



Research paper

Vibrational relaxation of $S_2(a^1\Delta_g)$ by collisions with SF_6 and CF_4 Shogo Tendo, Haruka Tanimoto, Tohru Uchiyama, Hiroki Goto, Ayano Hara¹, Keigo Fujihara, Hiroshi Kohguchi, Katsuyoshi Yamasaki*

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ABSTRACT

Irradiation of the pulsed laser light at 248 nm to the gaseous mixture of OCS and He generated vibrationally excited $S_2(a^1\Delta_g, v = 2 - 4)$ by the $S(^1D) + OCS$ reaction. A single vibrational level of $S_2(a^1\Delta_g)$ was detected with laser-induced fluorescence (LIF) via the $f^1\Delta_u - a^1\Delta_g$ transition. The rate coefficients for energy transfer from vibrational levels $v = 2$ and 3 of $S_2(a^1\Delta_g)$ to SF_6 and CF_4 have been determined from the time-resolved LIF intensities recorded at varying pressures of SF_6 and CF_4 . The reduced probability of energy transfer per collision derived from the rate coefficients enabled us to identify the v_4 mode of SF_6 and CF_4 as the energy-accepting vibration.

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1. Introduction

Oxygen and sulfur are in group 16 of the periodic table, and O_2 and S_2 have the identical ground electron configuration $(n\sigma_g)^2(n\pi_u)^4(n\pi_g^*)^2$, generating three lowest electronic states $X^3\Sigma_g^-$, $a^1\Delta_g$, and $b^1\Sigma_g^+$. Vibrational energy transfer of O_2 has been attracting researchers engaged in atmospheric and combustion chemistry, and there have been many reports of the rate coefficients for vibration-to-translation ($V-T$) and vibration-to-vibration ($V-V$) energy transfer by a variety of collision partners: He, O_2 , N_2 , O_3 , CO_2 , NO_2 , N_2O , and CH_4 [1–10]. On the other hand, there have been few reports on the kinetic study of vibrational energy transfer of S_2 . The lack of reports on S_2 is due mainly to the difficulty of generation of vibrationally excited S_2 . The reaction $S(^1D) + OCS \rightarrow S_2 + CO$, which newly forms S–S bond, is a candidate for generation of vibrationally excited S_2 . Veen et al. [11], however, reported that $S_2(X^3\Sigma_g^-)$ and $S_2(a^1\Delta_g)$ were formed only in $v = 0$ and $v \leq 2$, respectively. Richter et al. [12] detected higher vibrational levels of $S_2(a^1\Delta_g)$ up to $v = 6$; however, less than 1.7% of the heat of reaction is deposited into vibrational motion and more than 70% of $S_2(a^1\Delta_g)$ is in $v = 0$. We [13] have succeeded in detecting highly vibrational levels up to $v = 19$ and 11 of $S_2(X^3\Sigma_g^-)$ and

$S_2(a^1\Delta_g)$, respectively, by dispersed LIF technique. The time profiles of $S_2(a^1\Delta_g)$ recorded at different pressures of He have given the rate coefficients for $V-T$ energy transfer from $S_2(a^1\Delta_g)$ to He [14].

In the present study, He as a collision partner has been replaced with SF_6 and CF_4 . Both molecules have vibrational modes whose quantum energies are close to those of $S_2(a^1\Delta_g)$, and efficient vibrational energy transfer ascribed to the $V-V$ mechanism has been observed as expected. There, however, is a large difference in the rate coefficients between SF_6 and CF_4 ($k_{SF_6}/k_{CF_4} \approx 5-6$) albeit with nearly identical energy gap. We have elucidated the cause of the difference in efficiencies of SF_6 and CF_4 by the long-range interactions due to the quadrupole moment of $S_2(a^1\Delta_g)$ and the transition dipole moments of the specific vibrational modes of SF_6 and CF_4 .

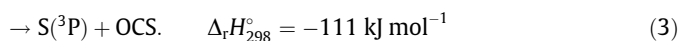
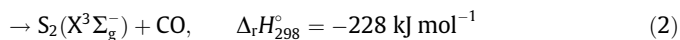
2. Experimental

The details of the experimental apparatus have been described in the previous report [15]. A gaseous mixture of OCS/SF_6 or OCS/CF_4 in buffer He, was irradiated with the light at 248 nm from a KrF excimer laser (Lambda Physik LEXtra50). Typical partial pressures of the sample gas were $p_{OCS} = 10-40$, $p_{SF_6} = 0-300$, $p_{CF_4} = 0-600$ mTorr, and $p_{He} = 5$ or 10 Torr at 295 ± 2 K. The photolysis of OCS at 248 nm yields an electronically excited sulfur atom $S(^1D)$ followed by the three exothermic channels:



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The initial concentration of $S(^1D)$, $[S(^1D)]_0$, was estimated to be $\approx (0.4\text{--}1.5) \times 10^{11}$ atoms cm^{-3} from the following typical values: $[OCS]_0 = (0.3\text{--}1.3) \times 10^{15}$ molecules cm^{-3} ; the quantum yield of $S(^1D)$, 0.95 [16]; the photoabsorption cross section of OCS at 248 nm, 2.36×10^{-20} cm^2 [17,18]; and the fluence of the photolysis laser 4.2 mJ cm^{-2} . Reported branching ratio between the channels $\phi_1 + \phi_2 : \phi_3 = 0.2 : 0.8$ [19] gives the upper limit of the initial concentration of total $S_2(a^1\Delta_g)$ to be about $\approx 3 \times 10^{10}$ molecules cm^{-3} (no report on the relative yield ϕ_1/ϕ_2 was made).

The vibrational levels of the $a^1\Delta_g$ state were excited via the $f^1\Delta_u - a^1\Delta_g$ transition with a $\text{Nd}^{3+}:\text{YAG}$ laser (Spectra Physics GCR-130 or 170) pumped frequency doubled dye laser (Lambda Physik LPD3002 with SHG crystal (BBO III)). The typical pulse energies introduced into the cell were $100\text{--}500 \mu\text{J pulse}^{-1}$. The wavelength of the vibrational band $v' - v''$ of the $f^1\Delta_u - a^1\Delta_g$ transition is nearly identical with that of $(v' + 3) - (v'' + 2)$, making the vibrational spectra congested. The LIF passing through an appropriate optical filter was detected with a photomultiplier tube (PMT, Hamamatsu R1104). When a few vibrational levels are excited simultaneously with the probe laser, the filter was replaced with a monochromator (JEOL JSG-125S, $f = 125 \text{ cm}$, $\Delta\lambda$ (full width at half-maximum) = 3 nm) and observed a single vibrational band with a PMT (Hamamatsu R928).

To record the time profiles of the LIF intensity of a vibrational level, the wavelength of the dye laser was tuned to that of a rotational line, and the delay times of the probe laser from the photolysis pulse were scanned automatically. The time constant τ_r of rotational relaxation is estimated to be $\tau_r \approx 1.5$ and $0.75 \mu\text{s}$ at 5 and 10 Torr, respectively, from $p\tau_r \approx 7.5 \times 10^{-6}$ Torr s, in which p is the total pressure [20]. τ_r is shorter than the time constant, $3\text{--}10 \mu\text{s}$, for generation of $S_2(a^1\Delta_g)$ in the present experiments, indicating that rotational relaxation is completed before vibrational relaxation occurs. The time profiles of a rotational line, therefore, represents that of the vibrational level of interest.

The total pressure of a sample gas was monitored with a capacitance manometer (Baratron 122A). The calibration factors of mass flow controllers (STEC SEC-400 mark-III and Tylan FC-260KZ) and sensors (STEC SEF-410 and KOFLOC 3810) for different gases were measured and used to convert the outputs of the controllers to the flow rates. The partial pressures of the reagents were calculated by proration of the total pressure with the flow rates. Highly pure grade OCS (Sumitomo Seika, 99.9%) diluted with He (OCS: He = 60:40), SF_6 (Showa Denko, 99.999%), CF_4 (Sumitomo Seika, >99.99%), and He (Japan Fine Products, >99.99995%) were used without further purification.

3. Results and discussion

3.1. Time profiles of the LIF intensities of the vibrational levels of $S_2(a^1\Delta_g)$

The LIF excitation spectra of $S_2(a^1\Delta_g)$ were reported in the previous study (Ref. [14] and Fig. 1 therein), and the excitation wavelengths for detecting a single vibrational level also were found. Fig. 1 shows the time profiles of the vibrational levels $v = 3$ and 4 recorded at varying pressures of SF_6 , and Fig. 2 shows those of the identical levels in the presence of CF_4 . OCS was found to be an inefficient relaxant of $S_2(a^1\Delta_g)$ in the previous study [14], and all the profiles in Figs. 1 and 2 remained unchanged over a range

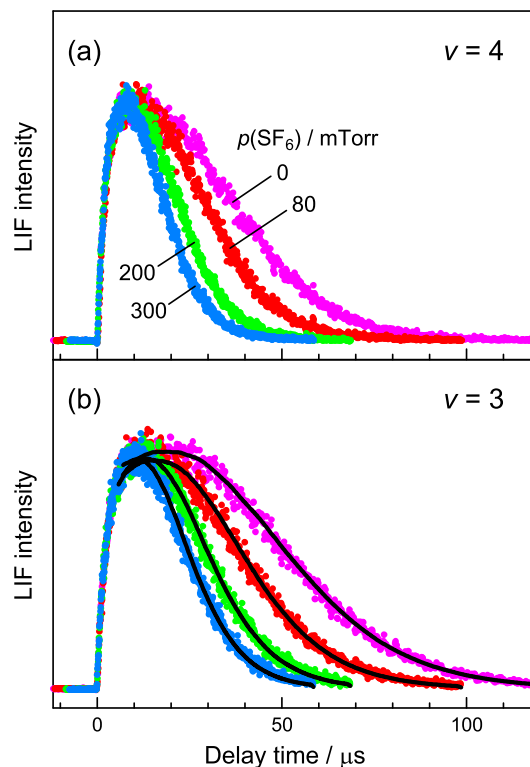


Fig. 1. Time profiles of the vibrational levels of $S_2(a^1\Delta_g)$ at varying pressures of SF_6 . The vibrational levels are $v = 4$ (a) and $v = 3$ (b). The abscissa represents the delay time between the photolysis and probe lasers. The pressures in the sample gas are $p_{\text{OCS}} = 40 \text{ mTorr}$ and $p_{\text{He}} = 10 \text{ Torr}$. p_{SF_6} is directly shown in (a). The colored dots represent the recorded data and the black dots show the time profiles calculated by Eq. (21) in the text.

of $10\text{--}40 \text{ mTorr}$ of OCS. He also does not relax the vibration of $S_2(a^1\Delta_g)$ effectively; nevertheless the relaxation by He was not able to be neglected because the pressure of He was higher than that of OCS by 2 to 3 orders of magnitude. Consequently, the low total (buffer) pressure was suitable for observing the effects of the addition of SF_6 and CF_4 . Preliminary experiments showed SF_6 to be more efficient in energy transfer than CF_4 , suggesting that a relatively low total pressure is appropriate for the experiments of CF_4 . Experiments were performed at 10 and 5 Torr of He buffer for the measurements in the presence of SF_6 and CF_4 , respectively.

All the profiles shown in Figs. 1 and 2 show faster decay at high pressures of SF_6 and CF_4 , indicating the vibrational relaxation occurs by collisions with SF_6 and CF_4 . The growths mainly correspond to the generation of $S_2(a^1\Delta_g, v)$ by the $S(^1D) + \text{OCS}$ reaction whose time constants were calculated to be about 3 and $10 \mu\text{s}$ in measurements with SF_6 and CF_4 , respectively, from the pressures of OCS and the overall rate coefficient ($\approx 3.0 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) [11,13,21]. We [13] have recently reported that vibrational levels of $S_2(a^1\Delta_g)$ are populated up to $v = 11$. The fact indicates that the recorded time profiles are not simple biexponential with growth and decay but multiexponential convoluted time profiles of the vibrational levels higher than the observed level. A nonlinear fit using multiexponential expression requires too many fitting parameters to determine the rate coefficients of interest. Integrated profiles method [22,23] (IPM) has, therefore, been applied to the analysis of the recorded profiles, determining the rate coefficients for the energy transfer from $S_2(a^1\Delta_g, v = 2, 3)$ to SF_6 and CF_4 . The details of the analysis will be described in the following section.

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