2A3b

Direct Determination of the Rate Coefficient for the Reaction of O(^{1}D) with OCS

○K. Orimi[1], S. Watanabe[1],H. Kohguchi[1], K. Yamasaki[1]
[1] Grad. Sc. Sci., Hiroshima Univ.

1. Introduction The reaction of O with OCS, leading to SO and CO, is one of the important reactions in the atmosphere. There have been many reports on the reactions of O(^{3}P). The rate coefficient of reaction O(^{3}P) + OCS, 1.3×10^{-14} cm^3 molecule^{-1} s^{-1}, is small due to the barrier along the reaction coordinate.[1] The reaction of O(^{1}D) with OCS; on the other hand, has rarely been studied. In the present study, we have detected vibrationally excited SO($X^3\Sigma^-$) generated in the O(^{1}D) + OCS reaction, and determined the overall rate coefficient.

2. Experiments A gaseous mixture of O_3/OCS/He at 298 K in a flowing cell was irradiated at 266 nm from a YAG laser. Vibrationally excited SO($X^3\Sigma^-$, v = 6 – 8 and 18 – 21) was detected via laser–induced fluorescence (LIF) of the $B^3\Sigma^- – X^3\Sigma^-$ transition with a YAG pumped dye laser. To record the time profiles of the LIF intensities, the wavelength of the probe laser was tuned to a rotational line, and time delays between the photolysis and probe laser were scanned with a pulse delay controller.

3. Results and discussion The rotational lines in the LIF excitation spectrum with $0-8$ band were assigned to the main branches of the $^3\Sigma^- – ^3\Sigma^-$ transition (Fig. 1). The LIF excitation spectra of $2-19$, $2-20$, and $2-21$ bands were also observed. The facts suggest that O(^{1}D) + OCS instead of O(^{3}P) + OCS governs the generation of SO($v \geq 19$), because the heat of reaction of O(^{3}P) + OCS → SO($X^3\Sigma^-$) + CO is smaller than the vibrational energies of SO($v = 19$).

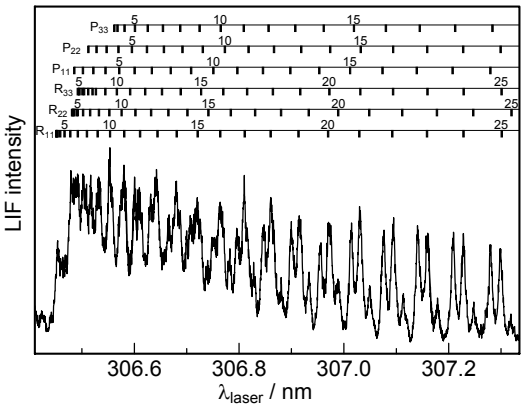

Fig. 1. LIF excitation spectrum of SO($B^3\Sigma^- – X^3\Sigma^-$, 0 – 8 band). p(OCS) = 40 mTorr, p(O_3) = 2.4 mTorr, and p(He) = 10 Torr.

Fig. 2 shows the time–resolved LIF intensities of SO($X^3\Sigma^-$, v = 8) observed at the various pressures of OCS. The gray lines denote the time–dependent LIF intensities fit by $A[1-\exp(-kt)]$ with adjustable parameters A and k. OCS pressure dependence of the first-order reaction rate k has given the overall rate coefficient of the O(^{1}D) + OCS reaction to be $[2.1 \pm 0.3(2\sigma)] \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}.

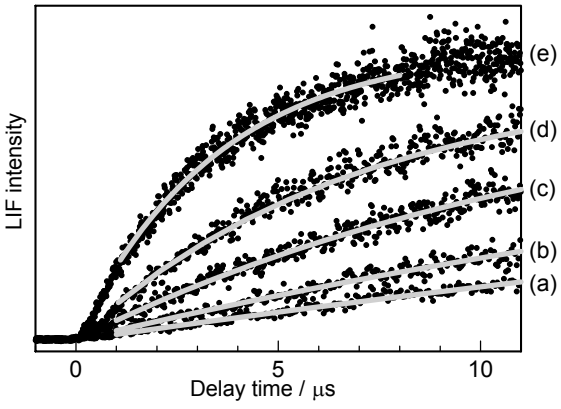

Fig. 2. Time profiles of SO($X^3\Sigma^-$, v = 8). The partial pressures of OCS were (a) 3, (b) 5, (c) 10, (d) 20, and (e) 41 mTorr. p(O_3) = 2.4 mTorr, p(He) = 10 Torr.

Reference

1. Chen et al., *Chem. Phys. Lett.*, **247**, 313 (1995).