報 文 3

Visible Emission Systems in Silicon Monoiodide

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The optical spectroscopic study of the Ar afterglow reaction of SiI_4 has led to the observation of two visible emission systems of SiI. A new red-degraded emission in the 430–480 nm region was assigned to the $A^2\Sigma^+ - X^2\Pi_{1/2}$ system by comparison with absorption spectrum. The $a(^4\Sigma_{1/2}^-) - X^2\Pi_{3/2}$ system was detected in the 490–560 nm region. The intensity was so strong that several new bands could be identified in longer wavelengths. The excitation source of SiI emission was concluded to be metastable Ar^+ ions.

1. Introduction

Although ultraviolet and visible band systems of SiI have been well known in absorption, only one system has been detected in emission. Lakshminarayana and Haranath¹⁾ first discovered a SiI emission in the 480–550 nm region excited by a radio frequency discharge through gaseous I_2 over silicon metal. The spectrum was composed of two subsystems; a weaker subsystem was located at 650 cm^{-1} to the red of the main subsystem. They have attributed this doublet system to the $A^2\Sigma^+ - X^2\Pi_7$ transition by analogy with previously known systems of silicon monohalides. Billingsley²⁾ re-examined the main subsystem under a higher resolution and re-assigned it to the

$A' - X^2\Pi_{3/2}$ transition. He suggested that the A' state is possibly the case $(a')^4\Sigma_{1/2}^-$ state which interacts with the $A^2\Sigma^+$ state. Therefore, Huber and Herzberg³⁾ have listed the A' state as tentatively the $a^4\Sigma_{1/2}^-$ state. Billingsley²⁾ reported that the weaker subsystem could not be observed in his spectrum obtained from a microwave discharge through Si and I_2 .

We have studied emission spectra produced from the Ar afterglow reaction of SiI_4 . Two visible emission systems of SiI have been observed and analyzed vibrationally. They are attributed to the $A^2\Sigma^+ - X^2\Pi_{1/2}$ and $a(^4\Sigma_{1/2}^-) - X^2\Pi_{3/2}$ transitions by comparison with reported absorption and emission spectra. The former emission system is detected for the first time in this work.

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2. Experimental

The flowing afterglow apparatus used has been described previously⁴⁾. Emission spectra produced from reactions of active Ar species with SiI₄ (CERAC Chem. Co.) were measured in the 200–700 nm region by using a Jarrell Ash 1 m monochromator. The pressure of Ar was 0.2–0.6 Torr. In order to obtain a sufficiently high pressure of SiI₄ in the reaction zone, it was necessary to heat the sample at about 370 K. Available atomic lines in the flame spectra were used as wavelength standards. The error in the measurement of sharp bandheads was less than 0.05 nm.

3. Results and analysis

Emission spectrum of SiI₄ in an Ar afterglow consists of sharp lines of Si and I atoms and characteristic SiI emissions in the visible region. Figure 1 shows a typical emission spectrum in the 430–560 nm region. Spectrum (a) was obtained by the Ar*, Ar⁺, and Ar^{+M}

+SiI₄ reactions, while spectrum (b) was detected after removing ionic species. Spectrum (a) is composed of intense atomic lines of iodine and two systems of SiI in the 430–480 and 490–560 nm region. The former system of SiI is a new emission observed in this work. A great suppression of emission intensity of SiI in spectrum (b) indicates that the dominant excitation source is ionic species, Ar⁺ and/or Ar^{+M} (metastable ions). Because of lack of thermochemical data on SiI₄ and SiI molecules, it is difficult to determine accurate minimum energies required for processes (1) and (2):

The sum of ionization potential of I₂ (9.3 eV) or I (10.4 eV) and excitation energy of SiI (2.6–2.9 eV) is smaller than the recombination energies of Ar⁺ (²P_{3/2}: 15.76 eV and ²P_{1/2}: 15.94 eV) by 2.5–4.0 eV. The minimum energy for dissociation process (3) is expected to be larger than 4.0 eV on the basis of thermochemical data on similar processes (4)–(6)^{5, 6)}:

Fig. 1. Emission spectra produced from the (a) Ar*, Ar⁺ and Ar^{+M}+SiI₄ and (b) Ar⁺+SiI₄ reactions. Lines marked • and * are I I and stray Ar I lines, respectively.

Fig. 2. New emission system of SiI in the 430-480 nm region.

It was therefore concluded that the dominant excitation source was Ar^{+M} with available energies of 16.23–20.27 eV for $\text{Ar}^{+M}-\text{Ar}^+$ excitation transfer and of 17.87–22.18 eV for $\text{Ar}^{+M}-\text{Ar}^*$ ($3p^53d$) charge transfer⁷⁾.

In Fig. 2 is shown the SiI emission in the 430–480 nm region. This emission was absent in the He and Ne afterglow reactions of SiI_4 . The bands are single-headed and red-degraded. The observed wavelengths of bandhead and corresponding vacuum wavenumbers are listed in Table 1. The wavenumbers of dominant bandheads agree well with those of the $X \rightarrow A$ transition of SiI obtained from absorption spectrum²⁾. We therefore attributed the new emission to the $A^2\Sigma^+ - X^2\Pi_{1/2}$ transition of SiI. In addition to 9 ($v', 0$) bands identified in absorption, 11 new bands could be detected in this work. The observed wavenumbers are compared with those predicted from reported molecular constants. The calculated wavenumbers are reproduced the experimental observation within 6 cm^{-1} , indicating the validity of our vibrational assignment. The absence of emission from low v' levels such as $v'=0$ and 1 and the observation of intense $v''=0$ v' -progression imply that internuclear separations of the $A^2\Sigma^+$ and $X^2\Pi_{1/2}$ states are dif-

Table 1. Bandheads for the $A^2\Sigma^+ - X^2\Pi_{1/2}$ emission system of SiI.

v'	v''	Wavelength (Å)	Wavenumber (cm^{-1})	
			Observed	Obs.-Cal.*
11	0	4304.7	23224	-3
9	0	4369.8	22878	0
8	0	4405.0	22695	-1
7	0	4440.8	22512	2
6	0	4478.3	22324	3
5	0	4518.0	22128	-1
4	0	4557.0	21938	5
7	2	4587.6	21792	2
5	1	4593.9	21762	-5
3	0	4599.3	21736	0
6	2	4628.1	21601	0
4	1	4634.8	21570	-2
2	0	4642.2	21535	0
5	2	4669.6	21409	1
3	1	4676.2	21379	5
4	2	4712.4	21215	2
2	1	4722.7	21168	-6
5	3	4748.9	21052	0
6	4	4784.8	21894	3
4	3	4793.2	21857	0

* Calculated from the following molecular constants (cm^{-1})²⁾: $\nu_e=21204.9$, $\omega_e'=208.6$, $\omega_e x_e'=1.66$, $\omega_e y_e'=0.079$, $\omega_e z_e'=0.0055$, $\omega_e''=363.8$ and $\omega_e x_e''=1.25$.

$\text{SiI}(\alpha\text{-X}^2\Pi_{3/2})$

Fig. 3. The $\alpha(^4\Sigma_{-1/2})\text{-X}^2\Pi_{3/2}$ emission system of SiI in the 485-560 nm region.

ferent significantly.

In Fig. 3 we show an enlarged spectrum in the 485-560 nm region. The spectrum is composed of a number of red-degraded bands. Thirteen dominant bands extending in the 485-530 nm region were ascribed to the $\alpha(^4\Sigma_{-1/2})\text{-X}^2\Pi_{3/2}$ transition of SiI according to the assignment of Billingsley²⁾. In this work, we could identify 13 additional bands as indicated in Fig. 3 by arrows. Their bandhead data are listed in Table 2 together with calculated

Table 2. Bandheads for the $\alpha(^4\Sigma_{-1/2})\text{-X}^2\Pi_{3/2}$ emission system of SiI.

v'	v''	Wavelength (Å)	Wavenumber (cm^{-1})	
			Observed	Cbs.-Cal.*
2	2	4985.1	20054	1
3	4	5102.8	19592	-1
0	3	5211.0	19185	2
4	6	5227.0	19126	-4
1	4	5234.3	19099	2
3	6	5289.7	18899	0
4	7	5323.1	18781	-5
2	6	5358.1	18658	1
3	7	5388.2	18554	-1
4	8	5421.2	18441	-4
2	7	5459.4	18312	-1
4	9	5523.0	18101	-5
5	10	5557.9	17687	-1

* Calculated from the following molecular constants (cm^{-1})²⁾: $\nu_e=20289.7$, $\omega_e'=275.7$, $\omega_e x_e'=5.6$, $\omega_e''=359.0$ and $\omega_e x_e''=1.1$.

values. A good agreement between the observed and calculated bandheads supports our vibrational assignment. Our assignment on the (2, 2), (0, 3), (1, 4), (3, 6) and (4, 7) bands are consistent with the numbering of Lakshminarayana and Haranath¹⁾, though there is a discrepancy of 3-14 cm^{-1} between the wavenumbers of bandheads. The weak second subsystem reported by them could not be observed in this work as in the measurement of Billingsley²⁾. The $\alpha(^4\Sigma_{-1/2})\text{-X}^2\Pi_{3/2}$ system from the lower vibrational levels, $v'=0-3$, could be found in the He afterglow, while it was absent in the Ne afterglow.

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