

## 1A2a

Nascent vibrational energy distributions of  $S_2(X^3\Sigma_g^-)$  generated in the  $S(^1D) + OCS$  reaction.Shogo Tendo,<sup>1</sup> Hiroshi Kohguchi,<sup>1</sup> Katsuyoshi Yamasaki<sup>1</sup><sup>1</sup> Department of Chemistry, Graduate School of Science, Hiroshima University

Bersohn and colleagues<sup>1</sup> reported that the  $S(^1D) + OCS$  reaction generated the only vibrationless level ( $v=0$ ) of  $S_2(X^3\Sigma_g^-)$ . We, however, have recently detected the highly excited vibrational levels up to  $v=19$ .<sup>2</sup> In the present study, the nascent vibrational distributions of  $S_2(X^3\Sigma_g^-)$  have been determined by kinetic analysis to ascertain the cause of the difference between the two studies.

A gaseous mixture of  $OCS(10 \text{ mTorr})/He(5 \text{ Torr})$  in a flow cell at 298 K was irradiated with laser light at 248 nm. The reaction of the photoproduct  $S(^1D)$  with  $OCS$  generates  $S_2(X^3\Sigma_g^-)$ . A single vibrational level of  $S_2(X^3\Sigma_g^-, v=1-4)$  was detected with laser-induced fluorescence (LIF) via the  $B^3\Sigma_u^- - X^3\Sigma_g^-$  transition.

The time-resolved LIF intensities of the vibrational levels were recorded at varying pressures of  $SF_6$  (Fig. 1). Kinetic analysis by the integrated profiles method (IPM) has given the pseudo first-order decay rates  $k_{1st}$ . The rate coefficients for vibrational relaxation of  $S_2(X^3\Sigma_g^-, v=1-3)$  by  $SF_6$  have been determined from the slopes of the straight line fit of the plots of  $k_{1st}$  vs  $[SF_6]$  (Fig. 2). The relative detectability of the adjacent vibrational levels also has been obtained in the IPM analysis, giving the nascent relative vibrational populations: 1.0/0.69/0.47/0.49 for  $v = 0/1/2/3$ . The findings indicate that vibrationally excited  $S_2(X^3\Sigma_g^-)$  is generated in the  $S(^1D) + OCS$  reaction.

$S_2(X^3\Sigma_g^-, v=0)$  with low reactivity probably accumulated by relaxation of the levels  $v \geq 1$  in their static cell of Bersohn's group, and they observed only  $v=0$  whose population was predominant over  $v \geq 1$ . On the other hand, the flow cell in the present study prevents  $v=0$  from accumulating in the observed volume.

## References

1. van Veen, N., et al. *J. Chem. Phys.* **1983**, *79*, 4295–4301.
2. Yamashita, J., et al. *J. Chem. Phys.* **2014**, *118*, 9330–9337.

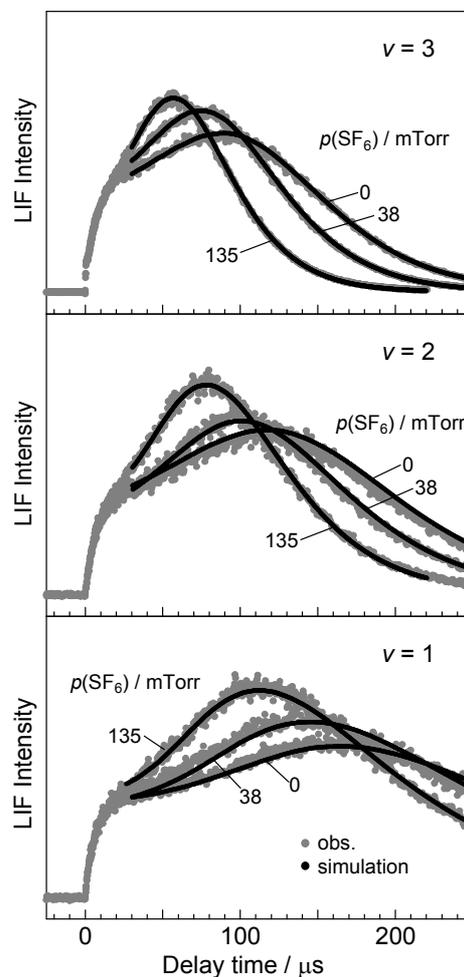


Fig. 1. Time-resolved LIF intensities of  $S_2(X^3\Sigma_g^-, v=1-3)$  at varying pressures of  $SF_6$ .

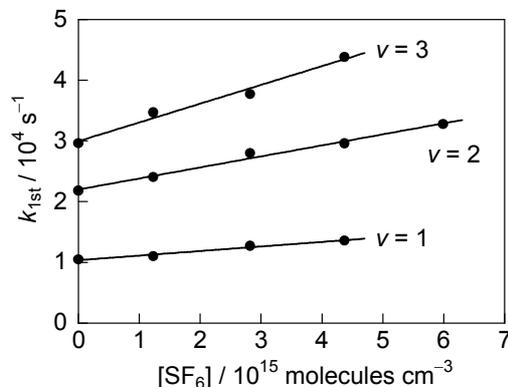


Fig. 2.  $[SF_6]$ -dependence of the pseudo first-order decay rates of  $S_2(X^3\Sigma_g^-, v=1-3)$ . The intercepts correspond to the relaxation by He.