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Magnetic field influence on the photolysis of the gaseous systems. I. Influence on the S_2 yield under the CS_2 photolysis excited below the dissociative limit

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Abstract

Photolysis of CS_2 was studied under excitation of this molecule by irradiation of the XeCl-excimer laser. Transient absorption observed here was assigned to S_2 (280.0–305.0 nm). The heterogeneous reactions define the S_2 decay. The S_2 photolysis yield as well as the fluorescence intensity of CS_2, were considerably reduced by an external magnetic field. The magnetic field dependences of the magnetic field effect of the CS_2 fluorescence and photolysis were used to identify the photolytically active states of CS_2. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Photolysis; CS_2; Transient absorption

1. Introduction

Every primary photochemical reaction may be considered a radiationless process, making detailed mechanistic investigation of radiationless relaxation one of the most fundamental tasks of photochemistry. Magnetic field influence upon radiationless processes in excited gas phase molecules provides important data on mechanisms of the energy transfer processes involving excited states. Magnetic field effect on the I_2 fluorescence discovered by Stoinbing in 1913 [1] was the first example of a magnetic field influence on the predissociation process of gas phase molecules. In the case of I_2, magnetic field induces a predissociation process from the levels of the $^3\pi_{0u+}$ bonded state to the levels of the $^1\pi_{1u}$ continuum state [2]. Later, the effects on the NO_2 fluorescence and photolysis were discovered by Solarz, Batler and Levy in 1973 [3] and Makarov in 1987 [4] under steady excitation of NO_2. It was the first example of an effect due to excited states of a polyatomic molecule. In NO_2 the magnetic field influence was observed for doublet excited states. Matsuzaki and Nagakura in 1974 [5], and Makarov and Bazhin in 1985 [6], discovered the magnetic field influence on fluorescence and photolysis efficiency of a non-magnetic singlet excited state of CS_2. These authors investigated magnetic field influence on the photolysis efficiency of CS_2 under steady state excitation. These works opened a new research field for investigation of the excited state dynamics in gaseous systems. Afterwards, magnetic field effect on gaseous fluorescence was found for a number of molecules such as SO_2 [7], carbonyls [8–10], diazines and triazine [11–13]. Note also that magnetic field influence on the photolysis efficiency of the SO_2-$n$$C_5H_{12}$ mixtures was studied by Makarov, Lavrik, Skubnevskaya and Bazhin [14] in 1980. It was shown [4,6,14] that the analysis of magnetic field effects in luminescence and in photolysis allows to resolve a problem related to the reactivity of various excited states of the molecules studied.

Given that the magnetic field influence on the efficiency of the NO_2, CS_2 and SO_2-$n$$C_5H_{12}$ photolysis has only been studied under steady state excitation [4,6,14], it becomes very important to extend such studies to time-resolved experiments, which would allow to record magnetic field influence on the yields of transient species. Such transients result from photochemical transformations of the excited molecule. Though the photolysis mechanism of the gaseous CS_2 has already been studied [6,15–17] while exciting CS_2 below the dissociative limit, one very important issue remained unsolved, namely, of whether the electronically

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excited CS_2 (CS_2^*) reacts with ground state CS_2, producing various intermediates? CS_2 has been flash-photolyzed close to the dissociative limit [15]. In these experiments, S_2 and CS intermediates were observed. The lifetime of the two species was found to be different. It was therefore assumed that these intermediates are produced in the reaction

$$CS_2^* + CS_2 \rightarrow S_2 + 2CS \tag{1}$$

This reaction is only possible for $\lambda_{exc} < 272.4$ nm [6,15–17].

Aerosol formation was observed under photolysis of CS_2 by radiation of a nitrogen laser ($\lambda_{exc} = 337$ nm) [18–22]. Given the absorption cross-section of CS_2 is very small in the 337 nm region, a two-photon CS_2 photolysis is impossible in this system. Therefore, it was assumed [6,16,17] that the reaction

$$CS_2^* + CS_2 \rightarrow S_2 + (CS)_2 \tag{2}$$

may be induced by $\lambda_{exc} > 272.4$ nm. However, no direct confirmation of this hypothesis has yet been obtained in time-resolved experiments.

The present paper addresses the exciting unresolved issues, studying the magnetic field effects in the CS_2 time resolved photolysis and fluorescence quenching under excitation at $\lambda_{exc} = 308$ nm.

2. Experimental

Field strength was continually variable from 0–1.2 T. The excitation source was A XeCl excimer laser, and the integrated pulse energy was 70–100 mJ, the pulse duration was 5 to 7 ns, maximum repetition rate 2 Hz. A FEU-79 photomultiplier detected the Cs_2 fluorescence exiting in a direction perpendicular to the laser beam and the magnetic field. Absorption spectra of transients were measured point-by-point using a monochromator, 1.0 nm mm^{-1} linear dispersion. A 120 W high pressure Xe lamp was used as a source of probe radiation. Data acquisition was performed using a DVK-3 PDP-11 compatible personal computer connected via a CAMAC interface to an ADC FK-4226 transient digitizer with 50 ns time resolution, a boxcar integrator and other devices. Commercial CS_2 was purified by vacuum trap-to-trap distillation.

3. Results.

3.1. Transient kinetics

Under the XeCl laser irradiation ($\lambda_{exc} = 308$ nm), transient absorption was observed in the 290.0 nm region. Optical density of this intermediate was linearly dependent on the laser pulse energy in the 18-100 mJ range.

We found that decay kinetics of the transient optical density ($D(\lambda_{prob})$) could be very well fitted by an exponential function, independent of the wavelength (λ_{prob}) of the probing radiation:

$$F(t) = A_0 \exp(-k_d t) \tag{3}$$

Here, A_0 and k_d are the initial amplitude and the decay rate constant of the exponential, respectively. Typical transient decay kinetics are shown in Fig. 1.

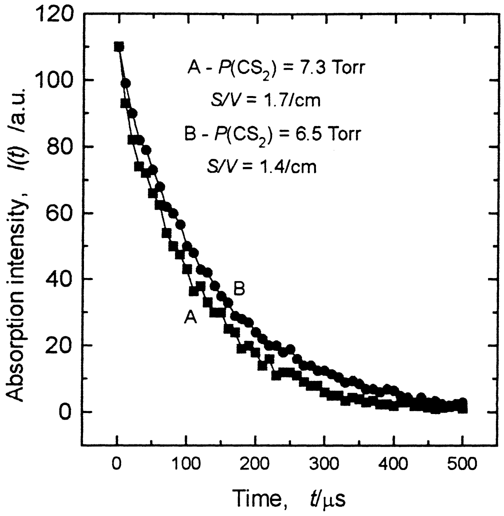

Fig. 1. Decay of the transient absorption under the CS_2 photolysis. (A) $P(CS_2) = 7.3$ Torr, $S/V = 1.7$ cm^{-1}; (B) $P(CS_2) = 6.5$ Torr, $S/V = 1.4$ cm^{-1}; $\lambda_{exc} = 308.0$ nm; $\lambda_{prob} = 290.0$ nm.

Given that the transient decay obeys a single-exponential law, we may assume that the observed absorption belongs to a single transient of the CS_2 photolysis; otherwise, a multi-exponential function should be expected. Judging by spectroscopic evidence, the observed transient is apparently the S_2 molecule [15,23,24].

We found that the S_2 decay time ($(k_d)^{-1}$) was independent on the CS_2 pressure in the 1.2–38.3 Torr range, depending, however, on the S/V ratio. Here, S and V are cell surface area and volume, respectively. Therefore, it should be assumed that S_2 decays heterogeneously on the cell surface. In this case, the k_d constant may be represented as follows:

$$k_d = \gamma\bar{v}\frac{S}{V} = \gamma\frac{S}{V}\sqrt{\frac{8kT}{\pi\mu_{mol}}} \tag{4}$$

where γ is the S_2 decay efficiency on the cell surface.

3.2. Photolysis of CS_2 in presence of magnetic field

We found that the integrated absorption D_B (290.0 nm) of S_2 is considerably reduced in presence of a magnetic field. Fig. 2 is a plot of the magnetic field effect in the CS_2 photolysis ($u(B) = D_B$ (290.0 nm)/D_0 (290.0 nm)) against the magnetic field strength. The magnetic field effect value was independent on the CS_2 pressure in the 1.2–38.3 Torr range.

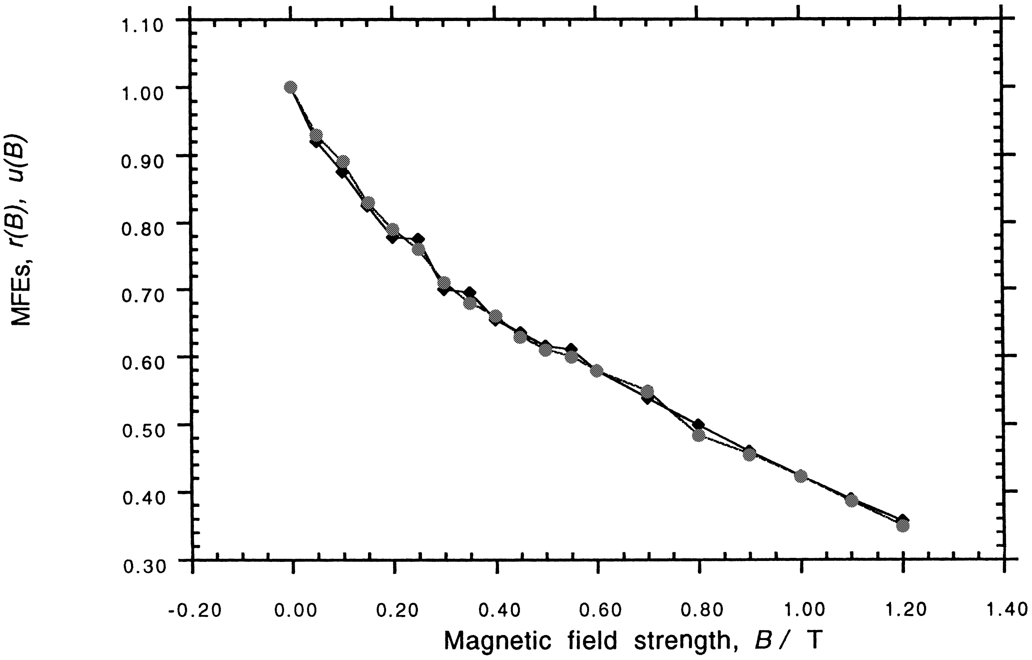

Fig. 2. Plots of the magnetic field effects of the CS_2 fluorescence: (a), $r(B) = A_s(B)/A_s(0)$ – $P(CS_2) = 11$ mTorr, and of the CS_2 photolysis: (b), $u(b) = D_B(290\ \mathrm{nm})/D_0(290\ \mathrm{nm})$ – $P(CS_2) = 6.5$ Torr vs. the magnetic field strength; $\lambda_{exc} = 308.0$ nm; $\lambda_{prob} = 290.0$ nm.

We measured the CS_2 fluorescence decay using $\lambda_{exc} = 308.0$ nm in the 6.3–152 mTorr range both in presence and in absence of the magnetic field. Magnetic quenching of the CS_2 fluorescence was independent of the gas pressure in the pressure range studied. We found that in this case the CS_2 fluorescence decay may be described by a biexponential function;

$$I(t,B) = A_S(B)\exp(-t/\tau_S) + A_L\exp(-t/\tau_L) \qquad (5)$$

Here, τ_s, $A_s(B)$, τL and A_L are the respective lifetimes and amplitudes of the short-and long-lived components. It was shown previously [25] using picosecond time resolution, that a fast component appears in the presence of a magnetic field, its amplitude and lifetime depending on B.

However, only the amplitude of the short-lived component is dependent on the magnetic field at the time resolution used in our experiments, because the time resolution of our setup is not enough for resolution of the fast component induced by a field [26–29]. The magnetic field effects in fluorescence ($r(B) = A_s(B)/A_s(0)$) and photolysis of CS_2 are shown in Fig. 2. The two magnetic field effect curves coincides within the experimental accuracy.

4. Discussion

It was shown [15] that with CS_2 excited close to the dissociative limit, the photolysis mechanism may be represented by the scheme:

$$CS_2 \rightarrow CS_2 \qquad (6)$$

$$CS_2 \rightarrow CS_2 + h\nu_f \qquad (7)$$

$$CS_2 \rightarrow CS_2 \rightarrow 2CS_2 \qquad (8)$$

$$CS_2 \rightarrow CS_2 \rightarrow 2CS + S_2 \qquad (9)$$

The reaction (9) is only active for $\lambda_{exc} < 272.4$ nm [3,4]. Given that in our present study we used $\lambda_{exc} = 308.0$ nm, and recalling that the transient absorption increases linearly with the pulse energy, the CS_2 photolysis may be explained as proceeding via the reaction

$$CS_2 + CS_2 \rightarrow (CS)_2 + S_2 \qquad (10)$$

The CS formation is impossible in this case, while an extra (CS_2) transient results due to Eq. (10). The spectrum of (CS_2) has not been published yet; furthermore, we failed to detect any additional absorption or fluorescence, which could be assigned to the (CS_2) transient. The only absorption observed was that of S_2.

Since the S_2 decay is independent on the CS_2 pressure, being dependent on *S/V*, the resulting decay of S_2 can be described as a heterogeneous process:

$$S_2 \rightarrow \text{products} \quad k_d = \gamma\bar{v}\frac{S}{V} = \gamma\frac{S}{V}\sqrt{\frac{8kT}{\pi\mu_{\mathrm{mol}}}} \qquad (11)$$

which means that the S_2 decay kinetics should be described by Eq. (3). The estimated value is about $4 \times 10^3\ \mathrm{cm}^{-1}$ at room temperature.

It had been assumed that the $\tilde{A} \leftarrow \tilde{X}$ (short-) and $\tilde{\mathrm{B}} \leftarrow \tilde{\mathrm{X}}$ (long-lived component) transitions may be assigned to the discrete and structureless spectral components of CS_2, respectively [25–29]. Here, the $\tilde{\mathrm{A}}$ and $\tilde{\mathrm{B}}$ states may be represented approximately as a superposition of the Born–Oppenheimer states mixed by electron–vibrational interactions [30]:

$$|\tilde{\mathrm{A}}\rangle = \alpha|{}^1\mathrm{A}_2\rangle + \beta|{}^1\mathrm{B}_2\rangle \qquad (12)$$

$$|\tilde{\mathrm{B}}\rangle = \alpha'|{}^1\mathrm{A}_2\rangle + \beta'|{}^1\mathrm{B}_2\rangle + \delta|{}^1\Sigma_g^+\rangle \qquad (13)$$

Here, the relation $\delta/(\alpha' + \beta') \gg 1$ is satisfied [31].

The magnetic quenching of the CS_2 fluorescence was studied and explained by the direct mechanism [25,32]. The magnetic field effect on the CS_2 photolysis has also been studied under steady state irradiation [6,17]. It was found that the CS_2 photolysis is mainly defined by the $\tilde{\mathrm{A}}$ state [6,17].

The present work is devoted to the time-resolved photolysis of CS_2. Based on the fact that the magnetic field effects on the S_2 yield and on the short-lived CS_2 fluorescence decay component, corresponding to the $\tilde{\mathrm{A}}$ state decay of CS_2, are the same, we conclude that the $\tilde{\mathrm{A}}$ state is the only CS_2 state sensitive to an external magnetic field, being also the only photochemically active CS_2 state at $\lambda_{\mathrm{exc}} = 308$ nm. This is most important conclusion of the present study, which will be crucial in the analysis of the CS_2 photolysis mechanism.

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