Beer-Lambert law. The valid pressures so obtained are then used for measuring the photoabsorption cross sections of the entire spectral region.

For the present work, the validity of Beer-Lambert law was studied for  $SO_2$  at a wavelength of 200.6 nm (See Figure 3.1(a)) for the first spectral region (188-230 nm)



Figure 3.1: The validity of Beer-Lambert law; (a) For  $SO_2$  first spectral region (b) For  $SO_2$  second spectral region. The solid curve shows the behavior of Beer-Lambert law as observed in the present experimental set-up. The dotted line indicates the straight line fit to the region where the Beer-Lambert law is valid.



Figure 3.2: The validity of Beer-Lambert law for CCl<sub>4</sub>.

and at a wavelength of 298.0 nm (See Figure 3.1(b)) for second spectral region (280-320 nm). As can be seen from Figures 3.1(a) and 3.1(b) for SO<sub>2</sub>, the valid pressure regions were up to 16 and 140 mtorr for first and second spectral regions respectively. In the second spectral region, the values of photoabsorption cross sections were at least one order of magnitude less than those in first spectral region and hence, the pressures required were at least one order of magnitude larger. It may be pointed out here that the corresponding values of absorbance for the limiting pressures are very nearly the same for both the spectral regions. The pressures chosen to measure the photoabsorption cross section for SO<sub>2</sub> varied from 10 to 16 mtorr for first spectral region and from 100 to 140 mtorr for the second spectral region. For CCl<sub>4</sub>, the Beer-Lambert law was studied at a wavelength of 200 nm (Figure 3.2). The absorbance versus pressure curve remains a straight line at all pressures between 20 and 1200 mtorr showing that the Beer-Lambert law does not get violated at these pressures. Hence for CCl<sub>4</sub>, there is no limitation for the applied pressure. However, for the present experiment the pressures were chosen such that at any temperature, the absorbance always lay within the limits between 0.15 to 0.8.

The reason for deviation of the Beer-Lambert law in case of structured photoabsorption spectrum of molecules is known to be due to the limiting instrumental resolution of the photoabsorption spectrometer (Nielsen et al., 1994; Okabe, 1978). The instrumental resolution plays a vital role in determining the extent of validity of Beer-Lambert law for structured photoabsorption (Hudson et al. 1967). The effect of resolution on the validity of Beer-Lambert law is briefly described below.

The incident intensity measured over the band width  $\Delta\lambda$  (The instrumental resolution) is determined by the slit width and grating parameters (Hudson et al, 1967). The intensity in the no gas scan is

deviates from Beer-Lamber

$$I_0(\lambda_m, \Delta \lambda) = \int_{\lambda_m - \Delta \lambda}^{\lambda_m + \Delta \lambda} S(\lambda) G(\lambda) \, d\lambda$$
(3.6)

where  $S(\lambda)$  is the source function and  $G(\lambda)$  is the instrumental response function. The instrumental response function is triangular when the entrance and exit slit widths are equal and the full width at half maximum (FWHM) is equal to the instrumental resolution  $\Delta \lambda$ .  $\lambda_m$  is the wavelength at the peak of the absorption band. For the gas scan the measured transmitted intensity consists of an additional factor due to photoabsorption by the gaseous column;

$$I(\lambda_m, \Delta \lambda) = \int_{\lambda_m - \Delta \lambda}^{\lambda_m + \Delta \lambda} S(\lambda) G(\lambda) \exp\left(-\sigma(\lambda) n l\right) d\lambda$$
(3.7)

For a continuum source,  $S(\lambda)$  is constant, since it has practically got no variation

with  $\lambda$ , within the band width  $-\Delta\lambda$  to  $\Delta\lambda$ . Therefore,

$$\begin{bmatrix} I_0(\lambda_m) \\ \overline{I(\lambda_m)} \end{bmatrix} = \frac{\lambda_m + \Delta\lambda}{\lambda_m - \Delta\lambda}$$

$$\begin{bmatrix} I_0(\lambda_m) \\ \overline{\lambda_m + \Delta\lambda} \\ \beta \\ \lambda_m - \Delta\lambda \end{bmatrix} (3.8)$$

when  $\sigma(\lambda)$  is a smoothly varying function of  $\lambda$  like the case of a continuous photoabsorption spectrum or when the number density of the target gas molecules is small i.e. when the target gas pressure is small in the case of structured photoabsorption spectrum. The factor  $\exp(-\sigma(\lambda)nl)$  in the integral of denominator of Equation 3.8 does not vary sharply within  $-\Delta\lambda$  to  $\Delta\lambda$ . Hence, it may be replaced by its value at  $\lambda_m$ . Then we have,

$$\ln\left[\frac{I_0(\lambda_m, \Delta\lambda)}{I(\lambda_m, \Delta\lambda)}\right] = \sigma(\lambda_m) n l$$
(3.9)

which indicates that Beer-Lambert law is valid. For structured photoabsorption spectrum, when there are fine structures within the width  $-\Delta\lambda$  to  $\Delta\lambda$ , for large values of number density (i.e. large target gas pressures) the factor  $\exp(-\sigma(\lambda)nl)$  also varies sharply within the width  $-\Delta\lambda$  to  $\Delta\lambda$  In such a situation,  $\ln\left[\frac{I_0(\lambda_m, \Delta\lambda)}{I(\lambda_m, \Delta\lambda)}\right]$  would have a functional dependence which is not necessarily linear in n and hence the absorption deviates from Beer-Lambert law for large values of n. The effect of various shapes and line widths of absorption lines on the measured  $\sigma(\lambda)$  was studied in detail by Nielsen et al (1944) and Hudson et al (1967).

### 3.3 Thermal Transpiration Effect

Consider two vessels, vessel 1 and vessel 2 containing a gas and held at temperatures  $T_1$  and  $T_2$  respectively and connected by a tubing of diameter d. If  $P_1$  and  $P_2$  are the pressures of the gas in the vessels 1 and 2 respectively, such that the mean free path of the gas molecules is very small compared to the diameter of the tube ( $\Lambda \ll d$ ), then from kinetic theory it may be shown that

$$P_1 = P_2$$
 (3.10)

However, for lower pressures when the mean free path is very large compared to the diameter of the tubing  $(\Lambda \gg d)$ , then there always exists a thermo-molecular flow of the gas from the colder vessel to the hotter vessel. This effects is known as thermal transpiration effect (Dushman, 1962). If thermal transpiration exists, then from kinetic theory of gases, it may be shown that

$$\frac{P_2}{P_1} = \sqrt{\frac{T_2}{T_1}}$$
(3.11)

In the intermediate pressure region, i.e. when the mean free path is either comparable or smaller than the diameter of the tubing ( $\Lambda \approx d$  or  $\Lambda < d$ ), the pressure conditions due to thermal transpiration can be described by empirical relations, which also satisfy the extreme pressure conditions described above. These empirical relations and the thermal transpiration relevant in the present work are described in Sections 3.3.1 and 3.3.2.

Knudsen (1910) has shown that the phenomenon of thermal transpiration is adequately explained by two opposing flows of gas - an axial flow from hotter to colder region and a surface flow along the walls in the reverse direction. As a result of these flows, there exists a forward momentum transfer towards the hotter side. Thermal transpiration is observed for cases where temperature differences are large while the pressures involved are small.

### 3.3.1 Thermal Transpiration Correction for MKS Capacitance Manometers

In the present work, an MKS Baratron capacitance manometer was used for absolute measurement of target gas pressures. The functioning of the Baratron capacitance manometer has been discussed in detail in Section 2.9. Since the material used in the Baratron is sensitive to ambient temperature fluctuations, it is always held at a constant elevated temperature of 318 K. For photoabsorption experiments at low temperatures, the temperature of photoabsorption chamber could be as small as 220 K. Due to this large temperature difference, there exists thermal transpiration effect which leads to a thermomolecular flow from the cold photoabsorption chamber to the hot MKS manometer. This thermomolecular flow produces an extra forward momentum transfer on the manometer apart from that due to the actual target gas pressure in the chamber. Hence, the manometer always overestimates the target gas pressure when the temperature of the photoabsorption chamber is lower than 318K. Hence, the pressures measured by Baratron capacitance manometer need to be corrected for this effect.

Theoretical calculations for thermal transpiration using kinetic theory of gases have been reported in literature, but these methods involve solving of complex numerical integral equations and therefore, are not practical for routine use in laboratory. Empirical relations exist in literature; namely the Liang's equation (Liang, 1953) and Takaishi-Sensui equation (Takaishi-Sensui, 1963). Liang studied the thermal transpiration for gases like He, Kr and Xe and gave the following empirical relation.

$$\frac{P_2}{P_1} = \frac{\alpha \Phi^2 X^2 + \beta \Phi X + \sqrt{T_2/T_1}}{\alpha \Phi^2 X^2 + \beta \Phi X + 1}$$
(3.12)

where

$$X = 0.133 P_2 d \tag{3.13}$$

 $P_2$  is expressed in pascals and d in meters  $\alpha$  and  $\beta$  are constants for the gas under study (to be experimentally determined) and  $\Phi$  is the pressure shift factor which is given by

$$0.27 \log \Phi = \log D + 9.59 \tag{3.14}$$

Where D is the molecular diameter (in meters) Baldwin and Gaertner (1973) conducted an extensive study on the thermal transpiration corrections in capacitance manometers. The corrections measured experimentally by them did not follow the Liang's equation. Poulter et al. (1983) conducted similar experiments for gases like He, Ne, Ar and SF6. They found that their experimental data could be fitted well using the Takaishi-Sensui equation and also their data agreed with the thermal transpiration corrections calculated by simple kinetic theory. The Takaishi-Sensui equation is given by :

$$\frac{P_2}{P_1} = \frac{A X^2 + B X + C\sqrt{X} + \sqrt{T_2/T_1}}{A X^2 + B X + C\sqrt{X} + 1}$$
(3.15)

where

$$A = A^* (T^*)^{-2} \tag{3.16}$$

$$B = B^* (T^*)^{-1} \tag{3.17}$$

$$C = C^* (T^*)^{-0.5} (3.18)$$

$$T^* = 0.5(T_1 + T_2) \tag{3.19}$$

$$X = 0.133 P_2 d \tag{3.13}$$

 $P_2$  and  $P_1$  are expressed in pascals; d is expressed in meters  $A^*$ ,  $B^*$ ,  $C^*$  are reduced constants given by

$$A^* = 1.4 \times 10^4 \exp(1.17 \times D \times 10^{10}) \tag{3.20}$$

$$B^* = 5.6 \times \exp(1.4 \times D \times 10^{10}) \tag{3.21}$$

$$C^* = (1.10 \times 10^{-8}/D) - 14$$
 (3.22)

D, the molecular diameter (in meters) can be calculated using the kinetic theory expression for viscosity of gases;

$$\eta = \frac{5}{16 D^2} \left(\frac{m \, k \, T}{\pi}\right)^{\frac{1}{2}} \tag{3.23}$$

Here, m is the molecular weight in kilogram,  $\eta$  is in poise and k is the Boltzmann constant. It may be pointed out here that the Liang's equation requires parameters like  $\alpha$ ,  $\beta$  which may not be easily available in literature for all gases of interest. The Takaishi-Sensui equation on the other hand has the following advantage. All the constants in the equation can be directly determined from the standard data

Molecule	$\frac{\text{mass } m}{(10^{-25} \text{ kg})}$	$\eta$ (poise)	$\begin{bmatrix} T_{\eta} \\ (K) \end{bmatrix}$	$\frac{D}{(10^{-10} \text{ meters})}$
CCl <sub>4</sub>	2.554215	13.34	400.9	5.557
$SO_2$	1.063716	12.54	293.5	5.402

Table 3.1: The viscosity data used for calculating Thermal transpiration corrections.

like viscosity which is easily available. Also according to Poulter et al (1983), this equation could satisfactorily represent the thermal transpiration corrections of gases in MKS Baratron capacitance manometers.

### 3.3.2 Thermal Transpiration Corrections for CCl<sub>4</sub> and SO<sub>2</sub>

In view of the above advantages discussed in Section 3.3.1, the Takaishi-Sensui equation was used for calculating the necessary thermal transpiration corrections to the pressures measured by MKS Baratron capacitance manometers. The diameter of the connecting tube was 6mm ( $d = 6 \times 10^{-3}$  meters). Thermal transpiration effect was studied for both the gases, CCl<sub>4</sub> and SO<sub>2</sub> in the temperature range 300 to 220 K. The molecular diameters of CCl<sub>4</sub> and SO<sub>2</sub> were determined from the viscosity data (CRC Handbook of Chemistry and Physics, 1984). The viscosity data and molecular data of CCl<sub>4</sub> and SO<sub>2</sub> relevant for thermal transpiration calculations is presented in Table 3.1. To estimate the thermal transpiration correction using Equation (3.15) the pressure  $P_2$  is taken to be the pressure measured by the manometer  $P_{brt}$  and hence the temperature  $T_2$  is the temperature of Baratron  $T_{brt}$  ( $T_{brt} = 318$ K).  $P_1$  is taken to be the true pressure of the target gas,  $P_{cmr}$  the pressure in the chamber which is at a temperature  $T_1$  ( $T_1 = T_{cmr}$ ).

Substituting all the above parameters in the Takaishi-Sensui equation, the factor  $\left(\frac{P_{cmr}}{P_{brt}}\right)$  was determined as a function of measured pressure  $P_{brt}$  at temperatures 300 to 200 K in steps of 20 K, for both CCl<sub>4</sub> and SO<sub>2</sub>. The factor so obtained was used for correcting the measured pressure during the experiment. The % thermal



Figure 3.3: The thermal transpiration corrections to be applied at different temperatures to the pressures measured by MKS capacitance manometer; (a)  $CCl_4$  (b)  $SO_2$ .

transpiration correction,  $\left(1 - \frac{P_{cmr}}{P_{brt}}\right) \times 100$  versus the measured pressure  $P_{brt}$  is plotted in Figures 3.3 (a) and 3.3 (b) for CCl<sub>4</sub> and SO<sub>2</sub> respectively. As can be seen from the figures, the thermal transpiration corrections are larger for lower temperatures and lower pressures. Also, the correction required is larger for SO<sub>2</sub> than CCl<sub>4</sub> as the molecular diameter for SO<sub>2</sub> is smaller than that for CCl<sub>4</sub>.

# 3.4 Vapour Pressure of the Target Gas

For molecules possessing low values of photoabsorption cross section ( $\approx 10^{-21}$  cm<sup>2</sup>), it is required to make measurements at higher target gas pressures in order to have appreciable absorbance. This in particular was necessary for CCl<sub>4</sub>, since its photoabsorption cross section values show a sharp decline on the longer wavelength side of its photoabsorption spectrum, by nearly two orders of magnitude (see Chapter 5). Carbon tetrachloride exists in liquid phase at room temperature and its vapors were extracted to the experimental chamber to study the photoabsorption (See Section 3.2). However at low temperatures, the target gas pressure cannot exceed its vapour pressure. In case, this target gas pressure exceeds the vapour pressure, the vapors would condense into their liquid phase inside the absorption chamber. Hence, for studying the photoabsorption of any target gas molecules at low temperatures, it becomes essential to know its vapour pressure characteristics. The vapour pressure at any given temperature can be determined from the equation given below:

$$\log 760 - \log (V.P)_{torr} = \frac{\Phi \Delta T}{T - 0.15 \Delta T}$$
(3.24)

where  $(V.P)_{torr}$  is the vapour pressure measured in torr,

$$\Phi = \frac{\Delta H_{vap}}{2.303 \, R \, T_b} \tag{3.25}$$

and

$$-\Delta T = T - T_b \tag{3.26}$$

ſ	Normal boiling point	Enthalpy of vaporization
Molecule	$T_b$	$\Delta H_{vap}$
	(Kelvin)	(cal/mole)
CCl <sub>4</sub>	349.6	7437.26
SO <sub>2</sub>	263.1	6684.72

Table 3.2: The Vapour pressure data of  $CCl_4$  and  $SO_2$ .

Here,  $\Delta H_{vap}$  is the enthalpy of vaporization, R is the gas constant (R = 1.98717 cal/deg/mole.  $T_b$  is the normal boiling point, the temperature at which the vapour pressure equals 760 mm. The data required for calculating the vapour pressure for CCl<sub>4</sub> and SO<sub>2</sub> are presented in Table 3.2.

### 3.4.1 Vapour Pressure Constraint on Absorbance.

In the present work, the target gas pressures for CCl<sub>4</sub> were chosen such that they produced at least a minimum absorbance of 0.15 even for the lowest measurable values of photoabsorption cross section. Figure 3.4(a) shows the vapour pressure curve for CCl<sub>4</sub>. Also, in the same figure are shown the curves indicating the pressures required at different temperatures to obtain a minimum absorbance of 0.15 for the cross section values of  $\sigma = 11.0 \times 10^{-21} \text{ cm}^2$  and  $\sigma = 68.5 \times 10^{-21} \text{ cm}^2$ . These curves for constant absorbance intersect the vapour pressure curve at temperatures at which the required pressure becomes equal to the vapour pressure. At temperatures lower than these critical temperatures obtained from the intersection of the curves, the photoabsorption cross sections cannot possibly be measured.

Measurement of such cross sections would require pressures larger than the vapour pressure which are not accessible, since the vapors would then undergo a phase transition into its liquid phase. Hence from the above argument and as may be seen from Figure 3.4(a), photoabsorption cross section cannot be measured below 240 K for  $\sigma = 11.0 \times 10^{-21} \text{ cm}^2$  and similarly below 220 K for  $\sigma = 68.5 \times 10^{-21} \text{ cm}^2$  in case of CCl<sub>4</sub>. Hence, at 240 K and 220 K for CCl<sub>4</sub>, measurement could not be





conducted beyond the wavelengths 207.5 and 195.5 mm where its cross section values were  $11.0 \times 10^{-21}$  cm<sup>2</sup> and  $68.5 \times 10^{-21}$  cm<sup>2</sup> respectively.

Figure 3.4(b) shows the vapour pressure curve for SO<sub>2</sub>. Also in the same figure are shown the curves indicating the pressures required at different temperatures to obtain an absorbance of 0.15 for a cross section value of  $5 \times 10^{-18}$  cm<sup>2</sup> and  $5 \times 10^{-19}$ cm<sup>2</sup>. This is typically the order of magnitude of cross sections measured for SO<sub>2</sub> in its first and second spectral region. As may be seen from the figure, the curves of constant absorbance do not intersect at any point with the vapour pressure curve at temperatures ranging from 300 to 220 K. Hence it is clear that in case of SO<sub>2</sub>, the absorbance is not constrained by vapour pressure at least in the temperature region of our interest.

### 3.4.2 Temperature of the Target Gas

In the present experiment, it was assumed that the temperature of the target gas is the same as the temperature of the walls of the photo absorption chamber, which were maintained at a desired low temperature. This assumption was based on the fact that the target gas molecules equilibrate to the temperature of the walls of the chamber in a few hours. An indirect proof for the above assumption could be established in the present experiment by using the vapour pressure properties of CCl<sub>4</sub>. At one instant when the temperature of the chamber was 228K, it was observed that the pressures higher than a value of 1.5 torr could not be achieved in the photoabsorption chamber, even when the Granville Phillips valve used to control the pressure in the chamber was completely open. This suggested that the vapour that was being introduced into the chamber was undergoing a phase transition and was condensing into its liquid phase inside the chamber. Substituting this value of pressure for the vapour pressure  $(V.P)_{torr}$  in Equation 3.24 the temperature of the target was estimated to be 227.73K. The above procedure was repeated for other temperatures also and it was found that the temperature of the gas agreed with the temperature of the walls within  $\pm 1.0\%$ .

### 3.5 Adsorption of the Target Gas

It was observed that at low temperatures, the transmission of the photoabsorption chamber reduced with time after the introduction of the target gas. The effect of reduction in the transmission with time at any wavelength was observed as an increase in the value of absorption cross section after each successive spectral scan. Each spectral scan was typically of 20 minutes duration. This reduction in transmission was attributed to the adsorption of the target gas molecules on the surfaces of the quartz windows at low temperatures.

It is well known that many materials adsorb the gas molecules at low temperatures. Quartz can adsorb both  $CCl_4$  and  $SO_2$  on its surface. The adsorbed target gas molecules can cause a reduction in transmission of the photoabsorption chamber. This change in transmission with time would depend on the rate of adsorption of these molecules on the quartz windows. The above effect was also observed by Wu et al. (1989), when they measured the photoabsorption cross sections for  $C_2H_2$  at low temperature (155K).

Hence, due to adsorption, there is a reduction in the transmitted intensity measured by the photo multiplier at the exit port of the absorption chamber, by a factor  $\zeta_T(t)$ , apart from the normal attenuation in the incident intensity caused due to photoabsorption. Thus Equation 3.4 may be modified by introducing the factor due to adsorption i.e.

$$I_{GA}(\lambda, T) = F I_{GB} \left[ \frac{I(\lambda, T)}{I_0(\lambda)} \right] \zeta_T(t)$$
(3.27)

The factor  $\zeta_T(t)$  due to adsorption is a function of time t and is a function of temperature, T of the target gas.

For the present work, a separate experiment was conducted to study the change in the transmission of photoabsorption chamber due to adsorption. The factor  $\zeta_T(t)$ was measured as a function time elapsed after the introduction of the target gas. The
procedure of the experiment is described below.

The absorption chamber was first evacuated to a pressure of  $10^{-6}$  torr and cooled to a desired low temperature T. At a time t = 0, the intensity  $I_B(t = 0)$ at the beam splitter and the transmitted intensity  $I_A(t = 0)$  at the exit port of the absorption chamber were measured. Then the target gas was filled in the absorption chamber at some known pressure. The quart windows were allowed to adsorb the target gas for 10 minutes; then immediately the target gas was flushed out and the intensity at the beam splitter  $I_B(t = 10)$  and the transmitted intensity  $I_A(t = 10)$ were measured. Assuming that there is no desorption immediately after flushing the target gas, the reduction factor in transmission due to adsorption after t = 10 min is calculated using the equation,

$$\zeta_T(10) = \frac{I_A(t=10)}{I_B(t=10)} \times \frac{I_B(t=0)}{I_A(t=0)}$$
(3.28)

The procedure was repeated and the factor  $\zeta_T(t)$  was measured in steps of 10 min at low temperatures (280-220 K at an interval of 20 K) for CCl<sub>4</sub> and SO<sub>2</sub>. The percentage change in transmission due to adsorption was estimated as a function of time for CCl<sub>4</sub> at 260, 240 and 220 K (no adsorption effect was observed at 280 K) and for SO<sub>2</sub>, it was measured from 280 to 220 K in steps of 20 K.

The percentage change in transmission  $(1 - \zeta_T(t)) \times 100)$  was plotted as a function of time for both CCl<sub>4</sub> and SO<sub>2</sub>. These curves are presented in Figures 3.5 (a) and 3.5(b) for CCl<sub>4</sub> and SO<sub>2</sub> respectively.

The function  $\zeta_T(t)$  was used to correct for the change in transmission during the gas scans of the photoabsorption experiment. Here, the time scale was converted to the corresponding wavelength scale by multiplying the time elapsed with the wavelength scanning speed of the monochromator and the transmission was corrected for adsorption.



Figure 3.5: Percentage change in transmission of quartz windows of the absorption cell due to adsorption of target gases; (a)  $CCl_4$  (b)  $SO_2$  at low temperatures.

1 Error in Pressure Measurement

# Chapter 4

# ERROR ANALYSIS

The errors in the photoabsorption experiment can conveniently be classified as follows : multiplicative errors relating to errors in pressure, temperature or absorption path length, additive errors caused by faulty counting statistics; and finally, cross section shape errors caused by gas impurities and uncertainties in the incident photon energies. A complete discussion of these error sources will now be given in order to obtain an estimate for the upper limit of the actual error. The most probable estimate of the accuracy of the experiment will also be given.

There were systematic errors in the measurement of pressure and absorbance at low temperatures. These are due to the thermal transpiration and adsorption effects. These effects and the methods adopted to correct the same have already been discussed in detail in Sections 3.3 and 3.5 respectively. The effect of bandwidth (instrumental resolution) on the measured photoabsorption cross section has also been discussed in detail in Section 3.2. The method adopted in the present experiment to avoid the temperature gradients at the edges of the optical path (edge effects) has been described in Chapter II.

refore the largest errors incurred in the measurement of temperature of the wall as absorption chamber, were taken to be the error in temperature of the targe

### 4.1 Error in Pressure Measurement

An MKS Baratron differential capacitance manometer was used to measure the target gas pressure in the absorption chamber. The measured pressure could be made absolute by evacuating the reference side of the manometer to a pressure of  $10^{-6}$ torr. The Baratron head (Model BH 310) was capable of measuring the pressures up to 10 torr. The systematic errors as given by the manufacturer for the pressures used in the present experiment were as follows. For CCl<sub>4</sub>, the highest pressure used was of the order of 4 torr where the systematic error was  $\pm 0.08\%$ , whereas the lowest pressure used was about 100 mtorr and the corresponding systematic error was  $\pm 0.1\%$ . The pressures used in the case of SO<sub>2</sub> were about 10 to 16 mtorr for the first spectral region where the systematic error in the pressure varied from 0.15% to about  $\pm 0.12\%$ . For the second spectral region, the pressures varied from 100-140 mtorr and the corresponding error varied from  $\pm 0.10\%$  to  $\pm 0.09\%$ . For all practical purpose, the highest error of  $\pm 0.15\%$  (after proper rounding off  $\pm 0.2\%$ ) has been considered in the calculation of overall error budget. The reference pressure end evacuated to  $10^{-6}$ torr introduced errors which should be negligibly small. An analog read-out unit was used for measuring the pressure sensed by the Baratron head. This could introduce another large error which under worst conditions could be as large as  $\pm 2\%$ .

### 4.2 Error in Temperature Measurement

Estimation of error in the temperature of the target gas is very important, in particular, for the measurement of temperature dependence of photoabsorption cross sections. It was shown in Section 3.4.2 that the temperature of the target gas was very nearly the same as the temperature of the walls of the photoabsorption chamber. Therefore the largest errors incurred in the measurement of temperature of the walls of the absorption chamber, were taken to be the error in temperature of the target gas. A calibrated thermocouple supplied by FTS System Inc, New York, was used to measure the temperature of the absorption chamber. As specified by the manufacturer, the error in the measurement of temperature by thermocouple could be as large as  $\pm 0.5^{\circ}$ C. This could introduce a maximum error of  $\pm 2\%$  at the highest temperature.

## 4.3 Error in Optical Path Length

The optical path length l in the present experimental set-up is the distance between the two quartz windows which are fused to the two quartz tubes in the absorption chamber. The absorption path length in the present experiment is 761 mm. The accuracy in the estimation of optical path length is due to the uncertainty in the extent of movement of the quartz tubes in the absorption chamber and the compression of the O-rings in the flanges at the ends of the chamber. A small misalignment of the photon beam with respect to the central axis of the photoabsorption chamber could also contribute to the error in the optical path length. In the worst case, the accuracy would be  $\pm 3$  mm giving an error of  $\pm 0.4\%$ .

### 4.4 Error in the Measurement of Intensities

In the present work, the error in the incident intensity is determined by the error incurred in the measurement of the intensity by the photo multiplier at the beam splitter. The error in the transmitted intensity is determined by the error in measurement of intensity by the photomultiplier at the exit port of the absorption chamber. Both the photo multipliers used in the present experiment were thermoelectrically cooled and were operated in the photon counting mode.

In the photon counting mode, the count rate will be linearly proportional to the intensity. The photon count rate is given by the number of photons counted divided by the integration time. The integration time is nothing but the gate width available per channel in the dual multi channel analyser which was operated in the multi scaling mode. Photon counting is a statistical process and it follows a Poissonian distribution. If the number of photons counted are n, then for a Poissonian distribution, the uncertainty in n is given by the standard deviation which is equal to  $\pm \sqrt{n}$ . The accuracy in intensity measurement could be increased by increasing the integration time or the gate width. The choice of gate width depends on the intensity available in a particular spectral region.

The counting statistics for the incident intensity,  $I_0$  measured by the beam splitter has introduced errors varying from  $\pm 1.5\%$  to 0.4% depending upon the spectral region where cross sections are measured. An error of  $\pm 2.5\%$  and  $\pm 0.5\%$  has been estimated due to counting statistics in the measurement of transmitted intensity, Iin different spectral regions. The larger errors of  $\pm 1.5$  and  $\pm 2.5\%$  for  $I_0$  and I were used to calculate the most probable estimate of accuracy of absorption cross sections.

## 4.5 Impurities of Target gases

 $CCl_4$  vapour was extracted from a spectroscopic grade liquid which was procured from Messrs Spectrochem, India. The purity of the liquid  $CCl_4$  was 99.9%. The vapour was further purified by fractional distillation before introducing into the absorption chamber.

scenar error. In the present experiment, it was found to be  $\pm$  3.0%. The incoherent sum represented the most probable estimate of the accuracy obtained by adding the squares of all of the errors and taking the square root of the total sum. In the present experiment, the most probable error was estimated to be  $\pm 4.1\%$  for photoabsorption cross section measurement. The error budget is presented in Table 4.1.

		Error %
Pressure		
	Measurement error	$\pm 0.2$
	Reading error	$\pm 2.0$
Temperature		$\pm 2.0$
· Optical path length		±0.4
Counting statistics in intensity		
	$I_0(\lambda)$	$\pm 1.5$
	$I(\lambda)$	$\pm 2.5$
Coherent sum		$\pm 8.6$
Incoherent sum or total		
r.m.s error	An office of the second	±4.1

e 4.1: Error budget for the measurement of photoabsorption cross sections

SO<sub>2</sub> used in the present experiment was procured from Messrs Grisheim, Ger-The gas was 99.98% pure and was used without further purification. The due to sample gas impurity could safely be considered negligible.

## Error in Photoabsorption Cross Section

herent sum of all these errors provides an estimate of the upper limit of the error. In the present experiment, it was found to be  $\pm$  8.6%. The incoherent presented the most probable estimate of the accuracy obtained by adding the s of all of the errors and taking the square root of the total sum. In the present nent, the most probable error was estimated to be  $\pm$ 4.1% for photoabsorption ection measurement. The error budget is presented in Table 4.1.

# Chapter 5

## **RESULTS AND DISCUSSION**

Carbon tetrachloride and sulphur dioxide were chosen as the target gases for the present study. The importance of studying the quantitative photoabsorption of these gases at low temperatures has already been discussed in Chapter 1. In the present, work, the photoabsorption cross section measurements for CCl<sub>4</sub> have been carried out in the spectral region from 186 to 240 nm at different temperatures from 220 to 300 K at an interval of 20 K. For sulphur dioxide, such measurements were carried out in two spectral regions 188 to 220 nm and 280-320 nm again in the same temperature region (220 to 300 K) and at the same interval of temperature as in the case of CCl<sub>4</sub>. The validity of Beer-Lambert law for both CCl<sub>4</sub> and SO<sub>2</sub> (in both the spectral regions) was studied in detail and has been discussed in Section 3.2. The measurement of photoabsorption cross sections were carried out at an instrumental resolution of 0.1nm and with an accuracy of about  $\pm 4\%$ .

## 5.1 Photoabsorption Cross Sections of CCl<sub>4</sub>

#### 5.1.1 Cross Sections at 300 K

The photoabsorption cross sections for  $CCl_4$  as a function of incident photon wavelength at 300 K are shown in Figure 5.1 in the wavelength region 186-240 nm. The



Figure 5.1: Photoabsorption cross sections of carbon tetrachloride at 300 K as a function of incident photon wavelength.

absorption cross sections show a sharp decline in their values from  $2.542 \times 10^{-18}$  cm<sup>2</sup> at 186 nm to  $9.16 \times 10^{-21}$  cm<sup>2</sup> at 240 nm. The decline is almost exponential in nature except for a small spectral region. Here an exceptionally large decrease has been observed in the region 186-208nm with a broad negative shoulder peaking around 197 nm. The continuous absorption of CCl<sub>4</sub> has been studied in detail by Majer and Simons (1964) and Sandorfy(1976). This has been interpreted as due to the existence of a transition involving excitation to a repulsive electronic state which

is anti-bonding in C-Cl (Dissociation energy = 3.00 eV). It may be difficult to explain the observed features (ie. the broad negative shoulder) quantitatively due to the complex nature of the potential energy surfaces of the molecule involved in the transition.

Photoabsorption cross sections at room temperature were also measured by Rowland and Molina (1975), Robbins (1976) and Simon et al. (1988). Cross section values reported by Simon et al (1988) at 295K only have been shown for comparison in Figure.5.1 along with those obtained at 300 K in the present experiment. Both these measurements were carried out at a spectral resolution of 0.1 nm. In the spectral region from 199 to 237 nm, the cross sections obtained by Simon et al (1988) and those measured in the present experiment are in close agreement within the quoted accuracy. But in the wavelength region from 186 to 198 nm, the values reported by Simon et al. (1988) were larger than those reported in the present experiment, varying from 22% at 186 nm to 8.3% at 198nm. Also, in the spectral region, 237-240nm, there is a discrepancy in the two results. At 238 nm cross sections obtained in the present case are lower by 5.5% whereas at 240 nm our values are higher by 9.4%.

#### 5.1.2 Cross Sections at Low Temperatures

Photoabsorption cross sections have been measured at four different temperatures varying from 220 to 280 K at an interval of 20 K. Since the photoabsorption cross sections decreased in their values with an increasing wave length it was necessary to use higher target gas pressures at longer wavelengths in order to achieve the requisite absorbance (0.15). Although there was no restriction on the target gas pressures from the consideration of Beer-Lambert Law, they were limited by the vapour pressure conditions at low temperature (see Section 3.3.1). Therefore, measurements at 260 and 240 K could be carried out up to 235 nm only and at 220 K, it was difficult to measure cross sections beyond 223 nm.

Wavelength	Absorption cross section $\times 10^{-21}$ cm <sup>2</sup> at							
(nm)	300 K	280 K	260 K	240 K	220 K			
186.0	2542	2542	2542	2542	2542			
186.5	2394	2394	2394	2394	2394			
187.0	2171	2171	2171	2171	2171			
187.5	2161	2161	2161	2161	2161			
188.0	1974	1974	1974	1974	1974			
188.5	1902	1902	1902	1902	1902			
189.0	1781	1781	1781	1781	1781			
189.5	1472	1472	1472	1472	1472			
190.0	1394	1394	1394	1394	1394			
190.5	1264	1264	1264	1264	1264			
191.0	1112	1112	1112	1112	1112			
191.5	934	934	934	934	934			
192.0	924	924	924	924	924			
192.5	808	808	808	808	808			
193.0	820	820	820	820	820			
193.5	778	778	778	778	778			
194.0	767	767	767	767	767			
194.5	662	662	662	662	662			
195.0	654	654	654	654	654			
195.5	649	649	649	649	649			
196.0	637	637	637	637	637			
196.5	632	632	632	632	632			
197.0	632	632	632	632	632			
197.5	623	623	623	623	623			
198.0	628	628	628	628	628			
198.5	634	634	634	634	634			
199.0	640	640	640	640	640			
199.5	638	638	638	638	638			
200.0	648	648	648	648	648			
200.5	642	642	642	642	642			
201.0	639	639	639	639	639			
201.5	647	647	647	647	647			
202.0	644	644	644	644	644			
202.5	671	671	671	671	671			
203.0	644	644	644	644	644			
203.5	655	655	655	655	655			
204.0	622	622	622	622	622			

Table 5.1: Photoabsorption cross sections of CCl<sub>4</sub> at low temperatures.

Wavelength	Absorption cross section $\times 10^{-21}$ cm <sup>2</sup> at						
(nm)	300 K	280 K	260 K	240 K	220 K		
204.5	609	609	609	609	609		
205.0	608	608	608	608	608		
205.5	588	588	588	588	588		
206.0	578	578	578	578	578		
206.5	572	572	563	563	555		
207.0	561	561	556	555	523		
207.5	555	555	534	490	470		
208.0	511	511	488	465	444		
208.5	493	494	477	448	460		
209.0	492	489	458	440	430		
209.5	484	474	428	417	418		
210.0	470	468	428	401	395		
210.5	453	448	419	395	382		
211.0	435	419	395	395	382		
211.5	421	414	387	364	332		
212.0	399	398	369	350	328		
212.5	393	375	353	323	313		
213.0	376	371	339	327	293		
213.5	360	336	325	296	283		
214.0	355	324	308	295	277		
214.5	331	309	290	272	242		
215.0	310	289	278	247	239		
215.5	300	276	257	240	224		
216.0	280	262	245	214	214		
216.5	272	249	241	222	202		
217.0	252	234	224	192	176		
217.5	240	225	206	176	158		
218.0	233	213	199	170	151		
218.5	216	204	185	162	144		
219.0	208	188	174	144	134		
219.5	203	176	169	139	134		
220.0	192	167	154	131	121		
220.5	178	162	146	119	97.7		
221.0	167	146	135	119	97.9		
221.5	153	136	125	108	90.3		
222.0	140	126	115	99.3	78.9		
222.5	131	123	108	90.3	77.0		

Table 5.1: Contd.

Wavelength	Absorption cross section $\times 10^{-21}$ cm <sup>2</sup> at							
(nm)	300 K	280 K	260 K	240 K	220 K			
223.0	124	109	101	89.7	68.5			
223.5	116	103	93.9	86.7	-			
224.0	108	96.2	87.2	75.1	-			
224.5	102	91.0	79.6	74.1	CC1 -			
225.0	93.3	83.8	73.3	67.4	-			
225.5	85.1	78.8	66.5	63.5	-			
226.0	76.6	71.5	62.1	58.2	-			
226.5	74.8	64.5	58.5	54.1	-			
227.0	69.2	59.3	53.8	48.4	-			
227.5	64.1	57.2	50.7	45.2	-			
228.0	59.5	53.8	47.4	41.7	-			
228.5	54.8	47.5	44.9	36.4	-			
229.0	52.3	46.5	39.9	34.2	-			
229.5	45.2	40.5	36.5	30.4	-			
230.0	42.6	35.4	33.7	28.5				
230.5	38.2	33.9	31.3	24.6	1 2 8 -			
231.0	37.0	31.4	28.9	22.6				
231.5	35.0	30.6	26.8	21.4	-			
232.0	33.0	28.2	23.1	19.3	-			
232.5	31.2	26.0	21.6	17.0	-			
233.0	25.6	23.0	19.5	15.7	-			
233.5	23.0	21.9	17.5	13.8	-			
234.0	21.4	19.5	15.2	12.2	-			
234.5	19.3	17.4	13.2	11.6	- 01			
235.0	18.1	16.7	12.2	11.0	-			
235.5	17.7	15.4	th (nm)	-	-			
236.0	15.5	14.1	-	-	-			
236.5	14.4	13.2	-	-	-			
237.0	12.6	11.3	of carb	in Letriu	Maride"			
237.5	12.4	10.1	100 K -	-				
238.0	11.0	10.3	-	-	-			
238.5	10.7	9.76	-	-	-			
239.0	9.33	8.54	-	-	-			
239.5	9.38	8.38	-	-	-			
240.0	9.16	8.41	-	-	-			

Table 5.1: Contd.



Figure 5.2: Photoabsorption cross sections of carbon tetrachloride at temperatures ranging from 220 to 300 K at an interval of 20 K.

Figure 5.3: Photodoscr**ption cross sections of carbon tetrachlariste at tennesstare** ranging from 230 to 300 K at considereal of 20 K pa) for wardenoth region from 12 to 22stany (h) for wavelength course from 200 to 24d nos





Figure 5.3: Photoabsorption cross sections of carbon tetrachloride at temperatures ranging from 220 to 300 K at an interval of 20 K (a) for wavelength region from 190 to 220 nm; (b) for wavelength region from 210 to 240 nm.

The photoabsorption cross sections of  $CCl_4$  measured in the present work at lower temperatures and also at 300 K are shown in Figure.5.2. The cross sections are also presented in Table 5.1 at an interval of 0.5 nm. As shown in Figure.5.2, the photoabsorption cross sections decrease with decrease in temperature by a factor which depends on the molecular structure of the target gas and also the incident photon wavelength. To get a better picture, the photoabsorption cross sections measured in the present experiment are being shown in two parts in Figures 5.3(a) and 5.3(b) for the wavelength regions 190 to 220 nm and 210 to 240 nm respectively. As may be seen from Figures 5.3(a) and 5.3(b), the effect of temperature on the photoabsorption cross section is most significant for the wavelength regions where the absorption is low (210-240 nm).

For shorter wavelengths (186-200nm) where the photoabsorption is high, there is no effect of temperature observed on the photo absorption cross section. The percentage decrease in the value of photoabsorption cross section at the incident photon wavelength of 223 nm and at a temperature 220 K was found to be as large as 45% as compared to the cross section values measured at 300 K whereas a decrease of about 16% was observed at 210nm when the temperature of the target gas decreased from 300 to 220 K. The threshold wavelength for the onset of temperature dependence in photoabsorption cross sections for  $CCl_4$  was found to be 209nm at 280 K and 206.5 nm for 220, 240 and 260 K respectively. The observed features of the temperature dependence of photoabsorption of  $CCl_4$  may be qualitatively interpreted on the same lines as described in section 1.6 for the case of continuous photoabsorption.

The only other measurement of photoabsorption cross sections of  $CCl_4$  at different temperatures has been reported by Simon et al. (1988). They used two thermostatic stainless steel cells, one of 2m optical path length and the other of 13.5cm. The smaller cell (13.5) was used to study the spectral region where the absorption cross sections were high. They measured photo absorption cross sections of  $CCl_4$  at 295K (ambient) and from 270-210 K in steps of 20 K in the spectral region



Figure 5.4: Photoabsorption cross sections of carbon tetrachloride as a function of temperature for five different wavelengths 210,216,230 and 234 nm. The cross sections reported by Simon et al are also shown in the figure.

174-250nm. The comparison of their (Simon et al. (1988)) results with those obtained in the present experiment is in order. The threshold wavelengths showing temperature dependence were found to be 204, 206, 208 and 210 nm at the temperatures of 210, 230, 250 and 270 K respectively. There is practically not much difference in the threshold wavelengths reported in the two cases. The small difference observed may be attributed to the different temperatures used in the two experiments.

The photoabsorption cross sections measured in the present experiment at different temperatures have been compared with those reported by Simon et al (1988) at five different wavelengths only i.e. at 210, 216, 220, 230 and 234 nm. The cross section values at these wavelengths are plotted at different temperature and are shown in Figure 5.4. Best straight line fit has been obtained through these points using the least squares fit technique. The slopes of these straight lines i.e. rates of change of

P	Wavelength (nm)	slope= $\left(\frac{d\sigma}{dT}\right)_{\lambda}$ as calculated from Figure 5.4						
		Present work	Simon et al					
	210	0.77	0.63					
-	216	0.91	0.72					
	220	0.89	0.59					
10	230	0.22	0.24					
	234	0.16	0.13					

Table 5.2: Rate of change of photoabsorption cross section with temperature at fivedifferent wavelengths.

photoabsorption cross section with temperature, in the two cases have been obtained for all the five wavelengths and are compared in Table 5.2. In both the cases, the slope increases from 210 to 216 nm and then shows decrease as the wavelength increases. Quantitatively, the increase/decrease of rate of change of photoabsorption cross sections with temperature are similar in both the cases. But in the present case, these values are larger than those given by Simon et al except at a wavelength 230 nm. It is difficult to point out the exact reason for such a discrepancy. After going through the work of Simon et al (1988), it appears that they may not have carried out thermal transpiration corrections of measured pressure at different temperatures. It is known that they are using a much longer absorption path length in their experiment; this would mean that they are working at comparatively lower pressures. It has been discussed in Section (3.3) that the thermal transpiration corrections needed at lower temperatures are larger for lower pressures. The quantitative differences in the rate of change of cross section with temperature may be attributed to the reasons described above.

sponding to the same 31 to KL, with a bread maximum which includes the bands from Q to NN. This is followed by a decrease in cross sections up to KL bands. As increase in cross sections has been observed between the bands KL to G but a sharp decrease in cross sections has been noticed subsequently tests hands G to A (Figure 5.5). An absorption cross section of  $9.11 \times 10^{-14}$  cm<sup>2</sup> has been spensured at hand G.

## 5.2 Photoabsorption Cross Sections of SO<sub>2</sub> (280 - 320 nm)

The photoabsorption cross sections for sulphur dioxide have been measured in the spectral region from 280 to 320 nm at different temperatures varying from 220 to 300 K at an interval of 20 K. This spectral region is a part of the absorption system which extends from 250 to 340 nm.

#### 5.2.1 Cross Sections at 300 K

The photoabsorption cross sections for sulphur dioxide at 300 K are shown in Figure 5.5 as a function of incident photon wavelength varying from 280 to 320 nm. It consists of discrete bands superimposed on an apparent continuum. The discrete absorption system was identified with the transition  $\tilde{A}^1A_2 \leftarrow \tilde{X}^1A_1$  by Hamada and Merer (1975). The continuous absorption underlying the structured bands is attributed to the  $\tilde{B}^1B_1 \leftarrow \tilde{X}^1A_1$  transition predicted theoretically by Hillier and Saunders (1971). The different bands of this system have previously been assigned and labeled by Clements (1935). In the present work, the nomenclature followed for different bands is the same as reported by Ahmed and Kumar (1992) and Clements (1935). The peaks in Figures 5.5, 5.6(a) and 5.6(b) have been labeled from **A** to **ST** from 320 nm to shorter wavelengths.

The photoabsorption cross sections for  $SO_2$  measured in the present experiment at 300 K vary from  $8.28 \times 10^{-19}$  to  $7.76 \times 10^{-19}$  cm<sup>2</sup> at wavelengths corresponding to the bands **ST** to **KL**, with a broad maximum which includes the bands from **Q** to **NN'**. This is followed by a decrease in cross sections up to **KL** bands. An increase in cross sections has been observed between the bands **KL** to **G** but a sharp decrease in cross sections has been noticed subsequently from bands **G** to **A** (Figure 5.5). An absorption cross section of  $9.11 \times 10^{-19}$  cm<sup>2</sup> has been measured at band **G**,



Figure 5.5: Photoabsorption cross sections of Sulphur dioxide at 300 K in the wavelength region 280 - 320 nm.

whereas the cross section at band A is  $2.29 \times 10^{-19} \text{ cm}^2$ .

A comparison of photoabsorption cross section obtained in the present experiment has been made at the incident photon wavelengths corresponding to peak values of the bands from **A** to **ST** (Table 5.3). The quantitative absorption data have been reported by Ahmed and Kumar (1992), McGee and Burris (1987), Leroy et al (1983), Brassington (1981), Thompson et al (1963), Warneck et al (1964) , Wu(unpublished) and Thompson et al (1975) under different experimental conditions. The data from Wu are unpublished and have been obtained between 300 and 338 nm with an instrumental resolution of 0.06 nm. The measurements by McGee and Burris (1987) were carried out between 300 and 324 nm with 0.03 nm instrumental resolution. Brassington (1981) used a frequency-doubled dye-laser source to obtain cross sections at 0.05 nm spectral resolution between 290 and 317 nm. Similar measurements were made by Leroy et al at 292 K between 280 to 312 nm. It may be pointed out here that, most of the available spectrometric data on absorption cross sections of 50, from 105 to 403 are at 203 ±10 K have been compiled and evaluated by Manatt and Lanc (1991) and have been reported at the same instrumental resolution of 0.1 am for proper comparison. For the sake of simplicity, the cross sections obtained in the present work are being presented in Table 5.3 along with those reported by a few researchers only, viz. We (unpublished), Loroy et al (1963)

Table 5.3: Values of photoabsorption cross sections for  $SO_2$  at 300 K as measured by various researchers.

		Absorption cross section $\times 10^{-19}$ cm <sup>2</sup>							
Band	Wavelength	Present		Leroy		Mc Gee	Manatt		
assignment	(nm)	work	Wu	et al	Brassington	and	and		
						Burris	Lane		
A	313.1	2.29	2.56	-	2.68	2.72	2.61		
В	310.7	2.55	3.34	3.2	3.91	3.83	3.67		
C	308.6	4.19	4.44	-	5.90	5.63	5.24		
D	306.5	5.26	5.29	Warge	7.38	7.17	6.77		
E	304.2	7.60	6.77	-	10.00	7.93	8.30		
F	302.1	7.64	7.49	-	9.85	9.33	9.05		
G	300.0	9.11	9.18	9.4	13.00	11.50	11.43		
Н	298.0	8.46	-	-	11.00	-	10.13		
J	296.2	8.20	-	-	11.25	-	10.84		
KL	294.2	7.76	not -b	een gi-e	n in Table 5-1	, these -	9.83		
MM'	292.3	8.30	-		-	-	9.95		
NN'	290.6	9.65	LA OUI	9.4	rue buccur e	-	10.38		
0	288.8	9.38	-	-	-	-	10.82		
Р	286.7	9.25	-	-	-	-	10.75		
Q	285.0	9.67	0.01	(emp)	ratures .	-	10.76		
R	283.1	8.80	-	-	-	-	10.43		
ST	281.4	8.28		9.1		1.0 -	10.01		

atures ranging from 220 to 280 K at an interval of 20 K. For the sake of convenience, these cross sections are shown in two parts, Figures, 5.6(x) and 5.6(b) at three temperatures only i.e. 220, 260 and 360 K. In Figure 5.6(x) are shown the photosbeorption cross sections for SO<sub>2</sub> in the spectral region ranging from 280 to 303 and whereas cross sections from 298 to 321 and at the above three temperatures are shown in pointed out here that, most of the available spectrometric data on absorption cross sections of SO<sub>2</sub> from 106 to 403 nm at 293  $\pm 10$  K have been compiled and evaluated by Manatt and Lane (1993) and have been reported at the same instrumental resolution of 0.1 nm for proper comparison. For the sake of simplicity, the cross sections obtained in the present work are being presented in Table 5.3 along with those reported by a few researchers only, viz. Wu (unpublished), Leroy et al (1983) , Brassington (1981), McGee and Burris (1987) and Manatt and Lane (1993). The cross section values reported in the present experiment are broadly comparable with those reported by Wu(unpublished) and Leroy et al(1983) but the values given by Brassington (1981), McGee and Burris (1987) and Manatt and Lane (1993) have been found to be much larger. It has been found that the measurements carried out in the continuously flowing systems are broadly similar both qualitatively and quantitatively but the cross section data reported using closed cell experiments are much higher. It may be pointed out here that in the experiments carried out by Wu, Leroy et al (1983), Thompson et al (1975), Warneck et al (1964) and in the present experiment, continuously flowing systems were used whereas closed cell experiments were carried out by Brassington (1981), McGee and Burris (1987) and Thompson et al (1963). Even though the cross section values measured by Thompson (1963) et al and Warneck et al (1964) have not been given in Table 5.3, these seem to be comparable with the cross section data obtained in the present experiment.

#### 5.2.2 Cross Sections at Low Temperatures

Photoabsorption cross sections for  $SO_2$  have been measured at four different temperatures ranging from 220 to 280 K at an interval of 20 K. For the sake of convenience, these cross sections are shown in two parts, Figures. 5.6(a) and 5.6(b) at three temperatures only i.e. 220, 260 and 300 K. In Figure.5.6(a) are shown the photoabsorption cross sections for  $SO_2$  in the spectral region ranging from 280 to 303 nm whereas cross sections from 298 to 321 nm at the above three temperatures are shown in

Band	Wavelength	Absorp	Absorption cross section $\times 10^{-19}$ cm <sup>2</sup> at						
assignment	(nm)	300 K	280 K	260 K	240 K	220 K			
A	313.1	2.29	2.48	2.64	2.78	2.88			
B	310.7	2.55	2.74	2.90	3.04	3.14			
C	308.6	4.19	4.09	5.03	4.57	5.45			
D	306.5	5.26	5.35	6.74	6.76	7.63			
E	304.2	7.60	8.13	8.29	9.00	9.41			
F	302.1	7.64	8.12	8.70	9.30	9.21			
G	300.0	9.11	10.67	11.34	11.52	11.60			
Н	298.0	8.46	8.11	9.84	10.00	10.30			
J	296.2	8.20	8.86	9.41	9.65	9.91			
KL	294.2	7.76	7.61	8.73	8.75	9.01			
MM'	292.3	8.30	8.16	8.54	9.61	9.72			
NN'	290.6	9.65	9.55	9.33	9.66	10.36			
0	288.8	9.38	9.78	9.61	9.90	10.75			
P	286.7	9.25	9.50	9.42	9.52	10.50			
Q	285.0	9.67	9.69	9.61	9.68	9.80			
R	283.1	8.80	9.05	9.29	9.58	9.80			
ST	281.4	8.28	8.39	8.46	8.49	8.78			

Table 5.4: Values of photoabsorption cross section for SO<sub>2</sub> at different temperatures.

Figure.5.6(b). Also, the values of cross sections at the peaks of the bands have been given in Table 5.4.

As shown in Figures 5.6(a) and 5.6(b), the absorption cross sections at the peaks of different bands from ST to A have been found to be much higher at 220 K as compared to the values at 300 K. There does not emerge any definite pattern in the variation of cross sections at different temperatures when the cross sections values at 240, 260 and 280 K are also taken into account. There are three types of trends seen. In case of ST, R, J, G, F, E, B and A bands, there is an increasing trend noticed in the values of cross sections at all temperatures from 300 to 220 K. In the second case (bands Q, P, NN'), the cross section values remain more or less the same at temperatures from 300 to 240 K but increase drastically at 220 K. Thirdly, in case of all other remaining bands, the trend is entirely different and the change in cross section values between 300 to 240 K could be positive or negative followed by a definite increase at 220 K.



Wavelength (nm)

Figure 5.6: Photoabsorption cross sections of Sulphur dioxide at 220, 260 and 300 K (a) in the wavelength region 280 - 303 nm (b) in the wavelength region 298 - 321 nm.

The temperature dependence of photoabsorption cross sections of  $SO_2$  has been studied by a few researchers only. Leroy et al (1983) have made cross section measurements at the peaks of four bands only (281.5, 290.7, 300.0 and 310.6 nm) at the three different temperatures of 296, 263 and 218 K. McGee and Burris (1987) have made similar measurements in the wavelength region 300 to 324 nm at the two temperatures of 295 and 210 K only. It may not be easy to make an intercomparison at all wavelengths. That is why the temperature dependence studied by Leroy et al (1983) and McGee and Burris (1987) along with the measurement made in the present experiment is being shown in Figure.5.7 at the peak values of **ST** (281.4 nm), **G** (300.0 nm) and **B** (310.7 nm) bands only.

At 281.4 nm, the only other measurement as a function of temperature is that from Leroy et al (1983) besides the one carried out in the present experiment. In both the measurements, the decrease in cross sections with increase in temperature from 220 to 300 K follows a straight line fit. However, the slopes in the two cases are different; the slope as observed in the present experiment is -0.006 as compared to a value of -0.010 as reported by Leroy et al (1983). Similarly, at the wavelength of 310.7 nm, cross section decreases linearly with the increase in temperature in all the three experiments reported by the present authors, Leroy et al (1983) and McGee and Burris (1987) giving a slope of -0.007, -0.005 and -0.011 respectively. At the wavelength of 300.0 nm, the cross section values at different temperatures as observed in the present experiment and those reported by Leroy et al (1983) do not show a linear dependence. In the first case, the results could be fitted to a third degree polynomial whereas in the second case a line can be drawn giving a similar fit. However, it is difficult to discuss about the temperature dependence reported by McGee and Burris (1987) as measurements have been made only at two temperatures. At this wavelength (300.0 nm), the results obtained in the present experiment can be conveniently fitted to a third degree polynomial of the form  $\sigma =$  $a_0 + a_1T + a_2T^2 + a_3T^3$ , thereby giving the values of constants  $a_0 = 118.999$ ,  $a_1 =$ 



Figure 5.7: Photoabsorption cross sections of Sulphur dioxide at different temperatures for three different wavelengths 281.4, 300.0 and 310.7 nm. The cross sections reported by Leroy et al and Mc Gee and Burris are also shown in the figure.

-1.3664,  $a_2 = 0.0058$  and  $a_3 = -8.2292 \times 10^{-19}$ . However, as there are only three data points reported by Leroy et al , it becomes exceedingly difficult to get the values of the above constants,  $a_0, \ldots, a_3$ . The possible reasons of obtaining different slopes and different constants for fitting the third degree polynomial obtained in the different experiments are discussed below. It appears that the thermal transpiration corrections of the measured pressure at different temperatures have not been carried out in the experiments reported by Leroy et al (1983) and McGee and Burris (1987). It is known that lower the temperature, higher is the transpiration correction required at a given pressure. This has been discussed elsewhere in the text in detail. Also, the adsorption effects (on the quartz windows) which are highly temperature dependent have to be taken care of while doing such experiments as they lead to change in the value of  $I_0(\lambda)$  during the experiment. Corrections due to adsorption effects have also not been taken into account in the other two experiments.

It has already been pointed out that there does not emerge any definite pattern in the study of temperature dependence of photoabsorption cross sections at different wavelengths. It is very difficult to explain this fact quantitatively but a qualitative explanation is in order. It has been discussed in section 3.1 that the absorption system presently being studied consists of discrete bands ( $\tilde{A}^1A_2 \leftarrow \tilde{X}^1A_1$  transition) superimposed on an apparent continuum ( $\tilde{B}^1B_1 \leftarrow \tilde{X}^1A_1$  transition). In our experiment, we are studying the temperature dependence of photoabsorption cross sections of the whole band system which includes the contributions from both structured (discrete) as well as continuous absorption. It is well known that the cross sections at the peaks of the discrete bands increase with decrease in temperature in case of structured absorption whereas in case of continuous absorption, the cross section values decrease with decrease in temperature. The added effect of the two types of temperature dependence at different incident photon wavelengths would qualitatively explain the present results.

## 5.3 Photoabsorption Cross Sections of SO<sub>2</sub> (188-220 nm)

The photoabsorption cross sections for  $SO_2$  have been measured in the spectral region from 188 to 220 nm at different temperatures ranging from 300 to 220 K at an interval of 20 K. This spectral region is a part of the absorption system which extends from 188 to 231 nm. The results are discussed below.

#### 5.3.1 Cross Sections at 300 K

The photoabsorption cross sections for sulphur dioxide are shown in Figure 5.8 as a function of incident photon wavelength in the spectral region ranging from 188 to



Figure 5.8: Photoabsorption cross sections of Sulphur dioxide at 300 K in the wavelength region 188 - 220 nm.

220 nm.

Sulphur dioxide has a system of strong absorption bands beginning near 235 nm. This system was identified with the transition  $\tilde{B}^1B_1 \leftarrow \tilde{X}^1A_1$  by Hillier and Saunders (1971) and was further confirmed by Brand and Srikameswaran (1972) and Brand et al. (1976) from the rotational analyses for a few bands in this absorption system. Even though the assignment of the electronic transition of this system has never been in doubt, the assignment of the different bands of the system has never been straight forward. We have followed the same nomenclature for different bands as Ahmed and Kumar (1992) and Okabe (1971). The peaks in Figures 5.8, 5.9(a) and 5.9(b) have been numbered from 7 to 26 from 218.9 nm to shorter wavelengths.

The photoabsorption cross sections for  $SO_2$  measured in the present experiment at 300 K (Figure.5.8) show an increase in their values from  $5.49 \times 10^{-18}$  cm<sup>2</sup> at band 26 to  $11.77 \times 10^{-18}$  cm<sup>2</sup> at band 18 respectively with an exception of band 20

Table 5.5: Values of photoabsorption cross sections of  $SO_2$  at 300 K as measured by various researchers.

cens (1992) of	tained cross	Absorption cross section $\times 10^{-18}$ cm <sup>2</sup>							
Band	Wavelength	Present	Wu	Thompson	Martinez	Manatt			
Assignment	(nm)	work	&	et al	&	&			
te data svallate	e in literature	on abanta	Judge	s sections of	Joens	Lane			
26	188.7	5.49	-	-	-	7.7			
25	190.2	6.64	al_inted	p <u>⊻</u> Manattai	d_Lane (19	9.17			
24	191.9	6.81	-	= at 0.1 mm	Tenner	9.51			
23	193.0	8.24	-	8.82	-	11.69			
22	194.6	9.87	-	9.58	-	12.25			
21	195.9	11.4	- N	10.75	IL_WORK AD	15.17			
20	197.4	9.36	-	9.42	12	12.24			
19	199.0	11.72	-	12.4	15.5	15			
18	200.6	11.77	6 <u>2</u> ), Ma	11.4	15.3	10.69			
17	202.2	11.1	-	10.4	15.3	14.35			
16	203.6	11.6	-	10.7	15.8	14.97			
15	205.3	9.45	n4 Judg	10.0	12.3	12.5			
14	206.8	10.78	-	11.6	15.3	14.24			
13	208.3	7.87	8.05	7.68	10.2	10.25			
12	210.2	6.75	7.43	7.12	9.8	9.91			
11	211.7	6.8	6.63	6.29	8.9	8.81			
10	213.5	4.02	5.52	5.21	5.9	6.04			
9	215.2	3.4	4.77	4.65	6.15	6.01			
8	217.2	3.04	3.96	3.75	4.15	3.3			
7	218.8	2.9	12 close	2.6	3.5	3.7			

where the cross section peak value of  $9.36 \times 10^{-18} \text{ cm}^2$  is much lower than that at the band 21 ( $11.40 \times 10^{-18} \text{ cm}^2$ ). This, in general, is followed by a decrease in the cross sections values from  $11.60 \times 10^{-18} \text{ cm}^2$  at band 16 to  $2.90 \times 10^{-18} \text{ cm}^2$  at band 7. There is however an exception for the band 14 where the cross section is slightly larger than that for the adjoining band.

A comparison of photoabsorption cross sections obtained in the present experiment has been made at the incident photon wavelengths corresponding to peak values of the bands from 26 to 7 (Table 5.5). The quantitative absorption data have also been reported by Ahmed and Kumar (1992), Martinez and Joens (1992), Wu and Judge (1981), Warneck et al. (1964), Thompson et al. (1963) and Golomb et al. (1962). The measurements by Ahmed and Kumar (1992) were carried out at a spectral resolution of 0.2nm whereas Wu and Judge (1981) and Martinez and Joens (1992) obtained cross sections in the spectral regions 208-220 nm and 197-240 nm at the instrumental resolution of 0.06 nm and 0.1 nm respectively. Most of the data available in literature on absorption cross sections of SO<sub>2</sub> from 106 to 403 nm at 293 $\pm$  10 K have been compiled and evaluated by Manatt and Lane (1993) and have been reported at the same instrumental resolution of 0.1 nm for proper comparison.

The cross sections obtained at 300 K in the present work are being presented in Table 5.5 along with the values reported by a few researchers, viz. Wu and Judge (1981), Thompson et al. (1963), Martinez and Joens (1992) and Manatt and Lane (1993). The cross section values reported in the present experiment are broadly comparable with those of Wu and Judge (1981) and Thompson et al. (1963) but the values given by Martinaez and Joens (1992) and Manatt and Lane (1993) have been found to be much larger. It is not possible to explain this discrepancy in an explicit way but it has been found that the measurements carried out in the continuously flowing systems are broadly similar both qualitatively and quantitatively, but the cross section data reported using closed cell experiments are much higher. It may be pointed out here that continuously flowing systems were used by Wu and Judge (1981), Thompson et al. (1963) and in the present work whereas Martinez and Joens (1992) used closed cells to carry out the experiments.

#### 5.3.2 Cross Sections at Low Temperatures

Photoabsorption cross sections for  $SO_2$  have been measured at four different temperatures ranging from 220 to 280 K at an interval of 20 K. For the sake of convenience, these cross sections are shown in parts. In Figure 5.9(a) are shown the cross sections for  $SO_2$  in the spectral region ranging from 188-206 nm at 220, 260 and 300 K whereas cross sections from 204-220nm at the above three temperatures are shown in Figure 5.9(b). Also the values of cross sections at the peaks of the bands have been given in Table 5.6. The absorption cross sections at almost all the peaks of the bands from 26 to 16 have been found to decrease when the temperature decreased to 280 K but the cross section values have been found to increase with decrease of temperature from 280 to 220 K. But in case of bands from 17 to 10 the cross section values broadly exhibit a consistent increase with a decrease in temperature from 300 to 220 K. For bands 9,8 and 7, the trend is not similar to what has been obtained in other cases. The trend is completely inconsistent and the cross sections did not get affected by a decrease in temperature from 300 to 280 K but showed a random increase or decrease in cross section values with a decrease in temperature from 280 to 220 K.

The photoabsorption cross sections of sulphur dioxide are plotted as a function of temperature at three incident photon wavelengths corresponding to the peaks of the bands 25 (190.2 nm), 14 (206.8 nm) and 9 (215.2 nm). The results are shown in Figure 5.10. Best straight line fit has been obtained through these points using the least squares fit technique. The slopes of these straight lines i.e the rates of change of photoabsorption cross section with temperature were found to be -0.015 and -0.036 for the wavelengths 190.2 nm and 206.8 nm respectively. The negative sign for the slopes indicates that the cross sections show an increasing trend with decrease in temperature for these wavelengths. For the wavelength 215.2 nm, the slope was found to be zero indicating that the change in cross section with temperature could not be observed. It may be pointed out here that the temperature dependence could not be observed for the adjoining bands 8 and 7 also. The reason for not observing any such dependence for the above three absorption bands may be attributed to the poor signal-to-noise ratio prevailing in this wavelength region where the absorption cross section values are rather small. There are no other measurements of photoabsorption cross sections of SO<sub>2</sub> reported at low temperatures in the spectral region (188 - 220 nm). Hence a comparison of the results obtained in the present work for this spectral region was not possible.



Figure 5.9: Photoabsorption cross sections of Sulphur dioxide at 220, 260 and 300 K (a) in the wavelength region 188 - 206 nm (b) in the wavelength region 204 - 220 nm.



Figure 5.10: Photoabsorption cross sections of Sulphur dioxide as a function of temperature at different wavelengths 190.2, 206.8 and 215.2 nm.

The temperature dependence of photoabsorption observed in this spectral region may be qualitatively explained as follows. SO, has structured absorption the temperature dependence of photoabsorption for structured absorption has already been discussed in Section 1.6. The increase in the peak values of the absorption bands with a decrease in temperature may be attributed to the decrease in the manber of molecules in the higher vibrational levels of the ground electronic state and the

10	Band	Wavelength	Absorp	Absorption cross section $\times 10^{-18}$ c					
	assignment	(nm)	300 K	280 K	260 K	240 K	220 K		
	26	188.70	5.49	4.46	6.08	6.38	6.89		
tor	25	190.20	6.64	5.72	6.44	6.99	7.55		
-	24	191.90	6.81	6.07	7.86	8.21	8.87		
	23	193.00	8.24	8.48	8.82	9.14	9.47		
	22	194.60	9.87	7.98	10.24	10.72	11.58		
	21	195.90	11.40	11.61	11.54	12.00	12.96		
e el	20	197.40	9.36	8.92	8.51	9.44	10.20		
	19	199.00	11.72	11.30	11.29	14.34	15.49		
1151	18	200.60	11.77	10.68	11.58	13.07	13.73		
	17	202.20	11.10	11.74	13.35	12.87	13.52		
	16	203.60	11.60	11.48	11.23	12.87	13.51		
	15	205.30	9.45	9.82	11.05	10.94	11.48		
	14	206.80	10.78	10.53	12.41	12.69	13.32		
	13	208.30	7.87	7.71	9.13	9.42	9.89		
1 1	12	210.20	6.75	7.01	8.98	8.44	8.86		
	11	211.70	6.80	7.52	8.41	9.02	9.47		
	10	213.50	4.02	4.20	4.42	5.37	5.69		
	9	215.20	3.40	3.40	2.88	3.21	3.37		
	8	217.21	2.04	2.04	2.38	2.19	2.38		
	7	218.80	2.90	2.90	2.78	2.39	2.51		

Table 5.6: Values of photoabsorption cross section of SO<sub>2</sub> at different temperatures.

The temperature dependence of photoabsorption observed in this spectral region may be qualitatively explained as follows.  $SO_2$  has structured absorption; the temperature dependence of photoabsorption for structured absorption has already been discussed in Section 1.6. The increase in the peak values of the absorption bands with a decrease in temperature may be attributed to the decrease in the number of molecules in the higher vibrational levels of the ground electronic state and the cooling of hot bands. The cooling of hot bands contribute to the sharpening of the absorption bands which has been observed in the present experiment (see Figures 5.9(a) and 5.9(b)). The fact that there is no definite pattern in the temperature dependence of all the observed bands in the spectrum may be attributed to the Franck-Condon factors which are different for each of the vibrational levels participating in the vibrational transitions in the given electronic transition.

The photoabsorption cross sections for  $SO_2$  obtained in the present experiment are given in Tables 5.7 and 5.8 at different temperatures and at an interval of 0.1 nm. It may be pointed out here that the cross section values already reported in Table 5.4 and 5.6 are only at the peaks of the absorption bands in the two spectral regions and not at all other incident photon wavelengths. That is why, it was it was necessary to report the cross section values in Tables 5.7 & 5.8 at all wavelengths at an interval of 0.1 nm. This would possibly make the picture complete.

Table 5.7: Photoabsorption cross sections for  $SO_2$  at different temperatures in the

Wavelength	Absort	otion cros	s section	×10-18	cm <sup>2</sup> at	Wavelength	Absorp	tion cros	s section	$\times 10^{-18}$	cm <sup>2</sup> at
(nm)	300 K	280 K	260 K	240K	220 K	(nm)	300 K	280 K	260 K	240 K	220 K
188.10	2.06	2.22	4.00	2.67	2.89	193.27	6.14	4.22	6.13	7.66	7.87
188.19	2.63	2.34	3.81	3.90	4.21	193.36	5.13	3.53	5.23	6.99	7.35
188.28	3.08	2.98	4.47	4.11	4.44	193.45	3.79	3.00	4.45	5.46	5.90
188.37	2.86	3.00	3.86	3.24	3.50	193.54	4.17	2.53	3.68	6.17	6.58
188.46	2.65	1.82	3.68	3.36	3.62	193.63	4.51	3.01	4.16	6.96	7.28
188.55	2.87	1.86	4.13	4.76	5.14	193.72	4.03	2.61	3.95	5.84	5.97
188.64	4.70	3.57	5.63	6.02	6.49	193.81	3.59	1.96	2.83	4.84	4.48
188.73	5.40	4.33	5.60	6.29	6.79	193.91	3.36	2.58	3.75	4.63	4.99
188.82	4.26	4.33	5.17	6.31	6.82	194.00	3.81	2.75	3.83	4.88	5.28
188.91	4.33	3.85	6.39	5.99	6.46	194.09	5.09	3.72	5.00	5.38	5.81
189.00	3.81	4.35	5.84	5.61	6.06	194.18	6.12	4.86	7.01	7.84	8.47
189.09	3.98	3.54	5.01	5.18	5.59	194.27	5.74	3.27	5.62	7.17	7.75
189.18	3.82	3.66	4.86	5.43	5.86	194.36	4.83	3.11	4.63	5.38	5.81
189.27	3.46	3.48	5.24	5.23	5.65	194.45	6.33	4.37	6.87	6.13	6.62
189.36	4.09	3.63	4.87	4.89	5.28	194.54	8.97	6.98	9.62	9.37	10.13
189.45	2.93	2.65	4.82	4.44	4.79	194.63	9.65	7.96	9.91	10.39	11.22
189.54	3.14	4.23	3.70	3.46	3.74	194.72	7.39	6.40	7.31	8.48	9.16
189.63	3.46	4.06	6.03	5.98	6.46	194.81	5.89	4.28	5.64	6.42	6.93
189.72	4.09	3.06	5.04	6.00	6.48	194.90	4.81	3.33	4.66	5.18	5.59
189.81	2.64	2.57	4.02	4.54	4.90	194.99	4.21	3.47	3.76	4.68	5.06
189.90	1.59	2.43	4.81	4.19	4.53	195.08	4.12	2.93	3.79	3.41	3.68
189.99	3.09	4.42	4.66	4.06	4.39	195.17	4.50	2.80	3.28	4.17	4.50
190.08	4.74	4.05	6.02	4.88	5.27	195.26	4.29	3.16	2.76	4.09	4.42
190.17	6.39	5.51	6.28	6.83	7.38	195.35	4.10	2.37	3.11	3.66	3.95
190.26	6.19	5.42	6.06	6.33	6.84	195.44	3.90	2.53	2.79	3.54	3.94
190.35	5.37	4.82	5.30	5.39	5.82	195.53	2.93	2.54	2.49	2.54	3.12
190.44	4.57	3.81	4.71	4.56	4.93	195.63	3.54	3.25	2.87	3.44	3.72
190.53	3.61	3.52	4.53	4.11	4.44	195.72	5.97	6.13	5.93	4.69	5.06
190.62	3.22	3.10	3.77	3.78	4.09	195.81	9.13	10.20	9.78	8.57	9.26
190.71	2.64	2.59	4.09	3.86	4.17	195.90	11.40	11.61	11.54	12.00	12.96
190.80	3.00	3.12	3.80	4.22	4.55	195.99	9.69	10.63	10.39	10.08	10.89
190.89	3.16	2.72	3.50	3.74	4.04	196.08	8.75	9.40	9.53	9.05	9.78
190.98	2.34	2.14	3.30	3.10	3.34	196.17	7.53	7.97	8.24	9.21	9.94
191.07	2.24	2.18	3.00	3.39	3.66	196.26	6.04	7.67	7.08	8.72	9.41
191.30	2.47	2.27	3.44	4.55	4.91	196.35	5.02	6.37	5.32	7.82	8.45
191.39	2.80	2.19	4.60	5.08	5.48	196.44	4.96	5.32	3.61	6.74	7.28
191.48	4.15	3.25	5.23	6.64	7.17	196.53	4.73	3.80	2.63	6.07	6.56
191.57	5.21	3.76	6.16	6.43	6.94	196.62	3.75	3.79	2.74	5.04	5.44
191.66	3.92	4.94	6.00	4.22	4.56	196.71	3.87	3.94	3.70	4.43	4.78
191.75	4.82	5.11	6.31	6.09	6.58	196.80	3.37	3.91	3.69	4.98	5.38
191.84	6.59	5.20	7.46	7.82	8.45	196.89	4.05	3.61	3.40	4.76	5.14
191.93	6.67	5.99	7.70	8.17	8.83	196.98	3.58	2.25	3.13	3.80	3.41
192.02	5.77	5.76	5.90	6.95	7.50	197.07	3.66	3.90	3.10	3.40	3.67
192.11	4.29	5.02	5.28	5.87	6.34	197.16	5.37	6.30	5.47	5.69	6.15
192.20	3.85	2.84	3.62	5.22	6.03	197.25	6.87	6.74	6.38	7.45	8.04
192.29	2.85	3.00	4.28	4.50	5.42	197.34	9.02	8.43	7.99	8.31	8.97
192.37	4.82	3.75	5.27	5.26	5.68	197.43	9.28	8.51	8.46	9.38	10.13
192.46	5.08	3.83	4.97	5.24	5.65	197.52	7.25	6.53	7.51	6.93	7.49
192.55	4.30	2.79	4.08	5.33	5.76	197.61	6.54	5.40	5.70	6.22	6.71
192.64	2.05	1.46	2.20	3.88	4.19	197.70	5.77	4.89	5.57	5.64	6.09
192.73	1.92	1.98	2.06	2.14	2.21	197.79	5.86	3.79	4.48	4.83	5.22
192.82	0.36	0.55	0.81	7.06	1.32	197.88	4.66	3.11	3.08	4.09	4.42
192.91	7.64	1.87	8.17	8.48	8.78	197.97	4.03	2.95	2.42	3.27	3.54
193.00	8.24	8.48	8.82	9.14	9.47	198.06	3.08	2.92	2.07	3.22	3.48
193.09	6.96	1.17	1.45	1.73	8.00	198.15	3.16	2.39	2.51	3.29	3.55
130.10	0.97	4 14	0.78	0.00	1.1/	130 74	1 44	/ 111	1 AU	/	1 44

wavelength region 186 - 220 nm.
	1 6.00	100	1. 1. 00	Tab	10 0.1.	Conta.			1 2 30	10-18	2 .
Wavelength	Absorp	tion cros	s section	×10 <sup>-18</sup>	cm <sup>2</sup> at	Wavelength	Absorp	tion cros	s section	×10-10	cm* at
(nm)	300 K	280 K	260 K	240 K	220 K	(nm)	300 K	280 K	260 K	240 K	220K
198.33	1.58	2.08	1.54	1.42	1.54	203.57	10.74	10.44	12.42	12.38	13.00
198.42	1.45	2.35	1.42	1.57	1.52	203.66	10.76	9.17	9.28	10.32	10.84
198.52	1.94	2.26	1.24	1.42	1.54	203.75	8.65	7.18	8.62	8.48	8.90
198.61	3.95	2.76	1.10	4.89	5.28	203.84	7.47	6.67	7.54	7.28	7.65
198.70	5.87	5.12	3.68	6.94	7.50	203.93	6.18	5.72	6.68	6.14	0.45
198.79	6.41	5.62	4.99	6.97	7.53	204.02	5,30	5.53	4.99	6.03	0.33
198.88	9.23	7.22	6.71	11.51	12.44	204.11	4.54	4.12	3.82	4.97	3.21
198.97	11.61	10.77	10.80	14.31	15.45	204.20	4.21	3.28	3.03	3.74	3.94
199.06	11.00	10.71	9.89	13.04	14.08	204.29	2.99	2.79	2.36	2.14	2.00
199.15	8.97	8.74	7.04	9.67	10.45	204.38	2.41	2.31	1.97	2.40	2.09
199.24	7.27	6.57	5.66	7.23	7.82	204.47	1.89	1.44	2.19	2.33	2.00
199.33	5.39	5.11	3.87	6.20	6.69	204.56	2.31	2.05	2.19	2.00	0.00
199.42	4.75	4.11	3.39	4.98	5.38	204.65	1.89	1.91	2.09	2.24	1.30
199.51	5.32	3.46	3.58	5.09	5.50	204.73	1.23	1.21	2.05	1.07	1.75
199.60	5.11	3.22	3.35	5.00	5.40	204.82	1.25	1.59	1.67	2.08	2.10
199.69	4.80	3.20	3.04	4.18	4.51	204.91	2.54	2.01	2.30	5.43	5.70
199.78	3.87	2.05	2.43	3.08	3.26	205.00	5.61	4.60	0.43	7.51	7.00
199.87	3.01	2.01	1.59	2.17	2.28	205.09	6.46	5.69	7.86	7.48	1.80
199.96	2.85	1.88	1.60	1.38	1.44	205.18	7.20	6.66	7.67	8.73	9.17
200.05	1.10	1.09	1.60	1.70	1.78	205.27	9.21	9.45	10.62	10.69	11.22
200.14	1.11	1.14	1.67	2.00	2.09	205.36	9.16	9.40	9.75	10.02	10.52
200.24	2.84	1.65	1.74	1.38	1.68	205.45	7.81	7.19	7.68	7.28	7.64
200.33	2.65	1.58	1.47	1.60	1.68	205.54	5.95	4.62	6.66	5.28	5.55
200.42	4.81	3.86	3.28	2.25	2.35	205.63	4.56	3.30	4.67	4.26	4.48
200.51	10.22	9.21 '	9.39	9.58	10.06	205.72	3.86	3.18	3.76	3.61	3.79
200.60	11.77	10.68	11.58	13.07	13.73	205.81	3.11	2.16	3.62	2.42	2.54
200.69	10.40	8.76	9.64	11.16	11.71	205.90	2.66	1.58	3.09	2.65	2.78
200.78	8.49	7.32	7.18	8.99	9.44	205.99	2.96	1.70	2.82	2.56	2.69
200.87	8.16	6.66	6.53	8.50	8.92	206.08	2.30	1.83	2.20	2.10	2.21
200.96	7.84	5.21	6.82	7.17	7.53	206.17	1.98	1.40	2.10	1.93	2.03
201.05	2.87	3.69	4.66	6.50	6.82	206.26	1.42	1.50	2.20	1.82	1.91
201.14	3.83	3.55	4.02	4.00	4.16	206.35	1.24	1.16	1.58	1.63	1.71
201.23	3.08	3.44	3.32	3.63	3.81	206.44	.74	1.13	1.39	1.47	1.55
201.32	2.84	2.95	3.07	3.00	3.16	206.53	1.18	1.34	2.47	1.71	1.80
201.41	2.60	1.26	3.35	2.98	3.13	206.62	.99	3.74	5.92	4.85	5.10
201.50	1.87	1.77	2.60	2.21	2.32	206.71	7.29	8.77	10.78	9.08	9.54
201.72	1.52	1.95	2.89	2.18	2.29	206.80	10.78	10.53	12.41	12.69	13.32
201.81	3.87	3.94	6.00	5.40	5.67	206.89	9.65	8.57	10.99	9.60	9.63
201.90	5.99	6.71	7.30	7.48	7.86	206.98	7.64	6.41	9.20	8.37	8.74
201.99	5.45	6.48	6.70	6.82	7.16	207.07	5.83	4.52	8.13	7.17	7.53
202.08	7.35	7.16	7.97	7.96	8.36	207.16	5.17	3.64	6.21	5.88	6.17
202.17	10.75	11.27	12.91	12.30	12.92	207.25	4.49	2.77	4.68	4.88	5.12
202.26	9.95	11.40	12.23	12.12	12.73	207.34	3.50	2.88	3.60	3.72	3.91
202.35	7.14	9.09	8.90	9.19	9.65	207.43	2.95	2.00	3.44	3.18	3.34
202.44	5.81	6.81	6.98	7.26	7.63	207.52	2.46	1.31	2.51	2.87	3.01
202.53	4.77	5.52	5.72	5.67	5.96	207.61	1.90	1.09	1.81	2.08	2.18
202.62	4.21	4.41	4.55	4.75	4.98	207.70	1.69	.65	1.94	1.60	1.68
202.71	3.70	3.74	3.55	3.90	4.09	207.82	1.62	.37	.92	1.03	1.08
202.80	3.37	3.17	3.56	3.59	3.77	207.91	.09	.02	1.14	.66	1.35
202.89	2.80	2.51	3.60	3.55	3.72	208.00	.92	.06	1.30	.83	.87
202.98	1.83	2.33	2.95	2.62	2.75	208.09	.49	2.25	1.88	2.59	2.72
203.12	1.29	1.54	1.96	2.17	2.28	208.18	4.25	6.25	6.36	6.75	7.09
203.21	1.31	1.51	1.70	1.52	1.60	208.27	7.76	7.66	9.01	9.34	9.80
203.30	1.27	1.40	1.56	1.96	2.06	208.36	7.61	7.11	8.95	8.90	9.35
203.39	1.20	1.10	2.53	1.04	1.09	208.45	6.64	5.74	7.82	7.41	7.78
203.48	4.58	2.53	9.27	4.72	4.96	208.54	6.16	5.41	7.47	7.37	7.73

Table 5.7: Contd.

				Tab	10 0.1.	Conta.				10=18	2 .
Wavelength	Absorp	tion cros	s section	×10-10	cm <sup>4</sup> at	Wavelength	Absorp	tion cros	s section	×10-10	cm* at
(nm)	300 K	280K	200K	240K	2201	(nm)	300 K	2001	2001	2401	4.03
208.63	5.73	5.07	6.06	6.90	1.24	213.98	2.20	2.50	2.90	3.04	3.02
208.72	5.22	3.87	5.98	5.72	0.01	214.07	2.00	1.51	3.11	3.14	3.52
208.81	3.96	2.84	4.87	4.82	5.07	214.10	2.00	1.01	3.50	2.44	2.56
208.90	3.05	2.25	3.66	3.05	3.20	214.25	1.51	1.82	2.04	2.44	2.30
208.99	2.47	1.62	2.58	2.11	2.22	214.34	1.82	1.77	2.13	2.30	2.41
209.08	2.44	1.30	1.95	2.14	2.25	214.43	1.77	1.76	1.95	2.18	2.40
209.17	1.92	1.21	1.77	1.79	1.88	214.51	1.61	1.61	1.60	2.49	2.50
209.26	1.93	.73	2.06	1.37	1.43	214.60	1.23	1.23	1.13	2.25	2.36
209.35	1.44	.79	1.71	1.38	1.45	214.69	1.18	1.17	1.41	1.74	1.82
209.44	.73	.64	1.48	.70	.74	214.78	1.04	1.04	1.73	1.86	1.95
209.53	.96	.50	.94	.33	.34	214.87	1.36	1.39	2.37	2.28	2.39
209.63	.91	.49	.60	.42	.52	214.96	2.52	2.51	3.01	2.66	2.80
209.72	.54	.36	.39	.61	.63	215.05 4	3.35	3.35	3.75	2.97	3.11
209.81	.29	.33	.72	1.79	1.89	215.14	3.11	3.11	3.35	3.16	3.32
209.90	3.75	2.59	1.32	4.12	4.32	215.23	3.25	3.25	2.10	3.20	3.36
209.99	6.04	3.62	5.13	5.66	5.94	215.32	1.50	1.50	1.63	3.06	3.21
210.08	6.34	5.27	6.48	7.19	7.55	215.41	1.31	1.31	1.76	2.70	2.83
210.17	6.65	7.00	8.83	8.31	8.72	215.50	1.49	1.49	1.80	2.08	2.18
210.26	6.53	6.63	8.39	8.07	8.47	215.60	1.11	1.11	1.56	1.09	1.14
210.35	5.13	5.69	6.51	6.20	6.51	215.69	.93	.93	.77	1.11	1.17
210.44	4.16	4.12	5.51	4.79	5.03	215.77	.65	.65	.86	1.26	1.32
210.53	3.42	3.06	4.42	4.07	4.27	216.09	.61	.61	.65	.64	.67
210.62	2.87	3.29	3.80	3.70	3.89	216.18	.56	.56	.38	.64	.50
210.71	2.67	3.46	2.94	3.96	4.21	216.28	.47	.47	.37	.25	.26
210.80	2.42	2.57	2.79	4.23	4.44	216.36	.15	.15	.47	.08	.05
210.89	2.08	2.22	3.12	3.47	3.65	216.46	.55	.55	.43	.19	.18
210.98	1.69	2.00	2.71	3.53	3.70	216.55	28	28	42	34	31
211.07	1 20	1 44	2 50	3 15	3 30	216.63	03	03	41	62	41
211.16	86	66	2.19	2 92	3.06	216 72	18	18	77	76	68
211.25	55	31	214	2.30	2.42	216.81	1 49	1 49	1.58	1.04	95
211.34	47	57	1 49	1.92	2.02	216.91	2.65	2.65	3.21	2 23	2 35
211.43	43	85	1.40	1.84	1.02	217.00	3.07	3.07	3.43	3.22	3 38
211 52	2.06	1 38	2 71	2.25	2.37	217.08	2.76	2.76	3.11	2.22	2.50
211.61	5 59	5 36	7.23	5.80	6.00	217.08	2.08	2.08	2.52	2.20	2.00
211.70	6.80	7 52	8 41	9.02	9.47	217.16	1.00	1.00	2.02	2.14	2.20
211 79	5.78	7 29	7.27	8 31	8 72	217.20	1.07	1.07	1.44	1 30	1 33
211 88	4.64	5 77	5.66	6.58	6.01	217.50	1.07	1.07	1.44	1.00	1.00
211.00	3.63	4 30	4.80	5.76	6.05	217.45	.50	.50	.44	1.02	1.55 OF
212.06	3.36	3.51	4.00	5.06	5 31	217.55	.01	.01	.00	.49	.00
212.00	2.30	3.01	4.40	1.00	1.01	217.03	.03	.03	.21	.00	.90
212.15	2.14	2.46	3.14	3.04	4.23	217.71	.10	.15	./1	,31	.52
212.24	2.40	2.40	2.09	3.94	9.14	217.01	.02	.02	.10	.05	.04
212.33	1.00	2.02	2.90	3.44	3.39	217.09	.09	.39	.07	.22	.09
212.42	1.99	2.03	3.40	3.01	3.19	217.98	.43	.23	.50	.12	.03
212.01	1.99	2.02	0.04	0.70	3.75	210.00	.00	.00	.43	.00	.00
212.60	1.80	1.49	2.25	2.70	2.89	218.17	.30	.30	.75	.10	.17
212.69	1.08	1.09	2.09	2.32	2.44	218.26	.29	.29	.38	.15	.16
212.78	1.09	.62	1.66	2.44	2.56	218.34	.30	.30	.62	.21	.22
212.87	.89	.67	1.35	2.03	2.13	218.43	.10	.10	.60	.44	.46
212.96	.22	.84	1.09	1.75	1.84	218.53	.16	.16	.51	.75	.78
213.08	.36	1.18	1.13	1.42	1.49	218.61	.88	.88	1.23	1.04	1.09
213.17	.98	1.43	1.27	2.79	2.94	218.71	2.26	2.26	1.65	1.61	1.69
213.26	2.90	2.61	3.33	3.84	4.08	218.80	2.90	2.90	2.78	2.39	2.51
213.35	3.38	3.41	3.42	4.43	4.70	218.88	2.22	2.22	2.36	2.45	2.57
213.44	3.93	3.97	4.02	5.08	5.39	218.97	1.63	1.63	1.41	1.63	1.72
213.53	3.99	4.15	4.14	5.27	5.58	219.06	1.40	1.40	1.11	.72	.76
213.62	3.79	3.42	3.01	4.38	5.32	219.16	.82	.82	.94	.62	.65
213.71	3.13	2.53	2.68	4.30	4.51	219.25	.86	.86	.74	.40	.43
213.80	2.24	1.56	3.60	3.62	3.79	219.33	.67	.67	.37	.37	.40
213.89	1.75	2.33	2.91	3.25	3.42	219.43	.60	.60	,20	.22	.22
213.98	2.20	2.56	2.90	3.84	4.03	219.51	.65	.65	.80	.78	.77

Table 5.7: Contd.

#### Table 5.8: Photoabsorption cross sections for $SO_2$ at different temperatures in the

Wavelength	Abeam	tion cros	e section	×10-19	cm2 at	Wave	length [	Absor	tion cro	es section	×10-19	cm <sup>2</sup> at
(nm)	300 K	280 K	260 K	240K	220 K	(n	m)	300 K	280 K	260 K	240 K	220 K
280.68	6.34	6.43	7.00	7.00	7.35	285	5.25	7.86	8.71	8.57	8.16	9.15
280.00	6.86	6.26	7.13	7.55	7.86	285	33	7.10	8 16	8.57	7.21	8 59
280.85	6.07	6.73	7.13	7.52	7.28	285	5.42	7.01	8.25	8.17	7.06	7.95
280.93	6.67	7 31	7 78	7 43	7.08	285	50	7 36	7 32	8.04	7.93	8 48
281.02	6.89	713	7 91	7.62	7 20	285	58	7.80	7 35	7.85	7 45	7 91
281.02	7 16	7.49	7.65	7.69	7.80	200	.00	6.90	7 25	7.00	7 45	7.01
201.10	7.08	8.02	7 79	7.40	7 52	200	05	7.26	7 20	7.50	7.40	7.01
201.10	7 72	8.02	8 44	7.70	9.42	200	2.02	7.50	7.50	7 30	7.49	7.40
281 35	8.08	8 21	8 30	8 47	8 55	286	3 1 2	6.05	7.00	7 32	7 43	7.50
281.00	8.00	8 30	8.46	8.40	9.79	200	2 20	6.47	7.10	6.90	7.45	6.72
281 51	7 72	8 35	8 36	7.96	8.64	200	2.28	6.32	6.22	6.80	6.75	0.15
281.60	8.08	8.31	8.26	8.51	8 34	286	37	6.32	6.73	6.74	7.03	8 03
281.68	8 18	8.41	8 40	8.94	8.04	200	2 45	6.34	6.13	7 10	0.00	0.55
281.00	8 28	8.95	8.96	8.09	0.94	200	5.40	7 20	7 21	7.19	9.02	9.04
281.85	8 16	7 55	8.30	8 12	8 10	200	62	9.46	7.51	1.00	9.10	9.00
201.00	7 49	7.65	7.57	7 79	0.19	200	2 70	0.40	1.19	0.03	9.24	10.08
281.33	7 12	7.03	7.04	7.14	7.55	200	70	9.20	9.50	9.42	9.52	10.50
202.02	6 54	6.07	7.04	7.02	7.10	200	0.10	9.15	9.32	9.22	0.09	10.00
202.10	0.54	0.0/	1.04	1.03	7.03	280	0.87	9.04	9.23	9.16	9.22	10.03
202.10	0.30	0.14	0.72	0.33	1.12	280	0.95	8.54	8.70	9.03	8.99	9.96
282.27	6.31 C.OF	0.48	6.39	5.97	0.43	287	.03	8.80	8.47	9.03	8.33	8.74
282.35	0.05	0.51	0.05	6.04	0.04	287	.12	8.14	8.59	9.22	8.78	8.94
282.43	5.95	6.59	6.26	5.88	6.22	287	.20	7.58	7.68	8.44	8.69	8.76
282.52	5.54	6.02	6.52	5.72	6.43	287	.28	7.68	7.52	8.17	8.38	8.89
282.60	5.76	5.95	6.00	5.52	6.07	287	.37	7.80	7.93	8.76	7.65	8.78
282.68	5.28	6.08	5.67	5.50	5.10	287	.45	7.61	7.91	8.76	7.78	7.74
282.77	5.60	5.80	5.80	5.43	4.64	287	.53	7.13	7.53	8.31	7.63	7.91
282.85	5.99	6.67	6.61	5.66	6.98	287	.62	6.67	7.04	8.17	8.16	8.18
282.93	7.78	8.64	7.85	7.45	9.15	287	.63	6.67	7.04	8.17	8.36	8.48
283.02	8.63	8.87	8.96	9.07	9.59	287	.72	6.43	6.71	7.91	8.16	8.18
283.10	8.80	9.05	9.29	9.58	9.80	287	.80	6.63	6.86	7.46	8.26	8.38
283.18	8.11	8.67	9.03	9.01	9.28	287	.88	6.22	6.63	7.85	8.16	8.18
283.27	8.30	8.45	9.03	8.74	8.90	287	.97	6.96	6.43	7.32	6.98	7.35
283.35	7.59	7.75	9.03	7.73	8.59	288	.05	7.08	6.27	7.65	7.72	7.87
283.43	7.44	7.86	8.37	7.81	8.14	288	.13	6.79	6.19	7.59	7.38	7.73
283.52	7.30	7.93	8.50	7.61	7.58	288	.22	6.52	6.62	7.32	7.48	7.04
283.60	6.88	7.47	8.04	6.19	7.11	288	.30	6.81	6.67	7.13	7.78	7.04
283.68	6.80	7.57	7.85	6.75	6.69	288	.38	7.10	6.91	7.46	7.31	7.76
283.77	6.82	7.03	7.52	6.76	7.07	288	.47	7.75	7.83	7.78	7.75	8.18
283.85	6.42	6.41	7.72	5.98	6.41	288	.55	7.45	8.53	7.59	7.23	8.73
283.93	6.19	6.77	7.32	5.96	6.03	288	.63	8.72	9.41	8.83	8.64	9.10
284.02	5.87	6.77	7.13	5.52	6.54	288	.72	9.27	9.78	9.42	9.64	10.40
284.02	5.87	6.77	7.13	5.52	6.54	288	.80	9.38	9.78	9.61	9.90	10.75
284.08	6.99	6.84	7.98	7.40	7.27	288	.88	8.55	9.32	9.55	9.61	10.08
284.17	7.00	7.10	7.65	6.44	7.40	288	.97	7.96	8.58	9.03	8.76	9.85
284.25	6.25	7.36	7.46	6.78	7.68	289	.05	7.39	8.07	8.50	8.33	9.44
284.33	6.49	6.99	7.85	6.72	7.36	289	.13	7.13	7.50	7.37	7.28	9.35
284.42	6.85	7.11	7.85	6.52	7.78	289	.22	6.16	7.50	7.78	6.88	8.12
284.50	7.60	7.57	8.57	6.94	8.82	289	.30	6.41	7.50	7.59	5.82	6.99
284.58	7.70	8.16	8.24	8.02	8.91	289	.38	6.46	6.71	7.06	5.32	6.93
284.67	7.84	8.01	8.57	7.38	8.97	289	.47	6.56	6.32	6.80	5.57	6.49
284.75	7.92	7.92	8.37	7.55	9.44	289	.55	6.38	5.91	7.13	4.96	6.89
284.83	8.73	8.23	8.96	8.84	9.21	289	.63	6.85	6.05	7.26	6.08	7.68
284.92	9.64	8.91	9.55	9.47	9.52	289	.72	6.29	6.99	7.39	6.31	7.66
285.00	9.67	9.69	9.61	9.68	9.80	289	.80	6.13	6.63	7.39	6.25	7.74
285.08	9.00	9.32	9.22	9.21	9.90	289	.88	6.36	6.58	7.59	6.29	7.41
285.17	8.19	9.19	9.29	9.00	9.56	289	.85	6.36	6.58	7.59	6.29	7.41

wavelenght region 280 - 320 nm.

Absorption cross section  $\times 10^{-19}$  cm<sup>2</sup> at Wavelength Wavelength Absorption cross section  $\times 10^{-19}$  cm<sup>2</sup> at 300 K 280 K 260 K 240K 220K (nm) (nm) 300 K 280 K 260 K 240 K 220 K 289.93 7.27 6.75 7.65 7.37 7.82 294.53 5.99 6.33 6.23 5.58 6.38 290.02 7.11 7.03 8.50 8.41 8.86 294.62 5.38 5.63 5.83 5.28 5.39 290.10 7.03 7.56 8.31 7.92 8.82 294.70 5.29 5.04 5.14 4.65 4.79 290.18 6.55 7.74 8.37 8.52 8.43 294.78 4.24 4.55 5.10 4.46 4.50 290.27 6.77 7.51 8.17 7.82 8.37 294.85 4.24 4.55 5.10 4.46 4.50 290.35 7.23 7.10 7.98 7.88 8.01 294.93 4.54 4.21 4.01 4.47 4.07 290.43 7.87 7.83 8.31 8.51 8.39 295.02 3.98 4.08 4.48 3.49 4.07 290.52 8.73 9.00 8.58 8.73 9.05 295.10 3.73 3.58 3.50 3.62 3.50 290.60 9.65 9.55 9.33 9.66 10.36 295.28 3.92 3.98 3.18 3.18 2.85 290.85 8.34 7.31 8.06 9.10 9.06 295.37 3.15 3.30 3.64 3.38 3.19 290.93 7.65 6.58 7.33 8.78 8.18 295.45 3.59 3.19 3.54 3.22 2.99 6.38 291.02 6.92 7.15 7.30 7.23 295.53 3.54 2.99 3.84 3.18 2.99 291.10 6.20 6.27 6.63 7.23 6.93 295 62 3.98 3.44 3.44 3.76 3.77 291.18 6.19 5.93 5.93 7.04 6.33 295.70 5.04 3.42 3.50 4.01 4.70 291.27 5.87 5.38 5.37 6.46 6.06 295.78 5.93 4.97 5.48 4.57 5.04 291.35 5.16 5.16 5.40 5.99 5.51 295.87 6.94 5.48 6.20 5.97 6.42 291.38 4.73 4.73 5.48 5.70 4.11 295.95 7.92 6.63 7.34 7.18 7.21 291.47 5.02 4.73 6.17 5.34 5.59 296.03 7.46 6.62 8.32 8.70 8.63 291.55 5.88 5.09 6.50 5.76 6.25 296.12 7.91 7.68 9.05 9.04 9.25 291.63 5.72 5.76 7.20 6.03 6.92 296.20 8.20 8.86 9.41 9.65 9.91 291.72 6.48 6.65 6.94 6.98 7.09 296.28 8.05 8.27 9.32 9.60 9.78 291.80 6.40 6.74 7.14 7.60 6.67 296.37 7.23 7.53 9.14 9.20 9.25 291.88 6.38 6.36 7.66 7.43 7.07 296.45 5.95 6.85 8.56 9.46 8.47 291.97 6.61 6.26 8.23 7.64 8.69 296.53 5.88 6.17 7.52 7.93 6.93 292.05 7.72 7.64 8.55 8.63 9.21 296.62 5.62 4.77 6.37 7.33 6.31 292.13 8.20 8.21 8.14 9.21 8.71 296.70 5.39 4.75 6.39 6.23 6.77 292.22 7.79 8.01 8.49 9.22 8.94 296.78 4.11 4.39 5.18 5.16 5.62 292.30 8.30 8.16 8.54 9.61 9.72 296.87 4.60 3.94 5.20 5.04 5.49 292.38 7.89 7.84 7.71 9.33 8.03 296.95 4.32 3.67 4.37 4.83 5.45 292.47 8.05 7.69 6.94 8.59 7.88 297.03 3.58 3.76 5.06 5.16 5.85 292.55 7.25 7.16 7.07 8.16 6.74 297.12 3.24 4.50 3.35 4.91 5.06 292.63 7.20 6.69 6.63 7.55 6.10 297.17 2.84 3.10 4.55 4.10 4.95 292.72 6.56 6.53 7.25 6.08 6.13 297.25 2.60 2.49 3.95 3.37 3.93 292.78 5.30 6.05 5.77 6.06 4.71 297.33 2.24 2.49 3.46 3.32 2.96 292.87 4.88 5.44 4.66 5.34 4.42 297.42 2.29 2.37 3.75 2.85 2.67 292.95 5.00 4.85 4.92 5.27 3.80 297.50 2.66 2.93 4.25 2.63 2.79 293.03 4.60 4.48 4.70 4.34 3.81 2.95 297.58 3.02 4.30 2.44 2.93 293.03 4.60 4.48 4.70 4.34 3.81 297.67 3.33 3.26 4.52 2.75 2.97 293.12 4.30 4.33 4.70 4.57 3.73 297.75 4.59 4.28 6.54 3.27 4.08 293.12 4.30 4.33 4.70 4.57 3.73 297.83 6.48 6.17 8.46 3.94 6.47 293.20 4.30 4.33 5.12 5.08 3.73 297.92 7.62 7.65 9.32 5.62 7.94 293.28 4.54 4.13 5.38 5.61 4.11 298.00 8.46 8.11 9.84 10.00 10.30 293.37 4.43 4.34 5.34 6.78 4.03 298.08 8.13 7.48 9.14 9.82 9.75 293.45 5.00 4.41 6.58 8.60 4.57 298.17 7.17 7.19 9.05 9.32 8.79 293.53 6.19 4.72 8.06 8.66 298.25 6.44 6.01 7.16 9.08 9.18 8.82 293.62 7.31 5.91 8.46 8.68 8.52 298.33 4.65 7.22 8.60 8.89 7.40 293.70 7.76 7.68 8.68 8.64 8.77 298.42 6.17 6.86 7.37 7.90 6.39 293.78 7.61 7.63 8.34 8.19 8.76 298.50 7.76 5.58 5.05 8.26 7.24 293.87 7.41 7.49 7.82 8.02 8.04 298.58 5.43 4.81 5.03 8.00 7.29 293.95 6.78 7.41 7.59 8.67 8.92 298.67 3.74 4.79 4.92 6.66 5.47 294.03 6.88 7.06 7.93 9.13 8.69 298.75 3.07 4.64 7.39 6.06 3.52 294.12 7.48 6.92 8.65 9.48 9.03 298.83 3.38 4.17 5.94 4.96 3.24 294.20 7.75 7.61 8.73 8.75 9.01 298.92 4.31 3.66 2.87 4.57 3.99 294.28 7.62 7.59 8.46 8.24 8.88 298.98 1.97 3 40 3.50 3.42 2.24 294.37 7.27 7.53 7.48 6.79 8.56 298.90 1.97 3.40 3.50 3.42 2.24 294.45 7.14 7.69 6.65 5.96 7.60 298.98 1.75 3.14 3.39 2.43 1.76

Table 5.8: contd.

				100						10-19	7 .
Wavelength	Absorp	tion cros	s section	×10-19	cm <sup>2</sup> at	Wavelength	Absor	otion cros	s section	×10-10	cm* at
(nm)	300 K	280 K	260 K	240 K	220 K	(nm)	300 K	280 K	260 K	240 K	220K
299.07	2.04	2.92	3.46	2.72	1.49	303.87	2.92	1.69	3.52	4.19	3.34
299.15	1.81	2.79	3.18	2.25	1.75	303.95	3.44	2.39	4.32	4.51	0.22
299.23	2.06	2.42	3.18	2.28	1.70	304.03	4.63	3.80	0.17	5.74	0.03
299.32	1.87	2.56	3.45	2.86	1.74	304.12	6.04	4.79	8.11	0.00	0.41
299.40	2.66	2.95	4.18	2.52	1.70	304.20	7.60	8.13	8.29	9.00	9.41
299.48	2.70	3.40	3.96	2.79	2.74	304.28	0.11	1.13	6.60	0.00	9.10
299.57	4.50	4.82	5.89	4.11	4.62	304.37	0.10	0.90 E 70	6.04	7.01	7 22
299.65	6.29	6.92	7.58	5.60	1.00	304.43	1.24	1.04	5.79	6.07	6.88
299.75	4.50	7.82	5.89	4.11	4.62	304.53	4.09	4.94	4.27	5.43	6.07
299.83	6.29	9.92	1.58	7.60	11.00	304.02	4.41	3.55	4.07	1 47	5 33
299.92	8.85	10.02	10.90	11.01	11.40	304.70	2.00	2.07	3.40	3.26	4.66
300.00	9.11	10.67	11.34	11.52	11.00	304.70	2.60	2.55	3.40	4 58	4.00
300.08	7.97	9.79	9.76	10.20	9.40	304.87	2.09	2.00	3.00	313	3.87
300.17	1.43	9.35	0.00	9.24	0.00	304.93	2.16	1.62	2.96	3.03	3.64
300.25	6.59	8.83	8.30	7.21	6 12	305.13	2.40	1.02	2.30	2.98	3.41
300.33	5.80	0.21	6.42	6.19	5.25	305.20	1 75	1.00	1.79	2.91	2.64
300.42	5.12	7.07	0.43	0.10	1.20	205.20	1.10	1.30	2.12	2.01	2.01
300.50	4.70	6.90	0.10	5.10	3.72	305.20	1.10	1.00	1.61	2 72	215
300.58	3.07	0.80	4.00	0.12	3.73	305.50	1.62	1.00	1.61	2.72	2.15
300.67	3.31	6.70	4.82	4.51	3.13	305.50	1.02	1 38	2.02	2.12	2.13
300.75	2.98	0.70	4.51	5.30	3.21	305.67	1 31	1.06	2.02	2.40	2.46
300.83	2.07	1.02	4.00	1.62	2.90	305.75	1 38	1.00	2.02	3.08	2.50
300.92	2.05	1.93	2.15	4.00	2.10	305.83	1.00	1.00	2.67	3.85	2.48
301.18	1.00	1.95	3.13	4.07	2.01	305.03	1.44	1.00	2.99	3 73	3.04
301.27	1.00	1.77	2.49	3.00	2.45	306.00	1.10	2.15	3 78	4.57	3.22
301.27	1.00	1.11	2.49	3.00	2.43	306.08	2 50	2.10	4 20	4.55	4.55
301.35	1.91	2.02	2.00	3.57	2.00	306.17	3.10	2 71	4.80	4.88	4.82
301.43	1.00	1.77	2.40	3.06	2.40	306.25	3 43	3.88	4 93	5.32	5.25
301.52	1.00	2.01	3.17	4 20	313	306.33	4 29	4.48	5.91	6.02	6.06
301.60	2.54	2.01	3.77	5.03	3.70	306.42	4 72	5.06	6.34	6.15	7.02
201.00	4.10	5.37	4.25	6.08	6.08	306 50	5 26	5 35	6.74	6.76	7.63
301.85	5.74	7.06	5.69	7.53	7.52	306.58	5.09	5.01	6.10	6.53	7.55
301.83	7.24	7.75	7.83	8 54	8 74	306.67	4.81	4.12	4.56	4.87	6.42
302.02	7 49	812	7.93	9 10	9.03	306.75	4.74	3.56	4.14	3.79	5.46
302.10	7.64	8 12	8 70	9.30	9.21	306.83	3.62	2.81	3.82	3.35	4.83
302.18	7.01	6.93	8.11	9.00	7.95	306.92	3.18	2.22	3.23	3.02	4.30
302.27	6.88	6.44	8.07	8.64	7.40	307.40	2.90	2.55	2.66	3.23	3.93
302.35	6.25	5.97	7.27	8.04	6.69	307.48	2.23	1.66	3.20	2.45	3.56
302.43	5.42	4.90	6.45	7.75	5.99	307.57	2.03	1.62	2.92	2.84	3.37
302.52	4.74	4.69	6.30	7.31	5.17	307.65	1.54	1.38	2.86	3.00	3.10
302.60	3.86	3.71	4.80	6.42	4.11	307.73	1.20	1.07	2.12	3.18	2.97
302.68	4.31	3.16	4.46	5.47	3.83	307.82	1.00	1.20	2.36	3.24	2.91
302.77	3.28	2.30	4.07	4.92	3.71	307.90	1.25	1.10	2.36	2.98	2.68
302.85	2.83	2.31	3.73	4.61	3.10	307.93	1.58	1.09	2.28	2.74	2.46
302.93	2.49	1.75	3.27	4.04	2.68	308.02	1.60	.91	2.48	2.43	2.25
303.02	2.74	1.84	3.32	4.27	2.53	308.10	1.40	1.29	3.19	2.92	2.68
303.10	2.08	1.31	2.71	3.85	2.58	308.18	1.79	2.20	2.96	3.03	3.21
303.18	1.82	1.59	2.32	3.68	2.25	308.27	2.08	1.57	3.13	2.96	3.10
303.27	1.99	1.59	2.66	3.28	2.21	308.35	2.49	2.98	4.13	3.50	2.90
303.37	1.99	1.59	2.66	3.28	2.21	308.43	2.70	3.08	4.33	4.20	3.99
303.45	1.63	1.67	2.86	3.48	1.89	308.52	4.05	4.06	4.28	4.60	5.02
303.53	1.61	1.60	2.47	3.32	2.33	308.60	4.19	4.09	5.03	4.57	5.45
303.62	1.80	1.11	2.64	3.52	1.99	308.68	3.81	3.39	4.17	4.44	5.19
303.70	2.16	1.51	2.70	4.23	3.02	308.77	3.16	3.77	4.43	4.25	4.65
303.78	2.16	1.49	3.35	4.10	2.94	308.85	3.37	2.84	4.44	4.50	4.21
									1		1010

Table 5.8: Contd.

Table 5.8: Contd.

Wavelength	Absorp	otion cros	s section	×10-19	cm <sup>2</sup> at	Wavelength	Absor	otion cros	s section	×10-19	cm <sup>2</sup> at
(nm)	300 K	280K	260 K	240K	220 K	(nm)	300 K	280 K	260 K	240 K	220 K
308.93	2.78	2.12	3.34	3.67	3.34	314.52	1.45	1.64	1.80	1.94	2.04
309.02	1.91	1.90	3.44	3.80	3.00	314.60	1.33	1.52	1.68	1.82	1.92
309.10	1.07	2.01	3.03	2.08	2.98	314.08	1.00	.03	1.09	1.40	1 50
309.18	1.49	1.00	2.12	2.40	4.46	314.77	64	1.19	1.35	1.49	1.39
309.35	1.14	1.00	2.40	2.30	2.26	314.03	1 11	1 30	1.46	1.15	1.20
309.43	96	1.00	2.76	2.20	1 99	315.02	1.60	1.50	1.40	2.09	2 19
309.58	.96	1.15	1.31	1.45	1.55	315.10	1.00	1.10	1.55	1.61	1 71
309.67	.91	1.10	1.26	1.40	1.50	315.18	.65	.84	1.00	1.14	1.24
309.75	.97	1.16	1.32	1.46	1.56	315.27	1.02	1.21	1.37	1.51	1.61
309.83	1.12	1.31	1.47	1.61	1.71	315.35	1.33	1.52	1.68	1.82	1.92
309.92	.91	1.10	1.26	1.40	1.50	315.43	1.24	1.43	1.59	1.73	1.83
310.00	1.45	1.64	1.80	1.94	2.04	315.52	1.43	1.62	1.78	1.92	2.02
310.08	.92	1.11	1.27	1.41	1.51	315.60	1.09	1.28	1.44	1.58	1.68
310.17	1.06	1.25	1.41	1.55	1.65	315.68	1.15	1.34	1.50	1.64	1.74
310.25	1.22	1.41	1.57	1.71	1.81	315.77	.11	.30	.46	.60	.70
310.33	.63	.82	.98	1.12	1.22	315.85	.79	.98	1.14	1.28	1.38
310.42	1.41	1.60	1.76	1.90	2.00	315.93	.90	1.09	1.25	1.39	1.49
310.50	.95	1.14	1.30	1.44	1.54	316.02	.11	.30	.46	.60	.70
310.58	1.48	1.67	1.83	1.97	2.07	316.10	.89	1.08	1.24	1.38	1.48
310.67	2.44	2.63	2.79	2.93	3.03	316.18	.60	.79	.95	1.09	1.19
310.70	2.55	2.74	2.90	3.04	3.14	316.27	.47	.66	.82	.96	1.06
310.83	2.30	2.49	2.65	2.79	2.89	316.35	.68	.87	1.03	1.17	1.27
310.92	2.30	2.49	2.65	2.79	2.89	316.43	1.03	1.22	1.38	1.52	1.62
311.00	1.51	1.70	1.86	2.00	2.10	316.52	.76	.95	1.11	1.25	1.35
311.08	2.77	2.96	3.12	3.26	3.36	316.60	.72	.91	1.07	1.21	1.31
311.17	2.44	2.03	2.79	2.93	3.03	316.68	1.09	1.28	1.44	1.58	1.68
311.23	2.30	2.00	2.11	2.80	2.95	310.77	1.18	1.37	1.53	1.67	1.77
311.33	2.09	2.20	2.44	2.00	2.00	310.85	.94	1.13	1.29	1.43	1.53
311.50	2.32	2.51	2.67	2.01	2.01	317.02	55	74	1.50	1.00	1.00
311.58	1.78	1.97	2.13	2.27	2.37	317.10	.50	73	.50	1.04	1 13
311.67	1.41	1.60	1.76	1.90	2.00	317.18	.64	.83	.99	1.13	1.23
311.75	1.44	1.63	1.79	1.93	2.03	317.27	.62	.81	.97	1.11	1.21
311.83	.95	1.14	1.30	1.44	1.54	317.35	.77	.96	1.12	1.26	1.36
311.92	.66	.85	1.01	1.15	1.25	317.43	.78	.97	1.13	1.27	1.37
312.00	1.19	1.38	1.54	1.68	1.78	317.52	.58	.77	.93	1.07	1.17
312.02	.09	.28	.44	.58	.68	317.60	.49	.68	.84	.98	1.08
312.10	.00	.19	.35	.49	.59	317.68	.34	.53	.69	.83	.93
312.18	.37	.56	.72	.86	.96	317.77	.72	.91	1.07	1.21	1.31
312.27	1.36	1.55	1.71	1.85	1.95	317.85	.61	.80	.96	1.10	1.20
312.35	1.39	1.58	1.74	1.88	1.98	317.93	.23	.42	.58	.72	.82
312.43	.93	1.12	1.28	1.42	1.52	318.02	.52	.71	.87	1.01	1.11
312.52	1.01	1.20	1.36	1.50	1.60	318.10	.44	.63	.79	.93	1.03
312.60	1.52	1.71	1.87	~2.01	2.11	318.18	.30	.49	.65	.79	.89
312.68	1.81	2.00	2.16	2.30	2.40	318.27	.33	.52	.68	.82	.92
312.77	2.09	2.28	2.44	2.58	2.68	318.35	.12	.19	.35	.49	.59
312.85	2.10	2.35	2.51	2.65	2.75	318.43	.54	.73	.89	1.03	1.13
312.93	2.15	2.34	2.50	2.04	2.74	318.52	.21	.29	.45	.59	.69
313.02	2.01	2.20	2.30	2.50	2.00	318.60	.19	.38	.54	.68	.78
313 18	1.69	1 88	2.04	2.10	2.00	310.00	.22	.20	.41	.55	.05
313.27	1.00	1.00	1.56	1.70	1.80	310.77	.10	.19	.35	.49	.59
313.35	1.17	1.36	1.52	1.66	1.00	318.03	.00	20	.10	.04	.94
313.43	1.10	1.29	1.45	1.59	1.69	319.02	40	59	.50	.50	.00
313.52	.18	.37	.53	.67	.77	319.10	20	19	35	49	59
313.60	.88	1.07	1.23	1.37	1.47	319.18	26	45	61	75	85
313.68	.72	.91	1.07	1.21	1.31	319.27	.19	.19	.35	.49	.59
313.77	1.14	1.33	1.49	1.63	1.73	319.35	.18	.37	.53	.67	.00
313.85	.97	1.16	1.32	1.46	1.56	319.43	.54	.73	.89	1.03	1.13
313.93	.83	1.02	1.18	1.32	1.42	319.52	.32	.51	.67	.81	.91
314.02	.96	1.15	1.31	1.45	1.55	319.60	.41	.60	.76	.90	1.00
314.10	.89	1.08	1.24	1.38	1.48	319.68	.11	.19	.35	.49	.59
314.18	.72	.91	1.07	1.21	1.31	319.77	.13	.19	.35	.49	.59
314.27	1.04	1.23	1.39	1.53	1.63	319.85	.17	.36	.52	.66	.76
314.35	.94	1.13	1.29	1.43	1.53	319.93	.12	.19	.35	.49	.59
314.43	.93	1.12	1.28	1.42	1.130	320.02	.16	.35	.51	.65	.75

# Chapter 6

# CONCLUSION AND SCOPE FOR FUTURE WORK

### 6.1 Conclusion

The temperature dependence of photoabsorption cross sections has been studied for the two target gases, carbon tetrachloride and sulphur-dioxide at both room temperature as well as at lower temperatures. The photoabsorption cross sections for carbon tetrachloride were measured in the spectral region 186-320 nm and for SO<sub>2</sub> at 188-220 nm and 280-320 nm at temperatures varying from 300 to 220 K. Such measurements were carried out with an accuracy of  $\pm 4.1\%$  at an instrumental resolution of 0.1 nm.

The study of photoabsorption at low temperatures for carbon tetrachloride revealed the following problems : the thermal transpiration effects, the problems related to vapour pressure of the target gas and the adsorption effect. All the above said problems have already been discussed in detail in Chapter 3. This is the first time that corrections due to the above effects have been fully incorporated and the most reliable values of absorption cross sections at low temperatures have been reported.

The thermal transpiration affects the measured pressure when the target gas

and manometer are at dissimilar temperatures. The measured pressure in general could be overestimated or underestimated as compared to the actual target gas pressure depending upon whether the manometer is at a temperature higher or lower than that of the target gas. It is known that the magnitude of the correction to be applied to the measured pressure increases with an increase in temperature difference between the manometer and target gas particularly for low target gas pressures. After going through the literature it seems that many of the earlier workers who conducted the photoabsorption experiment at low/high temperatures have not corrected their data for this effect. It may be pointed out here that the corrections needed for such experiments could be appreciable; in the present experiment the largest correction needed in the case of CCl<sub>4</sub> was about 8% at 220 K and about 13% at 220 K for SO<sub>2</sub>. In view of the above, it is suggested that the photoabsorption cross sections measured as a function of temperature should necessarily be corrected for the thermal transpiration effect.

It has been pointed out in Chapter 3 that the measurement of photoabsorption cross sections at lower temperatures are constrained by the vapour pressure of the target gas for certain wavelength regions where the absorption was low. In order to overcome this problem it is necessary to increase the absorption path length so that the pressures required to measure such low cross sections would always be below the pressures where the condensation of the target gas occurred.

It has been found in the present work that the adsorption of the target gas molecules on the quartz windows used in the absorption chamber reduced its transmission as a function of the time elapsed after introduction of the target gas. Such effects have been observed by other workers also (Wu et al, 1988). The Belgium group (Gillotay et al (1989), Simon et al (1988)) in their measurement of absorption cross section for halogenated methanes and chlorofluorocarbons at low temperatures apparently seem to have corrected for this effect. They used a reference cell which was also maintained at the same temperature and pressure conditions as the main absorption cell. Although they do not seem to explicitly report this effect or the necessary corrections applied, it appears that the reference cell was incorporated by them in order to nullify the effect of adsorption by taking the ratio of intensities at the reference and main absorption cells. In the present work, a separate experiment was conducted to study the effect of adsorption of target gas molecules on the transmission of the absorption chamber (see Chapter 3). The necessary corrections were incorporated during the actual experiment. In any case, the change in transmission due to adsorption of target gas molecules is an important effect that has to be considered for photoabsorption studies at low temperatures. The earlier researchers Leroy et al (1983) and McGee and Burris (1987) have not considered this effect. It may be pointed out here that the largest corrections required in the present experiment in case of  $CCl_4$  and  $SO_2$  were about as high as 14% and 6% respectively.

Thus in conclusion, it may be said that the photoabsorption cross sections measured in the present experiment at lower temperatures, in all probability, are highly reliable and more accurate. This is so because corrections for all the possible systematic errors as discussed above, have been incorporated in the present study. All these corrections unfortunately have not been incorporated simultaneously in the earlier measurements.

#### 6.2 Scope for Future Work

The present experimental setup can be used to measure photoabsorption cross sections for many other molecules like chlorofluorocarbons,  $CS_2$ ,  $NH_3$  etc. in the same spectral region and at temperatures as low as 220 K. Also, by modifying the current rating of the power supply of the argon mini-arc source, the intensity of the part of the continuum from 105 to 180 nm can be increased tremendously and the photoabsorption cross sections could be measured in the extended wavelength region from 105 to 340 nm. Also, by suitably changing the design of the absorption chamber the cross section measurements could be carried out at higher temperatures also say up to 450 K. Both these modification can make the present experimental set-up more versatile.

At 300 K, the present experiment set-up has the capability to measure cross sections above a value of  $10^{-21}$  cm<sup>2</sup> with an accuracy of about ±4%. But for temperatures below 300 K, the cross section measurements are constrained by vapour pressure (condensation conditions) of the target gas. The lower limit on the cross section values that could be measured depends on the vapour pressure at the temperature of interest. This problem can be over come by increasing the absorption path length so that the target gas pressures required to measure such cross sections are always below the vapour pressure in the temperature range of interest. Longer path lengths would also facilitate the measurement of photoabsorption cross section of molecules having very low cross sections.

The absorption path length of photoabsorption chamber may be increased by increasing its geometrical length. However, this would be disadvantageous particularly for carrying out temperature dependent studies, since it would be necessary to cool/heat the entire geometrical path length uniformly. It is advantageous to build a multipass cell (White cell, 1942) as the required absorption path lengths can be achieved within a chamber of moderate geometrical path length. The multipass cell consists of highly reflecting concave mirrors on both the ends of the cell. These mirrors are coated with special materials (e.g. Al+ MgF<sub>2</sub>, gold etc.) which can enhance the reflectivity in the spectral region of interest. The photon beam which enters the multipass cell suffers multiple reflections at these end mirrors and hence passes through the gas column in the cell several times before leaving the cell. Thus, the absorption path length can be increased manifolds over its actual geometrical path length.

These multipass cells can be heated/cooled and the temperature dependent

studies of photoabsorption of molecules having very low absorption cross sections can be carried out. A typical example of such a molecular system is NO<sub>2</sub> which is of great interest to aeronomers. But major discrepancies exist in the value of cross sections reported by many researchers in different spectral regions. The discrepancy is attributed to the difficulty in estimating the number density of NO<sub>2</sub> molecules in the absorption cell, since NO<sub>2</sub> is known to be in a dynamic equilibrium with N<sub>2</sub>O<sub>4</sub>. It would be particularly interesting to study the temperature dependence of photoabsorption of NO<sub>2</sub>; it would involve the thermo chemical study of NO<sub>2</sub> $\Rightarrow$  N<sub>2</sub>O<sub>4</sub> equilibrium.

### List Of Publications

Temperature dependence of photoabsorption cross sections of carbon tetrachloride at 186-240 nm. V.Prahlad and V.Kumar J. Quant. Spectrosc. Radiat. Transfer.,(1995) 54, 945.

Temperature dependence of photoabsorption cross sections of sulphur dioxide at 280-320 nm. V.Prahlad, S.M.Ahmed and V.Kumar submitted for publication to J. Quant. Spectrosc. Radiat. Transfer.

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