1D3b Detection of Sulfur Atoms (^{1}D and ^{3}P) and Branching Ratio between Reaction and Quenching in the S(^{1}D) + OCS System

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Carbonyl sulfide (OCS) is a sulfur compound at the highest concentration in the atmosphere. In the stratosphere, sulfur atoms in the two electronic states ^{3}P and ^{1}D are generated in the photolysis of OCS over the wavelengths $\lambda \sim 200$–250 nm and the subsequent processes are closely related to the generation of SO_x in the atmosphere. We have constructed a highly sensitive detection system of sulfur atoms and performed experiments on the chemical kinetics of reaction and quenching.

A gaseous mixture of OCS (15–60 mTorr) and He (3–78 Torr) was introduced to a flow cell at 298 K. The sample gas was irradiated with a KrF laser (248 nm), and the resultant S(^{1}D) and S(^3P_J) were detected by two photon laser-induced fluorescence (2P - LIF) technique via the schemes shown as the insets in Fig. 1.

The time profiles of the 2P - LIF intensities of the two electronic states were recorded as a function of the delay time between the photolysis and probe laser (Fig. 2). The nice correspondence between the decay of S(^{1}D) and growth of S(^{3}P) indicates that S(^{3}P) is generated by quenching of S(^{1}D). Recorded profiles at varying pressures of OCS were fit to the single-exponential decay (^{1}D) and growth ($^3P_2$), and the pseudo first-order rate coefficients k were determined. The [OCS]-dependence of k has given the overall rate coefficients for the S(^{1}D) + OCS reaction to be $(2.8 \pm 0.3) \times 10^{-10}$ and $(2.7 \pm 0.3) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} from the profiles of S(^{1}D) and S($^3P_2$), respectively. Measurements of the 2P - LIF intensities of S($^3P_2$) in the absence and presence of N_2 (2 Torr), which is an efficient quencher of S(^{1}D), have determined the branching ratio between reaction and quenching of the S(^{1}D) + OCS system to be 0.19 : 0.81.

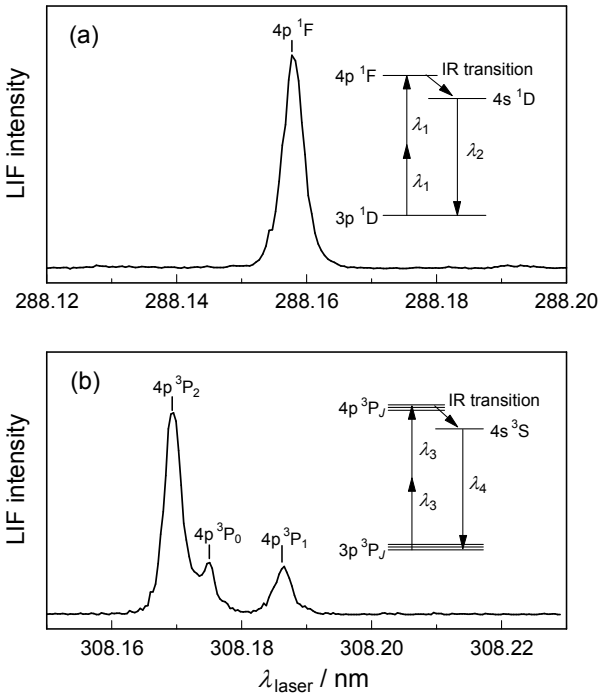

Fig. 1. 2P - LIF excitation spectra of (a) S(^{1}D) and (b) S($^3P_2$). The insets show the schemes of detection. (a) λ_1 = 288.16, λ_2 = 166.7 nm; (b) λ_3 = 308.17, λ_4 = 180.7 nm.

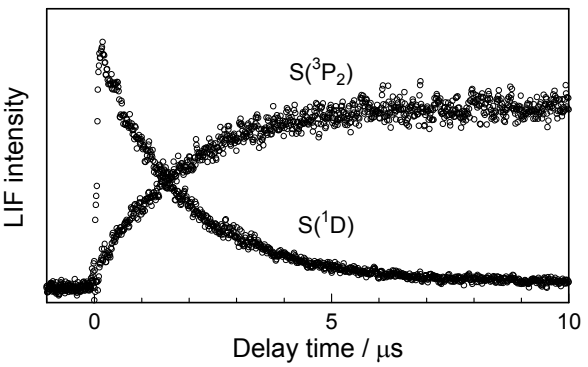

Fig. 2. Time-resolved 2P - LIF intensities of S(^{1}D) and S($^3P_2$). p(OCS) = 60 mTorr, p(He) = 3.0 Torr