energy for which the ion distribution function has its maximum value and that for  $k_{\lambda}$ . Furthermore, since  $k^*_E$  is different for  $C_4H_3^+$  and  $C_4H_4^+$ , it is expected that the value of  $E^*$  for which  $k_{\lambda}$  is maximum for these two fragment ions will be slightly different when a laser of wavelength  $\lambda$  is used. However, both shifts are expected to be small since the distribution function  $\psi_{E_i}^{\lambda}$  is expected to have a width which is small compared to the total energy of the parent ion (which is determined mostly by the third photon energy).

In light of the above discussion, the b value in eq 1 must then represent the energy difference between the value of the onset and that of the maximum of the  $\psi_{E_i}{}^{\lambda}k_{E_i}$  function (occurring at  $E^*_{\lambda}$ ). The nearly constant value of b, when  $S_2$  is an intermediate state in the ionization process, might result from the following: (1) as discussed above, the distribution function  $\psi_{E_i}^{\lambda}$  might be independent of  $\lambda$  if the photoionization probability from S<sub>2</sub> is much higher than that for energy redistribution in that state or is not very sensitive to small changes in  $\lambda$  if the energy redistribution is very rapid in the S<sub>2</sub> state, and (2) the slope of  $k_E$  vs. E is such that it does not shift greatly the maximum of the  $\psi_{E_i}^{\lambda}$  function when the energy of the third photon changes over the range used (0.7 eV as seen in Table I).

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# SO<sub>2</sub> Fluorescence from Vacuum Ultraviolet Dissociative Excitation of SO<sub>3</sub>

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The absorption and fluorescence excitation spectra of SO<sub>3</sub> were measured in the 145-160-nm region with synchrotron radiation as a light source. The fluorescence spectra produced by excitation of SO<sub>3</sub> at 147 and 157 nm were dispersed and compared with the laser-induced fluorescence spectrum of  $SO_2$ , from which the emitter is identified to be the excited  $SO_2^*$ . The photodissociation process of SO3 is discussed in accord with the fluorescence observed.

#### Introduction

There is a great concern about the oxidation processes of sulfur compounds because of their important roles in the formation of acid rain.  $SO_3$ , an important oxidation product of  $SO_2$  and other simple sulfur compounds,<sup>1</sup> reacts with ambient water to produce  $H_2SO_4$ . The reaction kinetics and spectroscopy of  $SO_3$  are of interest in the study of atmospheric photochemistry.

Since SO<sub>3</sub> is a strong oxidizer, there are experimental difficulties in the study of its gas-phase reaction kinetics and spectroscopy. For example, SO<sub>3</sub> reacts with optical windows to cause permanent window damage. SO<sub>3</sub> will react with H<sub>2</sub>O on walls and grease in joints to form acidic products that will attack O-ring material and metal. SO<sub>3</sub> also forms a surface polymer at room temperature. Because of these difficulties, the reaction kinetics and spectroscopy of SO<sub>3</sub> have not been extensively investigated.

While spectroscopic data for SO<sub>3</sub> have been reported in the infrared region,<sup>2-5</sup> very little is known about the ultraviolet (UV) and vacuum ultraviolet (vacuum-UV) regions. The absorption spectrum of SO<sub>3</sub> in the UV region was studied a long time ago;<sup>6,7</sup> however, the results were not certain. Aerosol formation from the SO<sub>3</sub> +  $H_2O$  reaction was observed in an early study,<sup>8</sup> but the kinetic measurement of the  $SO_3 + H_2O$  reaction in the gas phase was made only once.9

In this work, the photoexcitation process of  $SO_3$  is studied in the vacuum-UV region. Absorption and fluorescence excitation spectra are investigated with synchrotron radiation as a light source. Fluorescence produced by 147- and 157-nm excitation of SO<sub>3</sub> was dispersed and compared with the laser-induced fluorescence spectrum of SO<sub>2</sub>, from which the fluorescence is identified to be from the excited  $SO_2^*$ . This  $SO_2$  fluorescence is currently used as a means for the detection of SO<sub>3</sub> in our measurement of the reaction rate constant of  $SO_3 + H_2O$ .

### **Experimental Section**

Sample Preparation. Stabilized SO3 with a purity of 99% was supplied by Aldrich Chemical Co. in a sealed glass bottle. At

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room temperature,  $SO_3$  is a liquid with a portion of needlelike polymer. In this experiment, the glass bottle was placed inside a stainless steel container. Both the container and the glass bottle were baked under vacuum, and the H<sub>2</sub>O on walls was pumped out. The  $SO_3$  bottle was opened in a vacuum, and the sample was degassed at liquid  $N_2$  temperature. The gas handling system consisted of stainless steel tubing and Teflon valves without O-rings or grease. The gas cells used in the experiments were all made of stainless steel. The gas handling system and the gas cell were baked under vacuum for a few hours prior to performing the experiment. This treatment ensures that  $H_2O$  on walls is minimal, and  $SO_3$  does not convert to  $H_2SO_4$ .

SO<sub>3</sub> may decompose on stainless steel surfaces. Noticeable absorption and fluorescence from SO<sub>2</sub> were observed in the synchrotron radiation experiment. However, after the gas handling system and the gas cell were passivated with a flow of SO<sub>3</sub> gas, the decomposition was greatly reduced. All measurements were carried out in flow systems in order to reduce the buildup of decomposition products. In the synchrotron radiation experiment, pure SO3 was continuously introduced to the gas cell and pumped by a sorption pump. For the dispersion experiment, SO<sub>3</sub> diluted in He was continuously admitted to the gas cell and pumped by a mechanical pump with a liquid nitrogen cold trap. Pressures of SO<sub>3</sub> and SO<sub>3</sub>/He were monitored by Baratron capacitance manometers (MKS Instruments).

Synchrotron Radiation Experiment. The experimental setup for the synchrotron radiation measurement was described in a

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previous paper.<sup>10</sup> In brief, synchrotron radiation produced from the electron storage ring at the University of Wisconsin was dispersed by a 1-m vacuum monochromator (Seya type, grating blazed at 120 nm). The dispersed photon beam entered the gas cell through a sapphire window. LiF and MgF<sub>2</sub> windows were also used in the experiment. The optical path length of the absorption cell was 39.7 cm. The vacuum-UV light source was converted to UV light by sodium salicylate coated outside the exit sapphire window. The UV light was detected by a photomultiplier tube (PMT). The UV-visible fluorescence was monitored by a cooled PMT (EMI 9558QB) sensitive in the 180-800-nm region. The fluorescence intensity was observed in a direction perpendicular to the incident photon beam. The signal from the PMT was processed by an ORTEC photon counting system and then simultaneously recorded by an X-Y recorder and an IBM XT microcomputer. The data were later analyzed by the computer.

Fluorescence Dispersion. Fluorescence from dissociative excitation of SO<sub>3</sub> with a sealed Xe resonance lamp (147 nm) and a  $F_2$  excimer laser (157 nm, Lumonics) was dispersed by a 0.5-m monochromator (Acton, Inc.). The fluorescence was observed through a quartz window in a direction perpendicular to the light source beam.

The gas cell was a stainless steel six-way cross. Sapphire and  $CaF_2$  windows on the gas cell were used for the  $F_2$  laser and Xe lamp experiments, respectively. The section between the windows of the light source and the gas cell was flushed by pure  $N_2$  gas flow that allowed the vacuum-UV light transmission. Helium was used to flush the windows inside the gas cell to prevent SO<sub>3</sub> from reaching them.

The  $F_2$  laser was typically operated at 20 Hz with a pulse duration of 6 ns. The signal from the PMT was processed by a gated photon counting system with a sampling gate of about 35  $\mu$ s after each laser pulse. The  $F_2$  laser intensity was monitored by a copper diode with a sapphire window. The fluorescence signal detected in the Xe resonance lamp experiment was not gated.

Laser-Induced Fluorescence of  $SO_2$ . The laser-induced fluorescence of  $SO_2$  was observed in the excitation wavelength region of 275–285 nm, which was used to compare with the fluorescence observed from photodissociation excitation of  $SO_3$ . A Nd:YAG laser pumped dye laser (Quantel, YG581-30) was used as the light source. Output from rhodamine 590 was frequency-doubled into the UV light. The laser was operated at a repetition rate of 30 Hz with a pulse duration of 12 ns. The bandwidth of the laser light was about 1.6 cm<sup>-1</sup>.

A stainless steel gas cell with quartz windows was used for this experiment. Both pure  $SO_2$  and diluted  $SO_2$  in Ar were used in the flow system. The detection system (monochromator, PMT, and the gated photon counting system) was the same as for the  $F_2$  laser experiment.

#### **Results and Discussion**

Absorption and Fluorescence Excitation Spectra. The absorption spectrum was measured by attenuation of light source intensity by SO<sub>3</sub> at several pressures lower than 5 mTorr. The measurement was done with a sapphire window. As shown in Figure 1a, the spectrum in the 145–160-nm region is a continuum with broad discrete bands superimposed on it. Measurements with LiF windows were also carried out in this experiment. However, since the window transmission deteriorated with time due to a reaction with SO<sub>3</sub> during the measurements, the data were not considered to be reliable and are not presented in this paper. Nevertheless, it is worth noting that several sharp bands appeared in the 105-130-nm region similar to the absorption spectrum of  $SO_2$ .<sup>11</sup> These bands may be partly caused by  $SO_2$  produced from the decomposition of  $SO_3$  by walls. The broad bands shown in Figure 1a may also be partly due to  $SO_2$ , because  $SO_2$  also shows absorption structure in this wavelength region.<sup>12</sup> The photoab-

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Figure 1. (a) "Apparent" absorption cross section and (b) fluorescence excitation spectrum of SO<sub>3</sub>. The monochromator resolution was 0.2 nm. The cross section is measured in a unit of Mb  $(10^{-18} \text{ cm}^2)$ . The fluorescence excitation is a relative value. The lower limit of the fluorescence cross section at 147 nm is 0.15 Mb.

sorption cross section of  $SO_2$  was also measured in this experiment, and the result agrees with the published data.<sup>12</sup> Because of the possible interference by  $SO_2$ , the uncertainty for the measured absorption cross section is quite large, and the cross section shown in Figure 1a is therefore defined as an "apparent" one.

The absorption cross section<sup>12</sup> of SO<sub>2</sub> in the 145–160-nm region is about 5 Mb (1 Mb =  $10^{-18}$  cm<sup>2</sup>). O<sub>2</sub>, which is the other possible decomposition product, has a broad absorption band in the 135-155-nm region with a maximum absorption cross section of 14 Mb.<sup>13</sup> The "apparent" absorption cross section shown in Figure 1 has a peak cross section of about 26 Mb, which is much larger than the values of possible decomposition products. Thus, the measured absorption cross section in the 145-150-nm region is mostly due to  $SO_3$ . The "apparent" cross section represents the lower limit of the true absorption cross section of  $SO_3$ . By a detailed comparison between the absorption bands shown in Figure 1a with those<sup>12</sup> of  $SO_2$ , it is estimated that the concentration of SO<sub>2</sub> was not higher than 20% of the total gas pressure, and the  $O_2$  concentration should be about one-half of  $[SO_2]$ . The possible interference from these decomposition products may make the measured "apparent" absorption cross section of SO3 appear to be lower than the true value by about 25%.

Fluorescence was observed in the excitation wavelength region of 145–160 nm. The ratio of fluorescence intensity to light source intensity is shown in Figure 1b. The ratio represents the relative fluorescence cross section, which can be converted to absolute value by calibration at 147 nm (see discussion in the next section). The fluorescence excitation spectrum is a smooth function of excitation wavelength that increases with decreasing excitation wavelength. The fluorescence was observed with a LiF window down to 130 nm with a peak around 140 nm. However, because the transmission efficiency of the LiF window changed with time, the data were only qualitative.

The possible impurities of SO<sub>2</sub> and O<sub>2</sub> did not contribute to the fluorescence observed. The SO(A,B $\rightarrow$ X) fluorescence can be produced from photodissociation excitation of SO<sub>2</sub> at excitation wavelengths shorter than 134 nm, but not at the longer wavelengths.<sup>11</sup> Photoexcitation of O<sub>2</sub> in the 145–160-nm region will dissociate<sup>14</sup> into O(<sup>1</sup>D) + O(<sup>3</sup>P)...

dissociate<sup>14</sup> into  $O(^{1}D) + O(^{3}P)$ . *Fluorescence Spectra*. The fluorescence spectrum produced from photoexcitation of SO<sub>3</sub> at 157 nm (F<sub>2</sub> laser) is shown in Figure 2, where the monochromator resolution was set at 0.85

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Figure 2. Fluorescence spectrum produced from photodissociative excitation of  $SO_3$  at 157 nm (F<sub>2</sub> laser). The monochromator resolution was set at 0.85 nm. The SO3 pressure was about 10 mTorr mixed in 4.9 Torr of He.



Figure 3. Fluorescence spectrum produced from photodissociative excitation of SO<sub>3</sub> at 147 nm (Xe resonance lamp). The monochromator resolution was set at 0.85 nm. The SO<sub>3</sub> pressure was 15 mTorr in 1.6 Torr of He.

nm and SO<sub>3</sub> pressure was about 10 mTorr. The sapphire window on the gas cell was flushed by He so that the total pressure in the gas cell was about 4.9 Torr. The fluorescence was observed within 35  $\mu$ s after each laser pulse. No fluorescence was detected when  $SO_2$  at 55 mTorr was irradiated by  $F_2$  laser photons under the same experimental condition.

The fluorescence spectrum produced from photoexcitation of SO<sub>3</sub> at 147 nm is shown in Figure 3a where the monochromator resolution was set at 0.85 nm, and the partial pressure of SO3 was about 15 mTorr. The background signal caused by the scattered light from the Xe lamp is shown in Figure 3b. The scattered light is included in Figure 3a. A  $CaF_2$  window on the gas cell was used in this experiment and was flushed by He. The total pressure in the gas cell was 1.6 Torr. Pure  $N_2$  gas was used to flush the section outside the gas cell between the CaF2 window on the gas cell and the  $MgF_2$  window on the Xe lamp. Both spectra produced at 147 and 157 nm show several vibrational bands in the 380-480-nm region superimposed on an unresolved broad continuum from 270 to 500 nm. They are very similar to both the fluorescence spectra produced from optical excitation of  $SO_2^{16-19}$  and the chemiluminescence spectra produced from reactions of  $O_3$  with various sulfur compounds.<sup>20-23</sup> This similarity suggests that the observed

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Figure 4. Laser-induced fluorescence spectrum of SO<sub>2</sub> excited at 281.1 nm (frequency-doubled dye laser). The monochromator resolution was set at 0.43 nm. The SO<sub>2</sub> pressure was about 200 mTorr.

fluorescence is likely due to the excited SO<sub>2</sub>\* produced from photodissociative excitation of SO<sub>3</sub>. For a further identification of the fluorescence spectrum, the laser-induced fluorescence of  $SO_2$  was studied by using the same detection system for which the result is described in the next section. Comparing these spectra, it is conclusive that the fluorescence observed from vacuum-UV excitation of  $SO_3$  is indeed due to the excited  $SO_2^*$ .

The observed fluorescence is mainly produced from the direct photodissociation process of SO<sub>3</sub>. Optical emissions from other processes such as reactions among the chemical species  $SO_3$ ,  $SO_2$ , and  $O_2$  existing in either excited states or their ground states are believed to have a negligible contribution to the observed fluorescence. This assertion is based on the observation that the fluorescence is linearly dependent on the SO<sub>3</sub> concentration.

The fluorescence cross section at 147 nm was estimated by comparing its fluorescence intensity with that of C<sub>2</sub>F<sub>3</sub>Cl under the same experimental conditions. At 147 nm, C<sub>2</sub>F<sub>3</sub>Cl is dissociated into  $CF_2(\tilde{X}) + CFCl(\tilde{A})$  with a fluorescence cross section of about 0.25 Mb.<sup>15</sup> The CFCl( $\tilde{A}-\tilde{X}$ ) emission wavelength is in the 350-550-nm region, and the SO<sub>2</sub> fluorescence produced from dissociative excitation of SO<sub>3</sub> is in the 270-500-nm region. Since both the CFCl and SO<sub>2</sub> emissions are in the same wavelength region, the PMT response for the detection of both emissions was assumed to be the same. The fluorescence cross section of SO<sub>3</sub> at 147 nm, determined from the fluorescence intensity, is 0.15 Mb with an uncertainty factor of 2. This value is only a lower limit of the true fluorescence cross section, because the SO<sub>2</sub>\* fluorescence is subject to quenching<sup>16</sup> by He which was not corrected.

Laser-Induced Fluorescence of SO2. The laser-induced fluorescence (LIF) of SO<sub>2</sub> was observed in the excitation wavelength regions of 275–285 nm. Both pure  $SO_2$  and diluted  $SO_2$ in Ar were used in the experiment. It was observed that the LIF spectra were not dependent on SO<sub>2</sub> pressure. The fluorescence spectrum excited at 281.1 nm is shown in Figure 4. The LIF spectra at other excitation wavelengths in the 270-290-nm region are similar to this spectrum. The LIF spectrum is very similar to the spectra shown in Figures 2 and 3, except for the vibrational bands in the 380-470-nm region that do not appear in the LIF spectrum.

The excitation process of SO<sub>2</sub> fluorescence has been extensively studied and reviewed by Heicklen et al.<sup>16</sup> as well as by Lee and Loper.<sup>17</sup> Low-resolution fluorescence spectra were reported by Mettee<sup>18</sup> and Strickler and Howell,<sup>19</sup> wherein SO<sub>2</sub> was excited at several wavelengths between 265 and 313 nm. The broad semicontinuum is attributed to the  $\tilde{B}^1B_1 \rightarrow \tilde{X}^1A_1$  transition (fluorescence), and the vibrational structure in the 380-470-nm

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region is the  $\tilde{b}^3 B_1 \rightarrow \tilde{X}^1 A_1$  transition (phosphorescence).<sup>16,17</sup> The  $\tilde{b}$  state is not produced by a direct optical excitation of SO<sub>2</sub> but by collisional-induced intersystem crossing, SO<sub>2</sub>( $\tilde{B}$ ) + SO<sub>2</sub>  $\rightarrow$  SO<sub>2</sub>( $\tilde{b}$ ) + SO<sub>2</sub>. The intensity ratio of phosphorescence to fluorescence increases with increasing pressure and excitation wavelength.

The LIF spectrum of SO<sub>2</sub> shown in Figure 4 does not contain the  $\tilde{b}-\tilde{X}$  bands. This lack of triplet transition may be mainly caused by the detection method in which only the emission within 35  $\mu$ s after each laser pulse was detected. The time constant<sup>16</sup> for the collisional-induced crossing is estimated to be longer than 0.1 ms, which is much longer than the fluorescence observation time. On the other hand, the fluorescence spectrum produced from photodissociative excitation of SO<sub>3</sub> as shown in Figure 2, which was also detected within 35  $\mu$ s, clearly shows the  $\tilde{b}-\tilde{X}$  bands. This result indicates that the  $\tilde{b}-\tilde{X}$  bands are produced from a direct photodissociation of SO<sub>3</sub> into SO<sub>2</sub>( $\tilde{b}$ ) + O, but not from the collisional-induced crossing.

The yield for the production of  $SO_2(\tilde{b})$  is apparently larger than that of  $SO_2(\tilde{B})$ , because their emission intensities are of the same order of magnitude, but the radiative lifetimes of  $\tilde{b}$  (~8 ms) is much longer than that of  $\tilde{B}$  (~40  $\mu$ s). The quenching rate constants for  $SO_2(\tilde{b} \text{ and } \tilde{B})$  by  $SO_3$  are not known; however, it may be reasonable to assume that they are roughly equal to the quenching of SO<sub>2</sub>\* by SO<sub>2</sub>, which are<sup>16</sup> about  $10^{-12}$  and  $10^{-9}$  cm<sup>3</sup>/s, respectively. For the SO<sub>3</sub> partial pressure of 10 mTorr used in the experiment, the quenching rates of  $SO_2(\bar{b} \text{ and } \bar{B})$  by  $SO_3$  are about  $3 \times 10^2$  and  $3 \times 10^5$  s<sup>-1</sup>, respectively. For the quenching by He (4.9 Torr), the quenching rate for  $SO_2(\tilde{b})$  is at most equal to that by SO<sub>3</sub>, and for SO<sub>2</sub>( $\tilde{B}$ ) the quenching rate is negligible when compared with that of  $SO_3$ . The fluorescence intensity detected in a gated period, t, is proportional to nqE, where n is the population of the excited species, q is the PMT quantum yield which decreases systematically with increasing wavelength, E = $[1 - \exp(-t/\tau)]\tau/\tau_0$  is the fluorescence efficiency,  $\tau = \tau_0/(1 + \tau_0)$  $\sum_i \tau_0 k_i[\mathbf{M}_i]$  is the fluorescence decay time,  $\tau_0$  is the radiative lifetime,  $k_i$  is the quenching rate constant, and  $[M_i]$  is the concentration of a quenching species. In the current experimental conditions, E is about  $2 \times 10^{-3}$  for SO<sub>2</sub>( $\tilde{b}$ ) and  $7 \times 10^{-2}$  for SO<sub>2</sub>( $\tilde{B}$ ); namely, the fluorescence detection efficiency for the  $\tilde{b}$  state is much lower than that of the  $\tilde{B}$  state. The relative production yield for  $SO_2(\tilde{b})$  to  $SO_2(\tilde{B})$  is thus larger than that appearing in the spectra shown in Figures 2 and 3. The large production yield for  $SO_2(\tilde{b})$ may be due to the fact that the photodissociation of  $SO_3$  into  $SO_2({}^{3}B_1) + O({}^{3}P)$  is a spin-allowed process.

In the reactions of SO +  $O_3^{20}$  and SO + O + M,<sup>21</sup> the SO<sub>2</sub> emission was observed. In the SO-O<sub>3</sub> system, both the SO<sub>2</sub>( $\tilde{B}-\tilde{X}$  and  $\tilde{b}-\tilde{X}$ ) systems were observed. From the pressure dependence, it was estimated that about 30% of the  $\tilde{b}$  state is directly populated from the reaction.<sup>20</sup> In the SO-O system, SO<sub>2</sub> is mainly populated to high vibrational levels of the  $\tilde{B}$  state, because of its high exothermicity (132.1 kcal/mol). An emission band in the 230-400-nm region was observed from the recombination process of SO + O when the gas mixture of SO<sub>2</sub> in Ar was irradiated by intense F<sub>2</sub> laser pulse and the photon detection system was not gated. When the detection system was gated (35  $\mu$ s), the emission intensity was quite small.

Photodissociation Process of  $SO_3$ . From the above results, it is conclusive that the observed fluorescence is produced from photodissociative excitation of  $SO_3$ . The photodissociation processes that produce the observed emission are

$$SO_{3}(\tilde{X}) + h\nu \rightarrow SO_{2}^{*}(S) + O(^{3}P)$$
$$\rightarrow SO_{2}^{*}(T) + O(^{3}P)$$

where S and T represent the singlet and triplet states of SO<sub>2</sub>, respectively. The enthalpy change in the process SO<sub>3</sub>  $\rightarrow$  SO<sub>2</sub> + O is 83.3 kcal/mol (3.61 eV), where the heats of formation<sup>23</sup>  $\Delta H_f^{\circ}(SO_3) = -94.6 \text{ kcal/mol}, \Delta H_f^{\circ}(SO_2) = -70.9 \text{ kcal/mol}, \text{ and } \Delta H_f^{\circ}(O) = 59.6 \text{ kcal/mol} \text{ were used for the calculation}.$ 

The absorption spectrum of SO<sub>2</sub> in the UV region is assigned to four electronically excited states, namely, three singlet states  $(\tilde{A}^{1}A_{1}, \tilde{B}^{1}B_{1}, \text{and } \tilde{C}^{1}B_{2})$  and a triplet state  $(\tilde{b}^{3}B_{1})$ . The absorption spectrum in the 240–340-nm region is complicated by the overlapping between  $\tilde{A}$  and  $\tilde{B}$ . The origins of  $\tilde{A}$  and  $\tilde{B}$  are at 27 930 cm<sup>-1</sup> (3.46 eV) and 31 950  $\pm$  300 cm<sup>-1</sup> (3.96  $\pm$  0.04 eV), respectively.<sup>16,17</sup> The absorption to the  $\tilde{b}$  triplet state is in the 340–400-nm region with the origin at 25 766 cm<sup>-1</sup> (3.19 eV). Combining these excitation energies and the enthalpy change for the SO<sub>3</sub> dissociation, the threshold wavelengths for the production of SO<sub>2</sub>( $\tilde{A}$ ) and SO<sub>2</sub>( $\tilde{b}$ ) from photodissociative excitation of SO<sub>3</sub> are calculated to be at 175.3 and 182.3 nm, respectively. As shown in Figure 1, the threshold for the observed fluorescence is at 159 nm, which is about 0.7 eV higher than the calculated threshold for the production of SO<sub>2</sub>( $\tilde{A}$ ).

When SO<sub>3</sub> is irradiated at 157 nm, the excess energy above the SO<sub>2</sub>( $\tilde{X}$ ) + O dissociation limit is 4.28 eV. If all this excess energy is transferred to SO<sub>2</sub>, the shortest possible wavelength for the observed SO<sub>2</sub> emission is 290 nm, which does, in fact, correspond to the short limit of the spectrum shown in Figure 2. For the excitation at 147 nm, the excess energy is 4.82 eV. This excess energy could make the shortest emission wavelength to be 257 nm; however, the fluorescence actually starts around 270 nm, as shown in Figure 3.

SO<sub>3</sub> may also dissociate into SO + O<sub>2</sub>, for which the enthalpy change is 96.2 kcal/mol (4.17 eV). The photolysis of SO<sub>3</sub> in the near-UV region was studied by Norrish and Oldershaw,<sup>25</sup> in which the transient absorption of UV light by SO radical was observed. The photodissociation of SO<sub>3</sub> into SO(A and B) + O<sub>2</sub> is possible at wavelengths shorter than 139 and 133 nm, respectively. These processes are not included in the present study.

### Conclusion

The "apparent" photoabsorption cross section and fluorescence excitation spectrum of SO<sub>3</sub> were measured in the 145-160-nm region. The fluorescence spectra produced by 147- and 157-nm excitation of SO<sub>3</sub> were dispersed and compared with the laserinduced fluorescence spectrum of SO<sub>2</sub>. The fluorescence is attributed to the SO<sub>2</sub> ( $\tilde{B}, \tilde{b} \rightarrow \tilde{X}$ ) transitions. The lower limit for the absolute fluorescence cross section at 147 nm is determined to be 0.15 Mb. The observed fluorescence is currently used as a means for the detection of SO<sub>3</sub> in the measurements of reaction kinetics of SO<sub>3</sub> with various atmospheric species.

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<sup>(25)</sup> Norrish, R. G. W.; Oldershaw, G. A., Proc. R. Soc. London, A 1959, 249, 498.