CHEMISTRY LETTERS, pp. 1493-1496, 1985.

OBSERVATIONS ON THE $B^3\Sigma_u^-$ AND $B''^3\Pi_u$ STATES OF SULFUR DIMER BY N_2 LASER EXCITATION

Taketora BAN, Kazuo KASATANI, Masahiro KAWASAKI, and Hiroyasu SATO*
Chemistry Department of Resources, Mi'e University, Tsu 514

Time-resolved fluorescence spectra from the $B^3\Sigma_u^-$ and $B''^3\Pi_u$ states of sulfur dimer have been studied by pumping the ground state $^3\Sigma_g^-$ dimer with a nitrogen laser at 337.1 nm. A lifetime of the B state was measured by an effusive molecular beam technique while that of the B" state, by the bulb experiment. Quenching rates of these states were also obtained.

The sulfur dimer S_2 exists in a stable equilibrium with the atoms at >500 K and is expected to be a good laser medium. When S_2 molecules are excited by an UV light McGee and Weston[1] found two fluorescence lifetimes of ≈ 100 ns and ≈ 20 ns. The upper states are considered as $B''^3\Pi_u$ and $B^3\Sigma_u^-$, respectively. Various fluorescence lifetimes were reported for the B state, 36 ns (v' = 3, 4) by Crosley et al.,[2] 45.0 ± 0.6 ns (v' = 0 - 12) by McGee and Weston,[3] and 35 ± 5 ns (v' = 2 - 7) by Quick and Weston.[4] Compared to the B state, the information on the B" state is rather poor. In this report we intend to make clear the machanisms of N_2 laser-excitation of S_2 molecules from the time-resolved fluorescence spectra and fluorescence lifetimes in an effusive beam.

The effusive beam of S_2 was generated with a high temperature tube made of quartz. The upper part of the tube (2 mm i.d.) was kept at 730 K. The lower part was the sulfur reservoir heated separately. A home-made N_2 laser (≈ 10 ns pulse width) was used to excite S_2 molecules. Fluorescence lifetime measurement was made by a Hamamatsu 1P28A or R372 photomultiplier with glass filters and a fast circuitry.[5] Oscillograms on an oscilloscope (Tektronix 7904) were processed by a TV camera-microcomputer system which consisted of two gated counters. The oscillogram was measured by a TV camera. The signal height of the oscillogram was converted to the horizontal sweep extension of the video signal. The extension was counted until the video signal found the bright spot of the decay trace on the oscillogram. The count number was fed into a microcomputer while another counter was counting the signal height.

In a bulb experiment sulfur dimer was excited in a small T shaped ampoule, in which sulfur was contained at various reservoir temperatures of 376 to 543 K and at the fixed ampoule head temperature of 800 ± 5 K. At this temperature S_2 is dominant (>98%) in the ampoule head. The S_2 fluorescence induced by the home-made N_2 laser was recorded with a scanning monochromator (Nikon G-250). The time-resolved fluorescence spectra were measured by a photon counting unit (ORTEC 9301/9302/9315/9320) which normally opened the gate at 300 ns after the trigger signal. This delay in the unit was eliminated by the use of an external gate

circuit for the counting unit and an adjustable delay cable for the signal delivery. For lifetime measurement a home-made TEA N_2 laser ($\approx$ 1.5 ns pulse width) was used. Powdered sulfur (five nine, Wako Chemicals) of normal isotope content was used without further purification. The composition of isotopes is $^{32}S_2$ 90.25%, $^{32}S^{34}S$ 8.0%. Sulfur pressure was estimated from the reservoir temperature.

Figure 1 shows an example of the fluorescence spectra observed by the gated integrator of 0.3 μs gate width without delay between trigger and gate timing. The progression of $B^3\Sigma_u^-$ (v' = 2) of $^{32}S_2$ was observed along with that of $^{32}S^{34}S$.

When the gate (1 μs) was opened at 200 ns after the laser pulse, a structureless band was observed as shown in Fig. 2. This band is not attributable to the B → X transition, because the B → X transition has the shorter lifetimes and the structured spectra. A similar band was observed when S_2 was excited at 420 nm by an N_2 laser-pumped dye laser (Molectron DL-14). Although Patino and Barrow[7] have observed the B ← X (4, 21) transions at 514.5 nm and assigned 413.1 nm band as the B ← X (0, 11) of $^{32}S^{34}S$, the spectra observed by us would not correspond to the fluorescence of $B^3\Sigma_u^-$ from the reason mentioned above. The B" ← X transition has been reported in the visible and UV regions by Peterson and Schlie.[8] Quick and Weston,[4] who excited S_2 with a tunable dye laser,

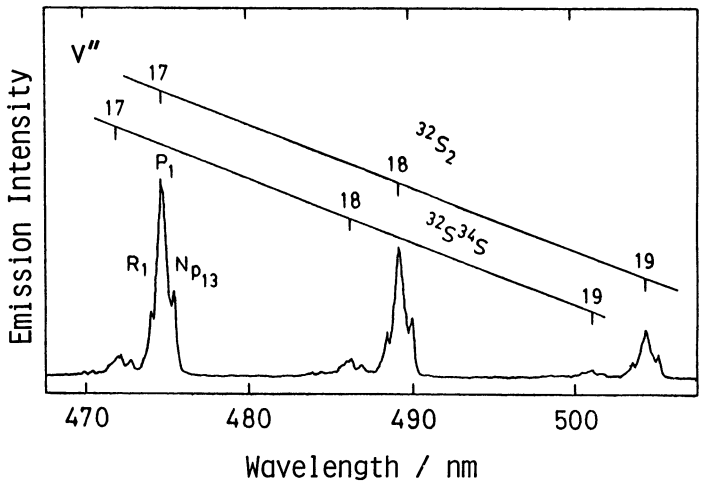

Fig. 1. A part of uncorrected emission spectrum obtained by an N_2 laser irradiation of sulfur dimer. Total Pressure is 25 Torr; Gate of 0.3 μs width is opened just after laser pulses. The transition is S_2 ($B^3\Sigma_u^-$ v'=2 → $X^3\Sigma_g^-$ v").

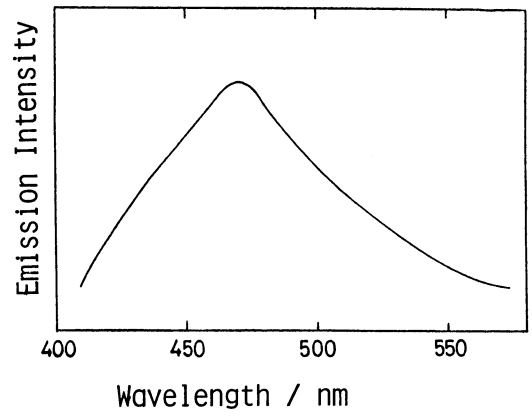

Fig. 2. Emission spectrum obtained by an N_2 laser irradiation of sulfur dimer. Gate of 1 μs width is delayed by 200 ns from the laser pulse. The transition is S_2 ($B''^3\Pi_u \rightarrow X^3\Sigma_g^-$).

observed both short- and long-lifetimes of 30-40 ns and 100-400 ns, respectively. They assigned the latter one to the B" → X transition. Since the unstructured spectra of Fig. 2 were observed only when the detector gate was delayed by 200 ns or longer, the relevant upper state must be B".

The fluorescence lifetimes and self-quenching rates of the $B^3\Sigma_u^-$ state were measured by the N_2 laser irradiation of S_2 both in the effusive beam and in the ampoules. In the effusive beam experiments, the emission decay curves, accumulated over two thousand laser shots, were analyzed as a single exponential with a lifetime of 52 ± 4 ns. This value is close to 45.0 ± 0.6 ns reported by McGee and Weston.[3] Matsumi et al.[9] have obtained the fluorescence lifetimes of 34-49 ns for single rovibronic-spin levels of various v'. Although the N_2 laser irradiation generates J = 13, 21, 23, and 25 levels of the (2,4) band of the B state,[10] the lifetimes are reported to be little dependent on the rotational quantum number.[9] The fluorescence decay observed presently is assumed to be single exponential. However, the fluorescence is contributed by various vibrational levels in the B" state which were excited simultaneously with those of the B state. As will be discussed later, the B" state has fluorescence lifetimes of submicrosecond, and hence the obtained lifetimes are longer than those obtained by Matsumi et al.[9]

In the bulb experiment, as Caughey and Crosly[2] suggested, the self-quenching of S_2(B-X) fluorescence is dominant and no vibrational relaxation was observed in the range of 0.3 - 30 Torr of S_2. The fluorescence lifetimes were shortened as shown in Fig. 3 by self-quenching according to Eq. 1,

$$1/\tau = 1/\tau_0 + k_q [S_2]. \qquad (1)$$

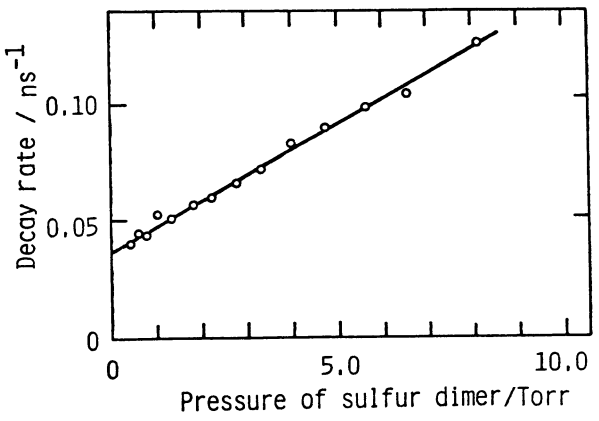

Fig. 3. Stern-Volmer plot for the short-lived component observed from the $B^3\Sigma_u^-$ state of sulfur dimer.

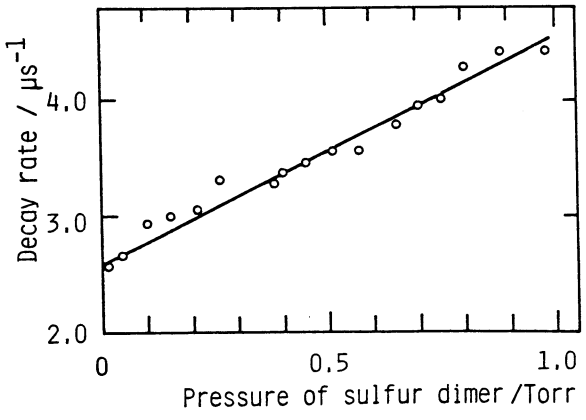

Fig. 4. Stern-Volmer plot for the long-lived component observed from the $B''^3\Pi_u$ state of sulfur dimer.

From Fig. 3 the electronic quenching rate constant k_q was found to be 8×10^{-10} cm^3 $molecule^{-1}s^{-1}$ and the fluorescence lifetime to be 27 ns. The present value of k_q is in good agreement with 6.18×10^{-10} $cm^3molecule^{-1}s^{-1}$ reported by McGee and Weston.[3] These large values are probably due to the fast complex formation, $S_2 + S_2 \rightarrow S_4$. The lifetime of 27 ns as obtained from the intercept of the Stern-Volmer plot was much shorter than that found by the beam method. This suggests that the Stern-Volmer plot is not so reliable in obtaining the fluorescence lifetime as the molecular beam method is.

The fluorescence lifetimes and self-quenching rate of the $B''^3\Pi_u$ were measured in the bulb experiment. Rather long emission decay lifetime was observed in the visible region along with the short lifetime. The lifetimes are shown in Fig. 4 as a function of sulfur pressure. The quantities of τ_0 and k_q in Eq. 1 were found to be 400 $\pm$ 50 ns and 1.7×10^{-10} $cm^3molecule^{-1}s^{-1}$, respectively.

Quick and Weston[4] reported that there are groups of lines within the structure of B-X band having a much longer fluorescence lifetime than the lines arised from the B state. Peterson and Schlie[8] suggested that the weaker $B''^3\Pi_u - X^3\Sigma_g^-$ transitions overlap the strong $B^3\Sigma_u^- - X^3\Sigma_g^-$ transitions. Matsumi et al.[9] have recently studied the B"-X transitions in detail by a supersonic beam technique and found that the radiative lifetimes of B" state fall in the range of 0.1-3.9 μs for various vibrational levels. In the vicinity of laser energy, the $B''^3\Pi_u^-$ state is excited in the v' = 5 level which has two components, Ω' = 0 and 1. The fluorescence lifetimes are reported to be 204 and 717 ns, respectively.[9] The present results correspond to their averaged values because the N_2 laser excitation of hot sulfur dimer is not state-selective.

The authors thank Dr. Yutaka Matsumi for sending a preprint prior to publication and Messers Tohoru Uchida and Shigeki Komoguchi for their help in experiment.

References

1) T.H. McGee and R.E. Weston, Jr., J. Chem. Phys., 68, 1736 (1978).
2) K.A. Meyer and D.R. Crosley, J. Chem. Phys., 59, 1933 (1973); T.A. Caughey and D.R. Crosley, Chem. Phys., 20, 467 (1977).
3) T.H. McGee and R.E. Weston, Jr., Chem. Phys. Lett., 47, 352 (1977).
4) C.R. Quick and R.E. Weston, J. Chem. Phys., 74, 4951 (1981).
5) G. Beck, Rev. Sci. Instrum., 47, 537 (1976).
6) W.R. Anderson, D.R. Crosley, and J. Allen, Jr., J. Chem. Phys., 71, 821 (1979).
7) P. Patino and R.F. Barrow, J. Chem. Soc., Faraday Trans. 2, 78, 1271 (1982).
8) D.A. Peterson and L.A. Schlie, J. Chem. Phys., 73, 1551 (1980).
9) Y. Matsumi, T. Munakata, and T. Kasuya, J. Chem. Phys., 81, 110 (1984); Y. Matsumi, T. Suzuki, T. Munakata, and T. Kasuya, Submitted for publication in J. Chem. Phys.
10) A.L. Smith and J.B. Hopkins, J. Chem. Phys., 75, 2080 (1981).

(Received July 8, 1985)