Vibrational Distributions of SO^+(A^2Π_i) Produced from Dissociative Ionization of SO- Containing Molecules in a Helium Flowing Afterglow

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Vibrational Distributions of SO\(^+\)(A\(^2\Pi\)) Produced from Dissociative Ionization of SO-Containing Molecules in a Helium Flowing Afterglow

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

1. Introduction

We have made systematic optical spectrocopic studies of gas-phase chemical reactions using a flowing-afterglow method \(^{1-9}\). 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 SO\(^+\)(A\(^2\Pi\) - X\(^2\Pi\)) emission system resulting from the He\(^+\)/SO\(_2\) and He\(^+\)/SOCl\(_2\) dissociative CT reactions at thermal energy \(^{10-12}\):

\[
\text{He}^+ + \text{SO}_2 \rightarrow \text{SO}^+(A^2\Pi) + \text{O} + \text{He}, \quad (1)
\]

\[
\text{He}^+ + \text{SOCl}_2 \rightarrow \text{SO}^+(A^2\Pi) + \text{Cl}_2 \ (\text{or} \ 2\text{Cl}) + \text{He}. \quad (2)
\]

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

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

2. Experimental

The flowing-afterglow apparatus used in this study was similar to that reported previously \(^{10-12}\). In brief, the metastable He (2\(^3\)S) atoms and He\(^+\) and He\(^2+\) ions were generated by a microwave
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 (2S), He⁺, and He₂⁺ are active species. The most prominent band in both spectra is the A²Π-X²Π 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 (A⁰Π-X⁰Σ⁻) transition and an OI atomic line are found in Fig. 1, while Si, OI, and CI⁺ atomic lines, Cl₂⁺ emission, and a broad band in the 260-380 nm region, which is probably associated with SCI⁺ or SCI₂⁺ 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 emission.
Fig. 2  Emission spectra resulting from the (a) He(2S), He+, He2+/SOCl2 and (b) He(2S)/SOCl2 reactions in a helium afterglow.

Table 1  Possible excitation processes of SO+ (A→Π; v' = 0) from the dissociative CT reactions of He+ with SO2, SOCl2, and SO2Cl2.

<table>
<thead>
<tr>
<th>Reactions</th>
<th>Processes</th>
</tr>
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<tbody>
<tr>
<td>He+ + SO2  \rightarrow SO+ (A) + O(3P) + He + 4.75 eV</td>
<td>(1A)</td>
</tr>
<tr>
<td>He+ + SO2  \rightarrow SO+ (A) + O(D) + He + 2.78 eV</td>
<td>(1B)</td>
</tr>
<tr>
<td>He+ + SO2  \rightarrow SO+ (A) + O(S) + He + 0.56 eV</td>
<td>(1C)</td>
</tr>
<tr>
<td>He+ + SOCl2 \rightarrow SO+ (A) + Cl2(X) + He + 8.17 eV</td>
<td>(2A)</td>
</tr>
<tr>
<td>He+ + SOCl2 \rightarrow SO+ (A) + 2Cl2(2P) + He + 5.70 eV</td>
<td>(2B)</td>
</tr>
<tr>
<td>He+ + SOCl2 \rightarrow SO+ (A) + Cl2(E) + He + 0.98 eV</td>
<td>(2C)</td>
</tr>
<tr>
<td>He+ + SO2Cl2 \rightarrow SO+ (A) + OCl2 + He + 5.70 eV</td>
<td>(3A)</td>
</tr>
<tr>
<td>He+ + SO2Cl2 \rightarrow SO+ (A) + Cl + Cl2(X) + He + 4.44 eV</td>
<td>(3B)</td>
</tr>
<tr>
<td>He+ + SO2Cl2 \rightarrow SO+ (A) + O(3P) + Cl2(X) + He + 4.17 eV</td>
<td>(3C)</td>
</tr>
<tr>
<td>He+ + SO2Cl2 \rightarrow SO+ (A) + O(D) + Cl2(X) + He + 2.20 eV</td>
<td>(3D)</td>
</tr>
<tr>
<td>He+ + SO2Cl2 \rightarrow SO+ (A) + O(P) + 2Cl2(2P) + He + 1.70 eV</td>
<td>(3E)</td>
</tr>
</tbody>
</table>

emission, while only the metastable He(2S) atoms are the excitation source of SO+, SI, OI, ClI, Cl2*, and SCI* or SC12* neutral emissions. The SO+ (A→X) emission was observed at low He pressures of 0.5-0.7 Torr, where the contribution of He2+ was insignificant. The dependence of emission intensity of SO+ (A→X) on the He pressure was similar to that of the (3,10) band of N2+ (C2Σu+→X2Πg+) resulting from the He+/N2 near-resonant CT reaction:  

\[ \text{He}^+ + \text{N}_2 \rightarrow \text{N}_2^+ (\text{C}^2\Sigma^+; \nu' = 3) + \text{He}. \]  

However, it was different from that of CO2+ (B2Σu+→X2Πg) emission resulting from the He2+/CO2
CT reaction\(^8\):

\[
\text{He}_2^+ + \text{CO}_2 \rightarrow \text{CO}_2^+ (\tilde{\text{B}}^2\Sigma_u^+) + 2\text{He}.
\]

It was, therefore, concluded that He\(^+\) was the excitation source of SO\(^+(A)\). Possible formation mechanism of SO\(^+(A)\) from the He\(^+\)/SO\(_2\) and He\(^+\)/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 He\((2^3S)\), He\(^+\), and He\(_2^+\). Although SI and BrI atomic lines and Br\(_2^+\) and Br\(_2^{++}\) molecular emissions are found, no SO\(^+(A-X)\) 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
the basis of this fact, the excitation source of the observed emissions was He (2S). The \( v' = 0 \)
and \( 1 \) \( v'' \)-progressions of the \( A_2^2\Pi_{u,\, \frac{1}{2}} - X_2\Pi_u \) and \( A_2^2\Pi_{u,\, \frac{1}{2}} - X_2\Pi_u \) 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 \( Br_2^+ (A) \) from \( SOBr_2 \) are as follows:

\[
\begin{align*}
SOBr_2 & \rightarrow Br_2^+ (A\Pi_u) + SO(X) + e^- - 18.41 \text{ eV}, \quad (5a) \\
& \rightarrow Br_2^+ (A\Pi_u) + S + O + e^- - 23.76 \text{ eV}. \quad (5b)
\end{align*}
\]

Since \( Br_2^+(A) \) is formed by the reaction with He (2S) with an available energy of 19.82 eV, only the following dissociative Penning ionization is energetically accessible for the formation of \( Br_2^+ (A) \):

\[
He (2S) + SOBr_2 \rightarrow Br_2^+ (A\Pi_u) + SO(X) + He + e^-.
\]

A HBr+ (A\Sigma^+ - X\Pi_u) 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 He (2S), \( He^+ \), and \( He_2^+ \) with \( SO_2Cl_2 \) in a helium afterglow is shown in Fig. 4(a). It consists of Cl\( ^+ \), Cl\( _2 \), SO (A-X), SO\( ^+ \) (A-X), and \( SO_2 (A^1B_1 - X^1X_1) \) emissions. When \( He^+ \) and \( He_2^+ \) ions are trapped, the 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 SO\( ^+ \) (A) is formed by the reaction with \( He^+ \) and/or \( He_2^+ \), while He (2S) is responsible for the formation of Cl\( ^+ \), Cl\( _2^+ \), SO (A), and \( SO_2 (A) \). The minimum energies required for the formation of SO\( ^+ \) (A) from \( SO_2Cl_2 \) is as follows:

\[
\begin{align*}
SO_2Cl_2 & \rightarrow SO^+ (A) + OCl_2 + e^- - 18.89 \text{ eV}, \quad (7a) \\
& \rightarrow SO^+ (A) + OCl + Cl(2P) + e^- - 20.15 \text{ eV}, \quad (7b) \\
& \rightarrow SO^+ (A) + O(3P) + Cl_2 + e^- - 20.42 \text{ eV}, \quad (7c) \\
& \rightarrow SO^+ (A) + O(3P) + 2Cl + e^- - 22.89 \text{ eV}. \quad (7d)
\end{align*}
\]

Since the recombination energies of \( He^+ (24.59 \text{ eV}) \) and \( He_2^+ (18.3-20.3 \text{ eV}) \) are higher than the
energies required for processes (7a) and (7b), both ions cannot be excluded from the excitation sources of \( \text{SO}^+ (A) \) from \( \text{SO}_2\text{Cl}_2 \). The dependence of emission intensity of \( \text{SO}^+ (A-X) \) on the He buffer gas pressure was similar to that of \( \text{He}^+ \). Therefore, the \( \text{He}^+ \) ion was concluded to be the responsible active species. Possible excitation mechanism of \( \text{SO}^+ (A) \) from the dissociative \( \text{He}^+/\text{SO}_2\text{Cl}_2 \) CT processes is (3A)-(3E) in Table 1.

An emission spectrum resulting from the reactions of \( \text{He} (2^3S) \), \( \text{He}^+ \), and \( \text{He}_2^+ \) with \( \text{SO}_2\text{FCl} \) is shown in Fig. 5. The only \( \text{SO} (A'\Pi-X'\Sigma^-) \) emission system is found. Since the emission intensity of \( \text{SO} (A-X) \) was independent of the electrostatic potential applied to the ion-collector grid, its excitation source was attributed to \( \text{He} (2^3S) \).

As described above, we found that dissociative ionization channels leading to \( \text{SO}^+ (A) \) are open for \( \text{SO}_2 \), \( \text{SOCl}_2 \), and \( \text{SO}_2\text{Cl}_2 \), and that the excitation source is only \( \text{He}^+ \). The vibrational distributions of \( \text{SO}^+ (A) \) from the reactions of \( \text{He}^+ \) with \( \text{SO}_2 \), \( \text{SOCl}_2 \), and \( \text{SO}_2\text{Cl}_2 \) are evaluated in the next section.

### 3.3 Vibrational distributions of \( \text{SO}^+ (A) \)

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

\[
I_{v'v''} = K N_{v'} \text{Re}^2 \langle \tilde{f}_{v'v''} \rangle q_{v'v''} \nu_{v'v''}^3.
\]  

where \( K \) is a constant depending on the units and geometry of the system, \( \text{Re} \langle \tilde{f}_{v'v''} \rangle \), \( q_{v'v''} \), and \( \nu_{v'v''} \) are the electronic transition moment, the Franck-Condon factor, and the transition frequency, respectively. The Franck-Condon factors of \( \text{SO}^+ (A-X) \) were calculated using Morse \( \text{SO}^+ (A-X) \) potentials. Then, the \( N_{v'} \) values were determined assuming \( \text{Re} \langle \tilde{f}_{v'v''} \rangle \) 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 \( \text{SO}^+ (A) \) due to collisions with the buffer He gas was insignificant in the present experimental conditions during its radiative lifetime of \( 2.4 \pm 0.4 \mu \text{s} \). It was found that the vibrational populations of \( \text{SO}^+ (A) \) decrease with increasing \( v' \) for all the three reactions, as shown in Figs. 6 (a)-8 (a). Since the vibrational distributions of \( \text{SO}^+ (A) \) decrease nearly exponentially with increasing \( v' \), effective Boltzmann vibrational temperatures \( (T_{v'}) \) are obtained from the relation,

\[
N_{v'} \propto \exp(-E_{v'}/kT_{v'}),
\]  

where \( E_{v'} \) is the vibrational energy of \( \text{SO}^+ (A : v') \) 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,
According to our previous studies on CT reactions of He+ with molecules, reactions proceed near-resonantly at thermal energy. Therefore, the recombination energy of He+, 24.59 eV, will be transferred nearly resonantly to SO2, SOCl2, or SO2Cl2, and the subsequent (pre) dissociation of near-resonant SO2+, SOCl2+, or SO2Cl2+ states will provide the fragment SO+(A) ion. Possible formation processes of SO+(A : v'=0) from the CT reactions of He+ with SO2, SOCl2, and SO2Cl2 are given in Table 1. The observed vibrational distributions of SO+(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 SO+(A). Although the formation of SO+(A : v'=0) from process (1C) is energetically allowed, the formation of the highest observed SO+(A : v'=11) from process (1C) is endoergic:

$$\text{He}^{+} + \text{SO}_2 \rightarrow \text{SO}^{+}(A) + \text{O}^{(1S)} + \text{He} - 0.43 \text{eV}.$$  

Therefore, process (1C) can be excluded from possible formation processes. It is known that the SO2+(F2A1) state at 20.06 eV is correlated with the SO+(A) + O(3P) dissociation limit. Therefore, process (1A) may be most important for the formation of SO+(A) from SO2. Assuming that SO+(A) is formed via a collision complex with a sufficient long lifetime to randomize its excess energy, the average vibrational energy deposited into SO+(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 SO+(A) from SOCl2 and SO2Cl2 are either comparable with or higher than that from SO2, even though the vibrational degrees of freedom in the He+-SOCl2 and He+-SO2Cl2 collision complexes are larger than those for He+-SO2. It is therefore reasonable to assume that the responsible excitation processes of SO+(A) from SOCl2 and SO2Cl2 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.

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