71359-63-2;  $CF_2(CF_2CO_2Cl)_2$ , 71359-64-3;  $CF_3C(O)OSO_2Cl$ , 71359-65-4;  $CF_3C(O)OC(O)Cl$ , 71359-66-5;  $C_3F_7C(O)OC(O)Cl$ , 7150, 71359-67-6; CF<sub>3</sub>COOH, 76-05-1; CClF<sub>2</sub>COOH, 76-04-0; CF<sub>2</sub>H-COOH, 381-73-7; C<sub>2</sub>F<sub>5</sub>COOH, 422-64-0; C<sub>3</sub>F<sub>7</sub>COOH, 375-22-4; CF2(CF2CO2H)2, 376-73-8; CIF, 7790-89-8.

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# Raman and Infrared Spectra, Normal-Coordinate Analysis, and Thermodynamic Properties of (Methylene- $h_2$ )sulfur Tetrafluoride and (Methylene- $d_2$ )sulfur Tetrafluoride

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Infrared spectra of gaseous and Raman spectra of liquid (methylene- $h_2$ ) sulfur and (methylene- $d_2$ ) sulfur tetrafluorides have been recorded and assigned. A normal-coordinate analysis is presented to check the compatibility of the assignment of the two molecules and to determine the nature of the bonding. The molecule has a totally rigid structure and the CS bond shows a strong double-bond character. The average methylene stretching frequency in this molecule is higher than for any other methylene compound.

### Introduction

The first published synthesis of methylenesulfur tetrafluoride, CH<sub>2</sub>SF<sub>4</sub>, was reported recently.<sup>1</sup> The molecule is of special interest because of its relationship to sulfur and phosphorus ylides. Electron diffraction<sup>2</sup> and NMR<sup>1</sup> studies indicate that the structure of  $CH_2SF_4$  is an almost regular trigonal bipyramid. The C atom is occupying one of the equatorial positions, and the hydrogen atoms are located in the axial plane.<sup>2</sup> In order to gain further insight into the structure of this novel molecule, we have studied its vibrational spectra. Room-temperature infrared spectra of gaseous and Raman spectra of liquid CH<sub>2</sub>SF<sub>4</sub> and CD<sub>2</sub>SF<sub>4</sub> are presented here along with a normal-coordinate analysis for the fundamental vibrations. The results are discussed in relation to the structure.

#### **Experimental Section**

(a) Material. (Methylene- $h_2$ ) sulfur tetrafluoride was prepared by metalation of SF<sub>5</sub>CH<sub>2</sub>Br and subsequent LiF elimination as described earlier.<sup>1</sup> (Methylene- $d_2$ )sulfur tetrafluoride was prepared according to the reaction scheme

$$CD_{3}COCD_{3} \xrightarrow{\Delta} CD_{2} = C = O \xrightarrow{+SF_{5}CI} SF_{5}CD_{2}COCl \xrightarrow{H_{2}O} SF_{5}CD_{2}COCl \xrightarrow{H_{2}O} SF_{5}CD_{2}COOl \xrightarrow{Ag_{2}CO_{3}} SF_{5}CD_{2}COO^{-}Ag^{+} \xrightarrow{Br_{2}} SF_{5}CD_{2}Br \xrightarrow{n-C_{3}H_{11}Li} CD_{2}SF_{4}$$

Chemically this synthesis is identical with the reported synthesis of  $CH_2SF_4$ . The isotopic purity of  $CD_2SF_4$  is estimated to be better than 98%, as indicated by proton NMR and infrared spectra.

(b) Spectra. Raman spectra were recorded by using the 6328-Å radiation of a He-Ne laser (OIP, Gent), ~120 mW, and two different monochromators: a modified Cary 81 and a Coderg PH 1. Both spectrometers are equipped with an RCA-C 31034 photomultiplier, Servogor-5 strip chart recorders, and necessary electronics. Spectra were obtained by using a DC amplification system, and the resolution used was about 2 cm<sup>-1</sup>. The liquid samples were sealed in a 5-mm o.d. NMR glass tube, and a 90° scattering geometry was used.

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Table I.	Infrared	and	Raman	Spectra	of	(Methylene-h,	)sulfur
Tetrafluo	ride at R	oom	Tempe	rature		-	

IR (gas)	Raman (	(liq)	
$\nu, a \text{ cm}^{-1}$	$\Delta \nu, a \text{ cm}^{-1}$	polarizn <sup>b</sup>	assign t <sup>c</sup>
3210 mw	3216 w	dp	$\nu_{10}$ (B <sub>1</sub> )
3092 mw	3092 s	p	$\nu_1$ (A, )
1630 vw		-	$2\nu_{12}$
1550 vw			$\nu_{4} + \nu_{12}$
1426 mw	· 4		$\nu_{2}^{\prime}$ (A <sub>1</sub> )
1307 m			$\nu_{11}$ (B <sub>1</sub> )
	1210 vw	р	$2\nu_{17}$
1157 s	1149 s	р	$\nu_3(\mathbf{A}_1)$
1124 m	1124 mw	p	$2\nu_{14}$
1018 s	1014 vw	dp	$\nu_{1,s}(B_{2})$
890 w			$2\nu_{18}$
818 vs			$\nu_{12}$ (B <sub>1</sub> )
	797 vw, br		$\nu_6 + \nu_7$
760 s			$\nu_{16} (B_1)$
	739 vs	р	$\nu_4(A_1)$
	693 vw	р	$2\nu_{9} + \nu_{7}$
676 ms	684 vw	dp	$\nu_{13}$ ( <b>B</b> <sub>1</sub> )
647 w	656 w	p	$\nu_5(A_1)$
604 w	590 m	dp	$\nu_{17} (B_2)$
565 ms	566 w	đp .	$\nu_{14}$ ( <b>B</b> <sub>1</sub> )
509 mw	502 vw	pp <sup>a</sup>	$\nu_{6}(A_{1})$
457 mw	449 ms	dp	$\nu_{18} (B_2)$
	<b>43</b> 0 vw, sh	dp	$\nu_8 (A_2)$
298 w	298 w	р	$\nu_{7}(A_{1})$
	207 s	dp	$\nu_9 (A_2)$
206 vvw			$\nu_{-} - \nu_{-}$

<sup>a</sup> s, m, w, v, sh, and br stand for strong, medium, weak, very, shoulder, and broad, respectively. <sup>b</sup> p, dp, and pp stand for polarized, depolarized, and partially polarized, respectively. <sup>c</sup> See Table V for the description of the normal modes and Table III for a listing of the internal and symmetry coordinates used. <sup>d</sup> Part of the observed depolarized intensity in this feature may be due to the combination  $\nu_1 + \nu_2$ .

Infrared spectra were recorded on a PE 283 spectrophotometer. Gaseous samples were contained in a 10 cm long gas cell with CsBr windows. At a later stage of this work a PE-180 spectrophotometer became available and the spectrum of CH<sub>2</sub>SF<sub>4</sub> was rerecorded in a

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Figure 1. Infrared spectra of gaseous methylenesulfur tetrafluoride at room temperature in a 10 cm long gas cell: (top)  $CH_2SF_4$  in CsBr-window cell, gas pressure about 20 mm; (bottom)  $CH_2SF_4$  in polyethylene-window cell, gas pressure about 60 mm; (middle)  $CD_2SF_4$  in CsBr-window cell, gas pressure about 20 mm.

10-cm gas cell with polyethylene windows down to  $100 \text{ cm}^{-1}$  to verify the low-frequency vibrations.

# **Results and Discussion**

(a) Spectroscopic Results. Infrared spectra of gaseous  $CH_2SF_4$  and  $CD_2SF_4$ , at room temperature, are shown in Figure 1. Their room-temperature Raman spectra, in the liquid phase, are shown in Figure 2. The spectra shown in Figures 1 and 2 are photocopies of the original spectra. The frequency values of the observed spectral features are listed in Table I for  $CH_2SF_4$  and in Table II for the deuterated compound. The frequency accuracy is believed to be  $\pm 2 \text{ cm}^{-1}$ . These tables also contain the relative intensities of the observed features as well as the depolarization character of the Raman bands.

(b) Assignment. The structure of methylenesulfur tetrafluoride as determined by electron diffraction measurements<sup>2</sup> is shown in Figure 3. The two axial fluorine atoms of the trigonal pyramid are denoted by  $F_1$  in Figure 3, while the other two, denoted by  $F_2$ , are equatorial. The axial atoms are marked  $F_1$  to signify the fact that they are in the XZ plane of the molecular symmetry group— $C_{2v}$ .<sup>3</sup> The molecule has 18 normal vibrations which can be classified as  $7 A_1 + 2 A_2$ + 5  $B_1$  + 4  $B_2$ .<sup>3-5</sup> The A<sub>2</sub> vibrations are only active in Raman spectra while A<sub>1</sub>, B<sub>1</sub>, and B<sub>2</sub> should be both Raman and infrared active. Further, in the Raman spectrum, only A1 modes can give rise to polarized bands;  $A_2$ ,  $B_1$ , and  $B_2$  bands must be depolarized. Thus by studying the depolarization ratios in Raman spectra and comparing the infrared and Raman spectra, it is possible to classify the observed spectral features as being due to the  $A_1$ ,  $A_2$ , or B modes. This does not disInorganic Chemistry, Vol. 18, No. 11, 1979 3209



Figure 2. Raman spectra of liquid methylenesulfur tetrafluoride at room temperature recorded with the spectral slit width  $\sim 2 \text{ cm}^{-1}$  and uncorrected for the spectral sensitivity. Upper curve shows the spectrum under parallel polarization and the lower curve shows the spectrum under perpendicular polarization: (top) CH<sub>2</sub>SF<sub>4</sub>; (bottom) CD<sub>2</sub>SF<sub>4</sub>.



Figure 3. Structure of methylenesulfur tetrafluoride as determined by electron diffraction studies.<sup>2</sup>

tinguish between  $B_1$  and  $B_2$  vibrations. In theory  $B_1$  and  $B_2$ vibrations can be separated by their band shapes in the infrared spectra of the gaseous state as they are functions of the moments of inertia. Moments of inertia calculated by using the structural data of Figure 3 are for CH<sub>2</sub>SF<sub>4</sub>  $I_x = 127.8$ ,  $I_y = 172.3$ , and  $I_z = 149.6$  and for CD<sub>2</sub>SF<sub>4</sub>  $I_x = 138.2$ ,  $I_y =$ 184.4, and  $I_z = 151.3$ , where the units are amu Å<sup>2</sup>. Ueda and Shimanouchi<sup>6</sup> have classified the asymmetric-top molecules according to the relative values of their moments of inertia. This classification, in favorable situations, separates gaseous infrared bands into A-type, B-type, or C-type bands which can be further correlated with the normal modes belonging to different symmetry species. Moments of inertia values for CH<sub>2</sub>SF<sub>4</sub> and CD<sub>2</sub>SF<sub>4</sub> presented above indicate that both these molecules are close to the type 36 of Ueda and Shimanouchi's

**Table II.** Infrared and Raman Spectra of (Methylene- $d_2$ )sulfur Tetrafluoride at Room Temperature

	Raman (liq	1)	
IR (gas) $\nu$ , $\alpha$ cm <sup>-1</sup>	$\Delta \nu, a \text{ cm}^{-1}$	polarizn <sup>b</sup>	assignt <sup>c</sup>
2435 mw	2432 w	dp	$v_{10}$ (B <sub>1</sub> )
2300 vw			$\nu_3 + \nu_7 + \nu_{15}$
2261 mw	2258 s	р	$\nu_1$ (A <sub>1</sub> )
2070 w			$2\nu_3$
1300 vw, br			$\nu_{5} + \nu_{13}$
1230 w	1222 w	р	$\nu_{4} + \nu_{6}$
1202 s	1193 s	р	$\nu_2$ (A <sub>1</sub> )
1125 mw			$2\nu_{17}$
1049 m	1054 vw	р	$\nu_3$ (A <sub>1</sub> )
981 m			$v_{11} (B_1)$
	974 vw, br		$v_{14} + v_{18}$
957 mw			$\nu_{15} (B_2)$
	870 vw		$\nu_{8} + \nu_{17}$
830 vs			$\nu_{12} (B_1)$
780 ms			$\nu_{9} + \nu_{17}$
741 s			$\nu_{16} (B_2)$
	721 vs	р	$\nu_4$ (A <sub>1</sub> )
668 w			$\nu_{13} (B_1)$
	646 w	р	$\nu_5(A_1)$
	584 w	dp	$\nu_{\gamma} + \nu_{8}$
568 ms	566 w	dp	$\nu_{17} (B_2)$
523 m	527 w	dp	$\nu_{6}$ (A <sub>1</sub> ), $\nu_{14}$ (B <sub>1</sub> )
448 m	445 s	dp	$\nu_{18} (B_2)$
	300 w	pp	$\nu_{7} (A_{1}), \nu_{8} (A_{2})$
	201 s	dp	$\nu_9 (A_2)$

<sup>a</sup> s, m, w, v, sh, and br stand for strong, medium, weak, very, shoulder, and broad, respectively. <sup>b</sup> p, dp, and pp stand for polarized, depolarized, and partially polarized, respectively. <sup>c</sup> See Table V for the description of the normal modes and Table III for a listing of the internal and symmetry coordinates used.

classifications.<sup>6</sup> The three infrared-active vibrations,  $A_1$ ,  $B_1$ , and B<sub>2</sub>, should have bands of B, A, and C types, respectively. As the shapes for A- and C-type bands are very similar for the type-36 molecules of ref 6, infrared band shapes are not of much help in distinguishing between  $B_1$  and  $B_2$  bands. Therefore, our assignment of the bands to the different modes is mainly based on the depolarization ratios in Raman spectra, the comparison of Raman and infrared spectra, and the available literature for related compounds.<sup>3,5,7-30</sup> Tables I and II also contain our suggested assignments for the observed features. The numbering scheme for the fundamental vibrations is according to that by Herzberg.<sup>3</sup> The spectra of CH<sub>2</sub>SF<sub>4</sub> were assigned first, and the assignment of the deuterated compound was deduced from that. Here we briefly discuss the assignment, only for the light compound. A complete list of the internal and symmetry coordinates is given in Table III. The three highest frequency  $A_1$  fundamentals,  $v_1$ ,  $v_2$ , and  $v_3$ , are expected to arise from the CH stretching, CH<sub>2</sub> deformation, and CS stretching vibrations and are easily assigned to bands at 3092, 1426, and 1157 cm<sup>-1</sup>, respectively. The literature values of the CS stretching frequencies, along with their CS bond distances, for a few related compounds are listed in Table IV for comparison purposes. The next two  $A_1$  fundamentals,  $\nu_4$  and  $\nu_5$ , arise from the SF stretching vibrations, and the last two  $A_1$  vibrations,  $v_6$  and  $v_7$ , arise from the skeleton deformation vibrations. These are assigned to the bands at 739, 656, 502, and 298 cm<sup>-1</sup> (Table I). Two  $A_2$ vibrations,  $\nu_8$  and  $\nu_9$ , arise from the torsion and  $F_1SF_2$  deformation modes (Table III) and are assigned to bands at 430 and 207 cm<sup>-1</sup>, respectively. We have assigned the  $F_1SF_2$ deformation,  $\nu_9$ , to the strong depolarized Raman band at 207 cm<sup>-1</sup> as its frequency is unaffected on deuteration and there is only a very weak feature in the infrared spectrum at about this frequency (Figure 1, Table I). The very weak infrared feature is probably due to a difference band such as  $\nu_6 - \nu_7$ . The depolarized Raman feature at about 430 cm<sup>-1</sup> is assigned

Table III

(a) Internal Coordinates of Methylenesulfur Tetrafluoride

coor- dinate	no.	description <sup>a</sup>	coor- dinate	no.	description <sup>a</sup>
r	1	CS str	$\beta_4$	12	F <sub>1</sub> SF <sub>2</sub> bend
<i>s</i> <sub>1</sub>	2	$SF_1$ str	ε,	13	F <sub>1</sub> SC bend
S 2	3	SF, str	ε,	14	F <sub>1</sub> SC bend
$t_1$	4	SF <sub>2</sub> str	θ,	15	F,SC bend
$t_2$	5	$SF_2$ str	θ,	16	$F_2$ SC bend
$u_1$	6	CH str	k	17	HCH bend
$u_2$	7	CH str	$i_1$	18	HCS bend
α	8	$F_2SF_2$ bend	$i_2$	19	HCS bend
$\beta_1$	9	$F_1 SF_2$ bend	$\gamma$	20	SHHC out-of-plane
β,	10	F, SF, bend			bend (wag)
$\beta_3$	11	F, SF, bend	au	21	torsion
			λ	22	$F_1SF_1$ bend

(b) Symmetry Coordinates Used for Methylenesulfur Tetrafluoride Normal-Coordinate Analysis

symmetry	coordinate <sup>b</sup>	description <sup>c</sup>
A <sub>1</sub>	$S_1$	$(1/2^{1/2})(u_1 + u_2)$
	$S_2$	ĸ
	$S_3$	r
	$S_4$	$(1/2^{1/2})(s_1 + s_2)$
	$S_5$	$(1/2^{1/2})(t_1 + t_2)$
	$S_{\epsilon}$	$(1/2)(\beta_1 + \beta_2 + \beta_3 + \beta_4)$
	$S_{\pi}$	$(1/2^{1/2})(\epsilon_1 + \epsilon_2)$
	S.	$(1/2^{1/2})(\theta_1 + \theta_2)$
	S <sup>°</sup>	α
	S.,	$(1/2^{1/2})(i_1 + i_2)$
	S	$\lambda$
Α.	<u>S.</u>	au
2	S. 2	$(1/2)(\beta_1 - \beta_2 + \beta_2 - \beta_3)$
В.	S.,	$(1/2^{1/2})(\mu_1 - \mu_2)$
	S. 4	$(1/2^{1/2})(i_1 - i_2)$
	S 15	$(1/2^{1/2})(s_1 - s_2)$
	S 16	$(1/2)(s_1 - s_2)$ $(1/2^{1/2})(s_1 - s_2)$
	5 <sub>17</sub>	$(1/2)(\theta_1 + \theta_2)$
D	S 18	$(1/2)(b_1 - b_2 - b_3 + b_4)$
$\mathbf{D}_2$	S <sub>19</sub>	$\gamma$ (1/21/2)/(((((((((((((((((((((((((((((((
	3 <sub>20</sub>	$(1/2^{-1})(l_1 - l_2)$
	3 <sub>21</sub>	$(1/2)^{(\sigma_1 - \sigma_2)}$
	0 <sub>22</sub>	$(1/2)(\beta_1 + \beta_2 - \beta_3 - \beta_4)$
	$S_{22}$	$(1/2)(\beta_1 + \beta_2 - \beta_3 - \beta_4)$

<sup>a</sup> In terms of atoms shown in Figure 3. <sup>b</sup> There are four redundant coordinates, all in the  $A_1$  block. <sup>c</sup> See part a for the description of the internal coordinates.

 Table IV.
 Comparison of CS Stretching Force Constants, Bond Distances, and Stretching Frequencies

molecule	<sup>r</sup> s-с, Å	f <sub>S-C</sub> , mdyn/A	$v_{S-C}, cm^{-1}$	ref
CS	1.5349	8.4	1274	7
		8.489	1278.6	8
SCS	1.555	7.86	1116 <sup>a</sup>	8
OCS	1.558	7.2	b	5
$F_2CS$	1.589	6.625	1365	9
-	1.56	6.084	1365	9,10
Cl <sub>2</sub> CS	1.60	6.12	1137	9,11
HÑCS	1.5609		963	5
			851	15
$(NH_2),CS$	1.71	4.21	b	12
сн=сн				
s	1.714	4.794	Ь	13
1 /			-	
CH = CH				
$(CH_3)_2 S = O$	1.84	3.03	Ь	14
$H_2CSF_4$	1.54	6.33	1157	с

<sup>a</sup> Average of symmetric and antisymmetric CS stretching frequencies. <sup>b</sup> CS stretch is mixed in more than one vibration. <sup>c</sup> This work.

to the other  $A_2$  mode,  $\nu_8$ , arising from the torsion vibration because (a) it is the only other depolarized band in the Raman spectrum below 700 cm<sup>-1</sup> which does not have an infrared counterpart (Table I) and (b) there is no band present in the Raman spectrum of the deuterated compound around this

Table V. Fundamental Frequencies and Assignments for (Methylene-h<sub>2</sub>)sulfur and (Methylene-d<sub>2</sub>)sulfur Tetrafluorides

	(		CH <sub>2</sub> SF <sub>4</sub>	$CD_2SF_4$		
	freq, cm <sup>-1</sup>			freq, cm <sup>-1</sup>		
mode	calcd <sup>a</sup>	obsd	description	calcd <sup>a</sup>	obsd	description
$\begin{array}{ccccccc} A_{1} & \nu_{1} & \\ & \nu_{2} & \\ & \nu_{3} & \\ & \nu_{4} & \\ & \nu_{5} & \\ & \nu_{6} & \\ & \nu_{7} & \\ A_{2} & \nu_{8} & \\ & \nu_{9} & \\ B_{1} & \nu_{10} & \\ & \nu_{11} & \\ & \nu_{12} & \\ & \nu_{13} & \\ & \nu_{14} & \\ B_{2} & \nu_{15} & \\ & \nu_{16} & \\ & \nu_{17} & \\ \end{array}$	3094 1434 1173 746 659 519 294 426 206 3217 1287 834 648 572 1022 779 624	3092 1426 1157 739 <sup>b</sup> 656 <sup>b</sup> 509 298 430 <sup>b</sup> 207 <sup>b</sup> 3210 1307 818 676 565 1018 760 604 457	CH <sub>2</sub> str HCH def CS str $SF_1$ str + SF <sub>2</sub> str $F_1SF_2$ def + $F_1SF_1$ def + $F_1SC$ def $F_2SC$ def + $F_2SF_2$ def + $F_1SF_2$ def torsion $F_1SF_2$ def CH <sub>2</sub> str HCS def SF <sub>1</sub> str $F_1SC$ def + $F_1SF_2$ def CH <sub>2</sub> wag ( $\gamma$ ) SF <sub>2</sub> str $F_2SC$ def $F_2SC$ def $F_2SC$ def $F_2SC$ def $F_2SC$ def $F_2SC$ def	2255 1186 1027 731 647 515 294 310 201 2418 1035 821 626 518 949 737 543 425	2261 1202 1049 721 <sup>b</sup> 646 <sup>b</sup> 523 300 <sup>b</sup> 201 <sup>b</sup> 2435 981 830 668 523 957 741 568 448	CD <sub>2</sub> str CS str DCD def $F_1 SF_2$ def + $F_1 SF_1$ def + $F_1 SC$ def $F_2 SC$ def + $F_2 SF_2$ def + $F_1 SF_2$ def torsion $F_1 SF_2$ def CD <sub>2</sub> str DCS def SF <sub>1</sub> str $F_1 SC$ def + $F_1 SF_2$ def CD <sub>2</sub> wag ( $\gamma$ ) SF <sub>2</sub> str $F_2 SC$ def F SF_2 def

<sup>a</sup> For carbon-12 and sulfur-32. <sup>b</sup> Frequencies for the liquid state (Raman spectra). All other are for the gas (infrared spectra).

frequency (Table II), and the torsion mode is expected to show the "deuterium shift". We believe that the  $\nu_8$  mode moves down to about 300 cm<sup>-1</sup> in the  $d_2$  molecule as indicated in Table II.

The two highest frequency  $B_1$  modes,  $v_{10}$  and  $v_{11}$ , arise from antisymmetric CH stretching and HCS deformation vibrations (Table III) and are easily assigned to bands at 3210 and 1307 cm<sup>-1</sup>, respectively (Table I). The CH<sub>2</sub> wagging motion,  $\nu_{15}$  $(B_2)$ , is assigned to the remaining highest frequency, unassigned, depolarized band at 1014 cm<sup>-1</sup>. There remain three  $B_1$  ( $\nu_{12}$ ,  $\nu_{13}$ ,  $\nu_{14}$ ) and three  $B_2$  ( $\nu_{16}$ ,  $\nu_{17}$ ,  $\nu_{18}$ ) fundamental vibrations to be assigned; of these,  $v_{12}$  and  $v_{16}$  arise from the antisymmetric stretching vibrations of SF<sub>1</sub> bonds and SF<sub>2</sub> bonds, respectively. These are expected to be strong in the infrared spectra. We have assigned them to strong infrared bands at 818 and 760 cm<sup>-1</sup>, respectively, which do not seem to have a counterpart in Raman spectra at the sensitivity and signal to noise ratio in the present work. The two lowest frequency vibrations in both  $B_1$  and  $B_2$  blocks arise from the skeleton deformations and are assigned to the four remaining, unassigned infrared bands below 700 cm<sup>-1</sup> at 676, 604, 565, and  $457 \text{ cm}^{-1}$  (Table I). There are depolarized bands in Raman spectra near these frequencies, which also support the assignment of the above four bands to the B modes. Further separation of these four vibrations into  $B_1$  or  $B_2$  is mainly based on normal-coordinate analysis which is discussed below.

(c) Normal-Coordinate Analysis and Structure. Normalcoordinate analysis was performed for both  $CH_2SF_4$  and  $CD_2SF_4$  in order (a) to check the compatibility of the assignment of the two molecules, (b) to obtain a detailed description of the vibrational modes, and (c) to get information about the stretching force constants of this molecule, especially that of the CS bond. The problem was set up by using all 22 internal coordinates (see Table III for internal and symmetry coordinates). The G matrices were calculated from the X matrices via B matrices by using Schachtschneider's GMAT program.<sup>31,32</sup> The X matrices were calculated by using the structural data shown in Figure 3 and the program CART.<sup>31</sup> Normal modes and their frequencies were calculated via Wilson's GF method<sup>4</sup> using a modified version of the FPERT program of Schachtschneider.<sup>32,33</sup> The use of a complete set of 22 internal coordinates introduces 4 redundant coordinates. These were carried through the calculations and resulted in 4 zero-frequency vibrations, all in the  $A_1$  block. Calculated and observed frequencies of the fundamental vibrations are compared in Table V. The calculated frequencies agree with

Table VI. Internal Valence Force Field for Methylenesulfur Tetrafluoride<sup>a</sup>

coordinate	value	coordinate	value
C-S	6.33	S-F <sub>1</sub> , S-F <sub>2</sub>	-0.036
S-F,	4.31	S-F, S-F,	1.11
S-F <sub>2</sub>	4.55	S-F <sub>2</sub> , S-F <sub>2</sub>	0.384
C-H	5.42	C-S, C-S-F <sup>b</sup>	0.479
$F_1 - S - F_1$	1.29	C-S, H-C-S	0.383
F,-S-F,	0.60	S-F, F <sub>1</sub> -S-F <sub>2</sub> <sup>b,c</sup>	0.439
F <sub>1</sub> -S-F <sub>2</sub>	3.52	S-F1, F1-S-F1	0.618
F <sub>1</sub> -S-C	2.03	S-F, F, -S-F,	0.253
F <sub>2</sub> -S-C	1.87	S-F, C-S-F <sup>b, č</sup>	0.731
н-с-н	0.207	H-C-S, H-C-S	0.023
H-C-S	0.884	F <sub>1</sub> -S-F <sub>2</sub> , F <sub>1</sub> -S-F <sub>2</sub> <sup>c</sup>	1.56
γ	0.237	F,-S-F,, F,-S-F,	0.60
torsion $(\tau)$	0.044	F,-S-F, F,-S-F,	-1.11
С-Н, С-Н	-0.013	F <sub>1</sub> -S-F <sub>2</sub> , F-S-C <sup>b,c</sup>	-0.145
C-S, S-F <sup>b</sup>	-0.576	C-S-F, C-S-F'	-0.681

<sup>a</sup> The units are mdyn  $A^{-1}$ , mdyn, and mdyn A for bond stretching, stretch-bend interaction, and angle deformation constants, respectively. <sup>b</sup> All of the force constants of this type were assumed to be equivalent. <sup>c</sup> Nonzero value shown was used only for the interaction constants with one common S-F bond.

the observed ones with an average error of less than 2% or 13  $\mbox{cm}^{-1}.$  The observed and calculated (in parentheses) ratios of the products of the frequencies for the  $A_1$ ,  $A_2$ ,  $B_1$ , and  $B_2$ blocks are 1.80 (1.98), 1.48 (1.41), 1.89 (1.92), and 1.18 (1.35), respectively. The "product rule" applies rigorously only for the zero-order frequencies (harmonic frequencies), and the differences in the observed and calculated "product values" given above are in the expected direction and magnitude.<sup>37</sup> Table V also contains an approximate description of the normal modes in terms of the internal coordinates and is based on their potential energy distribution and eigenvectors. Nonzero force constants on the final internal valence force field used to obtain the results of Table V are given in Table VI. The principal approximations assumed to reduce the number of interaction force constants are that all interactions between (a) the internal coordinates involving H atoms and those not involving H atoms, (b) the stretching coordinates not having a common atom, and (c) the stretch/deformation and deformation/ deformation without a common bond can be neglected. This force field was arrived at by a combination of the iteration process of FPERT with the trial and error method. Skeleton interaction constants and F<sub>2</sub>SF<sub>2</sub> deformation were held fixed in the final calculation at the values shown in Table VI. In order to check the values of the SF stretching force constant

 Table VII.
 Comparison of SF Stretching Force Constants

 and Bond Lengths
 Engths

·	bond length,	force const,	
molecule	Å	mdyn/Å	ref
SF <sub>6</sub>	1.564	5.01	8
		5.30	16
		4.35	17
		5.45	18
		4.895	19
SE CI	1.56 (av)	5.20	21
Sr <sub>5</sub> CI	1.50(ax) 1.576(ag)	4.03	21
	1.570 (eq)	4.52	19
	1.50	4 593	17
SF.Br	1.60 (ax)	4.50	22
01 521	1.60 (eq)	4.285	
SF <sub>2</sub> O <sup>-</sup>	1.60 (ax)	3.75	23
5	1.60 (eq)	3.60	
SF <sub>5</sub> <sup>-</sup>	1.62	4.12	24
	1.72	2.06	
SF₄O	1.56 (ax)	5.54	25
	1.56 (eq)	4.395	
$CH_2SF_4$	1.57	4.55	а
	1.59	4.31	
SF4	1.645	2.80	26
	1.545	5.25	27
	1.045	5.57	27
	1.545	3 30	20
	1.045	5.30	20
O SE	1.545	5.14	5
OSF.	1.585	3.8	5
SF.	1.59	4.72	28
<i>a</i> = 2			
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	1.55 1.60	(Å) <sup>1.65</sup>	.70
	-46		

Figure 4. Badger-rule plot of SF bond distances and force constants (data from Table VII). Solid points are for  $CH_2SF_4$ .

obtained here for CH<sub>2</sub>SF<sub>4</sub>, we have collected in Table VII the available literature data for the various sulfur fluorides. The data are plotted according to Badger's rule<sup>5</sup> in Figure 4. Clearly the values of SF stretching constants obtained here are compatible with the literature. The value of the CS stretching constant obtained here for CH<sub>2</sub>SF<sub>4</sub> is compared with the literature values for this constant in other compounds in Table IV. The value of  $f_{CS}$  for methylenesulfur tetrafluoride (6.33 mdyn/Å) is close to those reported for F<sub>2</sub>CS and Cl<sub>2</sub>CS (Table IV). One obtains a bond order of about 1.8 if one uses the data for the CS single bond from (CH<sub>3</sub>)<sub>2</sub>SO (Table IV).<sup>38</sup> Thus the ylidic formulation  $^{-}CH_2 - SF_4^{+}$  is not an important canonical form for this molecule. This is in contrast to the bonding systems suggested for phosphorus and sulfur ylides where the zwitterionic form reduces the double-bond character.

The strong double-bond character of the CS bond is also reflected in the high frequencies of the methylene stretching

Table VIII. Thermodynamic Properties of Methylene- $h_2$  and  $-d_2$  (in Parentheses) at 1 Atm Pressure and for the Ideal Gaseous State<sup>a</sup>

	,			
<i>T</i> , K	$(H_0 - E_0^0)/T$	$-(G_0 - E_0^0)/T$	S <sub>o</sub>	Cp
50	7.98 (7.99)	43.28 (43.48)	51.26 (51.47)	8.16 (8.20)
100	8.45 (8.56)	48.92 (29.15)	57.36 (57.71)	9.90 (10.33)
150	9.39 (9.66)	52.51 (52.82)	61.90 (62.48)	12.81 (13.49)
200	10.67 (11.05)	55.38 (55.78)	66.05 (66.84)	16.21 (17.01)
250	12.11 (12.59)	57.91 (58.41)	70.02 (71.01)	19.48 (20.41)
300	13.59 (14.15)	60.25 (60.85)	73.83 (75.00)	22.38 (23.42)
350	15.02 (15.67)	62.45 (63.14)	77.48 (78.81)	24.85 (25.98)
400	16.39 (17.09)	64.55 (65.33)	80.93 (82.42)	26.93 (28.12)
450	17.66 (18.42)	66.55 (67.42)	84.21 (85.84)	28.68 (29.90)
500	18.84 (19.65)	68.47 (69.42)	87.31 (89.07)	30.15 (31.40)

<sup>a</sup> Units are cal mol<sup>-1</sup> deg<sup>-1</sup>.

vibration in this compound. In fact, it seems that the average CH stretching frequency,  $(\nu_{asym} + \nu_{sym})/2$ , in the present compound is higher than any other reported methylene compound.<sup>29,30</sup> The average methylene frequency in  $CH_2SF_4$ is  $(3210 + 3092)/2 = 3151 \text{ cm}^{-1}$ . It is interesting to note here that the corresponding frequency in  $CH_2$ — $CF_2$  is only (3174  $+ 3057.3)/2 = 3116 \text{ cm}^{-1.30}$  (The second highest reported average methylene frequency seems to be that for  $CH_2NN$ , 3133 cm<sup>-1,29</sup>) One can use this average value of CH stretching frequency to predict the length of the CH bonds with the empirical plot of McKean et al.<sup>29</sup> The value of  $3151 \text{ cm}^{-1}$  suggests a CH bond distance ( $r^0$ ) of 1.0775 Å. Thus, the hybridization of carbon atom orbitals is such that it results in strong CH bonds. This indicates a maximum overlap of  $\pi$  orbitals between C and S which lends rigidity to the skeleton. In fact, no indication of "Berry-type exchange", 34-36 seen in SF<sub>4</sub>, is noticed in the infrared spectra of gaseous methylenesulfur tetrafluoride. Also no indication of hydrogen bonding is seen in the vibrational spectra. (The distance of the hydrogen atom from the neighboring "axial" F atom, as calculated from the electron diffraction data<sup>2</sup> (Figure 3) is 2.34 Å.) This absence of hydrogen bonding supports the bonding scheme suggested in ref 1 for the structure of  $CH_2SF_4$ .

(d) Thermodynamic Properties. Thermodynamic properties of (methylene- $h_2$ )sulfur and (methylene- $d_2$ )sulfur tetrafluorides were computed by using the geometry and moments of inertia given above, and the observed fundamental frequencies are listed in Table IV.<sup>32</sup> These calculations were done with the assumption of a rigid-rotor, harmonic-oscillator approximation and a symmetry factor of 2.<sup>3</sup> The calculated values of the enthalpy  $((H_0 - E_0^{\circ})/T)$ , the Gibbs free energy,  $(-(G_0 - E_0^{\circ})/T)$ , the entropy  $(S_0)$ , and the heat capacity  $(C_p)$ , are given in Table VIII. The average methylene- $h_2$  stretching frequency in CH<sub>2</sub>SF<sub>4</sub> predicts a value for the CH bond dissociation energy,  $D^{\circ}_{298}$ , of ~117 kcal/mol for this molecule, if one uses the correlation given by McKean et al. (Figure 3 of ref 29).

### Conclusion

Methylenesulfur tetrafluoride is a molecule of unique properties. It has a strong CS double bond and is a totally rigid species. Although its structure around the S atom is trigonal bipyramidal, its rigidity is in contrast with the related species, e.g.,  $SF_4$  and  $SOF_4$ . The methylene group has the highest stretching vibrations known. The covalent formulation  $CH_2$ — $SF_4$  describes the molecule best.

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**Registry No.** CH<sub>2</sub>SF<sub>4</sub>, 66793-25-7; CD<sub>2</sub>SF<sub>4</sub>, 71250-10-7.

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# Electron Paramagnetic Resonance Structural Studies of Molybdenum(V)-Oxo Complexes

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EPR and optical spectral data are reported for  $(NH_4)_2MoOCl_5$  and a series of its derivatives: MoOCl\_3L, where L = o-phenanthroline and  $\alpha, \alpha'$ -bipyridyl; MoOClL<sub>2</sub>, where L = acetylacetone, 8-hydroxyquinoline, and 8-mercaptoquinoline; MoOClL, where L = disalicylaldehyde o-phenylenediimine, N,N'-dimethyl-N,N'-bis(2-mercaptoethyl)ethylenediamine, and N,N'-bis(2-methyl-2-mercaptopropyl)ethylenediamine; Et<sub>4</sub>NMoOCl<sub>2</sub>L, where L = salicylaldehyde o-hydroxyanil. EPR measurements were made at both X (9.5 GHz) and Q (35 GHz) band frequencies. Several of the compounds have noncoincident g and nuclear hyperfine tensors which aid in assigning geometrical isomers in dimethylformamide solutions. The results are discussed in terms of the molecular and electronic structures of the above compounds and their relationship to the Mo center in xanthine oxidase. The spin-orbit coupling of chloride ligands does not appear to be the dominant mechanism contributing to the g shift.

## Introduction

The active sites of molybdenum enzymes have been investigated by using EPR to detect the Mo(V) (d<sup>1</sup>) species present during the catalytic cycles of these enzymes.<sup>2-5</sup> In order to obtain structural information about the molybdenum sites from EPR spectroscopy, we need data for a variety of well-characterized Mo(V) compounds. Some preliminary work in this area has been done recently on several monomeric Mo(V)-oxo complexes.<sup>2,6,7</sup> We now report the results of a more detailed EPR study of a series of ten such complexes.

As a consequence of the distribution of the naturally abundant isotopes, the EPR spectra of molybdenum(V)complexes are particularly amenable to analysis. The isotopes of even atomic mass, which comprise about 75% of the total, have no nuclear spin (I = 0). The intense lines observed with frozen-solution samples arise from the Zeeman term in the spin Hamiltonian for the I = 0 isotopes and provide a direct means of measuring the principal g factors. The remaining two isotopes (15.72% <sup>95</sup>Mo and 9.46% <sup>97</sup>Mo) have nuclear spins of  $I = \frac{5}{2}$  and nearly identical magnetogyric ratios. These isotopes produce six-line hyperfine patterns of low intensity which are distributed symmetrically with respect to the intense I = 0 lines. The ability to measure the g factors independently from the hyperfine interaction is especially helpful in the interpretation of EPR spectra of complexes of low symmetry, which may have noncoincident  $\mathbf{g}$  and nuclear hyperfine tensor axes. Knowledge of the relative orientation of the tensor axes can provide structural information in some instances.

The EPR spectra of  $(NH_4)_2MoOCl_5$  and a series of its derivatives, MoOCl<sub>3</sub>L (I, L = phen; II, L = trans-bpy; III, L = cis-bpy), MoOCl<sub>2</sub> (IV, L = acac; V, L= ox; VI, L = tox), MoOClL (VII, L =  $(sal)_2$ phen; VIII, L =  $C_8H_{18}N_2S_2$ ; IX,  $L = C_{10}H_2N_2S_2$ ), and  $Et_4NMoOCl_2L$  (X, L = sap), were measured at both X- (9.5 GHz) and Q-band (34.5 GHz) frequencies in dimethylformamide (DMF) solutions.<sup>8</sup> The magnetic properties are discussed in terms of the coordination geometry and bonding in these complexes.

#### **Experimental Section**

Synthesis. Syntheses of compounds I-III and V-X have been published previously.<sup>6,7,9-11</sup> Compound IV was prepared as described here.