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; $C_3F_7C(O)OC(O)Cl$, 71359-67-6; CF_3COOH, 76-05-1; $CClF_2COOH$, 76-04-0; CF_2HCOOH, 381-73-7; C_2F_5COOH, 422-64-0; C_3F_7COOH, 375-22-4; $CF_2(CF_2CO_2H)_2$, 376-73-8; ClF, 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_2SF_4, was reported recently.[1] The molecule is of special interest because of its relationship to sulfur and phosphorus ylides. Electron diffraction[2] and NMR[1] 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.[2] 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_2SF_4 and CD_2SF_4 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_5CH_2Br and subsequent LiF elimination as described earlier.[1] (Methylene-d_2)sulfur tetrafluoride was prepared according to the reaction scheme

$$CD_3COCD_3 \xrightarrow[-CD_4]{\Delta} CD_2{=}C{=}O \xrightarrow{+SF_5Cl} SF_5CD_2COCl \xrightarrow{H_2O}$$
$$SF_5CD_2COOH \xrightarrow{Ag_2CO_3} SF_5CD_2COO^-Ag^+ \xrightarrow[-AgBr,\ -CO_2]{Br_2}$$
$$SF_5CD_2Br \xrightarrow[-LiF]{n\text{-}C_5H_{11}Li} CD_2SF_4$$

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^{-1}. The liquid samples were sealed in a 5-mm o.d. NMR glass tube, and a 90° scattering geometry was used. 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_2SF_4 was rerecorded in a

Table I. Infrared and Raman Spectra of (Methylene-h_2)sulfur Tetrafluoride at Room Temperature

IR (gas) ν,[a] cm^{-1}	Raman (liq) $\Delta\nu$,[a] cm^{-1}	Raman (liq) polarizn[b]	assignt[c]
3210 mw	3216 w	dp	ν_{10} (B_1)
3092 mw	3092 s	p	ν_1 (A_1)
1630 vw			$2\nu_{12}$
1550 vw			$\nu_4 + \nu_{12}$
1426 mw			ν_2 (A_1)
1307 m			ν_{11} (B_1)
	1210 vw	p	$2\nu_{17}$
1157 s	1149 s	p	ν_3 (A_1)
1124 m	1124 mw	p	$2\nu_{14}$
1018 s	1014 vw	dp	ν_{15} (B_2)
890 w			$2\nu_{18}$
818 vs			ν_{12} (B_1)
	797 vw, br		$\nu_6 + \nu_7$
760 s			ν_{16} (B_1)
	739 vs	p	ν_4 (A_1)
	693 vw	p	$2\nu_9 + \nu_7$
676 ms	684 vw	dp	ν_{13} (B_1)
647 w	656 w	p	ν_5 (A_1)
604 w	590 m	dp	ν_{17} (B_2)
565 ms	566 w	dp	ν_{14} (B_1)
509 mw	502 vw	pp[d]	ν_6 (A_1)
457 mw	449 ms	dp	ν_{18} (B_2)
	430 vw, sh	dp	ν_8 (A_2)
298 w	298 w	p	ν_7 (A_1)
	207 s	dp	ν_9 (A_2)
206 vvw			$\nu_6 - \nu_7$

[a] s, m, w, v, sh, and br stand for strong, medium, weak, very, shoulder, and broad, respectively. [b] p, dp, and pp stand for polarized, depolarized, and partially polarized, respectively. [c] See Table V for the description of the normal modes and Table III for a listing of the internal and symmetry coordinates used. [d] Part of the observed depolarized intensity in this feature may be due to the combination $\nu_7 + \nu_9$.

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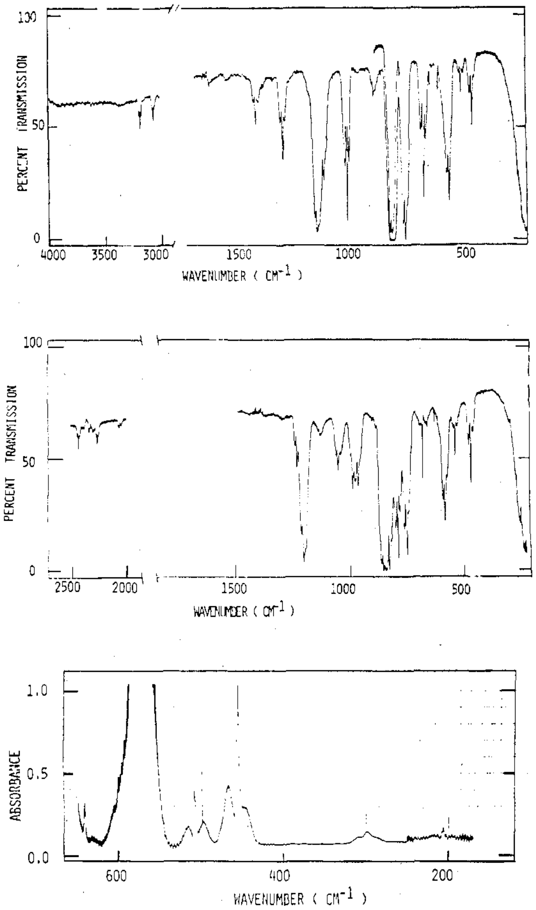


Figure 1. Infrared spectra of gaseous methylenesulfur tetrafluoride at room temperature in a 10 cm long gas cell: (top) CH_2SF_4 in CsBr-window cell, gas pressure about 20 mm; (bottom) CH_2SF_4 in polyethylene-window cell, gas pressure about 60 mm; (middle) CD_2SF_4 in CsBr-window cell, gas pressure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

10-cm gas cell with polyethylene windows down to 100 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 ±2 cm^{-1}. These tables also contain the relative intensities of the observed features as well as the depolarization character of the Raman bands.

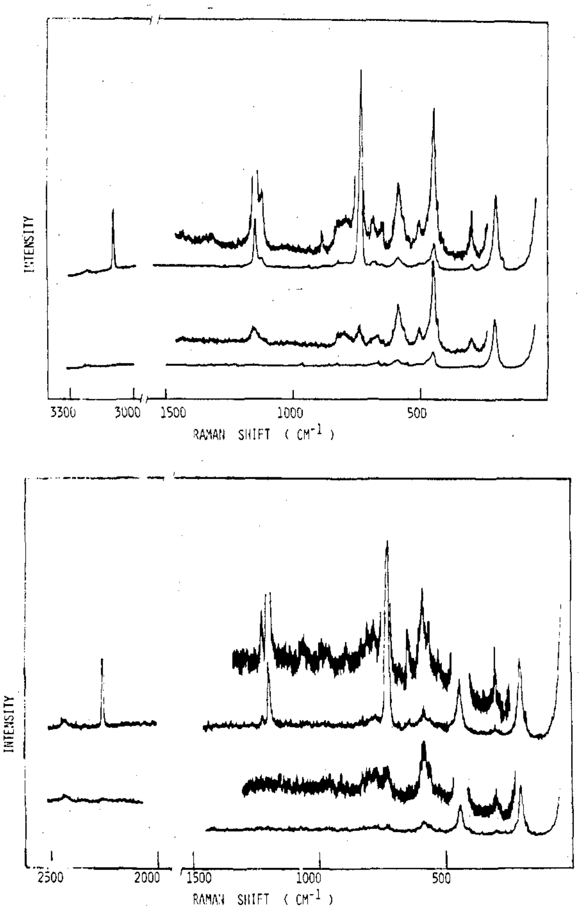


Figure 2. Raman spectra of liquid methylenesulfur tetrafluoride at room temperature recorded with the spectral slit width ~2 cm^{-1} and uncorrected for the spectral sensitivity. Upper curve shows the spectrum under parallel polarization and the lower curve shows the spectrum under perpendicular polarization: (top) CH_2SF_4; (bottom) CD_2SF_4.

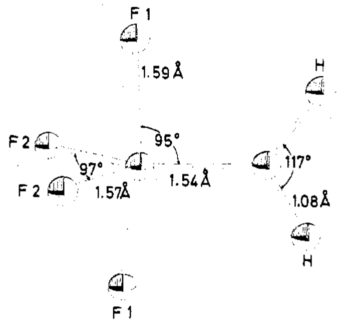


Figure 3. Structure of methylenesulfur tetrafluoride as determined by electron diffraction studies.[2]

(b) Assignment. The structure of methylenesulfur tetrafluoride as determined by electron diffraction measurements[2] 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}.[3] The molecule has 18 normal vibrations which can be classified as 7 A_1 + 2 A_2 + 5 B_1 + 4 B_2.[3-5] The A_2 vibrations are only active in Raman spectra while A_1, B_1, and B_2 should be both Raman and infrared active. Further, in the Raman spectrum, only A_1 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 distinguish 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_2SF_4 $I_x = 127.8$, $I_y = 172.3$, and $I_z = 149.6$ and for CD_2SF_4 $I_x = 138.2$, $I_y = 184.4$, and $I_z = 151.3$, where the units are amu Å^2. Ueda and Shimanouchi[6] 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_2SF_4 and CD_2SF_4 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

IR (gas)	Raman (liq)		
ν,^{a} cm^{-1}	$\Delta\nu$,^{a} cm^{-1}	polarizn^b	assignt^c
2435 mw	2432 w	dp	ν_{10} (B$_1$)
2300 vw			$\nu_3 + \nu_7 + \nu_{15}$
2261 mw	2258 s	p	ν_1 (A$_1$)
2070 w			$2\nu_3$
1300 vw, br			$\nu_5 + \nu_{13}$
1230 w	1222 w	p	$\nu_4 + \nu_6$
1202 s	1193 s	p	ν_2 (A$_1$)
1125 mw			$2\nu_{17}$
1049 m	1054 vw	p	ν_3 (A$_1$)
981 m			ν_{11} (B$_1$)
	974 vw, br		$\nu_{14} + \nu_{18}$
957 mw			ν_{15} (B$_2$)
	870 vw		$\nu_8 + \nu_{17}$
830 vs			ν_{12} (B$_1$)
780 ms			$\nu_9 + \nu_{17}$
741 s			ν_{16} (B$_2$)
	721 vs	p	ν_4 (A$_1$)
668 w			ν_{13} (B$_1$)
	646 w	p	ν_5 (A$_1$)
	584 w	dp	$\nu_7 + \nu_8$
568 ms	566 w	dp	ν_{17} (B$_2$)
523 m	527 w	dp	ν_6 (A$_1$), ν_{14} (B$_1$)
448 m	445 s	dp	ν_{18} (B$_2$)
	300 w	pp	ν_7 (A$_1$), ν_8 (A$_2$)
	201 s	dp	ν_9 (A$_2$)

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

Table III

(a) Internal Coordinates of Methylenesulfur Tetrafluoride

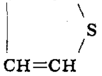
coordinate	no.	description^a	coordinate	no.	description^a
r	1	CS str	β_4	12	F$_1$SF$_2$ bend
s_1	2	SF$_1$ str	ϵ_1	13	F$_1$SC bend
s_2	3	SF$_1$ str	ϵ_2	14	F$_1$SC bend
t_1	4	SF$_2$ str	θ_1	15	F$_2$SC bend
t_2	5	SF$_2$ str	θ_2	16	F$_2$SC bend
u_1	6	CH str	k	17	HCH bend
u_2	7	CH str	i_1	18	HCS bend
α	8	F$_2$SF$_2$ bend	i_2	19	HCS bend
β_1	9	F$_1$SF$_2$ bend	γ	20	SHHC out-of-plane bend (wag)
β_2	10	F$_1$SF$_2$ bend			
β_3	11	F$_1$SF$_2$ bend	τ	21	torsion
			λ	22	F$_1$SF$_1$ bend

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

symmetry coordinate^b		description^c
A$_1$	S_1	$(1/2^{1/2})(u_1 + u_2)$
	S_2	k
	S_3	r
	S_4	$(1/2^{1/2})(s_1 + s_2)$
	S_5	$(1/2^{1/2})(t_1 + t_2)$
	S_6	$(1/2)(\beta_1 + \beta_2 + \beta_3 + \beta_4)$
	S_7	$(1/2^{1/2})(\epsilon_1 + \epsilon_2)$
	S_8	$(1/2^{1/2})(\theta_1 + \theta_2)$
	S_9	α
	S_{10}	$(1/2^{1/2})(i_1 + i_2)$
	S_{11}	λ
A$_2$	S_{12}	τ
	S_{13}	$(1/2)(\beta_1 - \beta_2 + \beta_3 - \beta_4)$
B$_1$	S_{14}	$(1/2^{1/2})(u_1 - u_2)$
	S_{15}	$(1/2^{1/2})(i_1 - i_2)$
	S_{16}	$(1/2^{1/2})(s_1 - s_2)$
	S_{17}	$(1/2^{1/2})(\epsilon_1 - \epsilon_2)$
	S_{18}	$(1/2)(\beta_1 - \beta_2 - \beta_3 + \beta_4)$
B$_2$	S_{19}	γ
	S_{20}	$(1/2^{1/2})(t_1 - t_2)$
	S_{21}	$(1/2^{1/2})(\theta_1 - \theta_2)$
	S_{22}	$(1/2)(\beta_1 + \beta_2 - \beta_3 - \beta_4)$

[a] In terms of atoms shown in Figure 3. [b] There are four redundant coordinates, all in the A$_1$ block. [c] See part a for the description of the internal coordinates.

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

molecule	$r_{\text{S-C}}$, Å	$f_{\text{S-C}}$, mdyn/Å	$\nu_{\text{S-C}}$, cm^{-1}	ref
CS	1.5349	8.4	1274	7
		8.489	1278.6	8
SCS	1.555	7.86	1116^a	8
OCS	1.558	7.2	b	5
F$_2$CS	1.589	6.625	1365	9
	1.56	6.084	1365	9, 10
Cl$_2$CS	1.60	6.12	1137	9, 11
HNCS	1.5609		963	5
			851	15
(NH$_2$)$_2$CS	1.71	4.21	b	12
	1.714	4.794	b	13
(CH$_3$)$_2$S=O	1.84	3.03	b	14
H$_2$CSF$_4$	1.54	6.33	1157	c

[a] Average of symmetric and antisymmetric CS stretching frequencies. [b] CS stretch is mixed in more than one vibration. [c] This work.

classifications.[6] The three infrared-active vibrations, A$_1$, B$_1$, and B$_2$, 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.[3,5,7-30] 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.[3] The spectra of CH_2SF_4 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, ν_1, ν_2, and ν_3, are expected to arise from the CH stretching, CH$_2$ deformation, and CS stretching vibrations and are easily assigned to bands at 3092, 1426, and 1157 cm^{-1}, 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, ν_4 and ν_5, arise from the SF stretching vibrations, and the last two A$_1$ vibrations, ν_6 and ν_7, arise from the skeleton deformation vibrations. These are assigned to the bands at 739, 656, 502, and 298 cm^{-1} (Table I). Two A$_2$ vibrations, ν_8 and ν_9, arise from the torsion and F$_1$SF$_2$ deformation modes (Table III) and are assigned to bands at 430 and 207 cm^{-1}, respectively. We have assigned the F$_1$SF$_2$ deformation, ν_9, to the strong depolarized Raman band at 207 cm^{-1} 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^{-1} is assigned to the other A$_2$ mode, ν_8, arising from the torsion vibration because (a) it is the only other depolarized band in the Raman spectrum below 700 cm^{-1} 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_2)sulfur and (Methylene-d_2)sulfur Tetrafluorides

		CH_2SF_4			CD_2SF_4		
		freq, cm^{-1}			freq, cm^{-1}		
mode		calcd[a]	obsd	description	calcd[a]	obsd	description
A_1	ν_1	3094	3092	CH_2 str	2255	2261	CD_2 str
	ν_2	1434	1426	HCH def	1186	1202	CS str
	ν_3	1173	1157	CS str	1027	1049	DCD def
	ν_4	746	739[b]	SF_1 str + SF_2 str	731	721[b]	SF_1 str + SF_2 str
	ν_5	659	656[b]		647	646[b]	
	ν_6	519	509	F_1SF_2 def + F_1SF_1 def + F_1SC def	515	523	F_1SF_2 def + F_1SF_1 def + F_1SC def
	ν_7	294	298	F_2SC def + F_2SF_2 def + F_1SF_2 def	294	300[b]	F_2SC def + F_2SF_2 def + F_1SF_2 def
A_2	ν_8	426	430[b]	torsion	310	300[b]	torsion
	ν_9	206	207[b]	F_1SF_2 def	201	201[b]	F_1SF_2 def
B_1	ν_{10}	3217	3210	CH_2 str	2418	2435	CD_2 str
	ν_{11}	1287	1307	HCS def	1035	981	DCS def
	ν_{12}	834	818	SF_1 str	821	830	SF_1 str
	ν_{13}	648	676	F_1SC def + F_1SF_2 def	626	668	F_1SC def + F_1SF_2 def
	ν_{14}	572	565		518	523	
B_2	ν_{15}	1022	1018	CH_2 wag (γ)	949	957	CD_2 wag (γ)
	ν_{16}	779	760	SF_2 str	737	741	SF_2 str
	ν_{17}	624	604	F_2SC def	543	568	F_2SC def
	ν_{18}	441	457	F_1SF_2	425	448	F_1SF_2 def

[a] For carbon-12 and sulfur-32. [b] 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 ν_8 mode moves down to about 300 cm^{-1} in the d_2 molecule as indicated in Table II.

The two highest frequency B_1 modes, ν_{10} and ν_{11}, arise from antisymmetric CH stretching and HCS deformation vibrations (Table III) and are easily assigned to bands at 3210 and 1307 cm^{-1}, respectively (Table I). The CH_2 wagging motion, ν_{15} (B_2), is assigned to the remaining highest frequency, unassigned, depolarized band at 1014 cm^{-1}. There remain three B_1 (ν_{12}, ν_{13}, ν_{14}) and three B_2 (ν_{16}, ν_{17}, ν_{18}) fundamental vibrations to be assigned; of these, ν_{12} and ν_{16} arise from the antisymmetric stretching vibrations of SF_1 bonds and SF_2 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^{-1}, 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^{-1} at 676, 604, 565, and 457 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.

Table VI. Internal Valence Force Field for Methylenesulfur Tetrafluoride[a]

coordinate	value	coordinate	value
C–S	6.33	S–F_1, S–F_2	−0.036
S–F_1	4.31	S–F_1, S–F_1	1.11
S–F_2	4.55	S–F_2, S–F_2	0.384
C–H	5.42	C–S, C–S–F[b]	0.479
F_1–S–F_1	1.29	C–S, H–C–S	0.383
F_2–S–F_2	0.60	S–F, F_1–S–F_2[b,c]	0.439
F_1–S–F_2	3.52	S–F_1, F_1–S–F_1	0.618
F_1–S–C	2.03	S–F_2, F_2–S–F_2	0.253
F_2–S–C	1.87	S–F, C–S–F[b,c]	0.731
H–C–H	0.207	H–C–S, H–C–S	0.023
H–C–S	0.884	F_1–S–F_2, F_1–S–F_2[c]	1.56
γ	0.237	F_1–S–F_2, F_2–S–F_2	0.60
torsion (τ)	0.044	F_1–S–F_2, F_1–S–F_1	−1.11
C–H, C–H	−0.013	F_1–S–F_2, F–S–C[b,c]	−0.145
C–S, S–F[b]	−0.576	C–S–F, C–S–F′	−0.681

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

(c) Normal-Coordinate Analysis and Structure. Normal-coordinate 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.[31,32] The X matrices were calculated by using the structural data shown in Figure 3 and the program CART.[31] Normal modes and their frequencies were calculated via Wilson's GF method[4] using a modified version of the FPERT program of Schachtschneider.[32,33] 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 the observed ones with an average error of less than 2% or 13 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.[37] 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_2SF_2 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

molecule	bond length, Å	force const, mdyn/Å	ref
SF_6	1.564	5.01	8
		5.30	16
		4.35	17
		5.45	18
		4.895	19
		5.26	21
SF_5Cl	1.56 (ax)	4.83	21
	1.576 (eq)	4.52	
	1.56	4.624	19
	1.576	4.593	
SF_5Br	1.60 (ax)	4.50	22
	1.60 (eq)	4.285	
SF_5O^-	1.60 (ax)	3.75	23
	1.60 (eq)	3.60	
SF_5^-	1.62	4.12	24
	1.72	2.06	
SF_4O	1.56 (ax)	5.54	25
	1.56 (eq)	4.395	
CH_2SF_4	1.57	4.55	*a*
	1.59	4.31	
SF_4	1.645	2.80	26
	1.545	5.25	
	1.645	3.57	27
	1.545	4.54	
	1.645	3.30	20
	1.545	5.37	
O_2SF_2	1.53	5.14	5
OSF_2	1.585	3.8	5
SF_2	1.59	4.72	28

[a] This work.

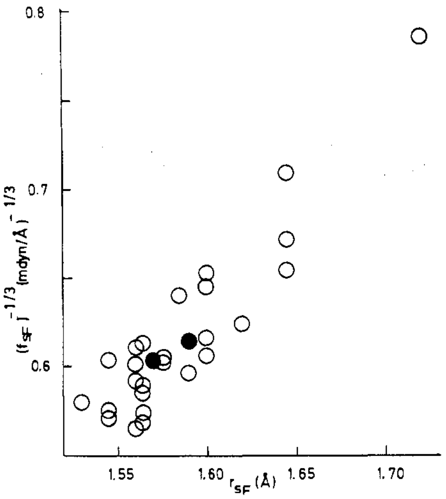


Figure 4. Badger-rule plot of SF bond distances and force constants (data from Table VII). Solid points are for CH_2SF_4.

obtained here for CH_2SF_4, we have collected in Table VII the available literature data for the various sulfur fluorides. The data are plotted according to Badger's rule[5] 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_2SF_4 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_2CS and Cl_2CS (Table IV). One obtains a bond order of about 1.8 if one uses the data for the CS single bond from $(CH_3)_2SO$ (Table IV).[38] 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 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.[29,30] The average methylene frequency in CH_2SF_4 is $(3210 + 3092)/2 = 3151$ cm^{-1}. It is interesting to note here that the corresponding frequency in $CH_2{=}CF_2$ is only $(3174 + 3057.3)/2 = 3116$ cm^{-1}.[30] (The second highest reported average methylene frequency seems to be that for CH_2NN, 3133 cm^{-1}.[29]) 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.[29] The value of 3151 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 π orbitals between C and S which lends rigidity to the skeleton. In fact, no indication of "Berry-type exchange",[34-36] seen in SF_4, 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[2] (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.

Table VIII. Thermodynamic Properties of Methylene-h_2 and -d_2 (in Parentheses) at 1 Atm Pressure and for the Ideal Gaseous State[a]

T, K	$(H_0 - E_0{}^0)/T$	$-(G_0 - E_0{}^0)/T$	S_0	C_p
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)

[a] Units are cal mol^{-1} deg^{-1}.

(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.[32] These calculations were done with the assumption of a rigid-rotor, harmonic-oscillator approximation and a symmetry factor of 2.[3] 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_2SF_4 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_2SF_4, 66793-25-7; CD_2SF_4, 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 α,α'-bipyridyl; $MoOClL_2$, 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; $Et_4NMoOCl_2L$, 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^1) species present during the catalytic cycles of these enzymes.[2-5] 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.[2,6,7] 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% ^{95}Mo and 9.46% ^{97}Mo) have nuclear spins of $I = {}^5/_2$ 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 **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, $MoOCl_3L$ (I, L = phen; II, L = *trans*-bpy; III, L = *cis*-bpy), $MoOClL_2$ (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.[8] 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.[6,7,9-11] Compound IV was prepared as described here.

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