

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

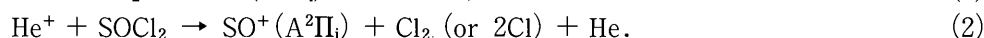
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Emission spectra resulting from the reactions of $\text{He}(2^3\text{S})$, He^+ , and He_2^+ with SO_2 , SOCl_2 , SOBr_2 , SO_2Cl_2 , and SO_2FCl have been measured in a helium flowing afterglow in order to examine dissociative-ionization processes 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 He^+ with SO_2 , SOCl_2 , and SO_2Cl_2 , it was absent from those of He^+ with SOBr_2 and SO_2FCl . 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 ± 230 , 4620 ± 760 , and 3100 ± 300 K for SO_2 , SOCl_2 , and SO_2Cl_2 , respectively.

1. Introduction

We have made systematic optical spectroscopic studies of gas-phase chemical reactions using a flowing-afterglow method¹⁾⁻³⁾. 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 He^+/SO_2 and $\text{He}^+/\text{SOCl}_2$ dissociative CT reactions at thermal energy⁴⁾⁵⁾:



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 SO_2 and 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 (SOBr_2 , SO_2Cl_2 , and SO_2FCl) are measured in a helium flowing afterglow. Although the $\text{SO}^+(\text{A-X})$ emission is observed from SO_2Cl_2 , it is absent from SOBr_2 and SO_2FCl . 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 He^+/SO_2 and $\text{He}^+/\text{SOCl}_2$ reactions.

2. Experimental

The flowing-afterglow apparatus used in this study was similar to that reported previously¹⁾⁻⁶⁾. In brief, the metastable $\text{He}(2^3\text{S})$ atoms and He^+ and He_2^+ ions were generated by a microwave

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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 (SO₂, SOCl₂, SOBr₂, SO₂Cl₂, or SO₂FCl) 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 D₂ and halogen lamps.

3. Results and Discussion

3.1 Emission Spectra of SO₂, SOCl₂, and SOBr₂

Figs. 1 and 2 (a) show typical emission spectra of SO₂ and SOCl₂ in a helium flowing afterglow, where He(2³S), He⁺, and He₂⁺ are active species. The most prominent band in both spectra is the A²Π_i-X²Π_r transition of SO⁺. The SO⁺(A-X) transition from v' = 0-11 is identified in the He⁺/SO₂ reaction, as shown in **Fig. 1**. In addition, the SO(A³Π-X³Σ⁻) transition and an OI atomic line are found in **Fig. 1**, while SI, OI, and ClI atomic lines, Cl₂^{*} emission, and a broad band in the 260-380 nm region, which is probably associated with SCl₂^{*} emission, are detected in **Fig. 2 (a)**. When ionic active species are removed using the ion-collector grids, the SO⁺(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 SOCl₂. On the basis of these facts, He⁺ and/or He₂⁺ are responsible for the formation of the SO⁺(A-X) ionic

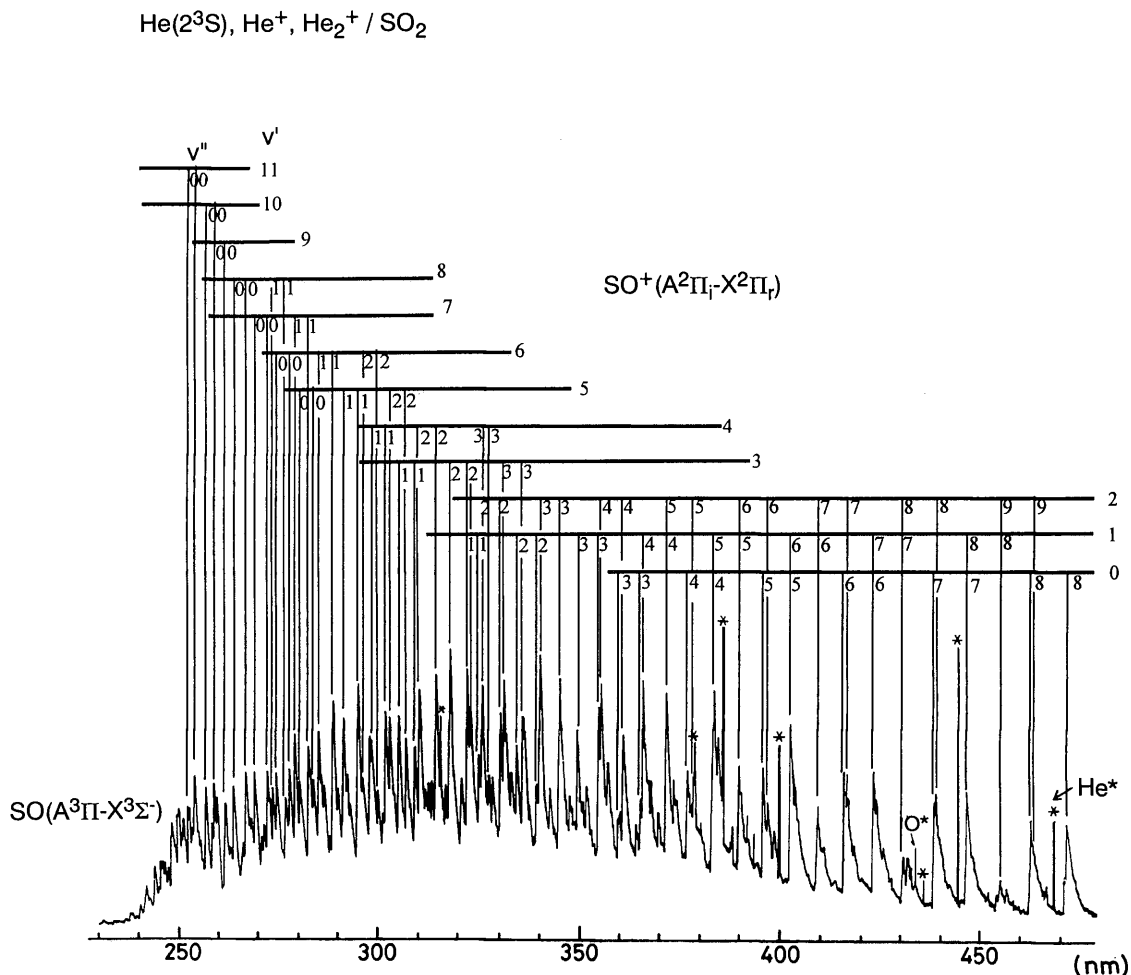


Fig. 1 Emission spectrum resulting from the He(2³S), He⁺, and He₂⁺/SO₂ reactions in a helium afterglow.

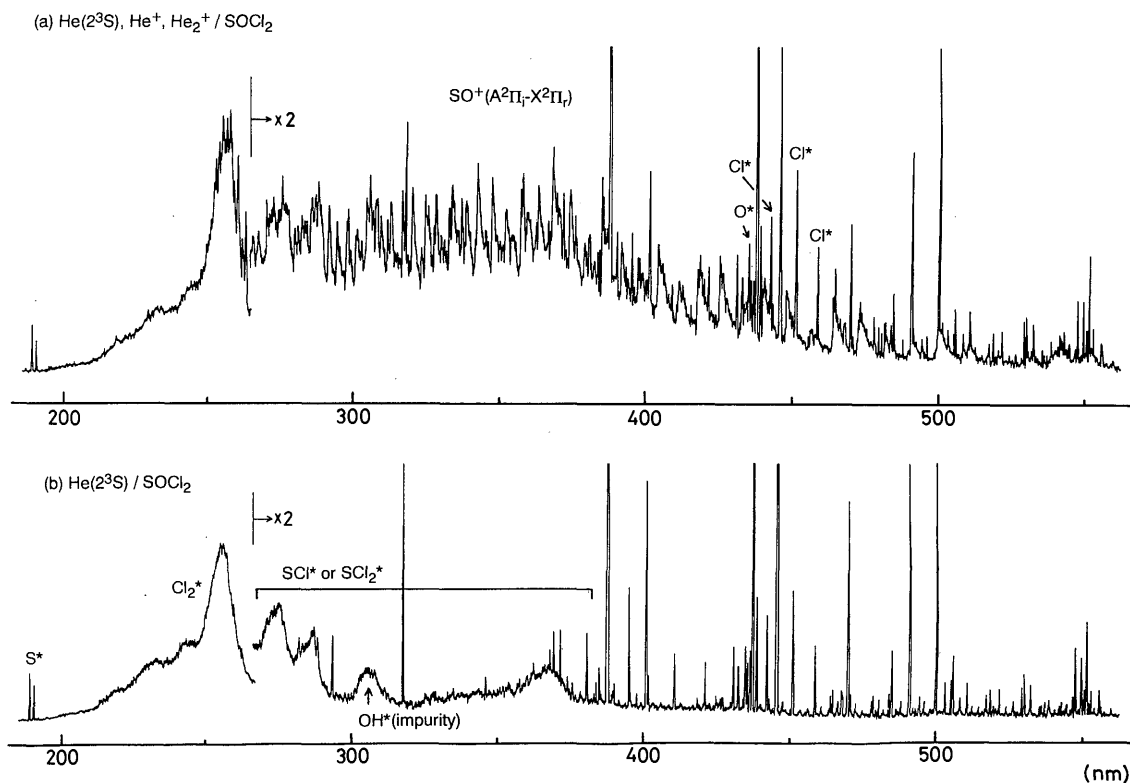
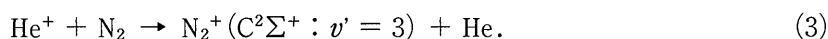


Fig. 2 Emission spectra resulting from the (a) $\text{He}(2^3\text{S})$, He^+ , and $\text{He}_2^+/\text{SOCl}_2$ and (b) $\text{He}(2^3\text{S})/\text{SOCl}_2$ reactions in a helium afterglow.

Table 1 Possible excitation processes of $\text{SO}^+(\text{A}^2\Pi; v' = 0)$ from the dissociative CT reactions of He^+ with SO_2 , SOCl_2 , and SO_2Cl_2 .

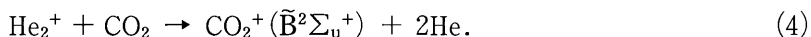
	Reactions	Processes
$\text{He}^+ + \text{SO}_2$	$\rightarrow \text{SO}^+(\text{A}) + \text{O}(^3\text{P}) + \text{He} + 4.75 \text{ eV}$	(1A)
	$\rightarrow \text{SO}^+(\text{A}) + \text{O}(^1\text{D}) + \text{He} + 2.78 \text{ eV}$	(1B)
	$\rightarrow \text{SO}^+(\text{A}) + \text{O}(^1\text{S}) + \text{He} + 0.56 \text{ eV}$	(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 SO^* , SI , OI , ClI , Cl_2^* , and SCI^* or 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 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 He^+/N_2 near-resonant CT reaction⁷⁾:



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 reaction⁸⁾ :



It was, therefore, concluded that He^+ was the excitation source of $\text{SO}^+(\text{A})$. Possible formation mechanism of $\text{SO}^+(\text{A})$ from the He^+/SO_2 and $\text{He}^+/\text{SOCl}_2$ 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_2 in a helium afterglow, where active species are $\text{He}(2^3\text{S})$, He^+ , and He_2^+ . Although SI and BrI atomic lines and Br_2^* and Br_2^{+*} molecular emissions are found, no $\text{SO}^+(\text{A-X})$ emission is detected. No appreciable change in the emission intensities was found, when He^+ and He_2^+ ions were removed using the ion-collector grids. On

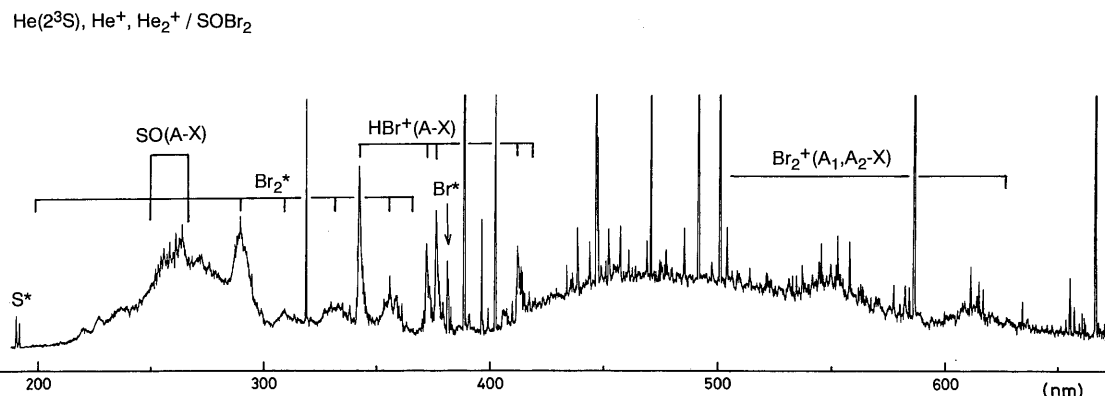


Fig. 3 Emission spectrum resulting from the $\text{He}(2^3\text{S})$, He^+ , and He_2^+ / SOBr_2 reactions in a helium afterglow.

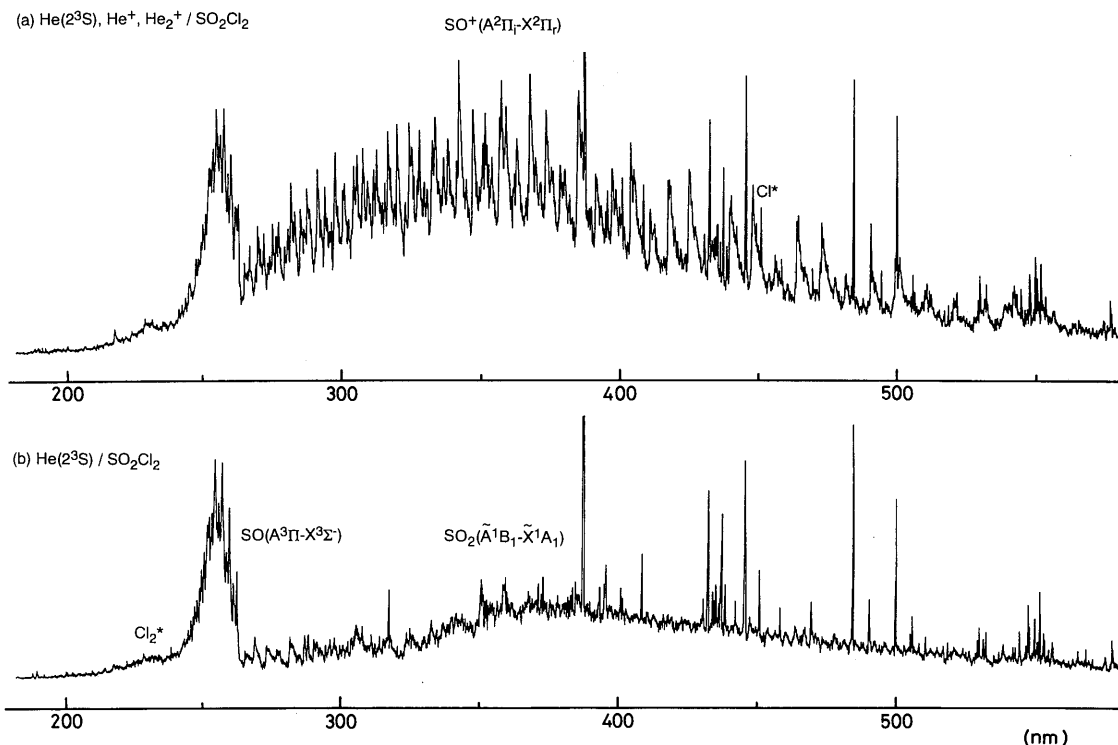
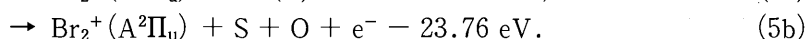
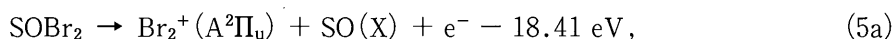
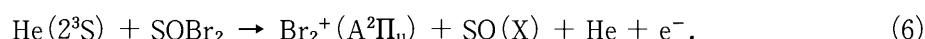


Fig. 4 Emission spectra resulting from the (a) $\text{He}(2^3\text{S})$, He^+ , and He_2^+ / SO_2Cl_2 and (b) $\text{He}(2^3\text{S})$ / SO_2Cl_2 reactions in a helium afterglow.

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 Br_2^+ are identified. Since these progression bands are heavily overlapped with each other, the Br_2^{+*} band becomes a broad continuous band. The minimum energies required for the formation of $\text{Br}_2^+(A)$ from SOBr_2 are as follows:



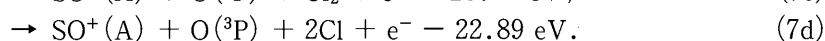
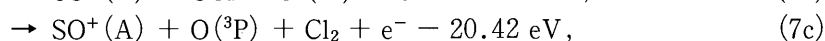
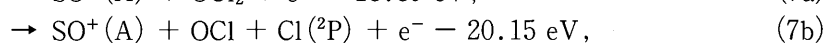
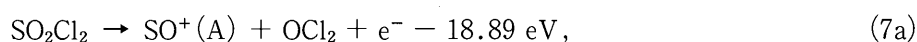
Since $\text{Br}_2^+(A)$ is formed by the reaction with $\text{He}(2^3\text{S})$ with an available energy of 19.82 eV, only the following dissociative Penning ionization is energetically accessible for the formation of $\text{Br}_2^+(A)$:



A $\text{HBr}^+(A^2\Sigma^+-X^2\Pi_i)$ emission probably due to some impurity involved in SOBr_2 is also identified in the 340-420 nm region.

3.2 Emission Spectra of SO_2Cl_2 and SO_2FCl

An emission spectrum obtained from the reactions of $\text{He}(2^3\text{S})$, He^+ , and He_2^+ with SO_2Cl_2 in a helium afterglow is shown in **Fig. 4(a)**. It consists of ClI , Cl_2 , $\text{SO}(A-X)$, $\text{SO}^+(A-X)$, and $\text{SO}_2(\tilde{A}^1B_1-\tilde{X}^1X_1)$ emissions. When He^+ and 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 He^+ and/or He_2^+ , while $\text{He}(2^3\text{S})$ is responsible for the formation of Cl^* , Cl_2^* , $\text{SO}(A)$, and $\text{SO}_2(\tilde{A})$. The minimum energies required for the formation of $\text{SO}^+(A)$ from SO_2Cl_2 is as follows:



Since the recombination energies of He^+ (24.59 eV) and He_2^+ (18.3-20.3 eV) are higher than the

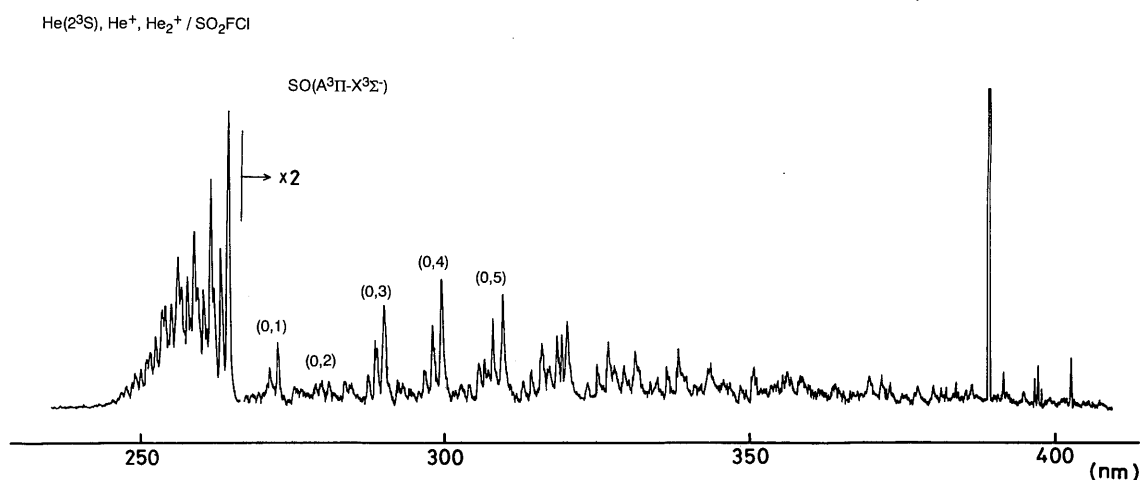


Fig. 5 Emission spectrum resulting from the $\text{He}(2^3\text{S})$, He^+ , and He_2^+ / SO_2FCl reactions in a helium afterglow.

energies required for processes (7a) and (7b), both ions cannot be excluded from the excitation sources of SO⁺(A) from SO₂Cl₂. The dependence of emission intensity of SO⁺(A-X) on the He buffer gas pressure was similar to that of He⁺. Therefore, the He⁺ ion was concluded to be the responsible active species. Possible excitation mechanism of SO⁺(A) from the dissociative He⁺/SO₂Cl₂ CT processes is (3A)-(3E) in **Table 1**.

An emission spectrum resulting from the reactions of He(2³S), He⁺, and He₂⁺ with SO₂FCl is shown in **Fig. 5**. The only SO(A³Π-X³Σ⁻) 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(2³S).

As described above, we found that dissociative ionization channels leading to SO⁺(A) are open for SO₂, SOCl₂, and SO₂Cl₂, and that the excitation source is only He⁺. The vibrational distributions of SO⁺(A) from the reactions of He⁺ with SO₂, SOCl₂, and SO₂Cl₂ are evaluated in the next section.

3.3 Vibrational distributions of SO⁺(A)

The relation between the emission intensity of a (*v'*, *v''*) band [*I*_{*v'**v''*}] and the population of the upper vibrational state [*N*_{*v'*}] 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*_{*v'**v''*}, and $\nu_{v'v''}$ are the electronic transition moment, the Franck-Condon factor, and the transition frequency, respectively¹²⁾. The Franck-Condon factors of SO⁺(A-X) were calculated using Morse SO⁺(A-X) potentials. Then, the *N*_{*v'*} values were determined assuming $\text{Re}(\bar{r}_{v'v''})$ to be constant. The *N*_{*v'*} 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⁺(A) due to collisions with the buffer He gas was insignificant in the present experimental conditions during its radiative lifetime of $2.4 \pm 0.4 \mu\text{s}$ ¹³⁾. It was found that the vibrational populations of SO⁺(A) decrease with increasing *v'* for all the three reactions, as shown in **Figs. 6(a)-8(a)**. Since the vibrational distributions of SO⁺(A) decrease nearly exponentially with increasing *v'*, effective Boltzmann vibrational temperatures (*T*_{*v'*}) are obtained from the relation,

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

where *E*_{*v'*} is the vibrational energy of SO⁺(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*_{*v'*} values of 3320 ± 230 ,

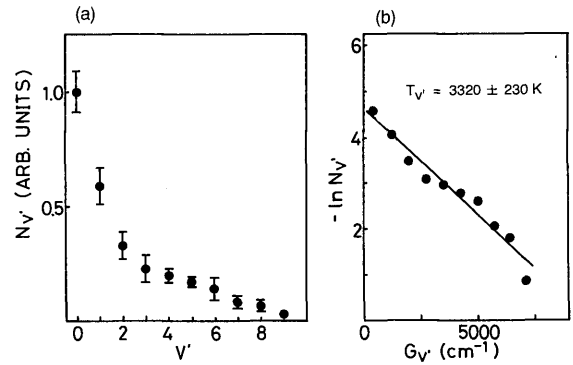


Fig. 6 Vibrational distribution of SO⁺(A) produced from the He⁺/SO₂ reaction.

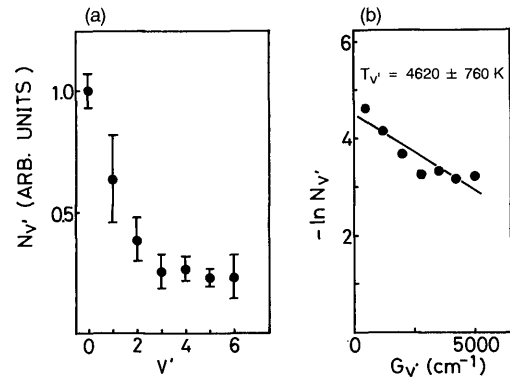


Fig. 7 Vibrational distribution of SO⁺(A) produced from the He⁺/SOCl₂ reaction.

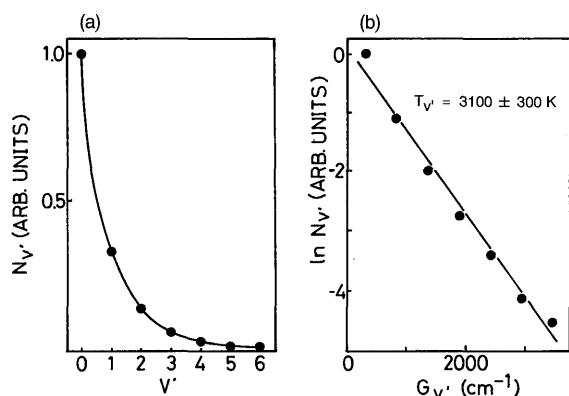
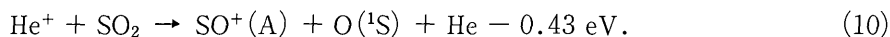


Fig. 8 Vibrational distribution of $\text{SO}^+(\text{A})$ produced from the $\text{He}^+/\text{SO}_2\text{Cl}_2$ reaction.

sequent (pre) dissociation of near-resonant SO_2^{+*} , 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 He^+ with SO_2 , SOCl_2 , and SO_2Cl_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 limit¹³⁾. Therefore, process (1A) may be most important for the formation of $\text{SO}^+(\text{A})$ from 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 SOCl_2 and SO_2Cl_2 are either comparable with or higher than that from 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 He^+-SO_2 . It is therefore reasonable to assume that the responsible excitation processes of $\text{SO}^+(\text{A})$ from SOCl_2 and SO_2Cl_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 SO_2 , SOCl_2 , and SO_2Cl_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 He^+/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 He^+ with molecules¹⁾⁻³⁾, reactions proceed near-resonantly at thermal energy. Therefore, the recombination energy of He^+ , 24.59 eV, will be transferred nearly resonantly to SO_2 , SOCl_2 , or SO_2Cl_2 , and the subse-

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