The Gas-phase Emission Spectrum of Carbon Disulfide Excited by an N_2 Laser—Magnetic Quenching Effect

Akiyoshi MATSUZAKI and Saburo NAGAKURA
The Institute for Solid State Physics, The University of Tokyo, Roppongi, Minato, Tokyo 106

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The time-resolved emission spectrum and its temperature dependence were observed with gaseous CS_2 excited by an N_2 laser. The spectrum was found to consist of three band systems, one of them being demonstrated to be emission from the $^1A_2$ state. The collision-free lifetimes and the collisional quenching constants were determined for the three band systems. The emission from the $^1A_2$ state was found to be quenched by a magnetic field because of the enhancement of an intramolecular energy-transfer process. This is the first observation of the magnetic quenching of emission from an excited singlet state.

The absorption spectrum of CS_2 in the region 290—370 nm has been studied by many researchers.[1—10] The longest wavelength absorption (the R system) in the region has been studied by Kleman,[4] by Douglas and Milton,[5] by Hougen,[6] and also by Hochstrasser and Wiersma[7] and has been assigned as the transition to the $^3A_2$ state which correlates with the $\pi\pi^{*3}\Delta_u$ state of the linear CS_2 molecule. Jungen *et al.*[9,10] studied in detail much stronger absorption (the V system) and assigned it, in accord with Mulliken's prediction,[11] to the transition to the $^1B_2$ state, the upper Renner-Teller component of the $\pi\pi^{*1}\Delta_u$ state of the linear molecule. Furthermore, they observed absorption due to the transition to the $^1A_2$ state, the corresponding lower component.

According to Jungen *et al.*,[9] there exist two absorption systems in the region of the N_2 laser wavelengths: one of them is due to a transition to a triplet state (the U band system) and the other to the transition to the $^1A_2$ state (the T band system). Brus[12] found that CS_2 emission excited by an N_2 laser shows two separate exponential decays. Mochiji *et al.* studied the emission spectrum of gaseous CS_2 and made a vibrational analysis with the aid of vibrational frequencies in the ground state.[13]

Under these circumstances, we have studied emission spectra of CS_2 excited by an N_2 laser, special attention being paid to the fluorescence from the $^1A_2$ state. We have found that the fluorescence is quenched by the magnetic field because of the enhancement of the intramolecular energy-transfer process. This is the first observation of magnetic quenching of emission from an excited singlet state.[14]

Experimental

An Avco Everett Model C950 N_2 laser was used for the excitation of CS_2. Emission from gaseous CS_2 was monochromatized by a Spex Model 1700 spectrometer and was detected by a combination of an EMI 6256S photomultiplier shielded by μ-metal and a PAR Model 160 boxcar integrator gated by a laser trigger. The signal is smoothed with an *RC* filter with a time constant of 0.2 μs. The N_2 laser intensity detected by this system was not affected by magnetic field. This shows that the shielding of the detecting system is good enough for our purpose. An electromagnet with a 6.5 cm gap was used for the magnetic quenching experiment, its field strength being calibrated by a Rowson-Lush gaussmeter indicator Type 789. A Pyrex glass cell of standard "cross" shaped design was used for the emission measurement which was made in the direction perpendicular to the excitation light. Temperature was controlled by flowing cooled nitrogen gas. Absorption spectra were measured by a Cary recording spectrophotometer model 14.

Wako reagent grade CS_2 was purified by distillation from calcium chloride. The sample pressure was measured by a calibrated Pirani gauge and an oil manometer. The vacuum system is free from Hg and background pressure is 10^{-6} Torr.

Results and Discussion

The Assignment of CS_2 Emission Excited by an N_2 Laser. Time-resolved emission spectra of CS_2 excited by the N_2 laser are shown in Fig. 1. The spectrum measured immediately after excitation ($t=0$) consists of sharp bands and a broad band. The latter decays more slowly than the former, as is clearly seen by a comparison of spectra a and b in Fig. 1.

Let us examine the sharp bands shown in Fig. 2. The most prominent band system labeled A forms a progression originating at the frequency of the N_2 laser, 29656 cm^{-1} and developing to the longer wavelength side with a interval of $2\nu''_2=850$ cm^{-1}[15]. The weaker bands labeled B, C, and D form similar progressions: their displacements from progression A are 210, 435, and 610 cm^{-1}, respectively. Progressions labeled a, b, c, and d appear at frequencies higher by 60 cm^{-1} than progressions A, B, C, and D, respectively. Pro-

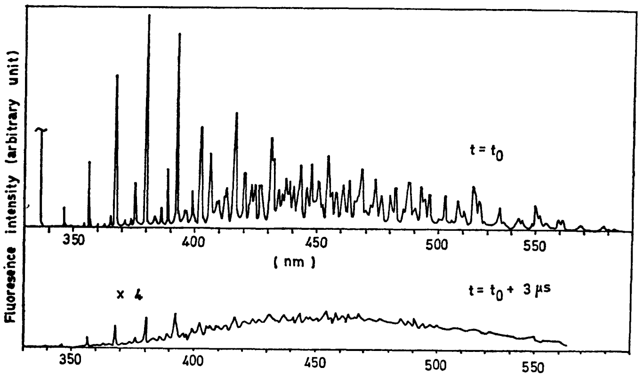

Fig. 1. The time-resolved emission spectra of CS_2 at 25 °C observed 0 μs (spectrum a) and 3 μs (spectrum b) after the fluorescence from the $^1A_2$ state of CS_2 reached the maximum intensity. The CS_2 pressure is 5×10^{-2} Torr.

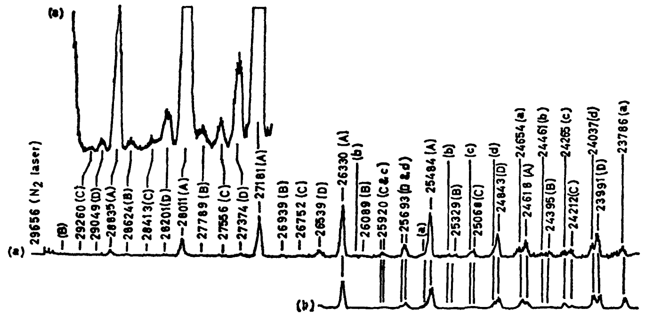

Fig. 2. The emission spectra of CS_2 at (a) 25 °C and (b) −90 °C. The pressure of CS_2 is 5×10^{-2} Torr.

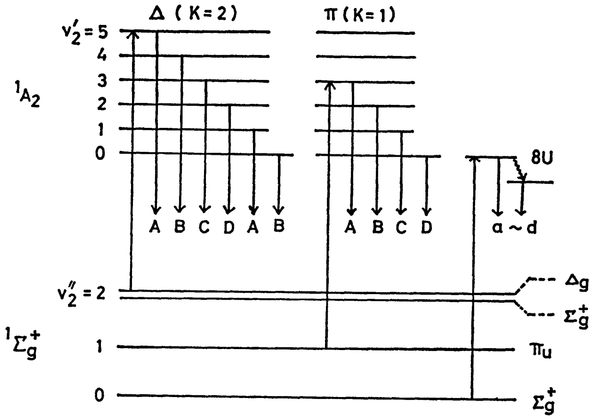

Fig. 3. The energy level diagram of CS_2: The $^1A_2$ and 8U excited states.

gressions a—d are too weak for their assignments to be made clear.

The temperature dependence of the emission spectra was studied at 25, −30, −45, and −90 °C. The spectra measured at 25 and −90 °C are shown in Fig. 2. The emission intensity at 25 °C is much stronger for progressions A—D than for progressions a—d. But progressions A—D rapidly decrease the intensity with lowering temperature and at −90 °C are weaker than progressions a—d. This means that progressions A—D and a—d belong to different electronic states.

According to Jungen *et al.*[9,10] who studied the absorption spectrum of CS_2, the N_2 laser excites the molecule to rovibronic levels of the $^1A_2$ state, say the $050(K=2)$ and $030(K=1)$ levels of $^1A_2$, and also to the upper level of the 8U band which corresponds to a transition to a triplet state and is known to display a Zeeman effect.[4] This is shown schematically in Fig. 3.

The transition from the ground state to the $^1A_2$ state is forbidden, but the mixing between the $^1A_2$ and $^1B_2$ components of the $^1\Delta_u$ state by the Renner-Teller effect can cause the hot bands to appear. In this case, the absorption intensity corresponding to the transition to the $^1A_2$ state is approximately proportional to K^2 [10] and also to the Boltzmann distribution in the lower state. This means that the fluorescence intensity from the $^1A_2$ state increases greatly with increasing temperature. Therefore, the A—D progressions sensitive to temperature are assigned to the transitions from the $^1A_2$ state. On the other hand, progressions a—d are regarded as emission from the excited levels of the 8U band system insensitive to temperature. The assignment of progressions A—D is supported by the fact that they shift each other by $\sim$210 cm^{-1}, ν'_2 of the $^1A_2$ state reported by Jungen *et al.*[10] Furthermore, this assignment is consistent with the fact that the bands belonging to progressions A—D show no splitting or broadening under magnetic field of 13.3 kG.[16] Thus progressions A—D are assigned to the fluorescence from the $050(K=2)$ and $030(K=1)$ levels, the $040(K=2)$ and $020(K=1)$ levels, the $030(K=2)$ and $010(K=1)$ levels, and the $020(K=2)$ and $000(K=1)$ levels, respectively. This is shown schematically in Fig. 3. Since their transition intensities are proportional to K^2, progression A is mainly from the $050(K=2)$ level of the $^1A_2$ state.

Let us turn to the broad band in Fig. 1 (b). This band is similar to emission of gaseous CS_2 excited optically at 290—330 nm,[17] excited by microwave discharge[18] or to that excited by electron impact of 200 eV[19] and also to emission of solid CS_2 or CS_2 in Ar and N_2 matrices excited at 260 nm.[19] The gas-phase emission was tentatively assigned by Douglas[17] and by others[18,19] to the transition from the excited state of the V system, say, the $^1B_2$ state. On the other hand, the solid-phase emission was assigned to the transition from the $^3A_2$ state. The decay times of the gas-phase emission and of the solid-phase emission are 15 μs and 1.8—2.1 ms, respectively. The former is very close to that of the broad band, 17 μs. This indicates that the broad band is tentatively assigned as the transition from the $^1B_2$ state.

Decay Times and Quenching Rates of the Emission. Figure 4 shows the plots of the decay rates, τ^{-1}, observed

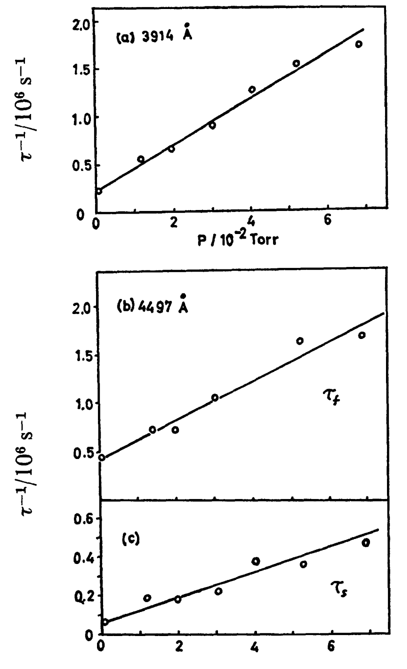

Fig. 4. The plots of decay rates *versus* the CS_2 pressure at 25 °C: (a) for the A band (391.4 nm); (b) for the a band (449.7 nm); (c) for the broad band (449.7 nm).

TABLE 1. COLLISION-FREE LIFETIMES (τ_0) AND COLLISIONAL QUENCHING RATE CONSTANTS (k)

λ (Å)	Band	τ_0 (μs)	k(10^{-10} cm^3/molecule s)
3923	A	4.5±0.2	5.6±0.2
4087	B	5.0±0.4	6.0±0.3
3988	C	5.0±0.5	8.1±0.2
4022	D	4.5±0.2	6.1±0.1
4475	a	2.9±0.3	6.0±0.3
4202	b	3.3±0.4	9.0±0.1
4475	broad	17.0±0.1	1.7±0.3

TABLE 2. THE EFFECT OF THE CS_2 PRESSURE (P) ON THE FLUORESCENCE INTENSITIES

P (Torr)	$I_{A'}/I_A$[a)]	I_B/I_A[a)]	I_C/I_A[a)]	I_D/I_A[a)]
2×10^{-3}	1.1	0.07	0.12	0.29
2×10^{-2}	1.1	0.08	0.14	0.32
1×10^{-2}	1.1	0.09	0.15	0.35
10	1.1	0.10	0.17	0.36
49	1.1	0.11	0.19	0.38

a) $I_{A'}$, I_A, I_B, I_C, and I_D are the fluorescence intensities of the bands at 3797(band A), 3923(band A), 3832(band B), 3857(band C), 3891 Å(band D), respectively.

with the bands belonging to progressions A and a and with the broad band *versus* CS_2 pressure. We can see that the linear relationship is satisfied for each band. This indicates that a Stern-Volmer mechanism holds for collisional quenching by the ground-state CS_2 molecule. The slope and intercept give a collisional quenching rate constant and a collision-free lifetime, respectively. The result is shown in Table 1.

As pointed out by Kleman,[4)] the $^1A_2$ state is perturbed by triplet states, as revealed by the observed perturbation to the vibrational and rotational structures of the corresponding absorption spectrum. However, since we can observe no effect of the magnetic field upon the positions and shapes of fluorescence bands belonging to progressions A, B, C, and D, it is clear that the mixing of triplet states is rather small and the singlet character is predominant for the $^1A_2$ state.

The appearance of the emission bands belonging to progression A suggests the "resonance limit". The effect of increasing collision frequency on the peak intensities of bands A—D is given in Table 2. Even at the CS_2 pressure of 10^{-3} Torr, under almost collision-free circumstances for instance, bands B—D have appreciable intensities.

Brus[12)] observed the non-exponential decay of the unresolved emission of CS_2 excited by an N_2 laser and evaluated the collision-free lifetimes (τ_0) and collisional quenching rates (k): $\tau_0=2.9$ μs, $k=(7.9\pm1.2)\times10^{-10}$ cm^3/molecule s for the short-lived component; $\tau_0=17$ μs, $k=(1.2\pm1.0)\times10^{-10}$ cm^3/molecule s for the long-lived component. His results agree quite well with our results. He assigned the short and long-lived emissions to the transitions from the B_2 and degenerate A_1 and B_1 components of the $^3A_2$ state,[5,6)] respectively, which has the zero-field splitting of 30—40 cm^{-1}.[7)] However, this assignment is very improbable for the following reasons: (1) The N_2 laser wavelengths coincide with no absorption lines of the R system corresponding to the transition to the $^3A_2$ state. (2) The absorption band of the R system is insensitive to temperature, whereas progressions A—D under consideration are very sensitive to temperature. (3) The vibrational frequency, ν'_2 in the upper state of progressions A—D, ~210 cm^{-1}, is not equal to that in the R system, 311 cm^{-1} [4)].

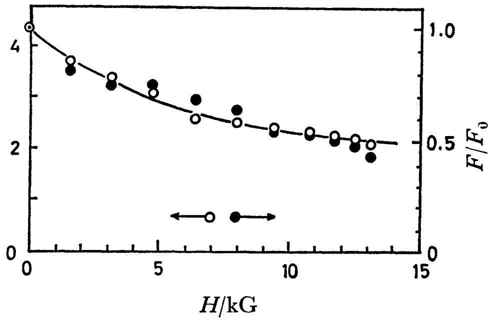

Fig. 5. Plots of F/F_0 and τ *versus* magnetic field(H): the pressure of CS_2 is 10^{-3} Torr.

Magnetic Quenching of Fluorescence. The effect of the magnetic field upon the emission intensity and lifetime of CS_2 was studied with a band at 379.7 nm which was assigned to the transition from the $^1A_2$ (0, 5, 0) state to the ground state. The lifetime, τ, and the integrated emission intensities in the absence and in the presence of the magnetic field, F_0 and F, respectively, were measured at 379.7 nm. The τ and F/F_0 values are plotted against the magnetic field in Fig. 5. As is clearly seen in this figure, the magnetic field effect is parallel for both quantities; they are reduced to about a half in the presence of the magnetic field of ~13 kG. This means that nonradiative energy-transfer (intramolecular or intermolecular) processes are enhanced in the magnetic field.

In order to study further the mechanism of the magnetic quenching observed with CS_2, we measured the pressure dependence of the fluorescence decay rate at 379.7 nm in the presence of the magnetic fields of 0, 4.7, and 12.6 kG. The Stern-Volmer plots of the observed decay rates *versus* the CS_2 pressure are shown in Fig. 6. From the straight lines obtained, the collision-free lifetimes, τ_0, and collisional quenching constants, k, were evaluated as given in Table 3. This table shows that the collision-free lifetime becomes shorter with an increase in the magnetic field, while the collisional quenching constant remains unchanged within the limits of experimental error.

The above-mentioned facts lead to the conclusion that the observed magnetic quenching of the fluorescence is due to an enhancement of an intramolecular nonradiative process. In view of the fact that the $^1A_2$ state is perturbed to some extent by the triplet states densely distributed in the appropriate energy region,[4)] it is reasonable to consider that the intersystem crossing to these triplet states occurs as one of the nonradiative processes and is enhanced by the magnetic field.

According to our experimental result shown in

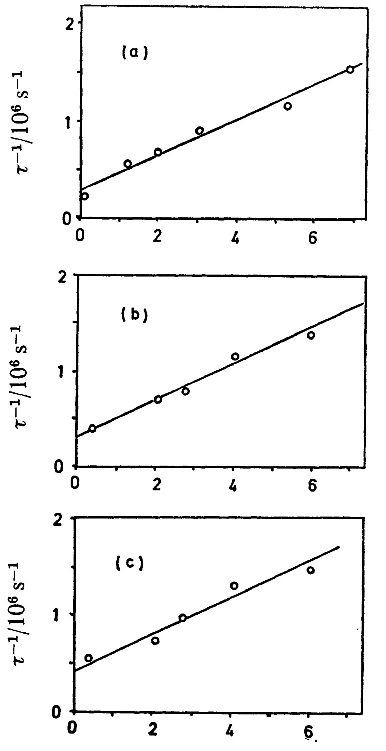

Fig. 6. Plots of τ^{-1} *versus* the CS$_2$ pressure.
(a) in the absence of magnetic field
(b) in the magnetic field of 4.7 kG
(c) in the magnetic field of 12.6 kG

TABLE 3. COLLISION FREE LIFETIMES (τ_0) AND COLLISIONAL QUENCHING CONSTANTS (k) IN THE PRESENCE OF MAGNETIC FIELD (H)

H (kG)	τ_0 (μs)	k(10^{-10} cm^3/molecule s)
0	4.1±0.2	5.6±0.2
4.7	3.2±0.2	5.6±0.2
12.6	2.2±0.3	5.5±0.2

Fig. 7, the $(F_0/F)-1$ value is proportional to the square of the magnetic field in the range higher than 5 kG and decreases rapidly with decreasing magnetic field below 4 kG. The extrapolation of the straight line representing the relation between $(F_0/F)-1$ and H^2 does not pass the origin. We measured very carefully the magnetic-field effect upon the $(F_0/F)-1$ value in the low-field region. The result is also shown in Fig. 7. It is emphasized that, below 700 G, the $(F_0/F)-1$ value decreases once and thereafter increases steeply with increasing magnetic field. Atkins has made theoretical studies to explain this phenomenon.[20)]

Emission from the B$^3\Pi$ 0_u^+ state of iodine is known to be quenched by a magnetic field.[21,22)] This phenomenon was explained by an induced predissociation caused by the magnetic mixing of an unbound 0_u^- state. Solarz *et al.* found that the fluorescence of nitrogen dioxide is quenched by magnetically induced collisional quenching.[23)] The quenched states of iodine and nitrogen dioxide are triplet and doublet, respectively, and are paramagnetic. In the present study, we found

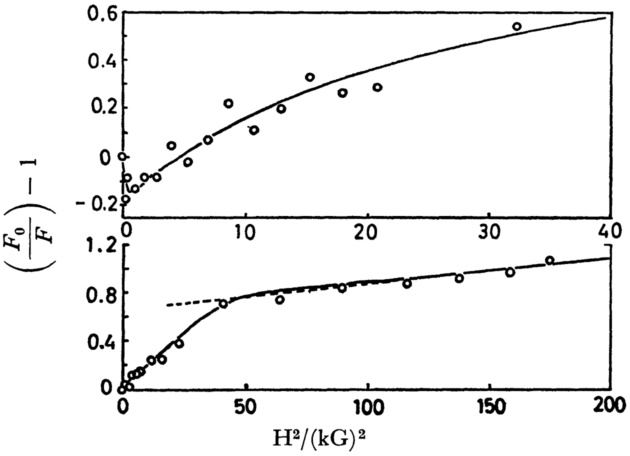

Fig. 7. Plots of $(F_0/F-1)$ *versus* the square of magnetic field: the pressure of CS$_2$ is 10^{-3} Torr.

that the fluorescence from the $^1A_2$ state of CS$_2$ was quenched by a magnetic field. This is the first example of the magnetic quenching of emission from a singlet state.

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