2F3b Generation of CH and H as the Photoproducts of Trihalomethanes and Chemical Reactions of CH with the Precursors.

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The methylidyne radical (CH) plays important roles in the combustion processes of the hydrocarbon and planetary atmospheres. UV two-photon photolysis of $CHBr_3$ and $CHCl_3$ is widely used for generating CH. In the $CHCl_3$ case, CH and H have been detected;[1,2] however, no report on the relative yield of CH and H has been made.

A gaseous mixture of $CHBr_3$ or $CHCl_3$ (0.5–4.0 mTorr) and He (10 Torr) in a flow cell at 298 K was irradiated with pulsed laser light at 193 or 248 nm. $CH(X^2\Pi)$ was detected with laser-induced fluorescence (LIF) via the $A^2\Delta$–$X^2\Pi$ transition (Fig. 1), and H atoms was observed with the Lyman-α fluorescence subsequent to two-photon excitation via the 2s ← 1s transition (Fig. 2).

The overall rate coefficients for the reactions of CH with $CHCl_3$ and $CHBr_3$ have been determined to be 5.3×10^{-10}, 5.5×10^{-10} cm^3 $molecule^{-1}$ s^{-1}, respectively for the first time. Addition of H_2 made it possible to convert CH into H via the CH + H_2 → CH_2 + H reaction. Time-resolved LIF intensity showed the increase in the yield of H (Fig. 3). The rate of the growth of H is shown in Fig. 3b. The upper limit of the relative yield of CH and H in the photolysis of $CHCl_3$ at 193 nm has been determined to be $\phi(CH)/\phi(H) < 0.7$.

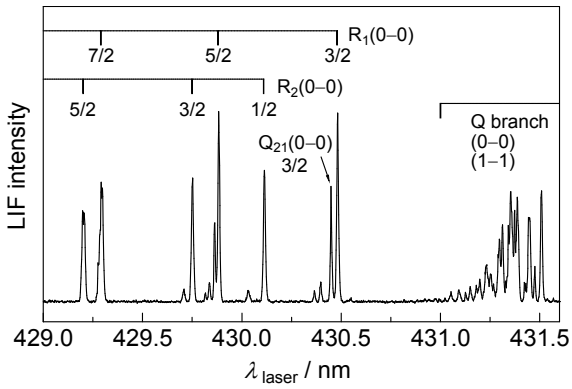

Fig. 1. LIF excitation spectrum of $CH(A^2\Delta - X^2\Pi)$. $p(CHCl_3)$ = 2 mTorr, p(He) = 10 Torr.

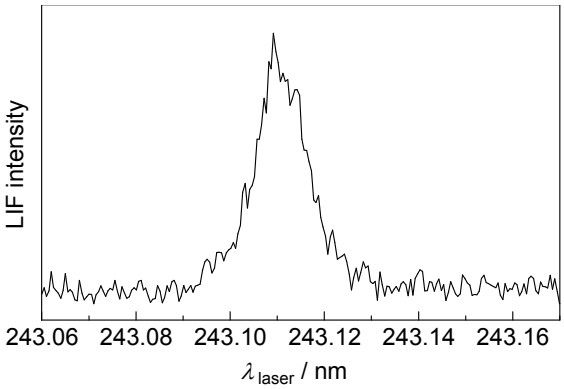

Fig. 2. Two-photon LIF excitation spectrum of H atom. $p(CHCl_3)$ = 2 mTorr, p(He) = 10 Torr.

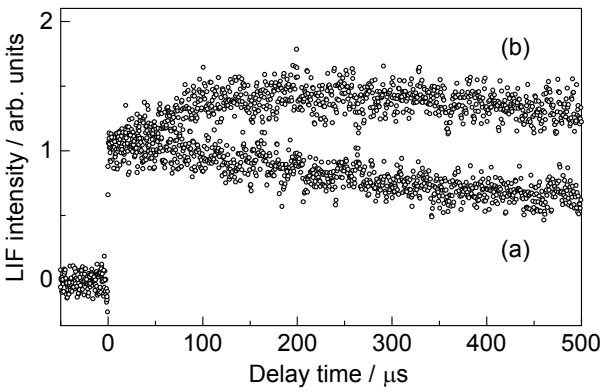

Fig. 3. Time-resolved two-photon LIF intensities of H atoms. $p(CHCl_3)$ = 1 mTorr, p(He) = 10 Torr, $p(H_2)$ = (a) 0; (b) 800 mTorr

References

1. Romanzin, C.; et al. *Chem. Phys.* **2008,** *351,* 77–82.
2. Brownsword, R. A.; et al. *J. Phys. Chem. A.* **1997,** *101,* 5222–5227.