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# $S_2(a^{1}\Delta)$ production in the photolysis of reduced sulfides: production chemistry, spectroscopy and interference potential in the LIF detection of OH

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### Abstract

Production of  $S_2(a {}^{1}\!\Delta, v = 2)$  has been observed in the UV photolysis of several reduced sulfur compounds by monitoring the  $f {}^{1}\!\Delta - a {}^{1}\!\Delta(2-3)$  laser excitation spectrum. There appears to be at least three production mechanisms including reaction of  $S({}^{1}D)$  with the precursor. The f-a(2-3) band shows several spectral overlaps with the OH A  ${}^{2}\Sigma - X {}^{2}\Pi(1-0)$  band including the Q<sub>1</sub>1 line. Since a significant fraction of the f-a emission from  $f {}^{1}\!\Delta(v = 2)$  overlaps the OH A-X(1-1) and (0-0) bands the potential for a significant 'interference' signal exists if the two species are produced simultaneously. © 1998 Published by Elsevier Science B.V. All rights reserved.

## 1. Introduction

The chemistry and photochemistry of gaseous sulfides is an area which has significant impact in both atmospheric and combustion chemistry. Biological production of sulfides is the major natural component of the atmospheric sulfur burden [1]. The hydroxyl radical (OH) initiated oxidation of sulfides, particularly dimethylsulfide (DMS,  $(CH_3)_2S$ ), produces sulfur dioxide (SO<sub>2</sub>) which undergoes further oxidation to produce sulfuric and methanesulfonic acids initiating the formation of condensation nuclei [2,3]. The non-sea salt/methanesulfonate aerosol which is ubiquitous in the marine boundary layer influences the earth's radiative balance both directly, as a scatterer of radiation, and indirectly as the precursor of the cloud condensation nuclei which affect the earth's albedo through cloud formation [4]. Carbonyl sulfide (COS) degrades slowly in the troposphere and, because of its long lifetime, is the most abundant tropospheric sulfide. It is a major source of stratospheric sulfur and contributes to the formation of the stratospheric sulfate aerosol which constitutes the Junge layer [5].

Experimental studies which utilize laser-induced fluorescence (LIF) to monitor the OH radical have played a significant role in increasing our understanding of the OH initiated oxidation of sulfides. The vast majority of these studies monitor OH via laser excitation of the  $A^2\Sigma - X^2\Pi(1-0)$  band followed by detection of fluorescence from the (1–1) and (0–0) bands at 315 and 308 nm, respectively. The significant wavelength difference between the off-diagonal excitation band and the diagonal detec-

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tion bands offers the opportunity to effectively discriminate against scattered excitation light. It might also be assumed to discriminate against co-incidental overlaps in excitation wavelengths which might result in detection of other species. In this work, we report the observation of a significant potential interference which can occur in the detection of OH in this scheme via the excitation of a vibrationally excited level of the metastable electronically excited state of diatomic sulfur, S<sub>2</sub> (a<sup>1</sup> $\Delta$ , v = 3).

LIF is typically an extremely sensitive and specific detection technique for atoms and small molecules. Nevertheless, the effects of photochemical interference on quantitative LIF measurements has been an issue of concern in both atmospheric and combustion chemistry. The most common example is the photochemical generation of the species of interest by the probe excitation pulse. This typically involves the photofragmentation of a parent molecule to produce the species of interest, either directly or via rapid chemical reaction. In both cases, the probe pulse produces the fragment and then also serves as the fluorescence excitation source. An example of the first case is the 2-photon detection of atomic oxygen in flames at 226 nm, since both water and molecular oxygen can photolyze to generate O atoms and hence produce an interference signal [6]. Similarly, generation of a 'reactive interference' is a major problem in the development of laser-based atmospheric sensors for OH [7]. In this case, probe beam photolysis of ozone,  $O_3$ , generates OH from the rapid reaction of O<sup>1</sup>D with water vapor. Accidental spectral coincidences of the type reported here are less common, particularly for excitation schemes which involve non-resonant detection.

To examine the potential of this interference, we have studied the laser photolysis of a variety of sulfur-containing molecules and found that  $S_2$  (a<sup>1</sup> $\Delta$ , v = 3) is frequently produced. Our results are consistent with at least three production mechanisms. In contrast to previous reports in the literature [8,9], we find that vibrationally excited  $S_2$  (a<sup>1</sup> $\Delta$ , v = 3) is a product of the reaction of S (<sup>1</sup>D) with both COS and carbon disulfide (CS<sub>2</sub>). As we discuss below, at least two other production mechanisms also appear to be operative. In this report, we focus on the spectroscopy of the interference with OH detection and give an overview of  $S_2$  (a<sup>1</sup> $\Delta$ ) production mechanism

nisms. A report of a detailed study of the dynamics of the  $S(^{1}D)$  reaction with COS, together with preliminary results on the reaction with  $CS_{2}$ , will include a more complete description of the experimental approach [10].

#### 2. Experimental

Our initial observation of  $S_2(a^{1}\Delta)$  occurred during a pulsed laser photolysis-pulsed LIF study of the kinetics of the reaction of OH with CS<sub>2</sub>. The experimental arrangement has been used extensively for studies of OH kinetics and has been described in detail elsewhere [2]. Experiments were performed in a jacketed Pyrex cell. A frequency quadrupled Nd:Yag laser was used for 266 nm photolysis of hydrogen peroxide  $(H_2O_2)$ . A frequency-doubled dye laser counterpropagated against the photolysis beam. OH was detected by exciting the  $Q_1$  line of the  $A^{2}\Sigma - X^{2}\Pi(1-0)$  band at 282 nm. Fluorescence was detected using a photomultiplier tube, at right angles to the laser propagation plane. The fluorescence was imaged onto the photocathode by two plano-convex collection lenses. A filter pack consisting of dichroic and solution filters was situated between the lenses and gave a bandpass of approximately 20 nm centered at 315 nm. It was designed to capture the OHA-X(0-0) and (1-1) fluorescence while minimizing scatter from the 282 nm probe. The photomultiplier output was processed by a 500 MHz digital oscilloscope or a boxcar averager. While studying a series of anomalous results, it became clear that a species other than OH was producing an LIF signal. This signal was present in the absence of  $H_2O_2$  and was produced by unfocussed 266 nm photolysis of CS<sub>2</sub> in nitrogen buffer. A laser excitation spectrum was obtained by scanning the probe laser between 279 and 284 nm, identifying the interference as the  $S_2 f^{1}\Delta - a^{1}\Delta$  band. Similar experiments using unfocussed 266 nm photolysis of COS and H<sub>2</sub>S also produced  $S_2(a^{-1}\Delta)$ , again identified by its LIF spectrum. In one set of experiments, the excitation beam was split with one segment being directed into the photolysis cell and the other into a Bunsen burner flame. The laser excitation spectra of both the  $S_2$  f-a bands in the photolysis cell and the OHA-X bands in the burner were then recorded simultaneously on two channels of the boxcar averager. In order to better characterize the production mechanism and spectroscopy, a further series of experiments examined the internal state distribution of the  $S_2(a^{1}\Delta)$ product and the spectrally resolved fluorescence from the laser excited  $S_2(f^{1}\Delta)$  state. A brief description of the configuration for these experiments is presented here and a detailed account will be given elsewhere [10]. One set of experiments was performed in an aluminum vacuum chamber pumped by a four inch diffusion pump. The basic experimental arrangement was the same as in the kinetics experiments with counterpropagating photolysis and probe beams. Fluorescence was detected using the same photomultiplier tube and filter pack. Pressures in the chamber were measured with capacitance manometers. For some experiments, concentrations were measured in situ by UV photometry using the 228 nm line from a cadmium lamp, an absorption cell and a 228 nm bandpass filter. The absorption cell was situated at the entrance of the reaction cell. The fourth (266 nm) or fifth (212.8 nm) harmonic output of a Nd:Yag laser was used as the photolysis beam. A series of resolved fluorescence experiments were carried out using a small aluminum fluorescence cell evacuated by a rotary pump. Fluorescence from the center of the cell was imaged onto the slit of a grating (1200 lines/mm) spectrometer. At the exit of the spectrometer, both a photomultiplier tube and an intensified, gated diode array detector could be used. The wavelength scale of this instrument was calibrated in the range of 250-380 nm using a mercury lamp. The relative sensitivity calibration of the detector was obtained using calibrated deuterium and tungsten/halogen lamps over the same wavelength range.

## 3. Results and discussion

# 3.1. $S_2 f^{l} \Delta - a^{l} \Delta$ spectroscopy

We have recorded LIF spectra of a number of vibrational bands of the  $S_2 f^1 \Delta - a^1 \Delta$  transition. Fig. 1 shows both the excitation spectrum of the (1–2) and (2–3) bands of the  $S_2$  f–a transition together with the OHA–X (1–0) transition. Both spectra were recorded simultaneously, the  $S_2$  f–a bands were recorded in the photolysis cell, the OHA–X bands in a burner. The  $S_2$  f–a excitation spectrum was obtained by photolyzing COS. The flame OH fluores-



Fig. 1. The excitation spectrum of the  $OH(A^2\Sigma^+ - X^2\Pi)(1-0)$  transition (in a Bunsen burner flame) recorded simultaneously with the  $S_2(f^1\Delta - a^1\Delta)$  spectrum. This OH spectrum was also used for wavelength calibration. The OH  $Q_11$  line, frequently used in kinetic experiments, is marked (\*).

cence was detected using a photomultplier tube and single dichroic filter with a similar bandpass to the filterpack used to detect the f-a fluorescence. The f-a spectrum shows rotational resolution, but most rotational features involve the excitation of multiple lines. The f-a spectrum was calibrated using the positions of the OHA-X lines. Fig. 2b shows the expanded f-a spectrum in the region of overlap together with a simulated spectrum (Fig. 2a) based on an S<sub>2</sub> ( $a^{1}\Delta$ ) rotational temperature of 500 K. The simulated excitation spectrum was calculated using the spectroscopic constants of Carleer and Colin [11] and compares well with the experimental spectrum. Any discrepancies cannot be resolved at our laser linewidth. An expanded OHA-X(1-0) spectrum is also included (Fig. 2c) showing the extensive overlap with the  $S_2$  f-a(2-3) lines. The OH  $Q_1$  lines are marked with a triangle ( $\blacktriangle$ ). The OH Q<sub>1</sub>1 line at 281.91 nm, which is frequently used in laboratory kinetic studies to monitor OH, is 'exactly' overlapped by  $S_2$  lines within our laser linewidth. It is clear that scanning on and off this line, an interference test which is frequently used in kinetic investigations, would not reveal the presence of an  $S_2(a^{-1}\Delta)$ interference. The  $Q_13$  line appears to offer the

'cleanest' OH excitation under these conditions, but it is clear that this will be a function of laser bandwidth, rotational temperature and Doppler width.

This type of spectral overlap is relatively rare, particularly when it involves detection of off-resonance fluorescence, since it requires a spectral coincidence within the excitation laser bandwidth and fluorescence lines which lie within the detector bandpass. The degree of overlap in the detection bandpass and the potential for minimizing the interference by tailoring this bandpass can be assessed by examining the resolved fluorescence spectrum. A knowledge of the appropriate vibrational transition probabilities is required. The only data on f-a transition probabilities are a limited set of Franck-Condon factors reported by van Veen et al. [8], which were calculated using harmonic oscillator wavefunctions. They acknowledged that these were not of the highest accuracy and did not attempt to experimentally verify their calculations. We recalculated Franck-Condon factors using the program CONFRON developed at Southampton University [12] (for application of the program, see, e.g., Ref. [13]). Both the  $f^{1}\Delta$  and  $a^{1}\Delta$  state potential energy surfaces were described using Morse functions generated from lit-



Fig. 2. Expanded view of (c) the OHA-X(1-0) excitation spectrum in the region of the  $Q_1 I$  band,  $Q_1$  lines are marked with  $\blacktriangle$ . Together with (b) the  $S_2$  f-a(2-3) band and (a) a simulation of the  $S_2$  f-a(2-3) band.

In order to verify the calculated Franck-Condon factors, resolved emission experiments were also performed. S<sub>2</sub> ( $a^{1}\Delta$ ) was generated by the reaction of S<sup>1</sup>D with COS at a total pressure of 100 Torr in He buffer. As the sensitivity of the resolved fluorescence experiments was low, the delay between the two lasers was optimized for maximum signal. Fig. 3 shows a resolved fluorescence spectrum obtained by exciting v = 2 of the f<sup>1</sup> $\Delta$  state. The excitation wavelength, 281.7 nm, corresponded to excitation of rotational levels around  $J \sim 30$ . A progression of vibrational bands originating from v = 2 are labeled. The relative magnitudes of the calculated Franck-Condon factors, shown by closed circles  $(\bullet)$ , are superimposed on the vibrational bands. There is reasonable agreement between the calculated and measured intensities. The discrepancy at the excitation band is associated with problems with subtraction of scattered laser excitation light. Low detection sensitivity at longer wavelengths leads to larger uncertainty and poorer signal-to-noise ratios. Weak fluorescence from v = 1 is also seen and is probably due to vibrational quenching. These bands are not labeled but the calculated Franck–Condon factors, shown by open circles ( $\bigcirc$ ), are again superimposed and indicate the band positions.

The potential for interference in detection of OH via the A-X(1-0) band occurs through excitation in the  $f_{-a}(2-3)$  band, followed by detection primarily in the (2-8) and (2-9) bands which account for approximately 14% of the fluorescence from the originally excited v = 2 level. Smaller contributions are present from the (2-7) and (2-10) bands. At higher pressures, vibrational relaxation within the f state could have a significant impact on this conclusion. Vibrational transfer to v = 1 results in fluorescence predominately outside the filter bandpass. while approximately 50% of the fluorescence from v = 0 falls within the filter bandpass. Our filter bandpass is designed to optimize collection of OHA-X fluorescence in kinetic experiments which are performed over a wide range of pressures and require detection of both the (1-1) and (0-0) bands which lie at 315 and 308 nm, respectively. In prac-



Fig. 3. Vibrationally resolved emission spectrum from  $S_2(f^{1}\Delta, v=2)$  recorded in helium. The approximate excitation wavelength is 281.7 nm corresponding to  $J(\sim 30)$  lines. Bands originating from v=2 are labeled and the relative magnitude of the calculated Franck–Condon factors are shown with  $\bullet$ . Bands originating from v=1 are not labeled, the relative magnitude of the calculated Franck–Condon factors are shown with  $\odot$ .

tice, narrowing the detection bandpass using narrower dichroic filters offers little prospect of further minimizing the potential interference.

In the region of the excitation spectrum shown in Fig. 2, transitions involving the  $S_2(X^3\Sigma^-)$  state are also expected. The (10–0) and (9–0) band of the  $B^3\Sigma-X^3\Sigma$  electronic transition have been reported at ~ 280 and 283 nm, with fluorescence lifetimes varying with J in v' = 9 [14]. The v' = 10 level is predissociative. Other vibrational bands of this transition have also been found perturbed and only recently re-analyzed [15]. In low pressure experiments, we have identified rotational lines with significantly longer fluorescence lifetimes around 283 nm. This region of the spectrum also contains the (0–2) band of the  $f^1\Delta-a^1\Delta$  transition, making an unambiguous assignment difficult.

# 3.2. $S_2(a^{l}\Delta)$ production

The potential problems associated with a 'coincidental' interference are related to the frequency of production of the interfering species. Our results are consistent with at least three production mechanisms for  $S_2(a^{1}\Delta)$ . Production was observed in the unfo-

cussed 266 nm photolysis of gas mixtures consisting of 1-2 Torr of COS, CS<sub>2</sub> and H<sub>2</sub>S in N<sub>2</sub> diluent at total pressures of approximately 500 Torr. Both the power dependence and temporal profiles of the f-a LIF signal were recorded, with the power being varied between 4 and 40 mJ/cm<sup>2</sup>. In similar experiments with DMS there was no observable f-a LIF signal. The observed power dependencies were 1.4 for H<sub>2</sub>S, 1.94 for CS<sub>2</sub> and 1.25 for COS. Fig. 4 shows four temporal profiles for  $S_2(a^{1}\Delta, v=3)$ production. These profiles were obtained sequentially following the 266 nm photolysis of a mixture of COS in N<sub>2</sub> at pressures of (a) 358, (b) 148, (c) 94 and (d) 490 Torr. The COS concentrations were all between 7 and  $8 \times 10^{15}$  molecules cm<sup>-3</sup>. These profiles are difficult to interpret for several reasons. If, as is the case for the reaction of  $S(^{1}D)$  with COS.  $S_{2}(a^{1}\Delta)$  is formed in a wide range of vibrational levels, then any temporal profile which monitors v = 3 has components resulting from direct production and also, potentially, production and loss terms from vibrational relaxation within the  $(a^{1}\Delta)$  manifold and loss to the ground electronic state,  $(X^{3}\Sigma^{-})$ . No kinetic data is available on these relaxation processes. In addition, a 'prompt' f-a LIF signal which



Fig. 4. Temporal profiles of  $S_2(a^{1}\Delta)$  signal following the photolysis of COS in the glass cell. (a)  $\bigoplus$ , 358 Torr; (b)  $\bigcirc$ , 148 Torr; (c)  $\blacksquare$ , 94 Torr; and (d)  $\Box$ , 490 Torr. Profiles were obtained in the sequence (a), (b), (c) and (d). Solid lines are meant to guide the eye and are not based on any kinetic analysis.

is coincident with the photolysis laser is observed in Fig. 4c,d and perhaps to a small extent in Fig. 4b. This 'prompt' signal is irreproducible and depends on factors such as the pumping speed and the length of the experiment. If the cell is evacuated and a fresh set of profiles obtained, the initial profiles contain no prompt signal and it again appears in later profiles. This behavior is not consistent with production via the  $S^{1}D$  reaction and suggests the buildup of a relatively stable reaction product which itself photolyses to give  $S_2(a^{1}\Delta)$ . Experiments using the vacuum chamber could be performed over a wider range of experimental conditions. An extensive study of the reaction of S<sup>1</sup>D with COS was performed using 212 nm photolysis of COS as the  $S^{1}D$  source. These results will be reported in detail elsewhere [10]. Based on previous literature reports [8,16,17], in low pressure pure COS experiments, the dominant processes are expected to be the reaction of  $S(^{1}D)$  with COS, leading to the production of  $S_2 a^{1}\Delta$  and  $X^{3}\Sigma$ in competition with electronic quenching to produce  $S(^{3}P)$ . At low pressures in pure COS and at higher pressures in He buffer, an  $S_2$  f-a signal with a very rapid rise time is observed. Fig. 5a shows such a profile of in 20 mTorr of COS. As rotational deactivation is usually expected to be fastest, the rise of the  $S_2$  signal was assumed to be limited by the reaction of  $S(^{1}D)$  atoms with COS. Therefore the observed profile was fitted to a general 'rise-and-fall' expression:

 $I = A \left[ \exp(-k_1 t) - \exp(-k_2 t) \right] + \text{background}$ 

where  $k_2$  and  $k_1$  represent the rise and fall rates, respectively. After dividing  $k_2$  by the OCS concentration, this treatment leads to a value of  $k_{rise} = 1.26$  $\times 10^{-10}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>. This number is consistent with previously reported values [8,16,17] of the rate constant for the  $S(^{1}D) + COS$  reaction, indicating that this process indeed dominates. Analysis of the excitation spectra indicate that  $S_2(a^{1}\Delta)$  is produced with a considerable degree of vibrational excitation with population of levels up to at least v = 6. In preliminary low pressure experiments on the  $S(^{1}D) + CS_{2}$  reaction, we find  $S_{2}(a^{1}\Delta)$  production with population in levels up to at least v = 3. Photolysis of  $7.3 \times 10^{15}$  molecule cm<sup>-3</sup> of OCS at a total pressure of 146 Torr in N2 gives very different behavior as shown in Fig. 5b. The profiles here are

similar to profiles 'a' and 'b' in Fig. 4, in that there is no evidence for  $S_2(a^{1}\Delta)$  formation on a timescale consistent with the  $S(^{1}D)$  reaction. At this pressure, quenching of  $S(^{1}D)$  by molecular nitrogen should be the dominant process with  $S(^{3}P)$  as the product.

Two potential routes to 'slow' production of  $S_2(a^{1}\Delta, v=3)$  are the reaction of  $S({}^{3}P)$  with the photolytic precursor, reaction 1b, or the three-body recombination of  $S({}^{3}P)$ , reaction 2.

$$S(^{3}P) + COS \rightarrow products$$
 (1a)

$$S(^{3}P) + COS \rightarrow S_{2}(a^{1}D) + CO(X)$$
 (1b)

$$S + S + M \rightarrow S_2(a^{\dagger}\Delta) + M$$
 (2)

The limited kinetic data on reaction 1a ranges from a rate coefficient of  $3.3 \times 10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> reported by van Veen et al. [8] to a value of  $3.5 \times$  $10^{-15}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> reported by Klemm and Davis [18]. In the only comprehensive study Klemm and Davis monitored the loss of  $S(^{3}P)$  by atomic resonance fluorescence but obtained no information on the reaction products. The van Veen et al. result appears to be based on the analysis of a single profile obtained at low pressures at high pumping speeds. Reaction 1b, while spin forbidden, is exothermic. If reaction 1b is as slow as reported by Klemm and Davis, it is difficult to determine a rate coefficient from the pseudo-first order rise time of a profile such as Fig. 5b, since the rate coefficient reflects all loss processes for S(<sup>3</sup>P) rather than simply loss to produce  $S_2(a^{1}\Delta)$  and, as noted above, other production and relaxation processes can influence the temporal profile. If the rise time of the profile in Fig. 5b is solely produced by reaction 1b, then our result is indicative of a rate coefficient of  $\sim 1.4 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  for the COS concentration used,  $7.3 \times 10^{15}$  molecule cm<sup>-3</sup>. If the decay actually reflects a significant pumping/diffusive loss of  $S({}^{3}P)$  then this profile could be consistent with the much slower rate reported by Klemm and Davis. However, profiles in Fig. 4a,b show very different temporal profiles at similar COS concentrations. The rise time is faster at higher pressure which would be consistent with production via reaction 2 rather than 1b. No data is available on the rate coefficient for reaction 2, but a limited series of power dependencies at a single delay showed a close



Fig. 5. Temporal profiles of  $S_2(a^{1}\Delta)$  signal following the photolysis of COS in the vacuum chamber: (a) low pressure pure COS (~20 mTorr), (2–3) transition; (b) high pressure  $N_2$  (~146 Torr), (1–2) transition. The line represents the best fit to a 'rise-and-fall' expression (see text), with the  $k_{rise}$  values of (a)  $1.26(\pm 0.5) \times 10^{-10}$  and (b)  $1.4(\pm 0.08) \times 10^{-13}$ , respectively.

to linear dependence of the S<sub>2</sub> ( $a^{1}\Delta$ , v = 3) signal on photolysis laser power. This would be consistent with reaction 1b rather than 2. Our limited data set

cannot eliminate either possibility and additional work is required to identify the production mechanism.

As noted above, the 'prompt'  $S_2(a^{1}\Delta)$  signal is suggestive of the buildup of a photolysis product which photolyses to produce  $S_2(a^{1}\Delta)$  directly. A previous flash photolysis-kinetic mass spectroscopic study of COS photolysis has identified a series of polymeric sulfur products including  $S_4$ ,  $S_5$ ,  $S_6$  and  $S_8$  [19]. These are potential candidates for the precursor to the 'prompt'  $S_2(a^{1}\Delta)$  signal.

Wahner and Ravishankara reported the observation of a similar interference in a kinetic study of the OH + COS reaction [20]. They observed the interference signal in both 193 and 266 nm photolysis of COS in He,  $N_2$  and SF<sub>6</sub> buffers. They noted that an LIF spectrum recorded between 281.96 and 283 nm showed line positions similar to the S<sub>2</sub> f-a and B-X transitions. Based on the observation of the interference in N2 and the risetime of the signal they discounted either  $S^{1}D$  or  $S^{3}P$  as playing a role in its formation, speculating that it might be due to reaction of a long-lived excited state of COS. Our results clearly identify the f-a transition as the origin of this interference and suggest that at least three mechanisms of production are possible. These mechanisms appear to be operative in photolysis of COS, CS<sub>2</sub> and  $H_2S$ . For both COS and CS<sub>2</sub> we have clear evidence that rapid reaction of S<sup>1</sup>D with the precursor produces  $S_2(a^1\Delta, v=3)$ . This is clearly a potential complication in studies of the fast equilibration of OH with  $CS_2$  in He buffer [2]. The origin of the 'slow' and prompt components of  $S_2(a^{1}\Delta)$  are much more difficult to identify. The fact that these components can be observed with three photolytic precursors may suggest that S atoms or  $S_2$  molecules, rather than a photolytically generated metastable state of the precursors, are responsible.

In previous work van Veen et al. observed production of  $S_2(a^{1}\Delta, v = 1)$  from the reaction of  $S(^{1}D) + COS$ , and concluded that there was negligible population in higher vibrational levels [8]. Sapers et al. studied the  $S(^{1}D) + CS_2$  reaction and were unable to observe the formation of any  $S_2(a^{1}\Delta)$ product [9]. In contrast we have observed  $S_2(a^{1}\Delta)$ , v = 3) production in both cases. Our results on DMS do not exclude the possibility that the reaction of  $S(^{1}D)$  with DMS also produces  $S_2(a^{1}\Delta)$ , or that it is produced by photolysis at other wavelengths. As noted above, our  $S(^{1}D)$  results and a comparison with previous work will be discussed in more detail elsewhere [10]. Our results demonstrate the importance of a detailed spectral characterization of LIF signals in kinetics experiments involving the reaction of OH with reduced sulfur compounds.

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#### References

- T.S. Bates, B.K. Lamb, A. Guenther, J. Dignon, R.E. Stoiber, J. Atmos. Chem. 14 (1992) 315.
- [2] A.J. Hynes, Reaction mechanisms in atmospheric chemistry: Kinetic studies of hydroxyl radical reactions, in: R.J.H. Clark, R.E. Hester (Eds.), Spectroscopy in Environmental Science, John Wiley, New york, NY, 1995.
- [3] H. Berresheim, P.H. Wine, D.D. Davis, Sulfur in the atmosphere, in: H.B. Singh (Ed.), Composition, Chemistry and Climate of the Atmosphere, Van Nostrand Reinhold, New York, NY, 1995.
- [4] R.J. Charlson, J.E. Lovelock, M.O. Andreae, S.G. Warren, Nature 326 (1987) 655.
- [5] M. Chin, D.D. Davis, J. Geophys. Res. 100 (1995) 8993.
- [6] J.E.M. Goldsmith, Appl. Opt. 26 (1987) 3566.
- [7] D.R. Crosley, in: J.R. Barker (Ed.), Progress and Problems in Atmospheric Chemistry, World Scientific, Singapore, 1995, p. 256.
- [8] N. Van Veen, P. Brewer, P. Das, R.J. Bersohn, J. Chem. Phys. 79 (1983) 4295.
- [9] S.P. Sapers, N. Andraos, D.J. Donaldson, J. Chem. Phys. 95 (1991) 1738.
- [10] R.C. Richter, A.R. Rosendahl, A.J. Hynes, in preparation.
- [11] M. Carleer, R. Collin, J. Phys. B 3 (1970) 1715.
- [12] J.M. Dyke, private communication.
- [13] L. Golob, N. Jonathan, A. Morris, M. Okuda, K.J. Ross, D.J. Smith, J. Chem. Soc. Faraday Trans. 2/71 (1975) 1026.
- [14] C.R. Quick Jr., R.E. Weston Jr., J. Chem. Phys. 74 (1981) 4951.
- [15] M.E. Green, C.M. Western, J. Chem. Phys. 104 (1996) 848.
- [16] G. Black, J. Chem. Phys. 84 (1986) 1345.
- [17] R.J. Donovan, L.J. Kirsch, D. Husain, Nature 222 (1969) 1164.
- [18] R.B. Klemm, D.D. Davis, J. Phys. Chem. 78 (1974) 1137.
- [19] H.E. Gunning, O.P. Strauss, The reactions of sulfur atoms, in: W.A. Noyes Jr., G.S. Hammond, J.N. Pitts Jr. (Eds.), Advances in Photochemistry, vol. 4, John Wiley, New York, NY, 1966.
- [20] A. Wahner, A.R. Ravishankara, J. Geophys. Res. 92 (1987) 2189.