

# Vibrational Distributions of $S_0^+(A^2\Pi_i)$ Produced from Dissociative Ionization of $S_0$ - Containing Molecules in a Helium Flowing Afterglow

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# Vibrational Distributions of $\text{SO}^+(\text{A}^2\Pi_i)$ Produced from Dissociative Ionization of SO-Containing Molecules in a Helium Flowing Afterglow

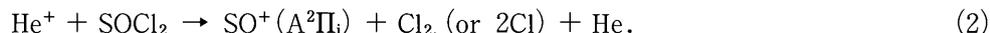
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Emission spectra resulting from the reactions of  $\text{He}(2^3\text{S})$ ,  $\text{He}^+$ , and  $\text{He}_2^+$  with  $\text{SO}_2$ ,  $\text{SOCl}_2$ ,  $\text{SOBr}_2$ ,  $\text{SO}_2\text{Cl}_2$ , and  $\text{SO}_2\text{FCl}$  have been measured in a helium flowing afterglow in order to examine dissociative-ionization processes leading to  $\text{SO}^+(\text{A}^2\Pi_i)$ . Although the  $\text{SO}^+(\text{A}^2\Pi_i\text{-X}^2\Pi_r)$  emission system was observed from the reactions of  $\text{He}^+$  with  $\text{SO}_2$ ,  $\text{SOCl}_2$ , and  $\text{SO}_2\text{Cl}_2$ , it was absent from those of  $\text{He}^+$  with  $\text{SOBr}_2$  and  $\text{SO}_2\text{FCl}$ . The vibrational distributions of  $\text{SO}^+(\text{A})$  decreased nearly exponentially with increasing  $v'$  for all the three reactions. The effective vibrational temperatures of  $\text{SO}^+(\text{A})$  were determined to be  $3320 \pm 230$ ,  $4620 \pm 760$ , and  $3100 \pm 300$  K for  $\text{SO}_2$ ,  $\text{SOCl}_2$ , and  $\text{SO}_2\text{Cl}_2$ , respectively.

## 1. Introduction

We have made systematic optical spectroscopic studies of gas-phase chemical reactions using a flowing-afterglow method<sup>1)-3)</sup>. One purpose of our studies is the detection of new emissions from reactive intermediates. The other is the clarification of Penning ionization by rare gas metastable atoms and charge-transfer (CT) reactions by rare gas ions at thermal energy. We have previously succeeded in identifying a new  $\text{SO}^+(\text{A}^2\Pi_i\text{-X}^2\Pi_r)$  emission system resulting from the  $\text{He}^+/\text{SO}_2$  and  $\text{He}^+/\text{SOCl}_2$  dissociative CT reactions at thermal energy<sup>4)5)</sup>:



On the basis of vibrational analysis, the vibrational constants of the  $\text{SO}^+(\text{A}^2\Pi_i, \text{X}^2\Pi_r)$  states were determined. However, the vibrational distributions of  $\text{SO}^+(\text{A}^2\Pi_i)$  in processes (1) and (2) were not measured.

In order to obtain more information on the formation processes of  $\text{SO}^+(\text{A}^2\Pi_i)$  from  $\text{SO}_2$  and  $\text{SOCl}_2$ , the vibrational distributions of  $\text{SO}^+(\text{A})$  in processes (1) and (2) are determined in this study. In addition, emission spectra of three new SO-containing molecules ( $\text{SOBr}_2$ ,  $\text{SO}_2\text{Cl}_2$ , and  $\text{SO}_2\text{FCl}$ ) are measured in a helium flowing afterglow. Although the  $\text{SO}^+(\text{A-X})$  emission is observed from  $\text{SO}_2\text{Cl}_2$ , it is absent from  $\text{SOBr}_2$  and  $\text{SO}_2\text{FCl}$ . The vibrational distributions of  $\text{SO}^+(\text{A})$  in the  $\text{He}^+/\text{SO}_2\text{Cl}_2$  reaction is determined and compared with those in the  $\text{He}^+/\text{SO}_2$  and  $\text{He}^+/\text{SOCl}_2$  reactions.

## 2. Experimental

The flowing-afterglow apparatus used in this study was similar to that reported previously<sup>1)-6)</sup>. In brief, the metastable  $\text{He}(2^3\text{S})$  atoms and  $\text{He}^+$  and  $\text{He}_2^+$  ions were generated by a microwave

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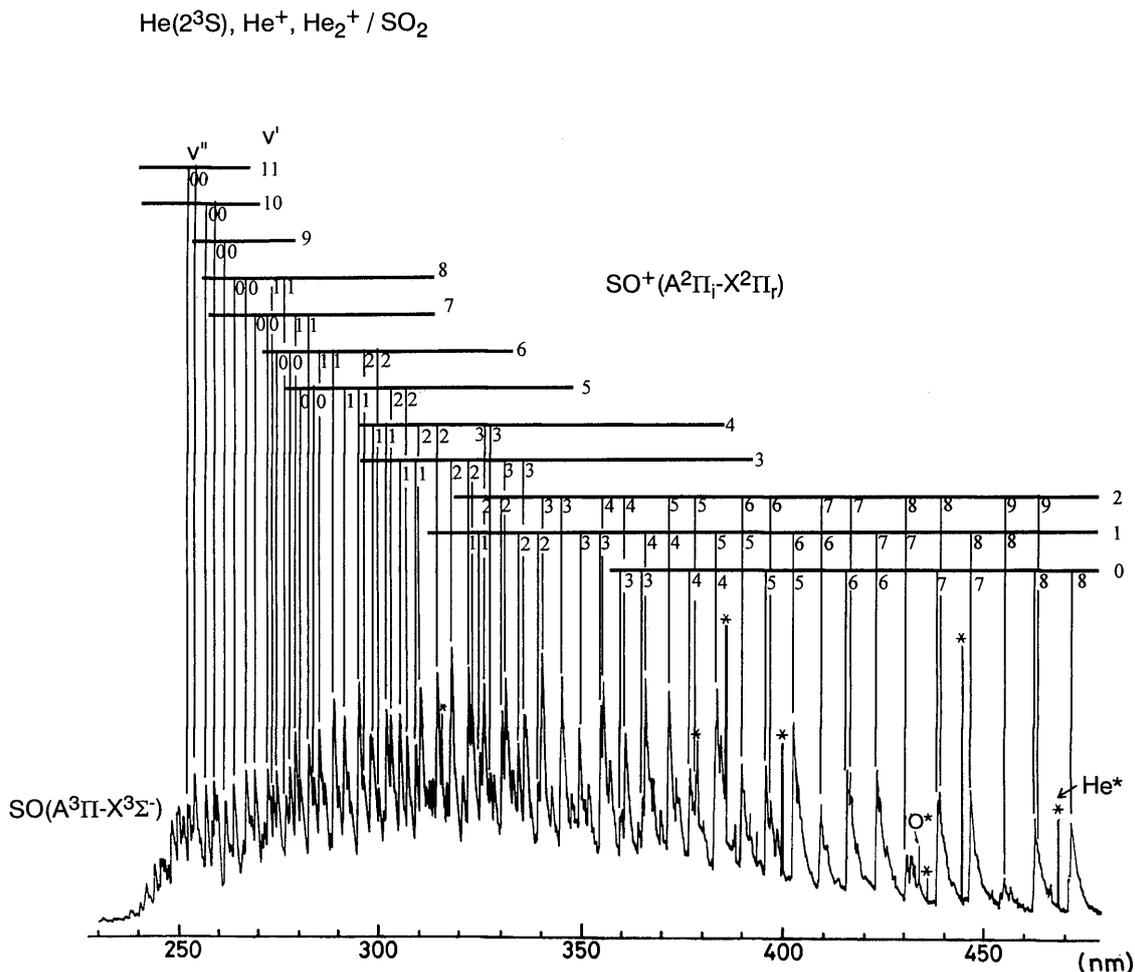
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discharge of high purity He gas. The contribution of ionic active species to the observed emissions was examined by using a pair of ion-collector grids placed between the discharge section and the reaction zone. A sample gas (SO<sub>2</sub>, SOCl<sub>2</sub>, SOBr<sub>2</sub>, SO<sub>2</sub>Cl<sub>2</sub>, or SO<sub>2</sub>FCl) was admixed with the He discharge flow operated at a He buffer gas pressure range of 0.5-1.5 Torr (1 Torr = 133.3 Pa). The emission spectra were dispersed with a Jarrell Ash 1 m monochromator equipped with a 1180 lines/mm grating blazed at 300 nm. The relative sensitivity of the optical detection system was calibrated using standard D<sub>2</sub> and halogen lamps.

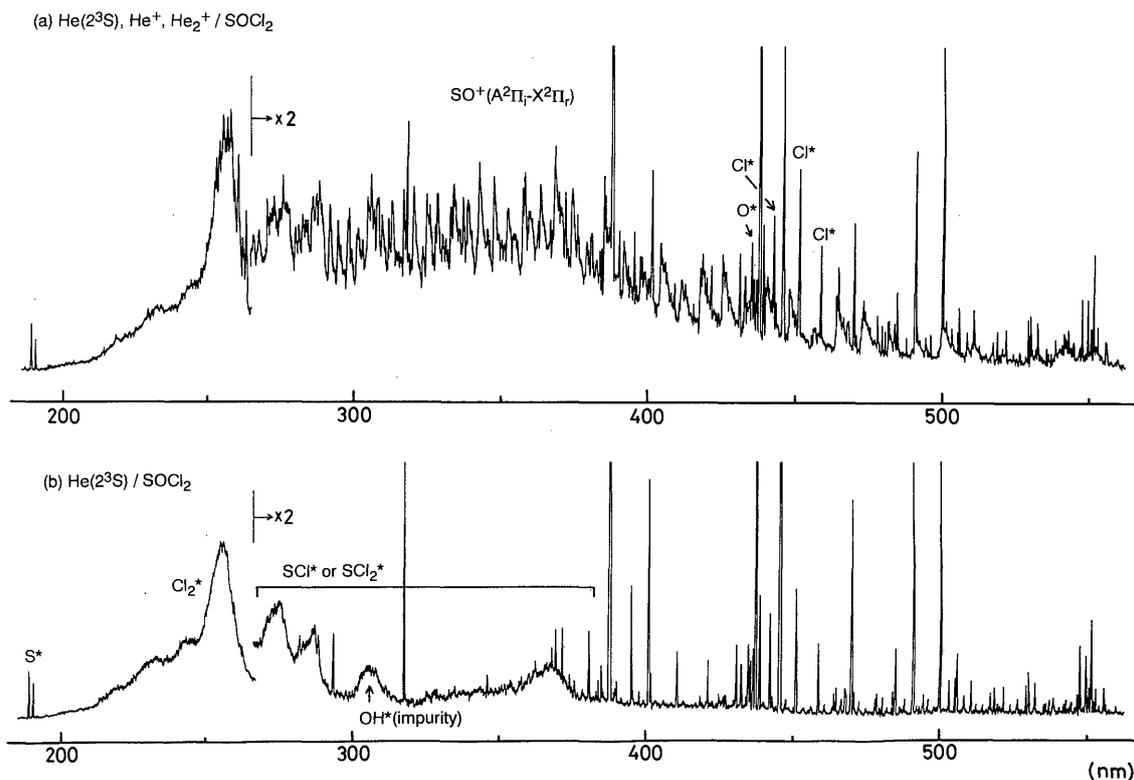
### 3. Results and Discussion

#### 3.1 Emission Spectra of SO<sub>2</sub>, SOCl<sub>2</sub>, and SOBr<sub>2</sub>

**Figs. 1 and 2 (a)** show typical emission spectra of SO<sub>2</sub> and SOCl<sub>2</sub> in a helium flowing afterglow, where He(2<sup>3</sup>S), He<sup>+</sup>, and He<sub>2</sub><sup>+</sup> are active species. The most prominent band in both spectra is the A<sup>2</sup>Π<sub>i</sub>-X<sup>2</sup>Π<sub>r</sub> transition of SO<sup>+</sup>. The SO<sup>+</sup>(A-X) transition from v' = 0-11 is identified in the He<sup>+</sup>/SO<sub>2</sub> reaction, as shown in **Fig. 1**. In addition, the SO(A<sup>3</sup>Π-X<sup>3</sup>Σ<sup>-</sup>) transition and an OI atomic line are found in **Fig. 1**, while SI, OI, and ClI atomic lines, Cl<sub>2</sub><sup>\*</sup> emission, and a broad band in the 260-380 nm region, which is probably associated with SCl<sub>2</sub><sup>\*</sup> emission, are detected in **Fig. 2 (a)**. When ionic active species are removed using the ion-collector grids, the SO<sup>+</sup>(A-X) emission disappears, while either no or very small change in intensities is found for the other emissions, as shown in **Fig. 2 (b)** for the case of SOCl<sub>2</sub>. On the basis of these facts, He<sup>+</sup> and/or He<sub>2</sub><sup>+</sup> are responsible for the formation of the SO<sup>+</sup>(A-X) ionic



**Fig. 1** Emission spectrum resulting from the He(2<sup>3</sup>S), He<sup>+</sup>, and He<sub>2</sub><sup>+</sup>/SO<sub>2</sub> reactions in a helium afterglow.

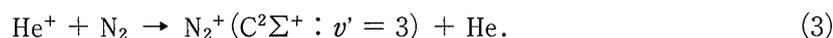


**Fig. 2** Emission spectra resulting from the (a)  $\text{He}(2^3\text{S})$ ,  $\text{He}^+$ , and  $\text{He}_2^+/\text{SOCl}_2$  and (b)  $\text{He}(2^3\text{S})/\text{SOCl}_2$  reactions in a helium afterglow.

**Table 1** Possible excitation processes of  $\text{SO}^+(\text{A}^2\Pi; v' = 0)$  from the dissociative CT reactions of  $\text{He}^+$  with  $\text{SO}_2$ ,  $\text{SOCl}_2$ , and  $\text{SO}_2\text{Cl}_2$ .

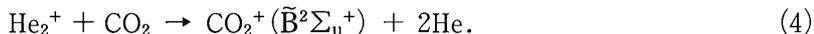
	Reactions	Processes
$\text{He}^+ + \text{SO}_2$	$\rightarrow \text{SO}^+(\text{A}) + \text{O}(^3\text{P}) + \text{He} + 4.75 \text{ eV}$	(1A)
	$\rightarrow \text{SO}^+(\text{A}) + \text{O}(^1\text{D}) + \text{He} + 2.78 \text{ eV}$	(1B)
	$\rightarrow \text{SO}^+(\text{A}) + \text{O}(^1\text{S}) + \text{He} + 0.56 \text{ eV}$	(1C)
$\text{He}^+ + \text{SOCl}_2$	$\rightarrow \text{SO}^+(\text{A}) + \text{Cl}_2(\text{X}) + \text{He} + 8.17 \text{ eV}$	(2A)
	$\rightarrow \text{SO}^+(\text{A}) + 2\text{Cl}(^2\text{P}) + \text{He} + 5.70 \text{ eV}$	(2B)
	$\rightarrow \text{SO}^+(\text{A}) + \text{Cl}_2(\text{E}) + \text{He} + 0.98 \text{ eV}$	(2C)
$\text{He}^+ + \text{SO}_2\text{Cl}_2$	$\rightarrow \text{SO}^+(\text{A}) + \text{OCl}_2 + \text{He} + 5.70 \text{ eV}$	(3A)
	$\rightarrow \text{SO}^+(\text{A}) + \text{OCl} + \text{Cl}(^2\text{P}) + \text{He} + 4.44 \text{ eV}$	(3B)
	$\rightarrow \text{SO}^+(\text{A}) + \text{O}(^3\text{P}) + \text{Cl}_2(\text{X}) + \text{He} + 4.17 \text{ eV}$	(3C)
	$\rightarrow \text{SO}^+(\text{A}) + \text{O}(^1\text{D}) + \text{Cl}_2(\text{X}) + \text{He} + 2.20 \text{ eV}$	(3D)
	$\rightarrow \text{SO}^+(\text{A}) + \text{O}(^3\text{P}) + 2\text{Cl}(^2\text{P}) + \text{He} + 1.70 \text{ eV}$	(3E)

emission, while only the metastable  $\text{He}(2^3\text{S})$  atoms are the excitation source of  $\text{SO}^*$ ,  $\text{SI}$ ,  $\text{OI}$ ,  $\text{ClI}$ ,  $\text{Cl}_2^*$ , and  $\text{SCI}^*$  or  $\text{SCl}_2^*$  neutral emissions. The  $\text{SO}^+(\text{A-X})$  emission was observed at low He pressures of 0.5-0.7 Torr, where the contribution of  $\text{He}_2^+$  was insignificant. The dependence of emission intensity of  $\text{SO}^+(\text{A-X})$  on the He pressure was similar to that of the (3,10) band of  $\text{N}_2^+(\text{C}^2\Sigma_u^+ - \text{X}^2\Sigma_g^+)$  resulting from the  $\text{He}^+/\text{N}_2$  near-resonant CT reaction<sup>7)</sup>:



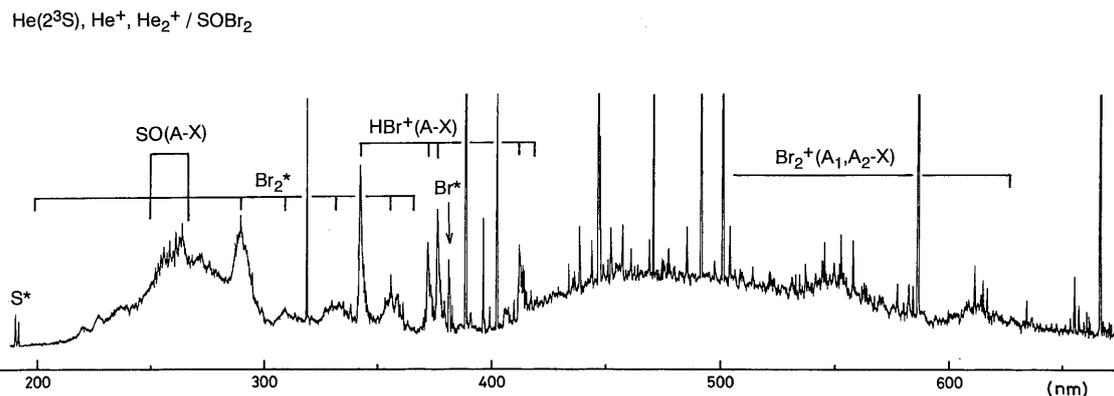
However, it was different from that of  $\text{CO}_2^+(\tilde{\text{B}}^2\Sigma_u^+ - \tilde{\text{X}}^2\Pi_g)$  emission resulting from the  $\text{He}_2^+/\text{CO}_2$

CT reaction<sup>8)</sup> :

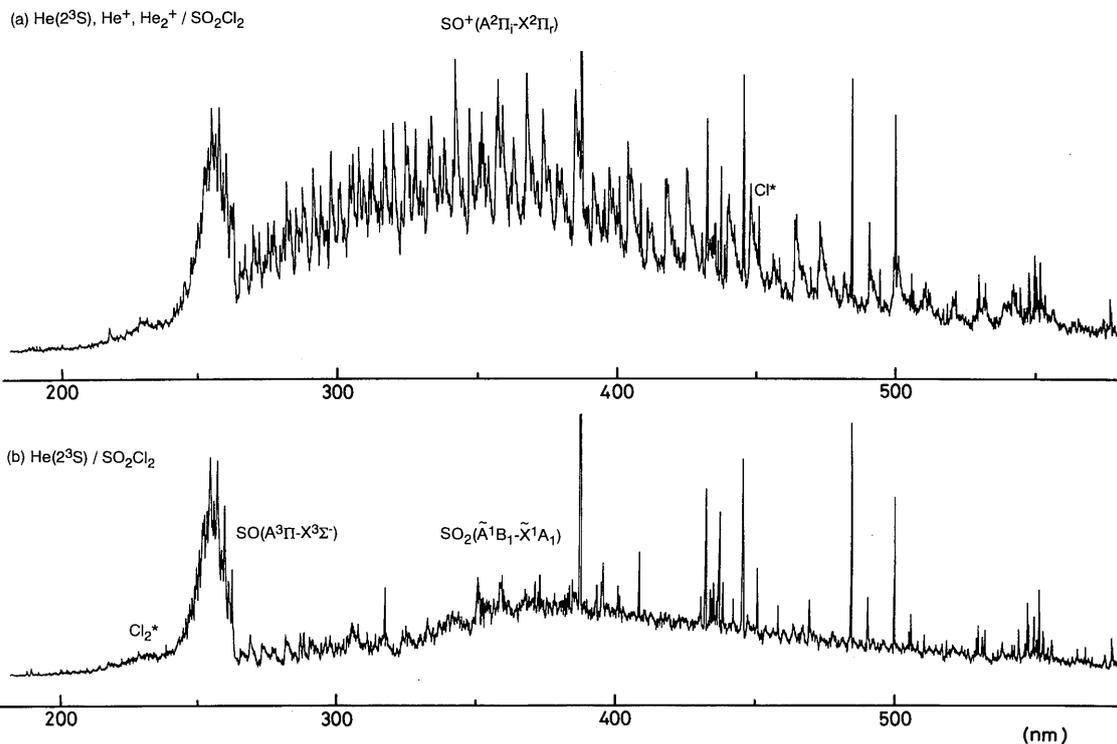


It was, therefore, concluded that He<sup>+</sup> was the excitation source of SO<sup>+</sup>(A). Possible formation mechanism of SO<sup>+</sup>(A) from the He<sup>+</sup>/SO<sub>2</sub> and He<sup>+</sup>/SOCl<sub>2</sub> reactions is given in **Table 1**. Thermochemical and spectroscopic data given in references 9-11 were used for the evaluation of heats of reactions reported in this work.

**Fig. 3** shows an emission spectrum of SOBr<sub>2</sub> in a helium afterglow, where active species are He(2<sup>3</sup>S), He<sup>+</sup>, and He<sub>2</sub><sup>+</sup>. Although SI and BrI atomic lines and Br<sub>2</sub><sup>\*</sup> and Br<sub>2</sub><sup>+</sup><sup>\*</sup> molecular emissions are found, no SO<sup>+</sup>(A-X) emission is detected. No appreciable change in the emission intensities was found, when He<sup>+</sup> and He<sub>2</sub><sup>+</sup> ions were removed using the ion-collector grids. On

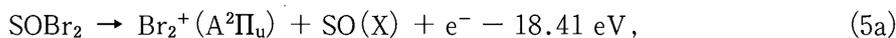


**Fig. 3** Emission spectrum resulting from the He(2<sup>3</sup>S), He<sup>+</sup>, and He<sub>2</sub><sup>+</sup>/SOBr<sub>2</sub> reactions in a helium afterglow.



**Fig. 4** Emission spectra resulting from the (a) He(2<sup>3</sup>S), He<sup>+</sup>, and He<sub>2</sub><sup>+</sup>/SO<sub>2</sub>Cl<sub>2</sub> and (b) He(2<sup>3</sup>S)/SO<sub>2</sub>Cl<sub>2</sub> reactions in a helium afterglow.

the basis of this fact, the excitation source of the observed emissions was  $\text{He}(2^3\text{S})$ . The  $v' = 0$  and 1  $v''$ -progressions of the  $A_1^2\Pi_u, 1/2-X^2\Pi_g$  and  $A_2^2\Pi_u, 3/2-X^2\Pi_g$  transitions of  $\text{Br}_2^+$  are identified. Since these progression bands are heavily overlapped with each other, the  $\text{Br}_2^{+*}$  band becomes a broad continuous band. The minimum energies required for the formation of  $\text{Br}_2^+(A)$  from  $\text{SOBr}_2$  are as follows:



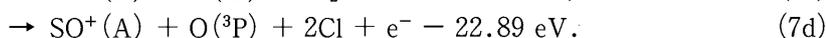
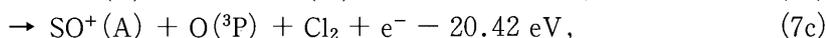
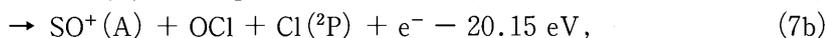
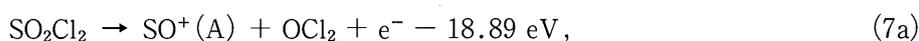
Since  $\text{Br}_2^+(A)$  is formed by the reaction with  $\text{He}(2^3\text{S})$  with an available energy of 19.82 eV, only the following dissociative Penning ionization is energetically accessible for the formation of  $\text{Br}_2^+(A)$ :



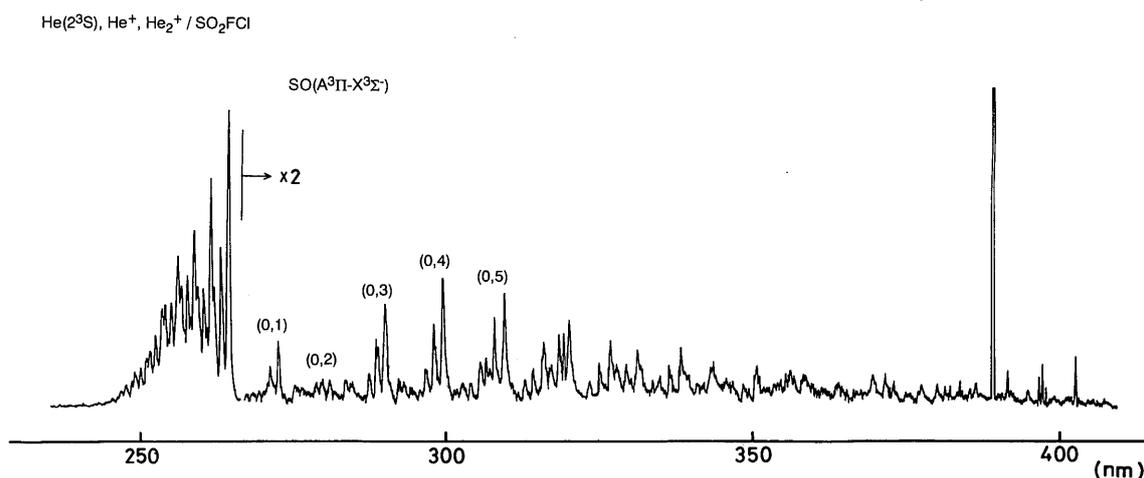
A  $\text{HBr}^+(A^2\Sigma^+-X^2\Pi_i)$  emission probably due to some impurity involved in  $\text{SOBr}_2$  is also identified in the 340-420 nm region.

### 3.2 Emission Spectra of $\text{SO}_2\text{Cl}_2$ and $\text{SO}_2\text{FCl}$

An emission spectrum obtained from the reactions of  $\text{He}(2^3\text{S})$ ,  $\text{He}^+$ , and  $\text{He}_2^+$  with  $\text{SO}_2\text{Cl}_2$  in a helium afterglow is shown in **Fig. 4(a)**. It consists of  $\text{ClI}$ ,  $\text{Cl}_2$ ,  $\text{SO}(A-X)$ ,  $\text{SO}^+(A-X)$ , and  $\text{SO}_2(\tilde{A}^1B_1-\tilde{X}^1X_1)$  emissions. When  $\text{He}^+$  and  $\text{He}_2^+$  ions are trapped, the  $\text{SO}^+(A-X)$  emission disappears, while the other emissions are essentially independent of an electrostatic potential applied to the ion-collector grids, as shown in **Fig. 4(b)**. This led us to conclude that  $\text{SO}^+(A)$  is formed by the reaction with  $\text{He}^+$  and/or  $\text{He}_2^+$ , while  $\text{He}(2^3\text{S})$  is responsible for the formation of  $\text{Cl}^*$ ,  $\text{Cl}_2^*$ ,  $\text{SO}(A)$ , and  $\text{SO}_2(\tilde{A})$ . The minimum energies required for the formation of  $\text{SO}^+(A)$  from  $\text{SO}_2\text{Cl}_2$  is as follows:



Since the recombination energies of  $\text{He}^+$  (24.59 eV) and  $\text{He}_2^+$  (18.3-20.3 eV) are higher than the



**Fig. 5** Emission spectrum resulting from the  $\text{He}(2^3\text{S})$ ,  $\text{He}^+$ , and  $\text{He}_2^+$ / $\text{SO}_2\text{FCl}$  reactions in a helium afterglow.

energies required for processes (7a) and (7b), both ions cannot be excluded from the excitation sources of SO<sup>+</sup>(A) from SO<sub>2</sub>Cl<sub>2</sub>. The dependence of emission intensity of SO<sup>+</sup>(A-X) on the He buffer gas pressure was similar to that of He<sup>+</sup>. Therefore, the He<sup>+</sup> ion was concluded to be the responsible active species. Possible excitation mechanism of SO<sup>+</sup>(A) from the dissociative He<sup>+</sup>/SO<sub>2</sub>Cl<sub>2</sub> CT processes is (3A)-(3E) in **Table 1**.

An emission spectrum resulting from the reactions of He(2<sup>3</sup>S), He<sup>+</sup>, and He<sub>2</sub><sup>+</sup> with SO<sub>2</sub>FCl is shown in **Fig. 5**. The only SO(A<sup>3</sup>Π-X<sup>3</sup>Σ<sup>-</sup>) emission system is found. Since the emission intensity of SO(A-X) was independent of the electrostatic potential applied to the ion-collector grid, its excitation source was attributed to He(2<sup>3</sup>S).

As described above, we found that dissociative ionization channels leading to SO<sup>+</sup>(A) are open for SO<sub>2</sub>, SOCl<sub>2</sub>, and SO<sub>2</sub>Cl<sub>2</sub>, and that the excitation source is only He<sup>+</sup>. The vibrational distributions of SO<sup>+</sup>(A) from the reactions of He<sup>+</sup> with SO<sub>2</sub>, SOCl<sub>2</sub>, and SO<sub>2</sub>Cl<sub>2</sub> are evaluated in the next section.

### 3.3 Vibrational distributions of SO<sup>+</sup>(A)

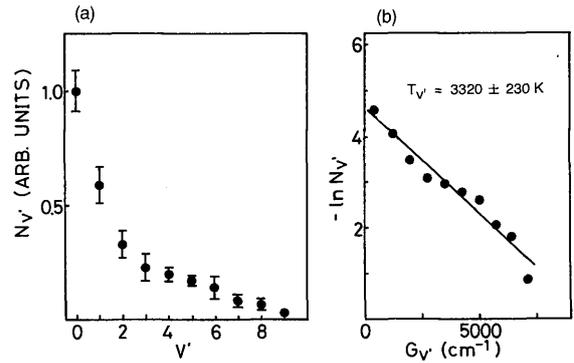
The relation between the emission intensity of a (*v'*, *v''*) band [*I*<sub>*v'**v''*</sub>] and the population of the upper vibrational state [*N*<sub>*v'*</sub>] is given by

$$I_{v'v''} = KN_{v'}\text{Re}^2(\bar{r}_{v'v''})q_{v'v''}\nu_{v'v''}^3, \quad (8)$$

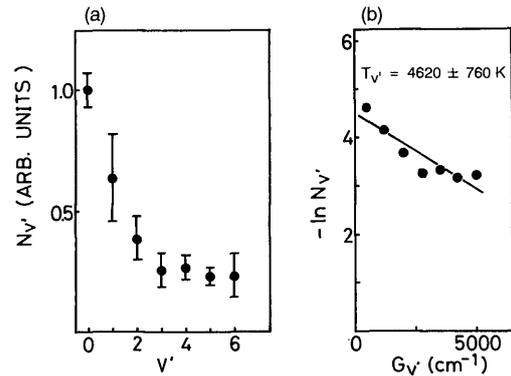
where *K* is a constant depending on the units and geometry of the system, and  $\text{Re}(\bar{r}_{v'v''})$ , *q*<sub>*v'**v''*</sub>, and  $\nu_{v'v''}$  are the electronic transition moment, the Franck-Condon factor, and the transition frequency, respectively<sup>12)</sup>. The Franck-Condon factors of SO<sup>+</sup>(A-X) were calculated using Morse SO<sup>+</sup>(A-X) potentials. Then, the *N*<sub>*v'*</sub> values were determined assuming  $\text{Re}(\bar{r}_{v'v''})$  to be constant. The *N*<sub>*v'*</sub> values were independent of the He buffer gas pressure over the range of 0.5-1.5 Torr, indicating that the vibrational relaxation of SO<sup>+</sup>(A) due to collisions with the buffer He gas was insignificant in the present experimental conditions during its radiative lifetime of  $2.4 \pm 0.4 \mu\text{s}$ <sup>13)</sup>. It was found that the vibrational populations of SO<sup>+</sup>(A) decrease with increasing *v'* for all the three reactions, as shown in **Figs. 6(a)-8(a)**. Since the vibrational distributions of SO<sup>+</sup>(A) decrease nearly exponentially with increasing *v'*, effective Boltzmann vibrational temperatures (*T*<sub>*v'*</sub>) are obtained from the relation,

$$N_{v'} \propto \exp(-E_{v'}/kT_{v'}), \quad (9)$$

where *E*<sub>*v'*</sub> is the vibrational energy of SO<sup>+</sup>(A : *v'*) and *k* is the Boltzmann constant. Of course, this vibrational temperature is not equal to any other temperatures (translational and rotational temperatures) that would exist in a fully equilibrium system. The *T*<sub>*v'*</sub> values of  $3320 \pm 230$ ,



**Fig. 6** Vibrational distribution of SO<sup>+</sup>(A) produced from the He<sup>+</sup>/SO<sub>2</sub> reaction.



**Fig. 7** Vibrational distribution of SO<sup>+</sup>(A) produced from the He<sup>+</sup>/SOCl<sub>2</sub> reaction.

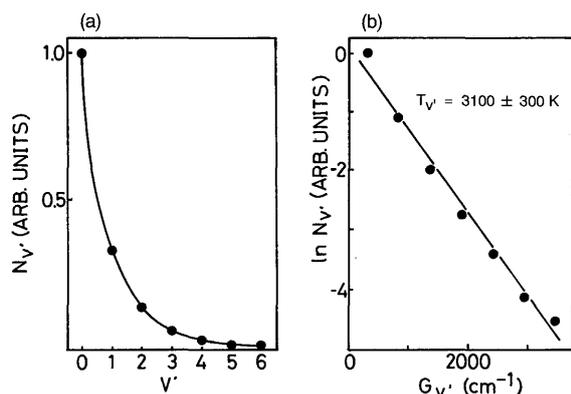
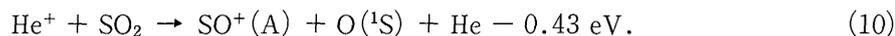


Fig. 8 Vibrational distribution of  $\text{SO}^+(\text{A})$  produced from the  $\text{He}^+/\text{SO}_2\text{Cl}_2$  reaction.

sequent (pre) dissociation of near-resonant  $\text{SO}_2^{+*}$ ,  $\text{SOCl}_2^{+*}$ , or  $\text{SO}_2\text{Cl}_2^{+*}$  states will provide the fragment  $\text{SO}^+(\text{A})$  ion. Possible formation processes of  $\text{SO}^+(\text{A} : v'=0)$  from the CT reactions of  $\text{He}^+$  with  $\text{SO}_2$ ,  $\text{SOCl}_2$ , and  $\text{SO}_2\text{Cl}_2$  are given in **Table 1**. The observed vibrational distributions of  $\text{SO}^+(\text{A})$  decrease single exponentially for all the three reactions. It is, therefore, reasonable to assume that one of the possible processes dominantly participates in the formation of  $\text{SO}^+(\text{A})$ . Although the formation of  $\text{SO}^+(\text{A} : v'=0)$  from process (1C) is energetically allowed, the formation of the highest observed  $\text{SO}^+(\text{A} : v'=11)$  from process (1C) is endoergic:



Therefore, process (1C) can be excluded from possible formation processes. It is known that the  $\text{SO}_2^+(\tilde{\text{F}}^2\text{A}_1)$  state at 20.06 eV is correlated with the  $\text{SO}^+(\text{A}) + \text{O}(^3\text{P})$  dissociation limit<sup>13)</sup>. Therefore, process (1A) may be most important for the formation of  $\text{SO}^+(\text{A})$  from  $\text{SO}_2$ . Assuming that  $\text{SO}^+(\text{A})$  is formed via a collision complex with a sufficient long lifetime to randomize its excess energy, the average vibrational energy deposited into  $\text{SO}^+(\text{A})$  is expected to be large for molecular ions having large excess energies and small vibrational degrees of freedom in collision complexes. The vibrational temperatures of  $\text{SO}^+(\text{A})$  from  $\text{SOCl}_2$  and  $\text{SO}_2\text{Cl}_2$  are either comparable with or higher than that from  $\text{SO}_2$ , even though the vibrational degrees of freedom in the  $\text{He}^+-\text{SOCl}_2$  and  $\text{He}^+-\text{SO}_2\text{Cl}_2$  collision complexes are larger than those for  $\text{He}^+-\text{SO}_2$ . It is therefore reasonable to assume that the responsible excitation processes of  $\text{SO}^+(\text{A})$  from  $\text{SOCl}_2$  and  $\text{SO}_2\text{Cl}_2$  are (2A) or (2B) and (3A), respectively. The excess energies of these processes are larger than that of process (1A). In order to confirm this assumption, further detailed experimental and theoretical studies will be required.

#### 4. Acknowledgments

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4620 ± 760, and 3100 ± 300 K are obtained for  $\text{SO}_2$ ,  $\text{SOCl}_2$ , and  $\text{SO}_2\text{Cl}_2$ , respectively, as shown in **Figs. 6 (b)**-**8 (b)**. These temperatures correspond to 0.29, 0.40, and 0.27 eV, respectively. The vibrational temperatures of  $\text{SO}^+(\text{A})$  in the  $\text{He}^+/\text{SO}_2$  and  $\text{He}^+/\text{SO}_2\text{Cl}_2$  reactions are similar, and they are lower than that in the  $\text{He}^+/\text{SOCl}_2$  reaction.

According to our previous studies on CT reactions of  $\text{He}^+$  with molecules<sup>1)-3)</sup>, reactions proceed near-resonantly at thermal energy. Therefore, the recombination energy of  $\text{He}^+$ , 24.59 eV, will be transferred nearly resonantly to  $\text{SO}_2$ ,  $\text{SOCl}_2$ , or  $\text{SO}_2\text{Cl}_2$ , and the subse-

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