

Measurement of photoabsorption and fluorescence cross-sections for CS₂ at 188·2–213 and 287·5–339·5 nm

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Abstract. The photoabsorption and fluorescence cross-sections for carbon disulphide have been measured in the 188·2–213 and 287·5–339·5 nm spectral regions using an argon mini-arc light source. The absorption cross-sections have been measured with an accuracy of $\pm 4\cdot2\%$ whereas the most probable error estimated in the case of fluorescence cross-sections is $\pm 5\cdot1\%$. The fluorescence quantum yields for CS₂ have also been obtained in the two spectral regions.

Keywords. Absorption; fluorescence; photon impact; photodissociation.

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1. Introduction

Carbon disulphide is a reactive trace constituent present in the earth's troposphere (Sandalls and Penkett 1977; Maroulis and Bandy 1980) and stratosphere (Turco *et al* 1980; Sze and Ko 1979). The presence of CS₂ in the Venusian atmosphere has been proposed by Barker (1979) and Young (1978) and in the interstellar medium by Goldsmith *et al* (1980). The data on photoabsorption and fluorescence cross-sections measured in the laboratory are required to model different aspects of the planetary atmospheres.

Absorption spectroscopy for CS₂ has been extensively studied both qualitatively as well as quantitatively in the UV and VUV spectral regions. A great majority of qualitative studies include the work carried out by Kleman (1963), Callear (1963), Rabalais *et al* (1971), Douglas and Zanon (1964) and Jungen *et al* (1973). Also, the photoabsorption cross-sections have been measured by Leroy *et al* (1983), Molina *et al* (1981) and Wu and Judge (1981). There seems to be large discrepancy in the absorption cross-section values reported by various researchers. It has been observed that the quantitative data on fluorescence of CS₂ is rather scarce. The only measurement reported by Black *et al* (1977) has been carried out at a few wavelengths between 190 and 210 nm. Some qualitative studies on fluorescence have been reported in the past which include the work carried out by Heicklen (1963) and Lambert and Kimbell (1973). In view of this, more measurements in this direction are needed, possibly using better techniques.

In the present experiment, photoabsorption and fluorescence cross-sections for CS₂ have been measured as a function of incident photon wavelength in the spectral regions 188·2–213 nm and 287·5–339·5 nm with an instrumental resolution of about 0·2 nm. From these cross-sections, the fluorescence quantum yield for CS₂ has been

obtained as a function of incident photon energy. The work has been carried out at low resolution so as to accommodate weak fluorescence intensity signals from CS₂ at different incident photon wavelengths.

2. Experimental set-up

An intense line-free UV continuum (115 to >360 nm) was produced from an argon mini-arc light source and the radiation was monochromatized by using a 1 m normal incidence asymmetrical monochromator (Jobin-Yvon, France) evacuated to a pressure of 10⁻⁵ Torr. A photon beam of about 0.2 nm instrumental bandwidth was selected so as to accommodate the low fluorescence signals in a few spectral regions. A beam splitter between the exit slit of the monochromator and the absorption/fluorescence chamber was used to monitor the incident photon intensity during the experiment. The beam splitter was simply a quartz plate mounted at 45° to the optic axis. About 95% of the photon beam was transmitted through the quartz plate and the rest was reflected to a photomultiplier (EMI 9558QB). The beam splitter region was evacuated through the exit slit of the monochromator. The transmitted photon beam enters the absorption chamber through a quartz plate which isolates the beam splitter from the absorption chamber vacuum wise. The absorption region, 24.8 cm long, was evacuated to a pressure of 10⁻⁵ Torr. The chamber was vacuum sealed at the other end by another quartz plate. Another monochromator was used after the absorption chamber and the gratings of the two monochromators were co-rotated so as to have the same wavelength. The 1 m monochromator decided the instrumental resolution and the other monochromator (0.2 m, Minuteman Inc., U.S.A.) was used to avoid detection of fluorescent emission produced by excited target molecules in the direction of the optic axis. A quartz plate was vacuum sealed to the exit slit of the 0.2 m monochromator which was evacuated to a pressure of 10⁻³–10⁻⁵ Torr depending upon the spectral range where absorption cross-sections were being measured. The transmitted intensity was measured using an EMI 9558 QB photomultiplier. The fluorescence intensity was measured in the direction of the optic axis. This could be done by removing the 0.2 m monochromator and the photomultiplier for measuring transmitted intensity in the absorption cross-section experiment. Instead, an appropriate colour glass filter having the spectral transmitting cut-offs matching with the CS₂ fluorescence spectrum, was placed after the quartz plate fixed at the end of the absorption/fluorescence chamber. The colour glass filter did not allow the incident photon beam to be transmitted but the fluorescence radiation could pass through the filter and was detected by a thermoelectrically cooled photomultiplier, EMI 9558QB. Because of low level signals in the fluorescence channel, it was essential to cool the photomultiplier but the other photomultipliers were also cooled thermoelectrically so as to have reduced dark current and large size photon pulses. All the photomultipliers were operated in the counting mode and after proper amplification, the signals were stored in a home-made microprocessor-controlled 1024 channel dual multi-channel analyzer operated in the multi-scaling mode. The data stored for each run were transferred to IBM compatible PC for data analysis.

Carbon disulphide vapour was obtained from an analytical-grade liquid. The vapour was purified by fractional distillation before being introduced into the absorption/fluorescence chamber. The gas was continuously flowing in the system

and the pressure in the chamber was measured absolutely using a MKS Baratron Capacitance manometer (head 310 MH-10). This was a differential manometer and the pressure was made absolute by evacuating the reference side to a pressure of about 10^{-6} Torr.

3. Method and error analysis

It is required to measure fluorescence quantum yield for CS₂ as a function of incident photon wavelength. The fluorescence quantum yield at a certain incident wavelength is defined as the ratio of fluorescence to photoabsorption cross-section. It is required to measure both these quantities absolutely at a given instrumental band width.

Photoabsorption cross-section at a certain incident photon wavelength is defined as the ratio of the number of photons absorbed by the target molecules to the number of photons incident on these molecules. The fluorescence cross-section is the ratio of the number of photons of different energies emitted by the target molecules to the number of photons absorbed by them. The wavelengths of fluorescing photons are essentially larger than that of the incident photon.

The photoabsorption cross-section, $\sigma_{T\lambda}$, for a given molecule could be measured using the Beer-Lambert law:

$$I_{\lambda} = I_{0\lambda} \exp(-\sigma nl), \quad (1)$$

where $I_{0\lambda}$ and I_{λ} are the fluxes incident on and transmitted through the gas, n is the concentration in particles per cubic centimeter and l is the path length in cm. In the above equation, n is given by

$$n = n_0 \frac{P}{760} \frac{273}{T}, \quad (2)$$

where n_0 is the Loschmidt's number, P is the absolute pressure in the absorption chamber measured in Torr and T is the temperature of the gas in degree Kelvin. When there is no gas in the absorption chamber, $I_{0\lambda}$ (measured by beam splitter photomultiplier) and I_{λ} are supposed to be the same. But in actual practice, there is a difference in the two values because of quartz windows intercepting the photon beam and the two photomultipliers even though they are of the same type. This gives a calibration for the incident intensity and with gas in, the beam splitter intensity is multiplied by this calibration factor to get $I_{0\lambda}$. This way, any change in intensity of the incident beam during the experiment can be taken care of. Thus, the absorption cross-section at a given photon wavelength could be measured by knowing the ratio of $I_{0\lambda}$ and I_{λ} , the number density of species under investigation and length of the absorbing column.

The fluorescence cross-sections for CS₂ are obtained as a function of incident photon wavelength by measuring the fluorescence intensity along the optic axis. As described previously in §2, an appropriate colour glass filter Wratten-3 has been used in combination with cooled photomultiplier just after the quartz plate at the end of the absorption chamber. This filter cuts off the incident photon wavelength ($\lambda_i < 320$ nm) but transmits the fluorescence signals at wavelengths larger than the incident photon wavelength. To extract the fluorescence intensity from the target

molecules alone is extremely difficult in this configuration as the quartz plate seems to fluoresce at UV and VUV wavelengths. A method developed to calculate fluorescence cross-sections is being given below.

When there is no gas in the fluorescence chamber, the fluorescence intensity from quartz plate Q_2 (figure 1) detected at the end of absorption/fluorescence chamber is given by

$$I_{f\lambda Q} = CK_1\gamma_{f\lambda Q}I_{0\lambda} \quad (3)$$

where $I_{0\lambda}$ is the intensity of photon beam detected by beam splitter photomultiplier, C is a constant which takes care of the reflectance and transmission of the beam splitter and Q_1 quartz plate, K_1 is a constant which takes care of the geometry of the system and quantum efficiency of the photomultiplier and $\gamma_{f\lambda Q}$ is the fluorescence quantum yield of quartz. $I_{0\lambda}$ and $I_{f\lambda Q}$ can be measured from the beam splitter photomultiplier and the other photomultiplier positioned behind the colour glass filter. Therefore, at each wavelength, the value of $CK_1\gamma_{f\lambda Q}$ can be obtained.

With gas inside the chamber, the total fluorescence intensity would have contributions both from quartz plate Q_2 and the target gas molecules. With gas in, the intensity of photon beam incident on the front edge of the quartz plate Q_2 would be $CI_{0\lambda}\exp(-n\sigma_{T\lambda}l)$. Therefore, the fluorescence intensity because of quartz alone would be given by

$$I_{f\lambda Q} = CK_1\gamma_{f\lambda Q}I_{0\lambda}\exp(-n\sigma_{T\lambda}l). \quad (4)$$

The fluorescence intensity because of gas alone would be given by

$$I_{f\lambda G} = KFC\gamma_{f\lambda G}I_{0\lambda}[1 - \exp(-n\sigma_{T\lambda}l)] \quad (5)$$

where K is the geometrical constant which depends upon the system, F is the photocathode quantum efficiency and $\gamma_{f\lambda G}$ is the fluorescence quantum yield for the target gas molecules alone. The two constants K and K_1 are different as the geometry involved in the production of fluorescence for gas and quartz is different.

The total fluorescence intensity at a given wavelength includes the fluorescence intensities because of quartz alone and also from the target gas molecules. This is given by

$$I_{f\lambda T} = CK_1\gamma_{f\lambda Q}I_{0\lambda}\exp(-n\sigma_{T\lambda}l) + KFC\gamma_{f\lambda G}I_{0\lambda}[1 - \exp(-n\sigma_{T\lambda}l)]. \quad (6)$$

The product $CK_1\gamma_{f\lambda Q}$ is known from (3) when there is no target gas in the cell. All

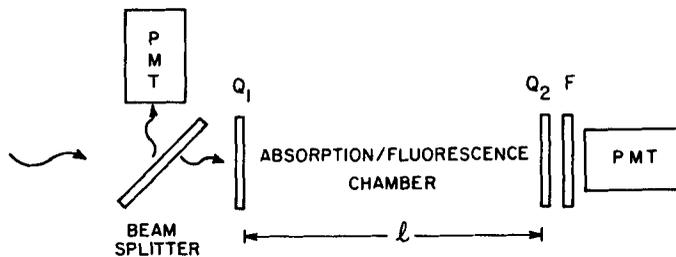


Figure 1 Schematic diagram showing the absorption and fluorescence region and position of quartz plates and colour glass filter.

other quantities like $I_{0\lambda}$, $I_{f\lambda T}$, n i.e. pressure and l are known from the experiment and $\sigma_{T\lambda}$ has been measured in absorption studies. The product $KFC\gamma_{f\lambda G}$ remains unknown with the result that the measurements for fluorescence intensity remain relative in nature. Different values of $I_{f\lambda T}/I_{0\lambda}$ are obtained at various target gas pressures and the slope of the graph between $I_{f\lambda T}/I_{0\lambda}$ and n i.e. pressure gives $KFC\gamma_{f\lambda G}$. A known target gas is chosen for which the $\gamma_{f\lambda G}$ value at a certain photon wavelength has previously been measured in an other experiment and reported in literature. For such a target gas (SO₂ in this case), absorption cross-section is first measured using the present experimental set up at the wavelength where $\gamma_{f\lambda G}$ has already been reported. Then at different gas pressures, $I_{f\lambda T}/I_{0\lambda}$ could be obtained. This would give the product of the constants, KFC . Now as both the products, $CK_1\gamma_{f\lambda G}$ and KFC are known, absolute fluorescence cross-sections could be obtained for any target gas. Thus, knowing absolute total photoabsorption and fluorescence cross-sections, fluorescence quantum yields could be obtained.

In the experimental set up described previously, the fluorescence light has to be sampled from very different regions of the fluorescence cell and this would vary in intensity with the change of target gas pressure. Therefore, K used in (5) and (6) should strictly depend on n and also on the nature of the gas. But in the present experiment, K has been considered to be constant for all practical purposes. Also, no effort, has been made to estimate error, if any, due to this effect.

The error budget in CS₂ measurements for both absorption and fluorescence cross-sections has been summarized in table 1. Only maximum possible errors due to measurement in pressure, temperature, optical path length and photon intensity have been given in table. The correction in pressure of CS₂ vapour due to thermal transpiration effects has already been taken care off while calculating the cross-sections from the observables. Errors introduced because of reference pressure in MKS capacitance manometer and sample gas impurity could safely be considered negligible. The error analysis has been discussed in detail by Ahmed and Kumar (1992).

The coherent sum of all these errors acted as an estimate of the upper limit of the actual error. In the present experiment, it has been found to be ± 5.8 and $\pm 6.8\%$ for absorption and fluorescence cross-section measurements respectively. The incoherent sum was obtained by adding the squares of all the errors and taking the

Table 1. Error budget in the measurement of photoabsorption and fluorescence cross-sections for CS₂ at room temperature.

	Error in $\sigma_{T\lambda}$ measurement (%)	Error in $\sigma_{f\lambda}$ measurement (%)
Pressure	± 1.0	± 1.0
Temperature	± 0.4	± 0.4
Optical path length	± 0.4	± 0.4
Counting statistics in intensity	± 4.0	± 5.0
Coherent sum	± 5.8	± 6.8
Incoherent sum or total r.m.s. error	± 4.2	± 5.1

square root of the total sum. The incoherent sum represented the most probable estimate of the accuracy of the experiment. In the present experiment, the most probable error was estimated to be ± 4.2 and $\pm 5.1\%$ for $\sigma_{T\lambda}$ and $\sigma_{f\lambda}$ measurements respectively. This gave the most probable error for fluorescence quantum yield to be $\pm 6.6\%$.

4. Result and discussion

4.1 Spectral region: 188-213 nm

The absorption studies were carried out at two typical incident photon wavelengths of 195.1 and 202.9 nm as a function of gas pressure. The $\ln(I_{0\lambda}/I_\lambda)$ dependence on pressure of the CS₂ vapour has been shown in figure 2. At both the wavelengths, 195.1 and 202.9 nm, the resultant curve is linear up to pressure less than 5 mTorr. At pressures larger than 5 mTorr, the curve is no more linear. At these pressures, not only the Beer-Lambert's law breaks down but there seems to be another factor also which is strongly contributing to this non-linear behaviour. This has been discussed in detail in the later part of the section. The photoabsorption cross-sections as measured in the present experiment are shown in figure 3. These cross sections have been measured at various CS₂ pressures ranging from 1 to 5 mTorr and the average cross sections are shown in figure 3.

The photoabsorption cross-sections in figure 3 show a sharp increase from band O to band H, varying from 144.1×10^{-18} to 794.0×10^{-18} cm². The cross-sections subsequently decrease rapidly from band H to band A with values varying from 794.0×10^{-18} to 34.3×10^{-18} cm². Not much quantitative work has been reported in this spectral region as the cross-sections in this region are pressure dependent to a large extent and therefore, it becomes difficult to obtain absolute values of cross-section which are pressure independent over a range of pressures. However, some comparison of cross-section values measured in the present work and those

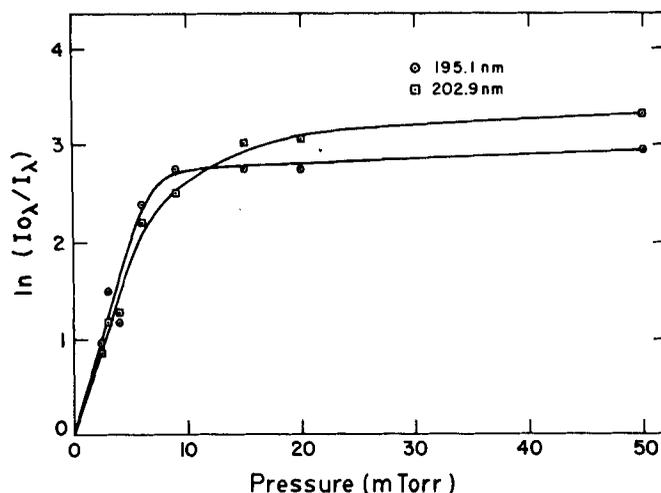


Figure 2. The $\ln(I_{0\lambda}/I_\lambda)$ dependence on CS₂ gas pressure at 195.1 and 202.9 nm.

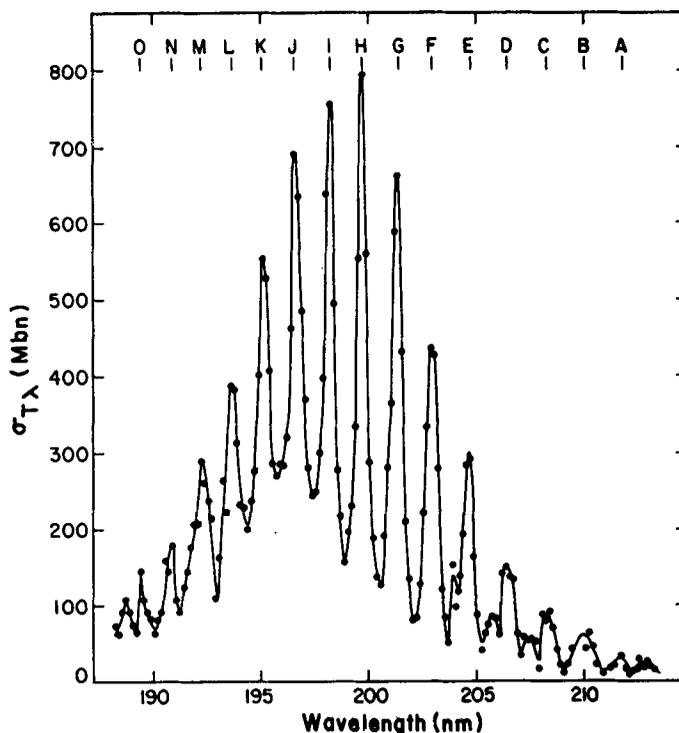


Figure 3. Photoabsorption cross-sections for CS₂ in the spectral region 188.2–213 nm.

Table 2. Photoabsorption cross-sections for CS₂ at peaks of a few bands in 188–213 nm spectral region.

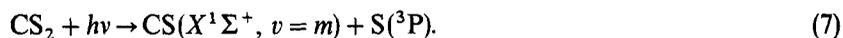
Band assignment	Present work (10 ⁻¹⁸ cm ²)	Molina <i>et al</i> (1981) (10 ⁻¹⁸ cm ²)
M	290.1	179
K	551.4	393
J	690.4	485
H	794.0	532
G	663.3	437
F	436.0	278
E	293.5	181

reported by Molina *et al* (1981) has been made in table 2 at peaks of some of the bands only. The cross-section values reported by Molina *et al* (1981) are, in general, 30 to 40% less as compared to those reported in the present work. In both the experiments, same photon beam resolution of 0.2 nm has been used for the measurement of photoabsorption cross-sections. This large discrepancy in the two measurements is perhaps due to larger pressures used for the target gas by Molina *et al* (1981) in their experiment. The main purpose of the experiment by Molina *et al* was to measure the photoabsorption cross-section for carbonyl sulphide. The main impurity in OCS is, in general, CS₂ which could affect the results to a great extent in this spectral region. The photoabsorption cross-sections for CS₂ were measured only to see the

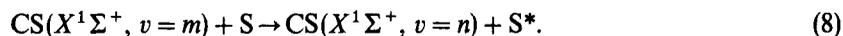
effect of impurity in OCS. It is, therefore, possible that the cross-sections for CS₂ were not measured over a range of those pressures where the results were pressure independent.

Studies on the pressure dependence of photoabsorption cross-sections for CS₂ have been carried out in detail in the present experiment. The cross-sections have been measured at large number of pressures e.g., at 6, 9, 12, 15, 20, 50 and 100 mTorr but for clarity, cross-section values measured at 9, 12, 15, 20 and 50 mTorr pressure are shown in figure along with the average values of cross-sections obtained at a few pressures less than 5 mTorr. At 50 mTorr, the peak intensities of the bands from L to F decrease by about 84 to 71% with the maximum decrease of about 90% at J, I and H bands. The peak intensities of the bands M to O decrease slowly and an attenuation of 71% for band M, 75% for N and 62% for band O has been observed. The bands E, D and C at 50 mTorr pressure are attenuated by about 71%, 46% and 28% respectively.

An attempt has been made to explain the pressure dependence of photoabsorption cross-sections for CS₂ in this spectral region. It was reported by Callear (1963) that vibrationally excited CS is produced directly by the photochemical dissociation of CS₂:



It was suggested that initially, at least three quarters of the molecules are distributed in levels with $v > 2$. It was also reported by Callear that the decay of the vibrationally excited CS may partly be due to CS₂ itself but may largely occur by multiple quantum transitions induced by interaction with transient species, e.g.



It was also pointed out that the atomic sulphur would decay by polymerization rather than by reaction with CS₂. From reaction (7), it is clear that more CS and sulphur atoms are produced at higher pressures of CS₂ vapour. The photoabsorption

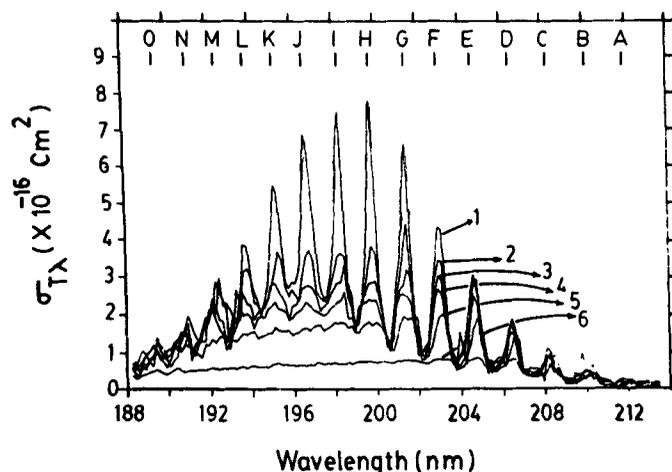


Figure 4. Photoabsorption cross-sections for CS₂ (188-213 nm region) at different pressures. Curve 1 shows average values of cross sections at pressure less than 5 mTorr; curves 2, 3, 4, 5 and 6 show cross section values at 9, 12, 15, 20 and 50 mTorr pressures.

cross-sections for both CS and S and polymerized S₂ are much smaller in this spectral region as compared to those reported for CS₂.

According to reaction (7), CS and S are both produced in the ground states. Therefore, the fluorescence emission is not possible. But it is known that energetically, sulphur atoms could be produced in ¹D state also. The threshold wavelength for the production of S(¹S) from CS₂ was found to be 172.0 nm using the value of 65 kcal for the heat of formation of CS (Okabe 1972). However, Hubin-Franskin *et al* (1976) reported a value of 34 kcal for the heat of formation for the CS radical which correspond to the value of 211.0 nm for the threshold wavelength for S(¹S) production. This shows that in this spectral region (188–211 nm), sulphur atoms are produced in ³P, ¹D and ¹S state and therefore fluorescence at 772.7 nm corresponding to ¹S → ¹D transition could be observed provided ¹S is deactivated collisionally by adding a buffer gas, argon at a pressure larger than 100 Torr. An attempt has been made in the present work to measure total fluorescence cross-sections as well as fluorescence quantum yields at a few wavelengths corresponding to the peaks of a few absorption bands in the spectral region 188–213 nm. A similar attempt has previously been made by Black *et al* (1977) at only five wavelengths between 190 and 210 nm. The relative fluorescence cross-sections at different photon wavelengths were obtained using the method discussed in §3. These cross-sections were made absolute by normalizing the results with SO₂ at 228 nm where the fluorescence quantum efficiency of 100% has been reported by Hui and Rice (1972). A similar experiment was performed at 228 nm using SO₂. Using $\gamma_{f\lambda G}$ as 100% at this wavelength and the absorption cross-section value of 0.45×10^{-18} as reported by Ahmed and Kumar (1992) and measuring $I_{fT\lambda}$ and $I_{0\lambda}$ at various pressures of SO₂, one could obtain the value of the product of constants KFC as given in (6). Knowing this constant, the fluorescence cross-sections were made absolute. The fluorescence cross-sections as well as fluorescence quantum yields as measured at peaks of some of the vibrational bands are given in table 3. The fluorescence quantum yield as obtained in the present experiment varies from about 30% to 19% at higher to lower photon wavelengths.

Table 3. Fluorescence cross-sections and fluorescence quantum yields for CS₂ at peaks of some of the bands. Also given are photoabsorption cross-section at these wavelengths.

Wavelength (nm)	$\sigma_{T\lambda}$ (10^{-18} cm ²)	$\sigma_{f\lambda}$ (10^{-18} cm ²)	$\gamma_{f\lambda}$ (%)
189.42	144.1	43.4	30.1
190.92	178.6	54.1	30.3
192.26	290.1	84.4	29.1
193.59	387.1	100.3	25.9
195.10	551.4	146.7	26.6
196.60	690.4	171.2	24.8
198.27	755.7	182.1	24.1
199.77	794.0	184.2	23.2
201.44	663.3	149.9	22.6
202.94	436.0	92.0	21.1
204.78	293.5	57.8	19.7
206.46	151.8	31.0	20.4
208.46	91.9	17.6	19.1

As compared to the results in the present work, the fluorescence quantum yield values reported by Black *et al* (1977) vary from 5 to 10% at wavelengths between 190 and 210 nm respectively.

The reason for large discrepancy in the two results could be explained in two ways. Firstly, as explained in §3, the fluorescence light has to be sampled from very different regions of the fluorescence cell and this would vary in intensity with the change of target gas pressure. Therefore, K used in (5) and (6) should strictly depend upon n and also on the nature of the gas. But in the present experiment, K has been considered constant. This could be responsible partly for the higher values of fluorescence quantum yields reported in the present experiment. Secondly, it is well-known that $S(^1S)$ atoms could be quenched fast by CS_2 . Therefore, it is desired to use low CS_2 pressures to provide sufficiently long-lived emission for detection. It is felt that the pressure of 0.7 Torr of CS_2 used by Black *et al* may be somewhat on the higher side so as to encourage fast quenching of sulphur atoms. That could explain why the quantum yields reported by Black *et al* are on the lower side.

4.2 Spectral region: 287.5–339.5 nm

The photoabsorption cross-sections as measured in the present experiment in the spectral range 287.5–339.5 nm are shown in figures 5 and 6. These cross-sections have been measured at various CS_2 pressures ranging from 1 to 5 Torr and the average cross-sections are shown in figures 5 and 6. It was found experimentally that the maximum pressure used in the experiment (i.e. 5 Torr) was well within the values of pressures where Beer-Lambert's law was valid.

Although the gas phase absorption spectrum of CS_2 in this spectral region has been studied extensively and the general features are now understood quite well, much of the detail is still lacking because the spectrum contains regions of extraordinary complexity. This absorption system assigned by Kleman (1963) as V system extends from 1 V band at 332.2 nm to 48 V band at 295.3 nm. The band extends to

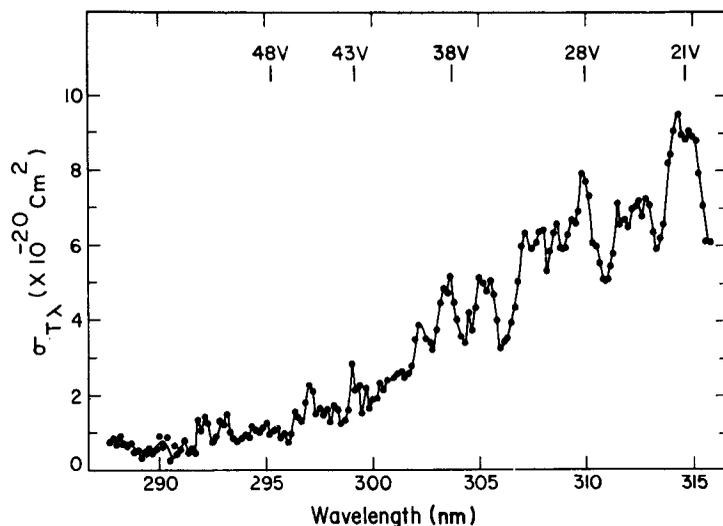


Figure 5. Photoabsorption cross-section for CS_2 in the spectral region 287.5–315.7 nm.

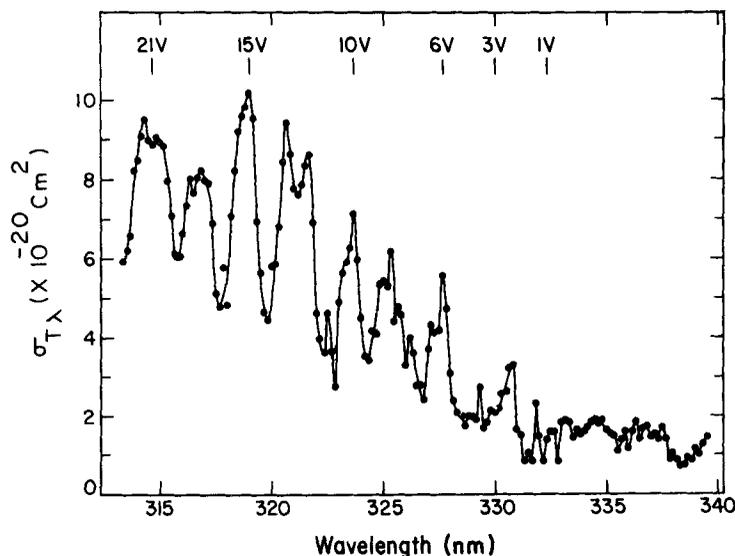


Figure 6. Photoabsorption cross-section for CS₂ in the spectral region 313.3–339.5 nm.

approximately 290 nm but no band assignment has been given by Kleman at wavelengths shorter than 295.3 nm. It has been established conclusively from the vibrational and rotational structure analysis of V system (Jungen *et al* 1973) that the absorption features of this system correspond to the ${}^1B_2({}^1\Delta_u) \leftarrow {}^1\Sigma_g^+$ transition. The absorption spectrum shown in figure 6 in the spectral region 334.0–339.5 nm which forms part of a bigger system extending up to 350.0 nm corresponds to ${}^1A_2({}^1\Delta_u) \leftarrow {}^1\Sigma_g^+$ transition. We have followed the same nomenclature for different bands as done by Kleman (1963). The peaks in figures 5 and 6 have been numbered from 1 V to 48 V which correspond to photon wavelengths from 332.2 nm to shorter wavelengths.

The photoabsorption cross-sections measured absolutely are shown in figures 5 and 6 for the spectral regions 287.5 to 315.7 nm and 313.3 to 339.5 nm respectively. The absorption cross-section values, in general, are less than $1.50 \times 10^{-20} \text{ cm}^2$ in the spectral region from 287.5 to 296.0 nm. The peak of the vibrational band 48 V has a cross-section value of $1.06 \times 10^{-20} \text{ cm}^2$ in this region. At wavelengths larger than 296.0 nm the band peaks show an increase in cross-section up to the vibrational band V 15 which corresponds to a photon wavelength of 318.9 nm. At the peak of 15 V, the absorption cross-section as measured in the present work is $10.16 \times 10^{-20} \text{ cm}^2$. Subsequently at larger wavelengths, decrease in cross-section values has been observed. The typical values at the peaks of vibrational bands 10 V and 6 V are 7.12×10^{-20} and $5.55 \times 10^{-20} \text{ cm}^2$ respectively. A comparison of photoabsorption cross-sections obtained in the present experiment at the peak of a few vibrational bands of the V-system has been made in table 4 with the values obtained by Wu and Judge (1981). The cross-sections reported by them have been obtained between 319 and 330 nm at the instrumental resolution of 0.06 nm. The values of the cross-sections obtained in the two cases are much different. This is expected as the instrumental resolutions in the two cases are different. A comparison on a large scale is not possible as the quantitative data on the photoabsorption cross-sections for CS₂ are scarce.

The total fluorescence cross-sections have been measured at a few pressures of CS₂ vapour from 10 mTorr to 850 mTorr around the peaks of some of the vibrational

Table 4. Photoabsorption cross-sections for CS₂ at peaks of a few bands in 320–330 nm spectral region.

Band assignment	Photon wavelength (nm)	$\sigma_{T\lambda}(10^{-20}\text{cm}^2)$	
		Present work	Wu and Judge (1981)
13 V	320.6	9.40	11.0
12 V	321.5	8.60	11.6
10 V	323.6	7.12	9.8
9 V	325.3	6.18	7.9
6 V	327.6	5.55	9.2

Table 5. Fluorescence cross-sections and fluorescence quantum yields for CS₂ at peaks of some of the vibrational bands of V-system. Both $\sigma_{f\lambda}$ and $\gamma_{f\lambda}$ are given at 20 mTorr and 850 mTorr of target gas pressure. Also given are photo-absorption cross-sections at these wavelengths.

Wavelength (nm)	$\sigma_{T\lambda}$ (10^{-20}cm^2)	At 20 mTorr		At 850 mTorr	
		$\sigma_{f\lambda}$ (10^{-21}cm^2)	$\gamma_{f\lambda}$ (%)	$\sigma_{f\lambda}$ (10^{-21}cm^2)	$\gamma_{f\lambda}$ (%)
302.09	3.88	2.85	7.3	0.33	0.9
303.59	5.17	4.11	7.9	0.36	0.7
304.92	5.12	3.47	6.8	0.34	0.7
307.09	6.35	3.84	6.0	0.29	0.5
308.59	6.59	0.80	1.2	0.25	0.4
309.76	7.93	1.34	1.7	0.28	0.4
311.42	7.16	2.23	3.1	0.27	0.4
312.76	7.26	1.36	1.9	0.24	0.3
314.26	9.49	0.64	0.7	0.25	0.3
316.76	8.19	1.02	1.2	0.22	0.3
318.92	10.16	1.22	1.2	0.21	0.2

bands of the V-system at incident photon wavelengths between 300 and 320 nm. The fluorescence cross-sections along with fluorescence quantum yields obtained from the measured $\sigma_{T\lambda}$ and $\sigma_{f\lambda}$ are given in table 5 at two typical pressures of 20 and 850 mTorr for the target gas.

The fluorescence quantum yields as measured in the present experiment at different photon wavelengths have been found to be different for different pressures of CS₂ vapour. The yields are highest at low pressures and decrease with increase in pressure in an unusual fashion. This shows that the fluorescing CS₂ molecules may be getting deactivated by CS₂ itself. This could be ascertained by using (6) which has been properly modified to take care of such deactivations. This is given by

$$I_{f\lambda T} = CK_1\gamma_{f\lambda Q}I_{0\lambda}\exp(-n\sigma_{T\lambda}l) + \frac{KFC\gamma_{f\lambda G}I_{0\lambda}[1 - \exp(-n\sigma_{T\lambda}l)]}{1 + k\tau n}, \quad (9)$$

here k is the quenching rate constant and τ is the radiative life time of the fluorescing

state. It may be pointed out that for the previous spectral region (188.2–213 nm), the product $k\tau n$ was negligible. For the present spectral region, k and τ values are not known by direct measurements. Using the approximate values of k and τ reported by Hecklen (1963) in an indirect measurement, one should be able to obtain the same value for fluorescence quantum yield at the two pressures. But the values obtained in the present experiment (table 5) have been found to be different at the two pressures. It shows that a more complex process may be occurring in this case. This process may involve vibrational relaxation of the upper excited state prior to deactivation by CS₂ itself as reported by Lambert and Kimbell (1973). Also, it may be pointed out here that the vibrational relaxation is a radiationless transition and is pressure dependent. Such measurements (table 5) have been made at a few absorption peaks of CS₂ which occur at different wavelengths ranging from 300 to 320 nm. The quantum yields vary from 7.3 to 1.2% and 0.9 to 0.2% at 20 and 850 mTorr of CS₂ pressure respectively at a few photon wavelengths from 302.09 to 318.92 nm. To the best of our knowledge, there are no other quantitative measurements for both fluorescence cross-sections and fluorescence quantum yields reported in literature in this spectral region. Therefore, a direct comparison is not possible.

5. Conclusion

The photoabsorption cross-sections, fluorescence cross-sections and fluorescence quantum yields were measured for carbon disulphide in the 188.2–213 and 287–339.5 nm regions with the instrumental resolution of 0.2 nm. The photoabsorption cross-sections measured in the 188.2–213 nm region were found to be pressure dependent and such a measurement, to the best of our knowledge, has been carried out for the first time. The fluorescence cross-sections in the present experiment, were measured along the photon-beam axis and a mathematical approach was put forward to obtain fluorescence cross sections. In the spectral region 300–320 nm, the fluorescence cross sections as well as fluorescence quantum yields measured at the peaks of some vibrational bands of the V system were found to have a special type of pressure dependence. A possible mechanism for this has been suggested.

It has been observed that the quantitative data on fluorescence of CS₂ in the two spectral regions mentioned above is rather scarce. More experiments with better technology are needed to be taken up in this direction in near future.

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