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MAGNETIC QUENCHING OF FLUORESCENCE OBSERVED WITH CARBON DISULFIDE EXCITED BY A NITROGEN LASER

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Fluorescence from the $^1A_2$ state of CS_2 was found to be quenched by a magnetic field. This is the first observation of the magnetic quenching of emission from the excited singlet state. The quenching was found to be due to the enhancement of intramolecular nonradiative energy transfer by a magnetic field.

Emission from the $B^3\pi_{0u}+$ state of iodine is known to be quenched by a magnetic field.1) This phenomenon was explained by an induced predissociation caused by the magnetic mixing of an unbound $0u^-$ state with the $B^3\pi_{0u}+$ state.2) In 1973, fluorescence in nitrogen dioxide was found to show magnetically induced collisional quenching.3) This is a second example of the magnetic quenching of emission from molecules. The quenched states of iodine and nitrogen dioxide are triplet and doublet, respectively. In the present study we found that fluorescence from the $^1A_2$ state of carbon disulfide was quenched by a magnetic field. This is the first example of magnetic quenching of fluorescence from a singlet state.

Experimental

An Avco Everett model C950 N_2 laser was used for excitation of CS_2. The emission from gaseous CS_2 was recorded through a Spex model 1700 spectrometer, an EMI 6256S photomultiplier shielded with μ-metal, and a PAR model 160 boxcar integrator gated with a laser trigger. The N_2 laser intensity detected by this system was not affected by the magnetic field. This shows that the shielding of the detecting system is good enough for our purpose. An electromagnet4) with a 6.5 cm gap was used, its field strengths being measured with a magnetic field scope.

Wako reagent grade CS_2 was purified through distillation over calcium chloride. The sample pressure was measured with a calibrated Pirani gauge. The vacuum system was free from Hg and the background pressure was 10^{-6} Torr. A Pyrex glass cell of a standard "cross" shaped design was used for the emission measurement made at right angles to the excitation light.

Results and Discussion

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 by us[5)] to the transition from the $^1A_2$ (0,5,0) state to the ground state. The observed lifetime, τ, and F/F_0 values are plotted versus magnetic field in Fig. 1. Here F_0 and F are the integrated emission intensities in the absence and in the presence of the magnetic field, respectively. As is clearly seen in this figure, both τ and F/F_0 are reduced to about a half in the magnetic field of ~13 kG. This means that nonradiative energy transfer (intramolecular or intermolecular) processes are enhanced in the magnetic field.

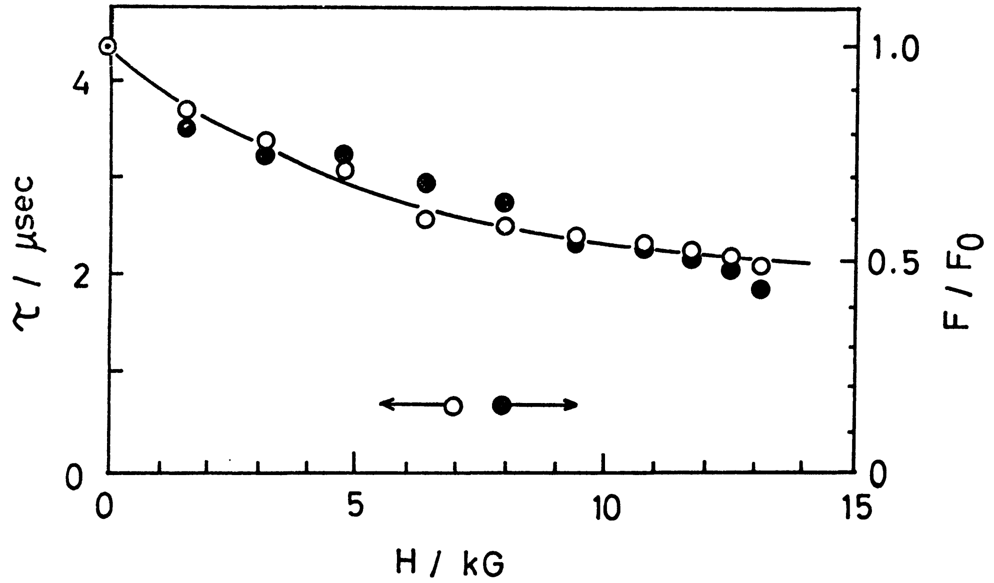

Fig. 1.
Plots of F/F_0 and τ versus magnetic field (H): the pressure of CS_2 is 10^{-3} Torr.

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. 2. From the straight lines obtained, the collision-free lifetimes, τ_0, and collisional quenching constants, k, were evaluated as given in Table 1. This table shows that the collision-free lifetime becomes shorter with an increase in magnetic field while the collisional quenching constant remains unchanged within the limits of experimental error.

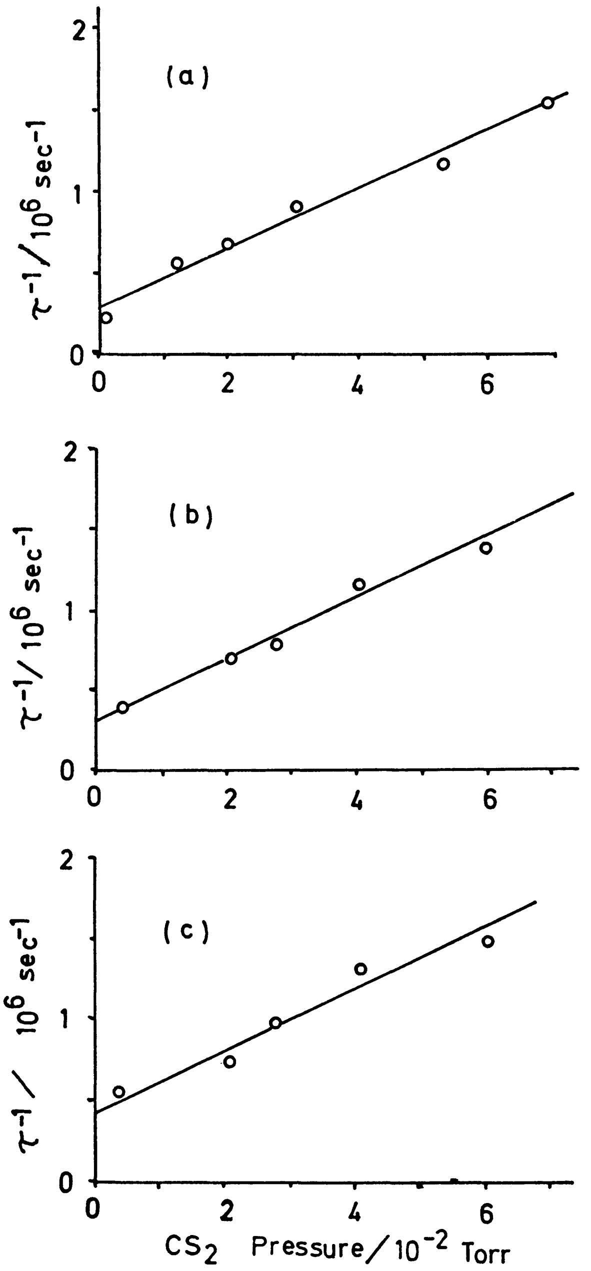

Fig. 2.
Plots of τ^{-1} versus magnetic field (H).
(a) in the absence of magnetic field
(b) in the magnetic field of 4.7 kG
(c) in the magnetic field of 12.6 kG

TABLE 1. COLLISION FREE LIFETIMES (τ_0) AND COLLISIONAL QUENCHING CONSTANTS (k) IN THE PRESENCE OF MAGNETIC FIELD (H)

H (kG)	τ_0 (μsec)	k (10^{-10} cm^3/molecule sec)
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

The above-mentioned facts lead to a conclusion that the observed magnetic quenching of the fluorescence is due to an enhancement of the intramolecular nonradiative processes. According to a study of the absorption spectra,6) the $^1A_2$ state is largely perturbed by the triplet states densely distributed in the appropriate energy region. This indicates that the mechanism of the observed magnetic quenching may involve intersystem crossing to the triplet states; the process may be enhanced by the magnetic field. In this connection, it may be noted that the observed (F_0/F - 1) value is proportional to the square of the magnetic field in the range higher than 5 kG, as is clearly seen in Fig. 3. Further details on the mechanism of this phenomenon will be published later.

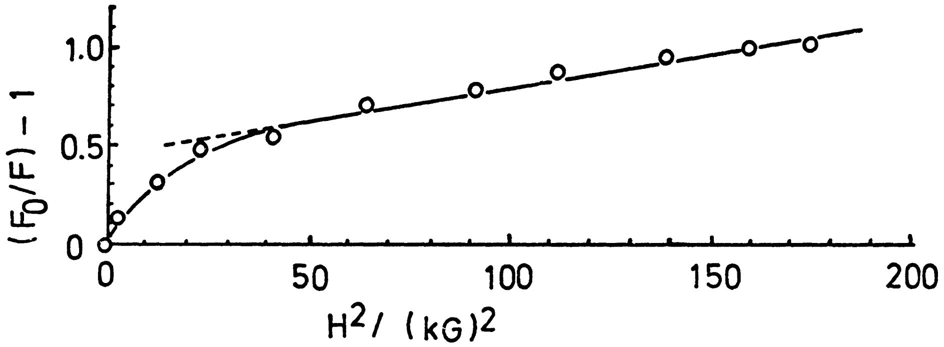

Fig. 3.
Plots of (F_0/F - 1) versus square of the magnetic field: the pressure of CS_2 is 10^{-3} Torr.

References and Note

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4) We wish to thank Professor Tatsuo Yajima for his kindness in putting the electromagnet at our disposal.

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