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# Recognition of the violet system of S<sub>2</sub>Cl in the pyrolysis of S<sub>2</sub>Cl<sub>2</sub>

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A total of 37 absorption bands, lying between 3785 and 4805 Å, have been observed during the pyrolysis of S<sub>2</sub>Cl<sub>2</sub> at 750 K. These bands have been tentatively assigned to transitions between the  $\bar{X}A''$  state of S<sub>2</sub>Cl to an unidentified electronically excited state with vibrational frequencies  $\omega_1' = 480 \text{ cm}^{-1}$  and  $\omega_2' = 407 \text{ cm}^{-1}$ . From this assignment it follows that the ground state vibrational frequencies are  $\omega_1'' = 659 \text{ cm}^{-1}$ ,  $\omega_2'' = 600 \text{ cm}^{-1}$ , and  $\omega_3'' = 336 \text{ cm}^{-1}$ . A simple molecular orbital diagram has been constructed from the frontier orbitals of S<sub>2</sub> and Cl. The predicted changes in the bond strengths and bond angles between the ground state and the excited state are consistent with experimental assignments.

## I. INTRODUCTION

The production of a violet band system in the flash photolysis of gas phase S<sub>2</sub>Cl<sub>2</sub> was first reported by McGrath<sup>1</sup> in 1960. Its carrier was suggested to be S<sub>2</sub>Cl. Donovan *et al.*<sup>2</sup> in 1968 did the same experiment and suggested SCl instead, in spite of the fact that only one progression was observed whereas SCl would have given two.

The first accepted evidence for the existence of the S<sub>2</sub>Cl radical as one of the photolytic products of S<sub>2</sub>Cl<sub>2</sub> was the result of an ESR study of inert matrices at 4.2 K.<sup>3</sup> Evidence of the SCl radical was reported in an infrared (IR) study using a microwave discharge and argon matrix technique.<sup>4</sup> An investigation of the pyrolysis of S<sub>2</sub>Cl<sub>2</sub> was undertaken here primarily to see if either of the radicals could be detected and identified at higher temperatures in the gas phase.

## II. EXPERIMENTAL

Commercial S<sub>2</sub>Cl<sub>2</sub> was purified by distillation *in vacuo* and then transferred into a 15 mm diam Pyrex absorption cell. The cell had a separately heated tail tube used to control the vapor pressure of S<sub>2</sub>Cl<sub>2</sub> in the main cell. The vapor in the main cell could be heated up to 750 K in order to produce sufficient band carrier species. It was not possible to investigate the region below 3700 Å because of the strong background absorption continuum of S<sub>2</sub>Cl<sub>2</sub>. Light from a 500 W halogen-quartz lamp passed through the absorption cell, and was sent to a 1/4 m Jarrell Ash monochromator equipped with 50 μm slits and an Oriel 7062 photomultiplier at the exit slit.

When the cell temperature was raised above 550 K, a sharp absorption band system began to appear over a steep background. When the radiation from the 500 W lamp was focused into the absorption area, the band intensity got stronger, probably due to both photolysis and local heating effects. The band absorption reached a maximum as the cell temperature was raised to about 750 K. Above that temperature, the band absorption declined.

## III. RESULTS AND DISCUSSION

As shown in Fig. 1, the absorption bands can be easily divided into seven groups. If the carrier is assumed to be S<sub>2</sub>Cl, rather than SCl, these groups can be rationalized. Each

group, as listed in Table I, is arranged in accordance with a  $\nu'$  progression of the  $\nu_1$  (S–S–Cl stretching) mode of the excited electronic state. The vibrational constant is about 480 cm<sup>-1</sup>. Most of the bands in group A have been reported before.<sup>1,2</sup> The very weak 4618 Å band is assigned to the 1<sub>0</sub><sup>0</sup> transition tentatively. Group B has a quantum of 407 cm<sup>-1</sup> above group A. This quantum can be attributed to the  $\nu_2$  (S<sub>2</sub>–Cl stretching) mode of the excited electronic state. Group C is composed of hot bands with  $\nu'' = 1$ . When compared with group A, a value of 659 cm<sup>-1</sup> for  $\Delta G''$  results. The magnitude of this vibrational quantum is smaller than that of S<sub>2</sub> (725 cm<sup>-1</sup>),<sup>5</sup> comparable to that of the S–SO stretch mode of S<sub>2</sub>O (680 cm<sup>-1</sup>),<sup>6</sup> but greater than that of SCl (617 cm<sup>-1</sup>).<sup>4</sup> It is therefore assigned to the  $\nu_1$  mode of the ground state of S<sub>2</sub>Cl. The observation of groups D and E further supports the above assignments. Group F consists of only two very weak members. Since their energies are about 600 cm<sup>-1</sup> below 1<sub>0</sub><sup>0</sup> and 1<sub>0</sub><sup>1</sup> bands and this energy difference is quite near to the fundamental frequency of SCl radical, they are assigned tentatively to the 1<sub>0</sub><sup>0</sup>2<sub>0</sub><sup>0</sup> and the 1<sub>0</sub><sup>1</sup>2<sub>0</sub><sup>0</sup> transitions, respectively. Members of group G are about 336 cm<sup>-1</sup> below the corresponding members of group A. Group G is thus

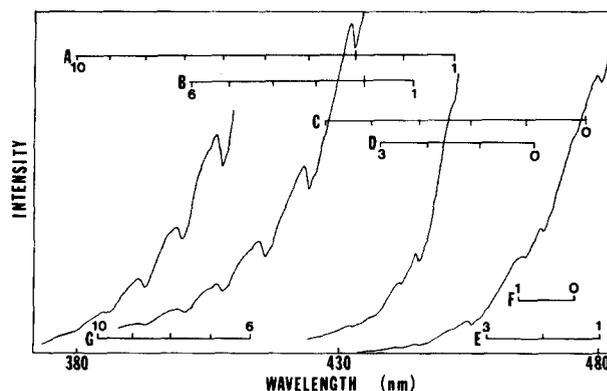


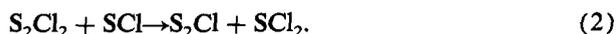
FIG. 1. Typical absorption spectrum of S<sub>2</sub>Cl from pyrolysis of S<sub>2</sub>Cl<sub>2</sub> at 750 K. The assignments for these progressions are: A(1<sub>0</sub><sup>0</sup>), B(1<sub>0</sub><sup>ν</sup>2<sub>0</sub><sup>0</sup>), C(1<sub>1</sub><sup>ν</sup>), D(1<sub>1</sub><sup>ν</sup>2<sub>0</sub><sup>0</sup>), E(1<sub>2</sub><sup>ν</sup>), F(1<sub>0</sub><sup>ν</sup>2<sub>0</sub><sup>0</sup>), and G(1<sub>0</sub><sup>ν</sup>3<sub>0</sub><sup>0</sup>). The members of each progression are marked by solid leading lines and some of their  $\nu'$  quantum numbers are given. Because of the strong absorption of S<sub>2</sub>Cl<sub>2</sub>, the spectrum has to be taken separately with different vapor pressures for each wavelength region.

TABLE I. Observed absorption peak wavelengths (Å in air) and their vibrational assignments of the violet system of S<sub>2</sub>Cl.

$\nu'$	A 1 <sub>0</sub> <sup>ν'</sup>	B 1 <sub>0</sub> <sup>ν'</sup> 2 <sub>0</sub> <sup>1</sup>	C 1 <sub>1</sub> <sup>ν'</sup>	D 1 <sub>1</sub> <sup>ν'</sup> 2 <sub>0</sub> <sup>1</sup>	E 1 <sub>2</sub> <sup>ν'</sup>	F 1 <sub>0</sub> <sup>ν'</sup> 2 <sub>1</sub> <sup>0</sup>	G 1 <sub>0</sub> <sup>ν'</sup> 3 <sub>1</sub> <sup>0</sup>
0	4618	4532		4671		4754	
1	4517	4435	4656	4568	4805	4643	
2	4420	4340	4553	4468	4693		
3	4327	4252	4454	4373	4587		
4	4239	4166	4360				
5	4154	4086	4271				
6	4074	4010					4130
7	3997						4052
8	3924						3976
9	3853						3903
10	3785						3834

considered to arise from the  $\nu'_3 = 1$  level since  $336 \text{ cm}^{-1}$  falls into the right region for a bending frequency expected for S<sub>2</sub>Cl.

The S<sub>2</sub>Cl may result from the cleavage of a chlorine atom from S<sub>2</sub>Cl<sub>2</sub> directly, or from the follow-up reaction of the S-S cleavage indirectly,



In Eq. (2), S<sub>2</sub>Cl is generated and SCl is consumed. This might be one of the reasons that S<sub>2</sub>Cl was observed here and SCl was not, although both of them are radicals.

Some of the bands in group A have been described as diffuse<sup>1,2</sup> although only medium resolution spectrographs have been taken. It remains possible that the *diffuseness* of this violet system is just the result of a dense overlap of the rotational lines of the heavy and asymmetric S<sub>2</sub>Cl top, but not the result of short radiative lifetime. To help clarify this point, a resolution variation method was applied. It is well-known that the absorption intensity of a diffuse band goes down relative to that of a sharp band as the resolution of the spectrometer gets higher. Absorption spectra in the region from 3800 to 4550 Å were remeasured for this purpose with a 3 m spectrometer. However, the relative absorption intensities of vibrational bands in each single run did not change much when the resolution was changed from 1.4 to 0.15 Å. This observation implies that most of the lines are broader than 1.4 Å in these bands, i.e., they are diffuse, as suspected by earlier workers.<sup>1,2</sup>

S<sub>2</sub>Cl can be formed from an S<sub>2</sub> molecule and a Cl atom. If we assume that only the frontier orbitals,  $\pi_x^*$  and  $\pi_y^*$  of S<sub>2</sub> and  $p_x$  and  $p_y$  of Cl, are involved in the formation, four new molecular orbitals result:  $M_1 = \pi_x^* + p_x$ ,  $M_2 = \pi_y^* + p_y$ ,  $M_3 = \pi_y^* - p_y$ , and  $M_4 = \pi_x^* - p_x$ . As far as the bonding between the central sulfur atom and the chlorine atom is concerned, the first two are "bonding" and the last two are "antibonding";  $M_1$  and  $M_4$  are the  $\sigma$  type and the other two are the  $\pi$  type. Figure 2 shows the shapes of these molecular orbitals with the order of their energies. There are five electrons, two from S<sub>2</sub> and three from Cl, to be placed in these orbitals. The electronic configuration of the ground state  $\tilde{X}$  based on these orbitals is  $M_1^2 M_2^2 M_3^1$ . That of the first excit-

ed state  $\tilde{A}$  is  $M_1^2 M_2^1 M_3^2$ . It is clear from Fig. 2 that both of these configurations give  $A''$  representation for their electronic states. When  $\tilde{X}A''$  to  $\tilde{A}A''$  transition occurs, the bonding in the molecule as a whole becomes weaker and the SCl moiety is the one which gets affected more seriously since one of its  $\pi$  electrons goes into the anti- $\pi$  type orbital. Our assignments for the vibrational modes lead to the same conclusion if one uses stretching frequency as the bond strength indicator: the stretching frequencies decreases by 1/4 for S-S and 1/3 for S-Cl when the molecule gets excited.

According to Fig. 2, ground state S<sub>2</sub>Cl is a bent radical with bond angle a few degrees greater than 90°. The orbital parities of  $M_2$  above and below the molecular plane are different in signs between the portions located at the two end atoms; hence these two portions repel each other. On the other hand, those of  $M_3$  are the same. This identity of the signs in  $M_3$  implies that a bonding molecular orbital may be

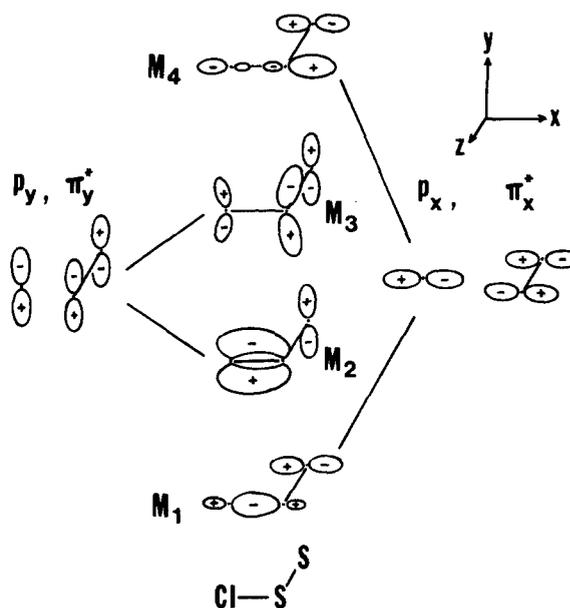


FIG. 2. Molecular orbital shape diagram for S<sub>2</sub>Cl radical formed from frontier orbitals of S<sub>2</sub> and Cl. Orbitals are shown from top to bottom according to the order of their energies from high to low.

formed between the end atoms if they ever get close enough to each other. This possibility tends to make the bond angle smaller. Nevertheless, this tendency is rather weak here because the end atoms are too far apart from each other; 2.8 Å is the distance if one assumes 2 Å for both the S–S and the S–Cl bonds and a 90° angle between them. As a consequence, when an  $M_2$  electron becomes an  $M_3$  electron, the bond angle will decrease, but not by much. This conclusion appears to be consistent with our spectroscopic results which give no  $\nu_3'$  progression and the only progression involving bending of the ground state, group G, is very weak.

The absorption spectrum of 15 Torr of S<sub>2</sub>Cl<sub>2</sub> in a 9.4 cm cell at room temperature was taken and it showed only a continuum in the same region. Besides, no band given in Table I can be correlated to any of the ground state vibrational frequencies of S<sub>2</sub>Cl<sub>2</sub>.<sup>7,8</sup> It seems therefore reasonable that S<sub>2</sub>Cl<sub>2</sub> is not the carrier of this band system although its concentration is the highest in the absorption cell.

Attempts have been made to search for other band systems for both S<sub>2</sub>Cl and SCl in the longer wavelength region down to 8500 Å, but none were found.

#### IV. CONCLUSION

The products of the pyrolysis of gas phase S<sub>2</sub>Cl<sub>2</sub> were examined by absorption spectroscopy and 37 bands were recorded. S<sub>2</sub>Cl is suggested to be the carrier of this band sys-

tem. The vibrational constants assessed from our measurements here are:  $\omega_1' = 480 \text{ cm}^{-1}$  and  $\omega_2' = 407 \text{ cm}^{-1}$  for the excited state and  $\omega_1'' = 659 \text{ cm}^{-1}$ ,  $\omega_2'' = 600 \text{ cm}^{-1}$ , and  $\omega_3'' = 336 \text{ cm}^{-1}$  for the ground state. This is the first time an electronic spectrum of S<sub>2</sub>Cl is recognized with partial vibrational analysis. The vibrational quantum number assignments are only tentative but the mode assignments are believed to be reasonable.

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