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COLLISIONAL RELAXATION OF H_2CS ($\tilde{A}^1A_2$, $v_4' = 1$)

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Fluorescence spectra of single vibronic levels of the first excited singlet state of H_2CS have been measured under effusive flow conditions as a function of pressure. Weak non-resonance bands grow in with increasing pressure, demonstrating the existence of collisional vibrational relaxation of the 4^1 level to the 4^0 level.

Formaldehyde has been known as a prototype for experimental and theoretical studies of intramolecular processes; radiative decay, internal conversion, and photodissociation.[1)] Concerning an isoelectronic C_{2v} molecule thioformaldehyde H_2CS, emission and absorption spectra of $^1A_2$ of H_2CS have been reported.[2,3)] The dynamical behaviour of this molecule, however, has not been reported except the fluorescence lifetimes that are rather long 99 ± 6 μs for the $\tilde{A}^1A_2$ ($v_4' = 1$) level because of the symmetry selection rule.[4)] The fluorescence spectra of H_2CS ($\tilde{A}$) would be easily affected by quenching molecules unless they are measured under low pressure condition. In order to study the dynamical behaviour of the $\tilde{A}$ state of thioformaldehyde, the collisional deactivation of $\tilde{A}^1A_2$ ($v_4' = 1$) has been observed under effusive flow conditions as a function of ambient pressures.

Thioformaldehyde is prepared by pyrolysis of dimethyl disulfide $(CH_3S)_2$ at 800°C using a Kanthal wire (1 mm diameter, 3 Ω) electric furnace and a quartz tube (OD = 12 mm, ID = 10 mm). Dimethylsulfide $(CH_3S)_2$ was obtained from Wako Chemicals.

By irradiation with dye laser light, fluorescence spectra (600 nm - 820 nm) were taken with a monochromator (f = 250 mm, 500 nm blazed). Under the pressure range of P = 1 - 300 mTorr a 6" vacuum chamber with a 6" diffusion pump was used for effusive flow conditions. The pressure was adjusted by changing the voltage to the heater of the diffusion pump and was measured 100 mm away from the emitting zone by a Pirani gauge. The pressure measured did not mean that of the observation zone. The effusive flow of H_2CS through a 3 mm i.d. tube was irradiated at 10 mm apart from the nozzle exit by a cw dye laser light from a Spectra-Physics DL-375 dye laser pumped with a Spectra-Physics 165 argon ion laser. Band widths were 10 cm^{-1}. Signals were obtained by a lock-in amplifier and a photomultiplier (HTX R-955, $\lambda_{cut\text{-}off}$ = 850 nm) as shown in Fig. 1.

Under high pressure conditions (total pressure P = 0.2 - 1.7 Torr) we used a box-type cell (70 x 70 x 70 mm) evacuated by a rotary pump (950 l/min) with two light baffles at each end.

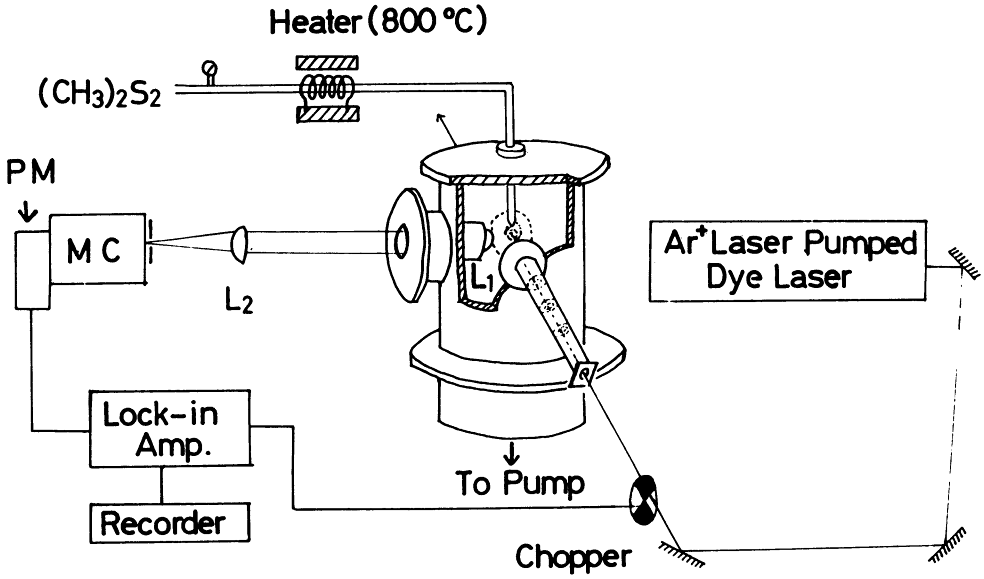

Fig. 1. Experimental setup for fluorescence measurement under effusive flow conditions. MC, 25cm monochromator; PM, photomultiplier; L_1 and L_2, lens for a telescope.

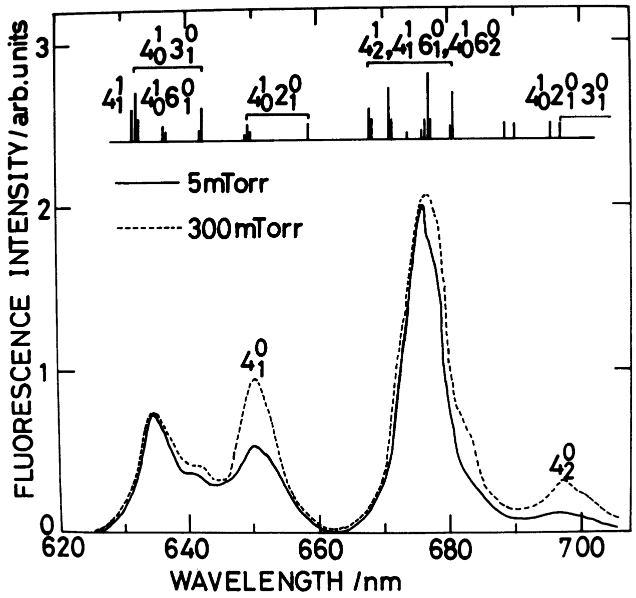

Fig. 2. Effect of the chamber pressure on the uncorrected emission spectrum of thioformaldehyde excited at 596 nm. The low and high pressure spectra are normalized at the 676 nm intensity. The excited level is the 4^1 level of the $\tilde{A}^1A_2$ state. Upper assignments are after Clouthier et al. (Ref. 3).

Figure 2 shows the pressure effect on fluorescence band intensities measured under the effusive flow conditions when the 4^1 level was pumped. The flow rate of $(CH_3S)_2$ was kept constant but the chamber pressure was changed by adjusting the voltage applied to the diffusion pump heater. The relative emission intensities at 635 nm and 676 nm that are purely from the 4^1 level were not affected by the pressure change while those at 650 nm and 697 nm increased with the total pressure from less than 1 mTorr to 300 mTorr. In Fig. 3, the relative peak fluorescence intensities of 676 nm and 650 nm bands with respect to 635 nm bands are plotted against the chamber pressures. The ratios of I (635 nm)/I (676 nm) do not change with the chamber pressure while the ratios of I (635 nm)/I (650 nm) decreased with the increasing pressure to approach an asymptotic value which is same as obtained in the high pressure region (P = 0.2 - 1.7 Torr). The transitions from the 4^0 level formed by collisions appear at 650 nm (4^0_1) in addition to the resonant $4^1_0 2^0_1$ transitions and at 697 nm (4^0_2) in addition to $4^1_0 2^0_1 3^0_1$.

This collision-induced vibrational deactivation process is similar to that reported in the SVL fluorescence of H_2CO ($\tilde{A}^1A_2$) by Shibuya et al.[5] or of Cl_2CS ($\tilde{A}^1A_2$) by Condirston et al.[6] They found that non-resonance bands grow in with a total pressure following a $4^1 \rightarrow 4^0$ transition. The unimolecular and bimolecular processes which populate and depopulate the 4^1 level of H_2CS ($\tilde{A}^1A_2$) are given as follows after Shibuya et al.[5] for H_2CO ($\tilde{A}^1A_2$),

$$\begin{aligned}
\tilde{X}\ (v'' = 0) &\xrightarrow{596.4\ \mathrm{nm}} \tilde{A}\ (v_4' = 1), \\
\tilde{A}\ (v_4' = 1) &\xrightarrow{k_r} \tilde{X}\ (v'') + h\nu, \\
&\xrightarrow{k_{10}[M]} \tilde{A}\ (v_4' = 0), \\
&\xrightarrow{k_q[M]} \tilde{X} \text{ or products}, \\
&\xrightarrow{k_{nr}} \text{non-emitting species},
\end{aligned}$$

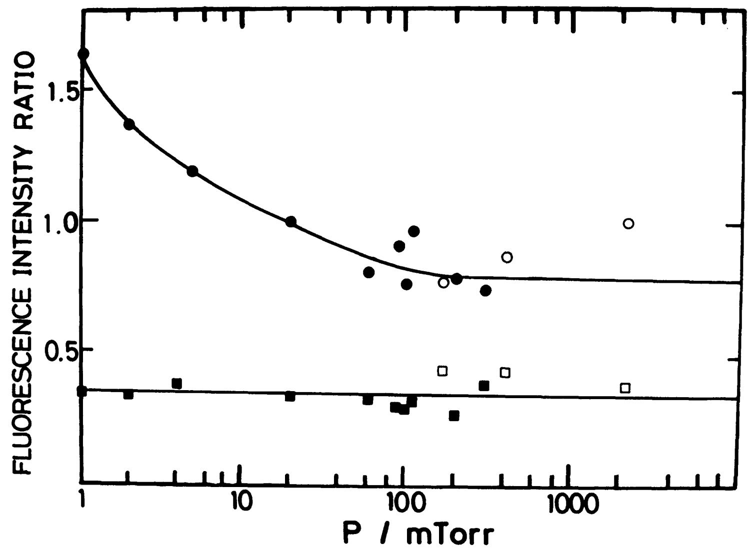

Fig. 3. Effect of the chamber pressures on the emission peak intensities at 650 nm and 676 nm relative to at 635 nm: I (635 nm)/I (650 nm), ●, measured in the 6" vacuum chamber, ○, in the box type cell; I (635 nm)/ I (676 nm), ■, in the 6" vacuum chamber, □, in the box type cell. At P < 1 mTorr, I (635 nm)/I (650 nm) and I (635 nm)/ I (676 nm) were 3.0 and 0.33, respectively.

$$\tilde{A}\ (v_4' = 0) \begin{cases} \xrightarrow{k_r'} & \tilde{X}\ (v'') + h\nu, \\ \xrightarrow{k_q'[M]} & \tilde{X} \text{ or products,} \\ \xrightarrow{k_{nr}'} & \text{non-emitting species.} \end{cases}$$

The microscopic rate constants are k_{10} for the 1 → 0 collision-induced vibrational deactivation process and k_q for the electronic quenching of the 4^1 level, while M denotes a parent molecule and by-products (H_2S, CH_3SH, CS_2 and SO_2) molecules of the pyrolysis of dimethyl disulfide.[7)] The subscripts r and nr denote radiative and nonradiative processes. The prime is used to identify the process originating from the 4^0 level. A steady state assumption of $dN_0/dt = 0$ gives,

$$N_1/N_0 = (k_r' + k_{nr}')/k_{10}[M] + k_q'/k_{10},$$

where N_0 and N_1 represent the number of molecules in the $\tilde{A}$ $v_4' = 0$ and $v_4' = 1$, respectively.

It is expected from this equation that the N_1/N_0 ratio and hence the emission intensity ratio $k_r N_1/k_r' N_0$ decreases with increasing the chamber pressure [M] to become constant. Actually, the expected decrease in the ratios of I (635 nm)/I (650 nm) is observed over the pressure range 1 - 50 mTorr while they are unchanged over the range P > 100 mTorr in Fig. 3. The pressure range over which the intensity change was observed is P < 100 mTorr. Because the k_r' and k_{nr}' are reported to be $\sim 10^4$ sec^{-1},[4)] these values are comparable with $k_{10}[M]$ only in P > 100 mTorr, assuming vibrational relaxation on almost every collision, i.e., $k_{10}[M] \sim 10^6$ sec^{-1} at 100 mTorr. The electronic (k_q) and vibrational (k_{10}) quenching rate constants are roughly estimated to be of the same order of magnitude, from the asymptotic value of 0.8 in I (635 nm)/I (650 nm).

Our observation of collisional relaxation of H_2CS seems in disagreement with those of Clouthier et al.,[3)] i.e., an increase in the total pressure from 0.1 to 2.0 Torr results in no change in the structure of the emission bands and only small variation in the intensity of the spectrum. Probably the total pressure was too high in their experimental conditions for the spectral change to be observable because Fig. 3 shows no change in the relative intensities of the spectra at P > 0.1 Torr.

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