

Study on gaseous CS₂ using laser - induced fluorescence*

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Abstract — The fluorescence of gaseous CS₂ was studied by laser - induced fluorescence (LIF) method. A working curve of gaseous CS₂ was obtained and the detection limit was less than 1 ppm. The time - resolved fluorescence emission spectrum of CS₂ vapor was recorded from 350 nm to 550 nm which consists of a discrete sharp band and a continuous part. The fluorescence lifetimes of the sharp band and the continuous part were measured to be 4-5 and 17 microseconds respectively. The self - quenching constant (Q) of CS₂ obtained is 80-150 torr⁻¹, and the quenching constants (Q_m) of CS₂ by foreign gases, CO₂, O₂, N₂, are 89.5, 45.6 and 30 torr⁻¹, respectively. All the data greatly help to understand the reactions of CS₂ in the atmosphere. The aerosol formation in CS₂ vapor after long time laser irradiation was also observed, and the mechanism of the aerosol formation was preliminarily discussed.

Keywords: fluorescence; gaseous CS₂; LIF method.

1 Introduction

Shanghai is the largest industrial and most densely populated city in China. The problem of air pollution in Shanghai is protruding. Besides SO₂, smoke dust, NO_x, and CO, the principal air pollutants in Shanghai include CS₂, Pb, hydrogen chloride, fluoride, hydrogen sulfide, chlorine, toluene and xylene, among which CS₂ is the most serious one. The release of CS₂ per year is about 3000 tons in Shanghai.

CS₂ is a neurotoxic chemical reagent because of its strong affinity with neurotic tissue. And more, irradiated with ultraviolet rays in the air CS₂ can conduct photochemical reactions with oxygen, OH radical and some organic compounds, and hence produce some other more harmful substances, the secondary pollutants (Wen, 1988). The environmental problem has become a focus of world attention in recent years. Determination of pollutants and studies of their changes in the environment play more and more important role in environmental protection. CS₂, an important pollutant in the atmosphere, especially its photochemical behavior in the atmosphere has been paid our attention.

In our work, the laser - induced fluorescence (LIF) method is used because of its high sensitivity and high resolution for studying gaseous CS₂. A working curve of gaseous CS₂ is obtained. The laser - induced fluorescence emission spectrum of gaseous CS₂ is presented and analyzed, fluo-

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rescence lifetime of CS₂ is measured, and fluorescence decay and quenching mechanism of CS₂ is studied by adding foreign gaseous. All these work is conducive to comprehension of the photochemical behavior of CS₂ in the air. The aerosol formation in CS₂ vapor irradiated by N₂ laser light is also observed for a long time and the mechanism of the CS₂ aerosol formation preliminarily discussed.

2 Experimental

The experimental setup is shown in Fig. 1. A N₂ laser is used as an exciting source ($\lambda = 337\text{nm}$). Fluorescence emission from gaseous CS₂, after being monochromatized, is detected by a combination of a Hamatsu R955 photomultiplier tube (PMT) and a 100 MHz transient recorder. The data is collected and processed in a microcomputer. A fluorescence cell made of stainless steel is used for the emission measurement which is made in the direction perpendicular to the excitation light. The CS₂ was purified by distillation and a repeated freeze(268K)-pump - thaw cycle. The purity of the foreign gases used in our experiment is superior to 99.99%.

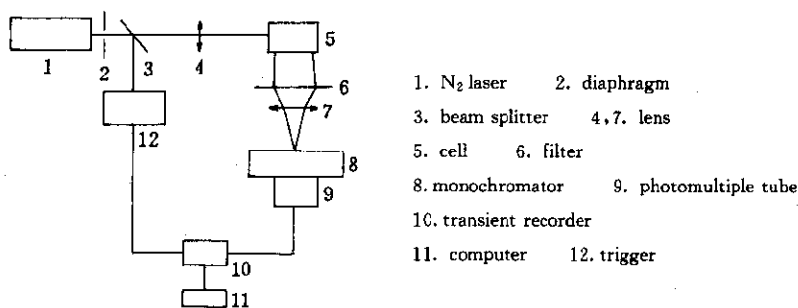


Fig. 1 Experimental setup

3 Results and discussion

Fig. 2 shows that at low pressure, intensity of fluorescence is linearly dependent on CS₂ pressure. In our experiment the detection limit obtained is about 10 millitorr, equivalent to 1 ppm.

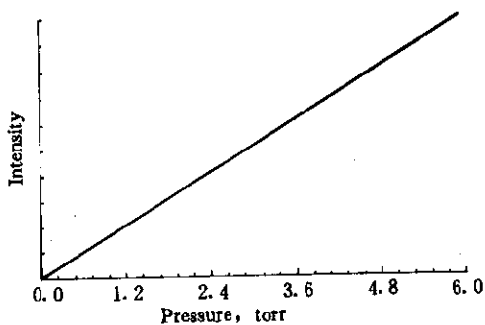


Fig. 2 Fluorescence intensity of CS₂ (the fluorescence emission wavelength, λ_{em} , is 392 nm versus pressure of CS₂)

The value is lower than the detection limit of 10 ppm by other conventional methods including colorimetric analysis, gas chromatography and so on.

Fig. 3 shows the fluorescence emission spectrum of CS₂ in the methanol solution and Fig. 4 shows the spectrum of gaseous CS₂ at 0.5 torr pressure. It can be seen that in the solution, the spectrum can not be clearly resolved because of the interaction between the solvent molecules and solute molecules. But in the gas phase, the fine structure can be resolved at very low pres-

sure. From the shape of the spectrum it can be seen that a discrete structure superimposes on an apparent continuum. This implies that there are two different processes after excitation.

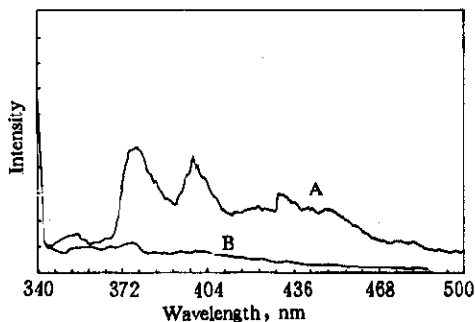


Fig. 3 A: Fluorescence emission spectrum of CS_2 -methanol solution ($V_{\text{CS}_2}:V_{\text{CH}_3\text{OH}}=1:1000$)
B: Fluorescence emission spectrum of methanol

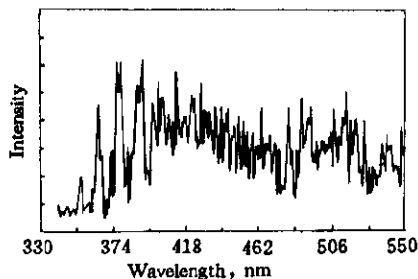


Fig. 4 Time-resolved fluorescence emission spectrum of gaseous CS_2 ($P_{\text{CS}_2}=0.5$ torr)

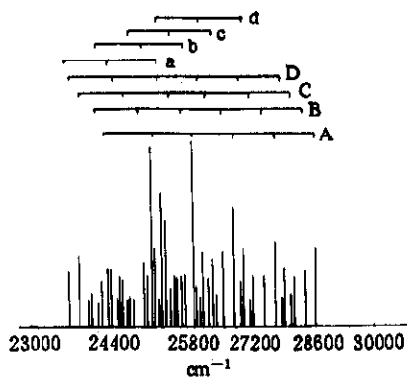


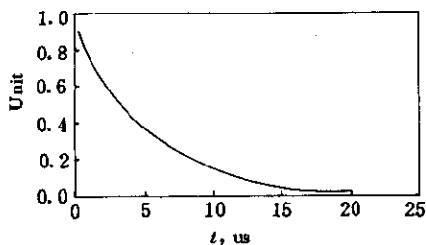
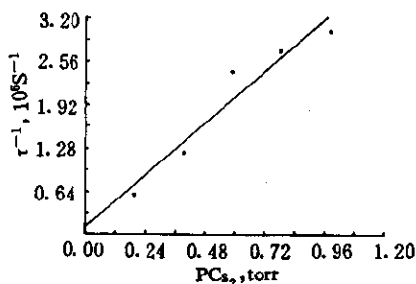
Fig. 5 Assignment of gaseous CS_2 fluorescence emission spectrum

The sharp bands are examined first (Fig. 5). The most prominent band system labeled A forms a progression originating at the frequency of the N_2 laser, 29656 cm^{-1} , and develops to the longer wavelength with an interval of $2V_2'' = 800\text{ cm}^{-1}$. The weaker bands labeled B, C, D form similar progressions and their displacements from progression A are about 210 cm^{-1} , 430 cm^{-1} and 610 cm^{-1} , respectively. Progressions labeled a, b, c and d appear at frequency higher by 60 cm^{-1} than progressions A, B, C and D, respectively. The CS_2 molecule is linear in the ground state, but not linear in its excited state which belongs to C_{2v} electronic configuration. The energy levels of the CS_2 molecule are partly shown in Table 1. The N_2 laser excites the molecule to the rovibronic levels, $050(K=2)$ and $020(K=1)$ levels of A_2 , and also to the 8U band which corresponds to a transition to a triplet state and is known to display a Zeeman effect. The transition from the ground state to the ${}^1\text{A}_2$ and ${}^1\text{B}_2$ components of ${}^3\Delta_u$ state by the Renner-Teller effect can cause the hot bands to appear. The A, B, C and D progressions are assigned to transitions from different vibrational levels of the A_2 state to the ground state (${}^1\Sigma_g^+$ state). The progressions a, b, c and d are regarded as emission from the excited levels of the 8U state to the ground state. As to the continuum part of the spectrum, it is believed that it comes from the complexity interior energy levels interaction of the CS_2 molecule. For example, the interaction between A_2 and some higher ground state levels may be one of the reasons.

Table 1 The energy levels of CS₂

Electronic configuration	D _{∞h} linear	C _{2v}	T ₀₀₀ cm ⁻¹	Bending angle °C
(Πg) ³ Πu	¹ Σ ⁺	¹ B ₂		
	¹ Σ _u ⁻	¹ A ₂	32000	180
	³ Σ _u ⁻	³ A ₂		
	¹ Δ _u	¹ B ₂ (V)	30300	150
		¹ A ₂ (T)	29430	135
(Πg) ³	³ Δ _u	³ B ₂ (S)		
		³ A ₂ (R)	29300	135
	³ Σ _u ⁺	³ B ₂		
	¹ Σ _g ⁺ (X)	¹ A ₁	0	180

In fixing the excitation light wavelength and monochromator wavelength, the transient recorder is used to record the decay of the CS₂ fluorescence signal with time, which is shown in Fig. 6. Through the exponential curve imitation of the plot in Fig. 6 by computer, the fluorescence lifetime (τ) of CS₂ in a certain pressure is obtained. Further, varying the CS₂ pressure, a series of lifetimes are obtained. In Fig. 7, the reciprocal of lifetime is plotted against the CS₂ pressure. The straight line in Fig. 7 is extrapolated and the intercept is the intrinsic fluorescence lifetime (τ_0) of gaseous CS₂ at a certain fluorescence emission wavelength (λ_{em}).

Fig. 6 The typical decay plot of CS₂ fluorescence signalFig. 7 The reciprocal of CS₂ fluorescence lifetime versus the CS₂ pressure ($\lambda_{em} = 392\text{nm}$)

The fluorescence lifetimes of CS₂ at different fluorescence emission wavelengths are determined in this way and shown in Table 2.

Table 2 The fluorescence lifetimes of CS₂ at different fluorescence emission wavelengths

λ_{em}, nm	τ_0, us	λ_{em}, nm	τ_0, us (Akiyoshi, 1976)
392	4.5	392.3	4.5
408	4.5	408.7	5.0
398	5.0	447.5	17.0
402	4.5		
420	3.9		
425	4.0		
448	17.0		

As shown in Table 2, the fluorescence lifetime of the sharp bands in Fig. 4 is 4–5 microseconds and the lifetime of the continuum part is 17 microseconds. This also indicates

that they are two different processes.

The Stern - Volmer model is introduced to study the quenching of CS₂ fluorescence caused by CS₂ itself and several foreign gases, CO₂, N₂, O₂, respectively.

Stern - Volmer model (Guo, 1990) is



The steady state concentration of CS₂* is

$$[CS_2^*] = \frac{k_a I_x [CS_2]}{k_f + k_q [CS_2]} \quad (4)$$

The intensity of fluorescence *I* is expressed as follows:

$$I = \alpha k_f [CS_2^*] \quad (5)$$

From Equation(4) and (5), we obtained

$$I = \frac{\alpha k_a I_x k_f [CS_2]}{k_f + k_q [CS_2]} \quad (6)$$

$$P/I = B(1 + QP) \quad (7)$$

In it, $Q = k_q/k_f$, $P = [CS_2]$, $B = \frac{1}{\alpha K_a I_x}$.

where α is collection efficiency of the fluorescence, I_x is the excitation light intensity, k_a is the rate constant of light adsorption, k_f is the fluorescence decay rate constant, k_q is the self-quenching rate constant.

Fig. 8 shows the ratio of the CS₂ pressure to the CS₂ fluorescence light intensity versus the CS₂ pressure.

From the ratio of the slope to the intercept of the plot in Fig. 8, the value of self-quenching constant is obtained. The results are shown in Table 3.

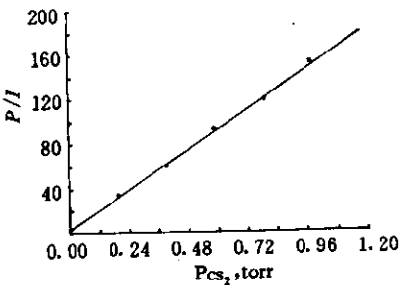


Fig. 8 The self-quenching of CS₂

Table 3 Self-quenching constant *Q* at different fluorescence emission wavelengths

λ_{em}, nm	$Q, torr^{-1}$	λ_{em}, nm	$Q, torr^{-1}$
392	150	390	204
402	126	430	116
428	97	480	119
430	104		
480	85		

Given the existence of foreign gas M, the following step should be added to the above model:



According to Equation (1)–(3) and (8), the following is obtained by the above method:

$$\frac{I_0}{I} = 1 + \frac{K_M[M]}{K_f + K_q[\text{CS}_2]} \quad (9)$$

$$\frac{I_0}{I} = 1 + CQ_m[M] \quad (10)$$

$$C = \frac{1}{1 + \frac{K_q}{K_f}[\text{CS}_2]} \quad Q_m = \frac{K_m}{K_f} \quad (11)$$

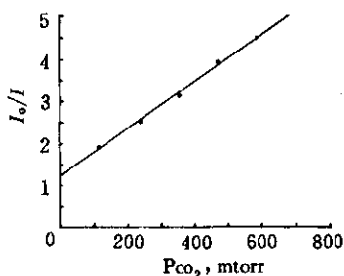


Fig. 9 The quenching of CS₂ by foreign gas, CO₂ (P_{CS₂} = 0.4 torr)

where I_0 is fluorescence intensity of CS₂ without any foreign gas, I is the fluorescence intensity of CS₂ with foreign gas M existing in the system under the study and K_M is the quenching rate constant of CS₂* by M.

Fig. 9 shows the ratio of I_0 to I versus pressure of the foreign gas, CO₂, with CS₂ pressure of 0.4 torr. From the slope of the plot in Fig. 9, combined with the Equation (10), (11) and the value in Table (3), we can contain the values of Q_M , shown in Table 4.

Table 4 Quenching constant Q_M of CS₂ by foreign gases

The foreign gases	Q_M, torr^{-1}	Q_M, torr^{-1} (Lambert, 1973)	Collision cross - section, $\text{cm}^2 \text{molecule}^{-1} \times 10^{-16}$
CO ₂	89.5	73.0	63.5
O ₂	45.6	34.8	55.8
N ₂	30	30	59.2

With the largest molecular size and the heaviest molecular weight among the three foreign gases, CO₂ has high efficiency in colliding with CS₂ and hence has a bigger value of Q_m as shown in Table 4. That the Q_m value of N₂ is close to that of O₂ lies in their close characters in molecular size, molecular weight and dipole moment and so on.

The aerosol formation in CS₂ vapor induced by N₂ laser light has been reported by several authors (Matsuzaki, 1992). In our experiment, we have observed a few brown deposits in the inner walls of the sample cell irradiated by N₂ laser light with high repetition rate for a long time. When a He-Ne laser light beam passed through the sample cell in the direction of overlapping the excitation light beam, it is observed that the light beam is scattered by CS₂ aerosol. The CS₂ aerosol may be composed of some polymers such as $(-S)_n$, $(-CS)_n$. Here it is preliminarily suggested the mechanism of CS₂ aerosol formation is as follows. The detailed studies were report-

ed elsewhere.

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