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The Vibrational Assignments of Sulfuryl-Fluoride, -Chloride and -Fluorochloride and Their Transferable Force Constants

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A normal coordinate treatment has been carried out on the basis of the Urey-Bradley force field in order to obtain a set of the most probable assignments and the transferable force constants for the sulfuryl fluoride, the chloride and the fluorochloride series. The assignments selected and the force constants obtained have been satisfactory. The potential energy distributions have been calculated and the vibrational modes have been estimated for each molecule.

Several infrared and Raman spectra of sulfuryl fluoride[1-3] and chloride[3-7] have already been recorded; their normal coordinate treatments have been made on the basis of the valence force field (VFF).[2,8-10]

Siebert[8] assumed the same angular geometry for both molecules and used a seven-parameter VFF. Stammrich et al.[9] simply reported $\nu_5(A_2) < \nu_9(B_2) < \nu_7(B_1)$ as holding for sulfuryl fluoride and $\nu_5(A_2) < \nu_7(B_1) < \nu_9(B_2)$ as holding for sulfuryl chloride, in connection with a normal coordinate analysis of chromyl chloride. Hunt et al.[10] applied the VFF described by Siebert to both the molecules and calculated several corresponding sets of force constants for probable sets of assignment of each molecule by using the correct geometry and the redundant condition. They could find a probable set of the force constants which predicted the fundamental frequencies for an assignment

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1) G. R. Hunt and M. K. Wilson, *Spectorchim. Acta*, **16**, 570 (1960).

2) W. D. Perkins and M. K. Wilson, *J. Chem. Phys.*, **20**, 1791 (1952).

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7) D. E. Martz and R. T. Lagemann, *J. Chem. Phys.*, **22**, 1193 (1954).

8) H. Siebert, *Z. anorg. u. allegem. Chem.*, **257**, 210 (1954).

9) H. Stammreich, K. Kawai and Y. Tavares, *Spectrochim. Acta*, **15**, 438 (1959).

10) G. R. Hunt and M. K. Wilson, ibid., **18**, 959 (1962).

of sulfuryl chloride, but they could not find a suitable one for the fluoride. However, one of the assignments for the fluoride unsuccssefully treated by Hunt et al. was recently supported, after a useful study of the microwave spectrum, by Lide et al.[11] For this reason, a normal coordinate treatment for both the molecules on the basis of the force field other than the VFF may be useful in the choice of probable assignments. Thus, we will try to carry out the treatment by using the simple Urey-Bradley force field (SUBFF). If necessary, the modified Urey-Bradley force field (MUBFF) will also be employed.

When the force constants obtained for sulfuryl fluoride and chloride predict satisfactorily the observed fundamental frequencies of corresponding molecules, consist with any tentative expectation and moreover they are transferable to sulfuryl fluorochloride, the assignment used is taken as the most probable one for each molecule.

Calculations

Sulfuryl fluoride and chloride both have a tetrahedral configuration and belong to the point group C_{2v}.[12,13] The nine normal vibrations of each molecule are distributed among the four symmetry species: four of the A_1 species, one of the A_2 species, two of the B_1 species, and two of the B_2 species. The A_2 mode is active only in Raman spectra, while the A_1, B_1 and B_2 are both infrared- and Raman- active.

Though we have, unfortunately, no configuration data on sulfuryl fluorochloride, the molecule is supposed to have a configuration similar to that of sulfuryl fluoride and chloride. If the OSO plane is assumed to be at right angles to the FSCl plane, the configuration belongs to the point group C_s. The nine normal vibrations are nondegenerate— six of the A′ species and three of the A′′ species. All the vibrations are both infrared- and Raman-active.

The following symmetry coordinates are used for the transformation into the factored $\boldsymbol{F}$ and $\boldsymbol{G}$ matrices defined by Wilson[14]:

For sulfuryl fluoride and the chloride:

$$A_1:\ S_1 = (1/\sqrt{2})(\varDelta R_1+\varDelta R_2)$$

$$S_2 = (1/\sqrt{2})(\varDelta r_3+\varDelta r_4)$$

$$S_3 = (1/\sqrt{P})(A\varDelta\alpha_{12}-\varDelta\theta_{13}-\varDelta\theta_{14}-\varDelta\theta_{23}-\varDelta\theta_{24})$$

$$S_4 = (1/\sqrt{Q})(B\varDelta\beta_{34}-C\varDelta\alpha_{12}-\varDelta\theta_{13}-\varDelta\theta_{14}-\varDelta\theta_{23}-\varDelta\theta_{24})$$

$$S_r = (1/\sqrt{R})(\gamma_1\varDelta\alpha_{12}+\gamma_2\varDelta\beta_{34}+\varDelta\theta_{13}+\varDelta\theta_{14}+\varDelta\theta_{23}+\varDelta\theta_{24})\equiv 0$$

$\gamma_1=2\cos(\beta/2)\sin(\alpha/2)/\sin\theta$, $\gamma_2=2\cos(\alpha/2)\sin(\beta/2)/\sin\theta$, $A=4/\gamma_1$, $B=(4+\gamma_1^2)/r_2$, $C=\gamma_1$, $P=A^2+4$, $Q=B^2+C^2+4$, $R=\gamma_1^2+\gamma_2^2+4$

$$\mathrm{A}_2:\ S_5 = (1/2)(\varDelta\theta_{13}-\varDelta\theta_{14}-\varDelta\theta_{23}+\varDelta\theta_{24})$$

$$\mathrm{B}_1:\ S_6 = (1/\sqrt{2})(\varDelta R_1-\varDelta R_2)$$

$$S_7 = (1/2)(\varDelta\theta_{13}+\varDelta\theta_{14}-\varDelta\theta_{23}-\varDelta\theta_{24})$$

$$\mathrm{B}_2:\ S_8 = (1/\sqrt{2})(\varDelta r_3-\varDelta r_4)$$

$$S_9 = (1/2)(\varDelta\theta_{13}-\varDelta\theta_{14}+\varDelta\theta_{23}-\varDelta\theta_{24})$$

and for sulfuryl fluorochloride,

$$\mathrm{A}':\ S_1 = (1/\sqrt{2})(\varDelta R_1+\varDelta R_2)$$

$$S_2 = \varDelta r_3$$

$$S_3 = \varDelta d_4$$

$$S_4 = (1/\sqrt{S})(D\varDelta\alpha_{12}-\varDelta\theta_{13}-\varDelta\theta_{14}-\varDelta\theta_{23}-\varDelta\theta_{24})$$

$$S_5 = (1/\sqrt{T})(E\varDelta\beta_{34}-F\varDelta\alpha_{12}-\varDelta\theta_{13}-\varDelta\theta_{14}-\varDelta\theta_{23}-\varDelta\theta_{24})$$

$$S_6 = (1/2)(\varDelta\theta_{14}+\varDelta\theta_{24}-\varDelta\theta_{13}-\varDelta\theta_{23})$$

$$S_r = (1/\sqrt{U})(\delta_1\varDelta\alpha_{12}+\delta_2\varDelta\beta_{34}+\varDelta\theta_{13}+\varDelta\theta_{14}+\varDelta\theta_{23}+\varDelta\theta_{24})\equiv 0$$

$\delta_1=2\cos(\beta/2)\sin(\alpha/2)/\sin\theta$, $\delta_2=2\cos(\alpha/2)\sin(\beta/2)/\sin\theta$, $D=4/\delta_1$, $E=(4+\delta_1^2)/\delta_2$, $F=\delta_1$, $S=D^2+4$, $T=E^2+F^2+4$, $U=\delta_1^2+\delta_2^2+4$,

$$A'':\ S_7 = (1/\sqrt{2})(\varDelta R_1-\varDelta R_2)$$

$$S_8 = (1/2)(\varDelta\theta_{13}-\varDelta\theta_{23}+\varDelta\theta_{14}-\varDelta\theta_{24})$$

$$S_9 = (1/2)(\varDelta\theta_{14}-\varDelta\theta_{24}-\varDelta\theta_{13}+\varDelta\theta_{23})$$

The internal coordinates used above are shown in Fig. 1.

The molecular constants of sulfuryl fluorochloride must be estimated because there are no experimental constants. The values of the equilibrium distance, S–F and S–Cl, are assumed to be equal to the corresponding one of sulfuryl fluoride and chloride. The S–O distance and the OSO angle proposed by Gillespie et al.[15] are used. This value of the OSO angle and the values of the OSF angle of sulfuryl fluoride and of the OSCl angle of sulfuryl chloride cause the FSCl angle to be 104.1 deg. On the other hand, an arithmetical mean value of the FSF and ClSCl angles shows the FSCl angle to be 103.9 deg. As a result, we regard the value of the FSCl angle as 104 deg. Since the difference between the observed angle, OSF (108.3 deg.), of sulfuryl fluoride and the OSCl angle (106.4 deg.) of the chloride is less than 2 deg., the bond angles, OSF and OSCl, in sulfuryl fluorochloride can be assumed to be equal in a normal coordinate treatment. The

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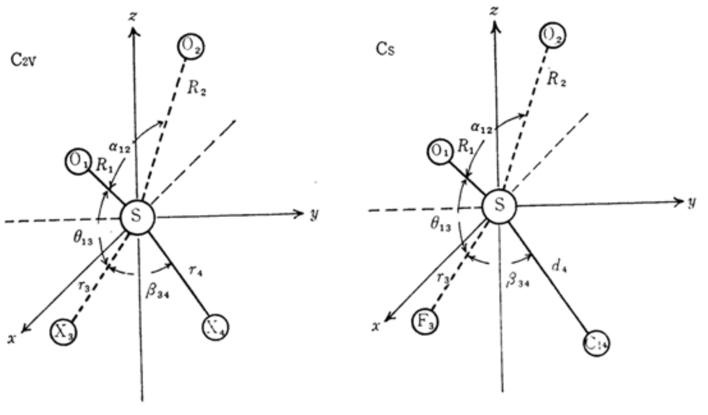
[11] D. R. Lide, Jr., D. E. Mann and J. J. Comeford, ibid., **21**, 497 (1965).

[12] D. R. Lide, Jr., D. E. Mann and R. M. Fristrom, *J. Chem. Phys.*, **26**, 734 (1957).

[13] K. J. Palmar, *J. Am. Chem. Soc.*, **60**, 2360 (1938).

[14] E. B. Wilson, *J. Chem. Phys.*, **9**, 76 (1941).

[15] R. J. Gillespie and E. A. Robinson, *Can. J Chem.*, **41**, 2074 (1963).



(X=F or Cl)

Fig. 1. The internal coordinates.

symmetry coordinates of sulfuryl fluorochloride have been made in accordance with these assumptions. The molecular constants of each molecule are summarized in Table I.

Table I. The molecular constants used in calculations

	SO_2F_2 12)	SO_2Cl_2 13)	SO_2FCl
R(S-O)Å	1.405	1.43	1.41 15)
r(S-F)Å	1.530		1.530
r(S-Cl)Å		1.99	1.99
∠OSO deg.	123.9	119.8	122 15)
∠FSF deg.	96.1		
∠ClSCl deg.		111.2	
∠FSCl deg.			104
∠OSF deg.	108.3		107.4
∠OSCl deg.		106.4	107.4

For the purpose of obtaining the force constants of sulfuryl fluoride and chloride in order to fit the calculated frequencies to the observed, the method of the minimization of functions described by Shimanouchi et al.16) is used, because the usual adjustment of least-squares was inadequate for these molecules. At the beginning of the calculation of force constants, the trial set of force constants are transferred from corresponding ones of thionyl halides, sulfur trioxide, sulfate ions, etc. The force constant, F', is assumed to be equal to $-0.1F$, as usual. The observed frequencies of sulfuryl fluoride assigned obviously by Lide et al. and those of sulfuryl chloride which were discussed by Hunt et al. are used in the calculations.

The calculation of the vibrational frequencies of sulfuryl fluorochloride are also carried out by the use of force constants transferred or predicted by applying the usual additive property from the values of sulfuryl fluoride and chloride. The results of calculation are then compared with the observed frequencies.

Results and Discussion

The convergence of force constants for sulfuryl fluoride is obtained readily in the SUBFF. Although Hunt et al. failed to make a normal coordinate analysis of this assignment with the VFF, we have obtained a good agreement between the calculated and the observed frequencies, as is shown in Table II. Moreover, the values of the force constants obtained are reasonable, as Table III shows.

On the other hand, the calculations on the basis of the SUBFF for Hunt et al.'s and our assignments of sulfuryl chloride show no great difference in the average deviation between the observed and the calculated frequencies. These results are listed as the set I and the calc.(1) of set II in Tables II and III. The values of the force constants obtained are reasonable, except for κ in set I having a large negative value. Since the deviation between the observed and the calculated frequencies in set I is found to be not great in the modes related by the κ, this exceptional value of κ in set I can not be corrected through a modification of the potential function. On the other hand, the calc.(1) of set II in Table II shows a great deviation in the rocking mode; this deviation can be corrected by applying the following modified UBFF (MUBFF), in which the l_{ijk} is the interaction force constant:

$$V = (\text{SUBFF}) + \sum l_{ijk}(\Delta\theta_{ij})(\Delta\theta_{ik})$$

The results of the calculation are shown in calc.(2) of set II in Tables II and III. It is not clear why such extra terms are necessary for sulfuryl chloride but unnecessary for sulfuryl fluoride.

The nonbonded O···O distances and the repulsion constants, F(OO)'s, picked up from previous reported data are shown together with our data in Table IV. The value of the constant obtained

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16) T. Shimanouchi and I. Suzuki, *J. Mol. Spectroscopy*, **8**, 222 (1962).

TABLE II. THE OBSERVED AND CALCULATED FREQUENCIES FOR SO_2F_2 AND SO_2Cl_2 (cm^{-1})

	SO_2F_2			SO_2Cl_2					
				Set I		Set II			
	obs.	calc.*	modes	obs.[10]	calc.*	obs.	calc.(1)*	calc.(2)**	modes
$A_1\nu_1$	1269	1290	$\nu_s(SO_2)$	1205	1223	1205	1231	1235	$\nu_s(SO_2)$
ν_2	848	852	$\nu_s(SF_2)$	577	578	577	571	569	$\delta(OSO)+\nu_s(SCl_2)$
ν_3	544	542	$\delta(OSO)+\delta(FSF)$	406	429	406	418	414	$\nu_s(SCl_2)+\delta(OSO)$
ν_4	384	382	$\delta(FSF)+\delta(OSO)$	209	205	209	208	206	$\delta(ClSCl)$
$A_2\nu_5$	388	393	twist.	363	349	280	274	280	twist.
$B_1\nu_6$	1502	1480	$\nu_{as}(SO_2)$	1434	1409	1434	1403	1402	$\nu_{as}(SO_2)$
ν_7	539	533	$r(SO_2)$	388	394	388	412	389	$r(SO_2)$
$B_2\nu_8$	885	887	$\nu_{as}(SF_2)$	586	560	586	587	599	$\nu_{as}(SCl_2)+w(SO_2)$
ν_9	553	543	$w(SO_2)$	280	281	363	333	351	$w(SO_2)+\nu_{as}(SCl_2)$

* SUBFF
** MUBFF
Set I: Hunt et al. supported from calculations using the VFF.[10]
Set II: This work.

TABLE III. THE FORCE CONSTANTS OF SO_2F_2 AND SO_2Cl_2

	SO_2F_2	SO_2Cl_2		
		Set I	Set II	
			(1)	(2)
$K(SO)$(md./Å)	11.01	10.43	10.30	10.31
$K(SF)$	4.38			
$K(SCl)$		2.13	2.08	1.97
$F(OO)$	0.725	0.425	0.610	0.655
$F(FF)$	0.381			
$F(ClCl)$		0.190	0.141	0.148
$F(OF)$	0.566			
$F(OCl)$		0.293	0.402	0.437
$H(OSO)$	0.617	0.553	0.536	0.549
$H(FSF)$	0.460			
$H(ClSCl)$		0.150	0.165	0.166
$H(OSF)$	0.512			
$H(OSCl)$		0.376	0.290	0.285
κ (md.Å)	0.428	−0.634	0.119	0.173
$l(OOCl)$				0.025
$l(ClClO)$				0.001
$l(OClCl)$				−0.135
$l(ClOO)$				0.054

TABLE IV. THE NONBONDED DISTANCES AND $F(OO)$

	$q(OO)$Å	$F(OO)$(md./Å)	Ref.
HCO_2^{2-}	2.24	3.00	17
CO_3^{2-}	2.27	1.72	18
BO_3^{3-}	2.36	1.05	18
$H_3N^+-SO_3^-$	2.43	0.76	19
SO_2F_2	2.47	0.725	This work
SO_2Cl_2	2.47	0.655(0.425)*	This work
SO_3	2.48	0.555	18
SiO_4	2.56	0.530	20
OsO_4	2.61	0.510	20
CrO_4	2.65	0.504	20
SeO_4	2.68	0.342	20
IO_4	2.87	0.226	20

* The value is calculated from the assignment-set I of SO_2Cl_2.

from our assignment of sulfuryl chloride seems to be adequate. The corresponding force constants between F and F and between Cl and Cl are approximately equal to the values calculated from the Lennard-Jones 6–12 potential; therefore, they may be considered to be appropriate. (As the force constants for other assignments of sulfuryl chloride treated by Hunt et al.[10] show inadequate values, their results are not reprinted here.)

In Table II, our assignment of sulfuryl chloride, shown as set II, is found to be more suitable than the assignment shown as set I in view of the force constants transferring from sulfuryl fluoride and chloride to sulfuryl fluorochloride, as is shown in Table V. We recorded the infrared spectrum of liquid sulfuryl chloride in the range from 400 cm^{-1} to 200 cm^{-1} with a Japan Spectroscopic spectrophotometer-402G. We can find no band near 280 cm^{-1}, and we find near 350 cm^{-1} the weak band observed at 363 cm^{-1} in the Raman spectrum.* This means that the Raman band at 280 cm^{-1} belongs to the infrared inactive A_2 species. These facts show that our assignment of sulfuryl chloride can be considered satisfactory. Therefore, the force constants of this molecule, listed in column 2 of set II in Table III, seem to be appropriate.

Gillespie et al.[21] reported a Raman band of sulfuryl fluorochloride at 195 cm^{-1} as one of

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* The far infrared spectrum in the gaseous state is now being studied; it will be reported on later.

17) T. Miyazawa, *J. Chem. Soc. Japan, Pure Chem. Sect. (Nippon Kagaku Zasshi)*, **77**, 381 (1956).

18) G. J. Janz and Y. Mikawa, *J. Mol. Spectroscopy*, **1**, 92 (1960).

19) M. J. Schmelz, T. Miyazawa, T. J. Lane and J. V. Quagliano, *Spectrochim. Acta*, **9**, 51 (1957).

20) K. Venkateswarlu and R. Thanalakshmi, *J. Sci. Ind. Res. (India)*, **21B**, 461 (1962).

21) R. J. Gillespie and E. A. Robinson, *Spectrochim. Acta*, **18**, 1473 (1962).

deformations connected with the chlorine atom, but, judging from our calculations, this frequency seems to be unsuitable as a fundamental one. We employ the Raman band at 308 cm^{-1} instead of that at 195 cm^{-1} and identify it as the FSCl deformation, $\nu_6(\text{A}')$, superimposed on the twisting, $\nu_9(\text{A}'')$, deformation, as is shown in Table V. The band at 195 cm^{-1} might rise from a difference between two vibrations.

TABLE V. THE OBSERVED AND CALCULATED FREQUENCIES OF SO_2FCl (cm^{-1})

	obs.[21]	calc. (Set I)	calc. (Set II)	modes
A′ ν_1	1224	1257	1263	$\nu_s(SO_2)$
ν_2	823	848	858	$\nu(SF)$
ν_3	627	604	616	$\nu(SCl)+r(SO_2)+\delta(OSO)$
ν_4	505	519	522	$\delta(OSO)+r(SO_2)$
ν_5	430	380	407	$\nu(SCl)+r(SO_2)$
ν_6	308	315	300	$\delta(FSCl)$
A″ ν_7	1455	1447	1442	$\nu_{as}(SO_2)$
ν_8	480	505	486	$w(SO_2)$ + twist.
ν_9	308	374	326	twist. + $w(SO_2)$

TABLE VI. THE ESTIMATED FORCE CONSTANTS OF SO_2FCl

K(SO)	10.66 (md./Å)	κ	0.301 (md.Å)
K(SF)	4.38	l (OOCl)	0.025
K(SCl)	1.97	l (FClO)	0.000
F(OO)	0.690	l (ClFO)	0.000
F(OF)	0.566	l (OFCl)	-0.068
F(OCl)	0.437	l (ClOO)	0.054
F(FCl)	0.256	l (OOF)	0
H(OSO)	0.583	l (FOO)	0
H(OSF)	0.512		
H(OSCl)	0.285		
H(FSCl)	0.313		

TABLE VII. THE POTENTIAL ENERGY DISTRIBUTION $F_{ii}L_{ia}^2/\lambda_a$ FOR THE NORMAL VIBRATIONS OF SO_2F_2

A_1 Vibration

	ν_1	ν_2	ν_3	ν_4
S_1	0.99	0.02	0.00	0.00
S_2	0.05	0.89	0.08	0.00
S_3	0.02	0.07	0.57	0.39
S_4	0.01	0.05	0.18	0.80

B_1 Vibration

	ν_6	ν_7
S_6	1.00	0.01
S_7	0.05	0.96

B_2 Vibration

	ν_8	ν_9
S_8	0.92	0.10
S_9	0.22	0.80

The force constants which lead to a good agreement between the observed and the calculated frequencies, as is shown in set II of Table V, are listed in Table VI. The assumed molecular constants of sulfuryl fluorochloride might not be so far from the true values.

The potential energy distributions for sulfuryl fluoride, chloride and fluorochloride are listed in Tables VII, VIII and IX respectively, while the vibrational modes for each molecule are added to Tables II and V.

TABLE VIII. THE POTENTIAL ENERGY DISTRIBUTION $F_{ii}L_{ia}^2/\lambda_a$ FOR THE NORMAL VIBRATIONS OF SO_2Cl_2

A_1 Vibration

	ν_1	ν_2	ν_3	ν_4
S_1	1.02	0.00	0.00	0.00
S_2	0.01	0.29	0.66	0.07
S_3	0.16	0.69	0.27	0.09
S_4	0.00	0.05	0.02	0.95

B_1 Vibration

	ν_6	ν_7
S_6	1.00	0.01
S_7	0.02	0.99

B_2 Vibration

	ν_8	ν_9
S_8	0.76	0.30
S_9	0.54	0.52

TABLE IX. THE POTENTIAL ENERGY DISTRIBUTION $F_{ii}L_{ia}^2/\lambda_a$ FOR THE NORMAL VIBRATION OF SO_2FCl

A′ Vibration

	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6
S_1	1.00	0.01	0.00	0.00	0.00	0.00
S_2	0.02	0.93	0.00	0.06	0.00	0.00
S_3	0.00	0.01	0.42	0.01	0.58	0.02
S_4	0.01	0.02	0.22	0.57	0.08	0.05
S_5	0.01	0.00	0.10	0.01	0.00	0.90
S_6	0.00	0.10	0.39	0.35	0.21	0.04

A″ Vibration

	ν_7	ν_8	ν_9
S_7	1.00	0.00	0.00
S_8	0.03	0.62	0.38
S_9	0.00	0.25	0.76

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