



Research paper

Vibrational relaxation of $S_2(a^1\Delta_g, v = 1-9)$ by collisions with HeJun Yamashita¹, Hiroki Goto, Keigo Fujihara², Ayano Hara, Hiroshi Kohguchi, Katsuyoshi Yamasaki*

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ABSTRACT

Vibrationally excited $S_2(a^1\Delta_g, v = 1-10)$ was generated by the $S(^1D) + OCS$ reaction and detected with dispersed laser-induced fluorescence (LIF) via the $f^1\Delta_u - a^1\Delta_g$ transition. The time profiles of the vibrational levels of interest were recorded at varying pressures of He. A kinetic analysis made by the integrated profiles method has given the rate coefficients for vibrational relaxation of $S_2(a^1\Delta_g, v = 1-9)$ by collisions with He. The energy gap law nicely correlates the probabilities of vibrational energy transfer per collision from $S_2(a^1\Delta_g)$, $O_2(X^3\Sigma_g^-)$, $NO(X^2\Pi)$, and $CO(X^1\Sigma^+)$ to He.

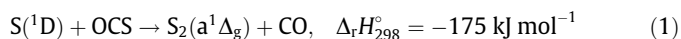
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1. Introduction

Sulfur is an important element in the cycles of earth's matters and biochemicals. There are many (about 30) allotropes, and disulfur (S_2) is the most basic molecule in the allotropes S_n [1,2]. Sulfur and oxygen are congeners, and the lowest three electronic states of S_2 and O_2 are identical: $X^3\Sigma_g^-$, $a^1\Delta_g$, and $b^1\Sigma_g^+$. The small interactions between nonpolar molecules and noble gases lead to a low efficiency of vibrational energy transfer. Parker [3] has observed vibrational energy transfer from $O_2(X^3\Sigma_g^-, v = 1)$ to He with an acoustic resonance tube, reporting the rate coefficient to be $7.1 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 296 K. Klatt et al. [4] have detected the vibrational levels of $v = 8-10$ of $O_2(X^3\Sigma_g^-)$ by the laser-induced fluorescence (LIF) technique and observed vibrational relaxation by collisions with He, determining the rate coefficients to be 1.4 ± 0.2 , 1.0 ± 0.1 , 1.3 ± 0.1 in units of $10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for $v = 8, 9$, and 10 , respectively. Hickson et al. [5] also have employed the LIF technique, giving the rate coefficients for relaxation of $v = 21$ and 22 of $O_2(X^3\Sigma_g^-)$ by He to be 1.65 ± 0.1 and 2.6 ± 0.1 in units of $10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, respectively. There have been few reports on the kinetics of the vibrational relaxation of $O_2(a^1\Delta_g)$ because the radiative lifetime of the $a^1\Delta_g - X^3\Sigma_g^-$ transition is too long ($\approx 72 \text{ min}$) [6] to detect and because there is no electronic state appropriate for being

excited in the LIF technique. Pejaković et al. [7] have recently detected the $a^1\Delta_g$ state by the $2 + 1$ or $2 + 2$ resonance-enhanced multiphoton ionization (REMPI) technique, reporting the rate coefficient for removal of the $v = 1$ level of the $a^1\Delta_g$ state by O_2 and CO_2 .

On the other hand, there has been no kinetic study on the vibrational relaxation of S_2 . The vibrational constant $\omega_e = 702.35 \text{ cm}^{-1}$ of $S_2(a^1\Delta_g)$, which is the target in the present study, is about half of 1580.19 and 1483.5 cm^{-1} of $O_2(X^3\Sigma_g^-)$ and $O_2(a^1\Delta_g)$ [8], respectively, and consequently, relatively high efficiency of relaxation of $S_2(a^1\Delta_g)$ by He is expected. We have generated $S_2(a^1\Delta_g)$ in the following reaction:



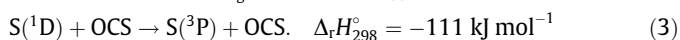
where $\Delta_r H_{298}^\circ$ is the heat of reaction for generation of $v = 0$ of $S_2(a^1\Delta_g)$. Unlike $O_2(a^1\Delta_g)$, $S_2(a^1\Delta_g)$ can be detected by the LIF technique via the $f^1\Delta_u - a^1\Delta_g$ transition. We have recently found that highly vibrationally excited levels up to $v = 11$ are formed by reaction (1) [9]. In the present study, the time profiles of a single vibrational level ($v = 1-10$) were recorded at varying pressures of He and analyzed by an originally developed integrated profiles method (IPM), giving the bimolecular rate coefficients for vibrational relaxation of the $v = 1-9$ levels of the $S_2(a^1\Delta_g)$ state by collisions with He. The resultant probabilities of relaxation per collision, $\approx 10^{-4} - 10^{-3}$ for $v = 1-9$, are higher than $10^{-6} - 10^{-4}$ for $v = 1-22$ of $O_2(X^3\Sigma_g^-)$ by He by more than an order of magnitude. Nevertheless the vibrational level dependence of the efficiency of relaxation of $S_2(a^1\Delta_g)$ by He is nicely correlated not only with that of $O_2(X^3\Sigma_g^-)$ by He but also with those of $NO(X^2\Pi)$ and $CO(X^1\Sigma^+)$ by He on the basis of the energy gap law.

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2. Experimental

The basic framework of the experimental apparatus has been described in the previous reports [10]. A gaseous mixture of OCS and He, typical pressures of which were $p_{\text{OCS}} = 40$ mTorr and $p_{\text{He}} = 10$ Torr, at 295 ± 2 K in a flow cell was irradiated with the pulsed light at 248 nm from a KrF excimer laser (Lambda Physik LEXtra50). The photolysis of OCS at 248 nm yields an electronically excited sulfur atom $S(^1D)$ followed by the highly exothermic reaction (1). The initial concentration of $S(^1D)$, $[S(^1D)]_0$, was estimated by an equation $[S(^1D)]_0 = [\text{OCS}]_0 \phi (1 - e^{-\rho\sigma})$, where $[\text{OCS}]_0$ is the initial concentration of OCS in the cell, ϕ the quantum yield of $S(^1D)$ in the photolysis, ρ the area number density of photons, and σ the photoabsorption cross section of OCS at 248 nm. $[S(^1D)]_0$ was estimated to be $\approx 1.5 \times 10^{11}$ atoms cm^{-3} from the following typical values: $[\text{OCS}]_0 = 1.3 \times 10^{15}$ molecules cm^{-3} , $\phi = 0.95$ [11], $\sigma = 2.36 \times 10^{-20}$ cm^2 [12,13], and $\rho = 5.3 \times 10^{15}$ cm^{-2} . There are two other exothermic channels for the $S(^1D) + \text{OCS}$ reaction:



The channels generating $\text{SO}(X^3\Sigma^-) + \text{CS}(X^1\Sigma^+)$ or $\text{O}(^3P) + \text{CS}_2(X^1\Sigma_g^+)$ are highly endothermic by +39 and +120 kJ mol^{-1} , respectively, and neglected at 295 K. Black [14] has reported that the yield of quenching (channel 3) is dominant over those of reactions; $\phi_1 + \phi_2 : \phi_3 = 0.2 : 0.8$. No report has given the branching ratio between channel 1 and 2. Therefore, the upper limit of the initial concentration of $S_2(a^1\Delta_g)$ was estimated to be about $\approx 3 \times 10^{10}$ molecules cm^{-3} .

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 Nd^{3+} :YAG laser (Spectra Physics GCR-130 or 170) pumped frequency doubled dye laser (Lambda Physik LPD3002 with SHG crystal (BBO III)). The typical pulse energy introduced into the cell was 500 $\mu\text{J pulse}^{-1}$. The vibrational constants, ω_e , of the $a^1\Delta_g$ and $f^1\Delta_u$ states of S_2 are 702.35 and 438.32 cm^{-1} [8], and consequently, the transition energies of the vibrational bands $v' - v''$ and $(v' + 3) - (v'' + 2)$ are nearly identical and their rotational lines are liable to overlap. To avoid simultaneous detection of different vibrational bands, fluorescence was collected with a quartz lens ($f = 80$ mm) and dispersed with a monochromator (JEOL JSG-125S, $f = 125$ cm, $\Delta\lambda(\text{fwhm}) = 3$ nm) with a photomultiplier tube (PMT, Hamamatsu R928). To record the time profiles of the LIF intensity of the vibrational level of interest, the wavelength of the dye laser was fixed to that of a rotational line, and the delay times between the photolysis and probe laser were scanned. In general, the product of the number density n of a gas and the time constant τ_r of rotational relaxation is $n\tau_r \approx 2.4 \times 10^{11}$ $\text{cm}^{-3} \text{ s}$ [15]. $\tau_r \approx 1.5$ μs at 5 Torr, which is the lowest pressure of the present experiments, is shorter than the time constant, 2.6 μs , for generation of $S_2(a^1\Delta_g)$ by reaction (1), 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 step size of the time scan was varied according to the time scales of the profiles. A single data point is an average of the signals from ten laser pulses and a single time profile consists of 1000 data points.

The total pressure of a sample gas was monitored with a capacitance manometer (Baratron 122A). The calibration factors of mass flow controllers (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) and He (Japan Fine Products, >99.99995%) were used without further purification.

3. Results and discussion

3.1. Laser-induced fluorescence excitation spectra of S_2 via the $f^1\Delta_u - a^1\Delta_g$ transition

Fig. 1 shows the laser-induced fluorescence excitation spectra observed in the present study. The excited and detected vibrational bands together with the laser dyes used are listed in Table 1. The $^1\Delta - ^1\Delta$ transition consists of two P, two Q, and two R branches according to the selection rule $\Delta J = 0$ and ± 1 . Sulfur atom ^{32}S has no nuclear spin and one of the two P, Q, and R branches is missing. Moreover, the intensity of the Q branch decreases rapidly with J . As a result, the rotational structures of the vibrational bands in the $f^1\Delta_u - a^1\Delta_g$ of S_2 appear to be those in the $^1\Sigma - ^1\Sigma$ transition. A large difference in the internuclear distance between the $f^1\Delta_u$ and $a^1\Delta_g$ states, 0.21551 and 0.1983 nm, respectively, makes the difference of the rotational constants, B_e , large: 0.29262 and 0.22704 cm^{-1} for the $f^1\Delta_u$ and $a^1\Delta_g$ states, respectively [8]. Because the rotational quantum number at the band head of the R branch is calculated to be $J_{\text{head}} \approx 2$, the R branch appears to turn back from the band origin to red with the P branch. The different features of the rotational lines between the bands result from the difference of the rotational constants of the relevant vibrational levels. Even if all the peaks in Fig. 1 are assigned with the rotational transitions, it cannot be judged whether or not the rotational lines of vibrational bands other than the level of interest are blended. We, therefore, observed dispersed fluorescence spectra by fixing the wavelength of the exciting laser (marked with asterisks in Fig. 1) and scanning that of the monochromator. All the dispersed fluorescence spectra showed the vibrational progression associated with a single vibrational level of the $f^1\Delta_u$ state and their intensity distributions were in good agreement with the Franck–Condon factors, indicating that a single vibrational level of interest was detected.

3.2. Kinetic analysis of the time-resolved LIF intensities

The rotational lines excited to record the time profiles of the vibrational levels of interest are marked with asterisks in Fig. 1. Fig. 2 shows the time-resolved LIF intensities of the $v = 2$ and 3 at varying pressures (5–40 Torr) of He. We first expected that OCS governs vibrational relaxation of $S_2(a^1\Delta_g)$ because the vibrational quantum of the ν_3 stretching mode of OCS, 859 cm^{-1} [16], can accept the vibrational quantum energies 696–647 cm^{-1} of $S_2(a^1\Delta_g, v = 1-9)$. Little difference of the time profiles of the vibrational levels of $S_2(a^1\Delta_g)$, however, was observed when the partial pressures of OCS in the system were changed over a range of 20–60 mTorr. The fact suggests that OCS makes no contribution to the vibrational relaxation of $S_2(a^1\Delta_g)$ under the present conditions.

The time profiles of the two levels show faster decay at higher pressures of He, indicating that the vibrational relaxation of $S_2(a^1\Delta_g)$ proceeds via vibration-to-translation (V–T) energy transfer. Although the time profiles show growth and decay and appear to be biexponential, a long cascade along the vibrational manifold is represented by multiexponential instead of biexponential. The number of exponential terms giving the time profiles of the level v is $v_{\text{max}} - v$, where v_{max} is the highest vibrational levels initially prepared by reaction (1). According to our recent observation [9], $v_{\text{max}} = 11$, nine exponential terms are needed for fitting the time profiles of $v = 2$. Moreover, the weight of each exponential term must be determined in the analysis. Too many parameters make nonlinear fit impractical and thus reliable rate coefficients cannot be derived.

Integrated profiles method (IPM) [17,18] is appropriate for making a kinetic analysis of the consecutive processes. The kinetic scheme relevant to the vibrational level v of $S_2(a^1\Delta_g)$ is given as follows:

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