Kinetic Study on the Relaxation of $S_2(X^3\Sigma_g^-, a^1\Delta_g)$
by Collisions with He

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There have been few reports on the vibrational relaxation of $S_2$ in contrast to those of the congeneric molecules $O_2$ and SO. We have determined the rate coefficients for relaxation of vibrationally excited $S_2$ in two electronic states $X^3\Sigma_g^-$ and $a^1\Delta_g$.

A gaseous mixture of OCS and He in a flow cell at 298 K was irradiated with a KrF laser (248 nm) and the following $S^1(D) + OCS$ reaction generated $S_2 (X^3\Sigma_g^-, a^1\Delta_g)$. The two electronic states were detected with laser-induced fluorescence (LIF) via the $B^3\Sigma_u^- - X^3\Sigma_g^-$ and $f^1\Delta_u^- - a^1\Delta_g$ transitions. The excited fluorescence was dispersed with a monochromator ($f = 125$ cm) to detect a single vibrational level. Time-resolved LIF intensities of a pair of adjacent vibrational levels were recorded at different He pressures (Fig. 1 shows $S_2(X^3\Sigma_g^-, v = 1, 2)$). Kinetic analysis based on the integrated profile method has given the pseudo first-order rate coefficients $k_v$. The bimolecular rate coefficients for relaxation of $S_2$ (Table 1) have been obtained from [He]-dependence of $k_v$ (Fig. 2 shows $S_2(X^3\Sigma_g^-, v = 1, 2)$).

![Fig. 1. Time-resolved LIF intensities of (a) $v = 2$ and (b) $v = 1$ of $S_2(X^3\Sigma_g^-)$. The gray dots denote observed data and the black dots in (b) are the results of simulation.](attachment:image1.png)

![Fig. 2. [He]-dependence of the pseudo first-order rate coefficient $k_v$ for $S_2(X^3\Sigma_g^-, v = 1, 2)$](attachment:image2.png)

| Table 1. Rate coefficients for vibrational relaxation of $S_2$ by He.$^a$ |
|---------------------------------|----------------|----------------|
| electronic state               | $v = 1$        | $v = 2$        |
| $X^3\Sigma_g^-$                | $(6.6 \pm 0.7)^b \times 10^{-14}$ | $(1.1 \pm 0.2)^b \times 10^{-13}$ |
| $a^1\Delta_g$                  | $6.3 \times 10^{-14}$ | $(1.2 \pm 0.2)^b \times 10^{-13}$ |

$^a$ in units of cm$^3$ molecule$^{-1}$ s$^{-1}$. $^b$ The stated confidence limits are $2\sigma$.

References