VIBRATIONAL SPECTRA AND NORMAL COORDINATE ANALYSIS OF DISULFURYL DIFLUORIDE $S_2O_5F_2$ AND DISELENONYL DIFLUORIDE $Se_2O_5F_2$

Jiří TOUŽÍN and Miloš ČERNÍK
Department of Inorganic Chemistry, Masaryk University, 611 37 Brno

Received December 20, 1991
Accepted March 10, 1992

Dedicated to Professor K. Dostál on the occasion of his 70th birthday.

Raman spectra (1 600 – 100 cm^{-1}) of liquid $S_2O_5F_2$ and $Se_2O_5F_2$ and infrared spectra (1 600 – 400 cm^{-1}) of liquid and gaseous $S_2O_5F_2$ were measured. A modified general valence force field was used for their interpretation by normal coordinate analysis. Refinement of the number of lines in the Raman spectrum of $S_2O_5F_2$ by means of numerical separation of the overlapping bands led to the conclusion that liquid $S_2O_5F_2$ consists at least of three rotamers at room temperature.

The ^{19}F NMR spectrum[1] of $S_2O_5F_2$ consists of a single line whose chemical shift is characteristic for fluorine bonded to S(VI) and gives a clear evidence for the chemical equivalence of both fluorine atoms. Since the infrared (IR) spectrum of this compound exhibits a band at 872 cm^{-1} which can be attributed to the S–F stretching, the acyclic structure of the disulfuric acid difluoride $FO_2S–O–SO_2F$ has been suggested for it (ref.[2]). This structure, with an oxygen bridge connecting the two sulfur atoms, is consistent with the fact that $S_2O_5F_2$ is a true fluorosulfuric acid anhydride[3] as well as with the structure data of the analogous molecule of disulfuryl dichloride[4] $S_2O_5Cl_2$. Two independent studies[5,6] concerned with analysis of vibrational spectra of $S_2O_5F_2$, $S_3O_8F_2$ and some other polysulfuryl halides had been performed.

Considering the polarization of Raman lines of the liquid, Gillespie and Robinson[5] suggested for $S_2O_5F_2$ a conformation with the trans arrangement of fluorine atoms and C_s symmetry. Simon and Lehmann[6] had available the Raman spectrum and the IR spectrum (1 800 – 400 cm^{-1}) of gaseous $S_2O_5F_2$ and its 10% solution in CCl_4. Lacking any informations on the Raman lines polarization, they interpreted the spectral data in accordance with the model of C_{2v} symmetry. Electron diffraction study[7] revealed later that in the gas phase, $S_2O_5F_2$ is present as a conformer with the trivial symmetry C_1 where the tilt angles of the two $–SO_2F$ groups with respect to the S–O–S plane are different and mutually independent.

Diselenonyl difluoride $Se_2O_5F_2$ was only recently isolated from a mixture of polyselenonyl difluorides formed during the reaction of selenonyl difluoride with selenium trioxide[8,9]. ^{19}F NMR and Raman spectra suggest that its structure is the same as that of disulfuryl difluoride. The Raman spectrum has been only tentatively assigned in the stretching vibrations region, since the ν(SeF), ν'(SeF) and ν'(SeOSe) stretching modes could not be discriminated reliably. Since the vibrational spectra of $S_2O_5F_2$ have not yet been unambiguously interpreted and the assignment of some vibrational frequencies in refs[5,6] is rather different, we employed the normal coordinate analysis to characterize in more detail the bonding in both compounds and to obtain an unambiguous assignment of all of their normal modes.

EXPERIMENTAL

Instrumental Methods

Raman spectra were recorded on a Spex Ramalog 3 spectrometer. The samples were filled under dry air into glass capillaries which were cooled with liquid nitrogen, evacuated and sealed off. The spectra were excited by the 488 nm line of a Spectra Physics Model 165-03 Ar^+ laser (200 mW). Emission lines of the Ar^+ plasma were employed for the spectral calibration.

The infrared spectra of $S_2O_5F_2$ were recorded on a Perkin–Elmer 783 spectrometer in a poly(chlorotrifluoroethylene) cell[10] equipped with AgCl windows. The instrument was frequency-calibrated by means of a polystyrene foil and of atmospheric water vapour and carbon dioxide, measured in the single-beam mode. The liquid $S_2O_5F_2$ sample thickness was 0.017 mm, the gas sample thickness was 0.7 mm at 34 kPa. For the liquid sample the thickness was too large to enable the positions of the most intense bands to be read reliably. However, the high volatility of the compound precluded the measurement of a thinner capillary layer in an unsealed cell.

^{19}F NMR spectra were measured on a Varian XL 100 spectrometer using $CFCl_3$ as the external standard.

Substances

$S_2O_5F_2$ was prepared by the reaction of IF_5 with SO_3 (ref.[11]) and purified by repeated distillation (b.p. 51 °C). The synthesis and isolation of $Se_2O_5F_2$ have been described in ref.[9]. The purity of the compounds was checked by ^{19}F NMR spectroscopy. The sample of $S_2O_5F_2$ gave a single signal whose chemical shift was 46.8 ppm, which agrees well with the published value[12] of 47.3 ppm. The singlet of $Se_2O_5F_2$ at 72.2 ppm was accompanied by a very weak signal of SeO_2F_2 at 55.6 ppm, whose presence in the sample is evidenced in the Raman spectrum by a very weak line at 275 cm^{-1} (ref.[13]).

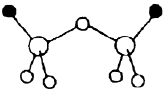
Calculations

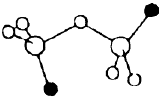
Normal coordinate analysis (NCA) was performed by the Wilson ***G*, *F*** matrix method using published programs[14,15]. The program for numerical separation of overlapping bands[16] was modified for a PC/AT. The band shape was approximated by the Cauchy–Lorentz profile function. The differences between the calculated and experimental intensities did not exceed 1%.

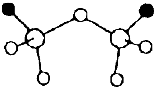
RESULTS AND DISCUSSION

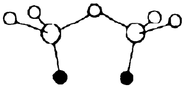
Vibrational Spectra

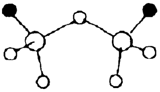
Molecules of $X_2O_5F_2$ (X = S, Se) can form rotamers with the C_{2v} (*Ia*, *Ib*), C_s (*II*, *III*), C_2 (*IV*) or C_1 symmetry, whose existence is due to the hindered rotation of the XO_2F bonds about the X–O groups of the nonlinear X–O–X bridge. The conformers *III* and *IV* form from *Ia* and *Ib*, respectively, by rotation of the $-XO_2F$ groups by the same angle smaller than 180° in the same or opposite directions, respectively. Conformer *II* is also generated from *Ia* or *Ib* by rotation of one of the $-XO_2F$ groups by 180°. If the mutual position of the $-XO_2F$ groups is general, the conformers *V* possess the trivial symmetry C_1.


Ia


II


III


Ib


IV

The vibrational representations belonging to the above rotamers, along with the symmetry of the two bridge stretching vibrations, are given in Table I. It is clear that identification based on the different activity of normal vibrations in the IR and Raman spectra is only feasible for the rotamers *Ia* and *Ib*, where four vibrations of the A_2 species are IR-inactive. The determination of the number of polarized bands should enable the discrimination of *Ia*/*Ib* from *II* or from the *III*/*IV* pair. Discrimination between the two C_s models should be based on the fact that in the spectrum of *II* both bridge stretching vibrations must be polarized whereas in the spectrum of *III* only the

TABLE I
Vibrational representations of $X_2O_5F_2$ molecules (X = S, Se). $N = 9$

Rotamer	Point symmetry group	Vibrational representation	Symmetry species	
			νXOX	$\nu' XOX$
Ia Ib	C_{2v}	$7A_1 + 4A_2 + 6B_1 + 4B_2$	A_1	B_1
II	C_s	$13A' + 8A''$	A'	A'
III	C_s	$11A' + 10A''$	A'	A''
IV	C_2	$11A + 10B$	A	B
V	C_1	$21A$	A	A

$\tilde{\nu}$(XOX) band will be polarized. The discrimination of the conformers *III* and *IV* cannot be based on their vibrational spectra.

Thus, attempts to ascertain the presence of the conceivable $X_2O_5F_2$ conformers requires a knowledge of the activity of the normal vibrations and of the polarization of the Raman lines. However, $Se_2O_5F_2$ is too aggressive and thermally labile to allow its IR spectrum to be recorded, and consequently the investigation was mostly concerned with $S_2O_5F_2$. Due to some differences in the reported numbers of observed infrared bands[2,6] and Raman lines[2,6], and Raman line polarization data have only be reported in ref.[5], we measured the Raman spectrum of liquid $S_2O_5F_2$ and the IR spectra of liquid and gaseous $S_2O_5F_2$. All the spectra obtained, along with the Raman spectrum published in ref.[5], are given in Table II and shown in Fig. 1. The IR spectrum of gaseous $S_2O_5F_2$ is basically consistent with the spectra reported in refs[2,6]. In the latter paper, the authors report weak absorptions at 493 and 1 180 cm^{-1}, which were not observed in our spectra due to the lower sample concentration. This is confirmed by the weak shoulder at 492 cm^{-1} in the IR spectrum of the liquid and by the corresponding Raman line at 488 cm^{-1}. On the other hand, the shoulder at 1 267 cm^{-1}, which apparently corresponds to the intense Raman line at 1 259 cm^{-1}, is absent from the IR spectrum reported in ref.[6].

All lines present in our Raman spectrum have been reported in the earlier papers except for the weak lines at 156, 302 and 1 242 cm^{-1} which Simon and Lehmann[6] failed to observe. The spectrum[5], however, includes additional bands at 350, 366, 435 and 540 cm^{-1}, and the spectrum[6] includes a band at 673 cm^{-1}; these are probably due to impurities. The agreement between the all three Raman spectra is satisfactory, the difference largely lying within ± 5 cm^{-1}.

Higher differences exist between the spectra of liquid and gaseous disulfuryl difluoride. Although the too high intensity of some absorptions in the IR spectrum of liquid $S_2O_5F_2$ precluded precise reading of their frequencies, comparison of spectra of the liquid and gaseous substance shows that transition from the gaseous to the liquid phase is accompanied by a marked intensity decrease of the bands at 1 511, 1 247, 873, 827 and 555 cm^{-1} and by the appearance of new intense absorptions with lowered wavenumbers at 1 495, 1 472, 1 236, 864, 808 and 539 cm^{-1}. Only for the shoulder at 890 cm^{-1} the new absorption has a higher frequency. With regard to the high band intensi-

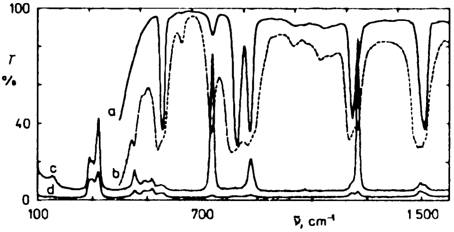


Fig. 1

Infrared (a, b) and Raman (c, d) spectra of gaseous (a) and liquid (b – d) disulfuryl difluoride $S_2O_5F_2$; polarization: c ||, d ⊥

TABLE II

Band and line positions (cm^{-1}) and relative intensities (0.1 – 10) in the vibrational spectra of $S_2O_5F_2$ and $Se_2O_5F_2$

$S_2O_5F_2$								$Se_2O_5F_2$	
IR (g)		IR (l)		RA^a (l)	RA^b (l)		RA^c	RA (l)	
								112 sh	1
								117	2
							152	202	4
				157 p	156 p	1	157	222	10
				290	290 p	2	288	275	0.5
				301	302	2	300		
							316	310 sh	3
				323 p	322 p	4	323	322	3
				350				360 sh	1
				366				365	1
								372 sh	1
								390	1
		429	1	435					
455	5	454	3	456 p	453 p	2	452		
							463		
		492 sh		487	488	1	488		
							502		
		513 sh		518 p	516	1	516		
		539 b	9	540	539 sh		539		
555	8	560 sh		560	552	1	552	558	4
621	1	625	3		629	0.1		674 sh	1
							728	693	5
737	2	733	8	733 p	732 p	8	732	711 sh	2
							735		
827	9	808 b	9	814	812 b	0.5	810		
							867		
873	8	864 b	9	872 p	872 p	2	875		
		890 sh						962 sh	2
		958 sh						969	6
1 034	1	1 036	3					1 054	2
		1 083 sh						1 060 sh	2
		1 130	4						
1 140	1	1 165 b	3						
1 247	8	1 236	8	1 249 p	1 242 sh		1 252		
							1 254		
1 267 sh		1 264	8	1 264 p	1 259 p	10	1 258		
		1 472 sh							
		1 495 b	9	1 490	1 485	1	1 480		
1 511	8	1 512 sh		1 511	1 504 sh		1 498		

[a] Ref.[5]; [b] this work; [c] wavenumber obtained by numerical resolution; sh shoulder, b broad band, p polarized band.

ties and their simultaneous occurrence for all stretching vibrations of $S_2O_5F_2$, the absorptions do not seem likely to be hot or combination bands.

When comparing the wavenumbers in the Raman spectrum of the liquid $S_2O_5F_2$ and the IR spectrum of the gaseous substance, the differences due to the different state of aggregation are less marked. Pronounced frequency differences only occur between the IR bands at 827 and 1 511 cm^{-1} and the corresponding Raman lines at 812 and 1 504 cm^{-1}, respectively.

The apparent asymmetry of some lines and the occurrence of many shoulders brought us to apply numerical separation of the overlapping bands in order to determine the number and parameters of the Raman lines of $S_2O_5F_2$. The wavenumbers of the resolved lines, which are included in Table II, were used in the NCA. The number of bands so detected was higher than would be expected for a single conformer of $S_2O_5F_2$. This is best seen in the region of the S–O–S bridge stretching vibrations, where three lines with the intensity ratio 6 : 7 : 7 were found at 728, 732 and 735 cm^{-1} (Fig. 2). The resolution of the corresponding absorption band at 733 cm^{-1} in the IR spectrum of liquid $S_2O_5F_2$ led to a similar result, viz. the occurrence of bands at 727, 732 and 736 cm^{-1} in the 5 : 6 : 9 ratio (Fig. 3). Since each of the conceivable conformers can have only one ν(SOS), one ν′(SOS) and one δ(SOS) vibration, the liquid $S_2O_5F_2$ probably comprises at least three rotamers. Attempted resolution of lines of the remaining two bridge vibrations was not unambiguous due to their low intensity. The bands of all the remaining normal vibrations occur in pairs corresponding to the in-phase ($\tilde{\nu}$) or out-of-phase ($\tilde{\nu}'$) vibrations of the two $-SO_2F$ groups; the wavenumber differences within each pair are from 4 to 188 cm^{-1}, which is also a complicating factor in the resolution.

Nevertheless, the concept of an equilibrium establishing between several rotamers in liquid $S_2O_5F_2$ is supported by the previously discussed differences between the IR spectra of the liquid and gaseous substances; for the latter, electron diffraction data[7] indicate the existence of a single conformer with the trivial symmetry C_1. The polarization measurements prove that this asymmetrical rotamer is not the major component

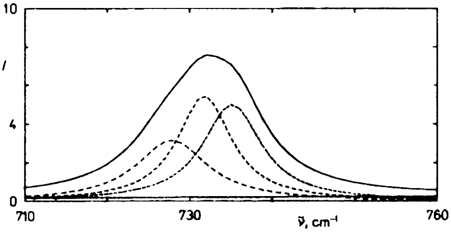


FIG. 2
Separation of the ν(SOS) band in the Raman spectrum of liquid $S_2O_5F_2$

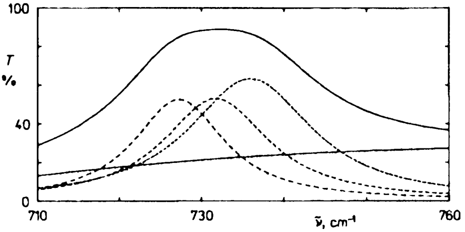


FIG. 3
Separation of the ν(SOS) band in the IR spectrum of liquid $S_2O_5F_2$

of liquid $S_2O_5F_2$. Actually, only seven lines are polarized beyond doubt, for the rest the degree of depolarization cannot be determined accurately due to their frequent overlap. In any case, however, the depolarization factors approach the limiting value of 0.75, so that, although some weakly polarized lines can occur, the overall picture rather corresponds to the expectation for the conformers *II* or *III*/*IV* with 13 or 11 polarized lines, respectively. This conclusion is consistent with the recent X-ray investigation[17] which gave evidence that at T = 100 K, crystalline $S_2O_5F_2$ contains rotamer *IV* solely. Thus, if the rotamer possessing the symmetry C_2 is energetically the most favourable conformation in the solid phase, it can be expected to be a major component in the liquid $S_2O_5F_2$, too.

Normal Coordinate Analysis

Although the above results document that liquid $S_2O_5F_2$ at room temperature constitutes an equilibrium mixture of at least three different, as yet unspecified rotamers, conformation *Ia* with the highest possible symmetry C_{2v} was chosen for the NCA. With regard to the number of available experimental fundamental frequencies, a substantial simplification of the general valence force field was necessary, and the choice of the conformer with the highest symmetry presents a reasonable solution. The geometry of the chosen model of the $X_2O_5F_2$ molecules (X = S, Se) is shown in Fig. 4, the structure parameters used are given in Table III. The set of internal symmetry coordinates used for the transformation of the $\boldsymbol{G}$ and $\boldsymbol{F}$ matrices into the diagonal block form is given in Table IV.

The calculation procedure was the same as applied to the $N(SO_3)_2^{3-}$ and $N(SeO_3)_2^{3-}$ anions[19]. As in that case, only twenty out of the set of observed bands could be attributed to the normal vibrations of the $X_2O_5F_2$ molecules (X = S, Se); the remaining torsion bands $\tau'(XO_2F)$ (A_2) lie at so low wavenumbers that they could be detected in none of the spectra obtained. Thus, only 20 independent parameters were available for the final adjusting of the four blocks. In three cases, linear combinations of quadratic potential constants (QPC) constituting elements of the factorized $\boldsymbol{F}$ matrix, rather than the constants themselves, could be adjusted. The nonzero elements of the $\boldsymbol{F}$ matrix are

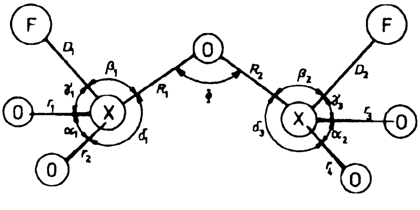


FIG. 4
Model of the $X_2O_5F_2$ molecules (X = S, Se) used for NCA calculations

expressed via the chosen set of potential constants as given in Table V. The final values of the 20 adjusted parameters are given in Table VI. By their re-insertion in the secular equation the experimental values of the fundamental frequencies are reproduced with an absolute error not exceeding 1 cm^{-1}.

The final assignment of all of the 21 normal vibrations and an overview of the potential energy distributions in the two molecules studied are given in Table VII. For $S_2O_5F_2$, NCA gave evidence that the weak band at 621 or 625 cm^{-1} in the IR spectrum and at 629 cm^{-1} in the Raman spectrum, which Gillespie and Robinson[5] attributed to $\rho'(SO_2)$, actually cannot be related with any of the normal vibrations of the molecule. The upper limit of deformation frequencies is the $\delta(SO_2)$ vibration at 552 cm^{-1}, and so the above band must be an overtone or combination frequency. Apparently, this also applies to the weak absorptions at 1 034 and 1 140 cm^{-1} in the IR spectrum of gaseous $S_2O_5F_2$ and to the five weak bands within the 1 165 – 958 cm^{-1} range in the spectrum of the liquid. The NCA also settled the discrepancies between the assignments of the bridge vibrations in refs[5,6]. The symmetric stretching vibration, $\tilde{\nu}_s(SOS)$, cannot be identified with the band at 323 cm^{-1} (refs[5,20]); actually, in accordance with ref.[6], it lies at 732 cm^{-1}, which agrees well with the values of 750 and 783 cm^{-1} observed for the isoelectronic anions $N(SO_3)_2^{3-}$ (ref.[19]) and $S_2O_7^{2-}$ (ref.[21]), respectively. On the other hand, the wavenumber of 488 cm^{-1} attributed to the bridge bending vibration, $\delta(SOS)$, in ref.[6] is unreasonably high; in agreement with ref.[5], that vibration can be attributed to the surprisingly low intense Raman line at 157 cm^{-1}. The correctness of this assignment is confirmed by the close values of 164 and 160 cm^{-1} found by NCA for the $\delta(SOS)$ vibration in the $S_2O_7^{2-}$ and $N(SO_3)_2^{3-}$ anions, respectively. The assignment of the $\nu'(SOS)$ vibration as well as the stretching vibrations of the S–F and S=O bonds corresponds well with the interpretation in refs[5,6], and the potential energy distribution

TABLE III
Structure parameters of $S_2O_5F_2$ and $Se_2O_5F_2$ molecules

Parameter	$S_2O_5F_2$[a]	$Se_2O_5F_2$[b]
R[c]	161.1	170
D[c]	152.5	168.5
r[c]	139.8	157.5
α[d]	126.8	126
β[d]	102.4	94
γ[d]	106.6	108
δ[d]	106.1	108
Φ[d]	123.6	120

[a] Ref.[6]; [b] estimated based on structure parameters of related compounds, e.g. ref.[18]; [c] bond lengths in pm; [d] angles in deg.

gives evidence that they can be regarded as sufficiently characteristic. This also applies to the $\tau(SO_2)$ and $\rho(SO_2)$ vibrations as well as to the two torsional vibrations of the $-SO_2F$ groups. The difference of 78 cm^{-1} between the $\nu(SOS)$ and $\nu'(SOS)$ vibrational frequencies confirms the conclusions of Brown and Ross[21] concerning the influence of the bridge angle value on the separation of both bridge stretching vibrations in condensed $[O_3XOXO_3]^{n-}$ anions and their derivatives.

TABLE IV
Set of internal symmetry coordinates used

A_1

$S_1 = 2^{-1}(\Delta r_1 + \Delta r_2 + \Delta r_3 + \Delta r_4)$
$S_2 = 2^{-1/2}(\Delta D_1 + \Delta D_2)$
$S_3 = 2^{-1/2}(\Delta R_1 + \Delta R_2)$
$S_4 = N_1^{-1}(A\Delta\alpha_1 + A\Delta\alpha_2 - \Delta\gamma_1 - \Delta\gamma_2 - \Delta\gamma_3 - \Delta\gamma_4 - \Delta\delta_1 - \Delta\delta_2 - \Delta\delta_3 - \Delta\delta_4)$
$S_5 = 8^{-1/2}(\Delta\gamma_1 + \Delta\gamma_2 + \Delta\gamma_3 + \Delta\gamma_4 - \Delta\delta_1 - \Delta\delta_2 - \Delta\delta_3 - \Delta\delta_4)$
$S_6 = N_2^{-1}(-B\Delta\alpha_1 - B\Delta\alpha_2 + C\Delta\beta_1 + C\Delta\beta_2 - \Delta\gamma_1 - \Delta\gamma_2 - \Delta\gamma_3 - \Delta\gamma_4 - \Delta\delta_1 - \Delta\delta_2 - \Delta\delta_3 - \Delta\delta_4)$
$S_7 = \Delta\phi$
$S_{R1} = N_3^{-1}(B\Delta\alpha_1 + B\Delta\alpha_2 + D\Delta\beta_1 + D\Delta\beta_2 + \Delta\gamma_1 + \Delta\gamma_2 + \Delta\gamma_3 + \Delta\gamma_4 + \Delta\delta_1 + \Delta\delta_2 + \Delta\delta_3 + \Delta\delta_4)$

A_2

$S_8 = 2^{-1}(\Delta r_1 - \Delta r_2 - \Delta r_3 + \Delta r_4)$
$S_9 = 2^{-1}(\Delta\gamma_1 - \Delta\gamma_2 - \Delta\gamma_3 + \Delta\gamma_4)$
$S_{10} = 2^{-1}(\Delta\delta_1 - \Delta\delta_2 - \Delta\delta_3 + \Delta\delta_4)$
$S_{11} = 2^{-1/2}(\Delta\tau_1 + \Delta\tau_2)$

B_1

$S_{12} = 2^{-1}(\Delta r_1 + \Delta r_2 - \Delta r_3 - \Delta r_4)$
$S_{13} = 2^{-1/2}(\Delta D_1 - \Delta D_2)$
$S_{14} = 2^{-1/2}(\Delta R_1 - \Delta R_2)$
$S_{15} = N_1^{-1}(A\Delta\alpha_1 - A\Delta\alpha_2 - \Delta\gamma_1 - \Delta\gamma_2 + \Delta\gamma_3 + \Delta\gamma_4 - \Delta\delta_1 - \Delta\delta_2 + \Delta\delta_3 + \Delta\delta_4)$
$S_{16} = 8^{-1/2}(\Delta\gamma_1 + \Delta\gamma_2 - \Delta\gamma_3 - \Delta\gamma_4 - \Delta\delta_1 - \Delta\delta_2 + \Delta\delta_3 + \Delta\delta_4)$
$S_{17} = N_2^{-1}(B\Delta\alpha_1 - B\Delta\alpha_2 + C\Delta\beta_1 - C\Delta\beta_2 - \Delta\gamma_1 - \Delta\gamma_2 + \Delta\gamma_3 + \Delta\gamma_4 - \Delta\delta_1 - \Delta\delta_2 + \Delta\delta_3 + \Delta\delta_4)$
$S_{R2} = N_3^{-1}(B\Delta\alpha_1 - B\Delta\alpha_2 + D\Delta\beta_1 - D\Delta\beta_2 + \Delta\gamma_1 + \Delta\gamma_2 - \Delta\gamma_3 - \Delta\gamma_4 + \Delta\delta_1 + \Delta\delta_2 - \Delta\delta_3 - \Delta\delta_4)$

B_2

$S_{18} = 2^{-1}(\Delta r_1 - \Delta r_2 + \Delta r_3 - \Delta r_4)$
$S_{19} = 2^{-1}(\Delta\gamma_1 - \Delta\gamma_2 + \Delta\gamma_3 - \Delta\gamma_4)$
$S_{20} = 2^{-1}(\Delta\delta_1 - \Delta\delta_2 + \Delta\delta_3 - \Delta\delta_4)$
$S_{21} = 2^{-1/2}(\Delta\tau_1 - \Delta\tau_2)$

S_{R1} and S_{R2} are redundant coordinates, N_i are normalization factors; for $S_2O_5F_2$ and $Se_2O_5F_2$: A = 3.492727 and 3.603797, B = 1.145237 and 1.109939, C = 7.234812 and 5.852776, and D = 0.734168 and 0.893928, respectively.

TABLE V
Elements of the factorized $\boldsymbol{F}$ matrix

A_1

$\boldsymbol{F}_{1,1} = f_r + f_r' + f_r'' + f_r'''$

$\boldsymbol{F}_{2,2} = f_D + f_D'$

$\boldsymbol{F}_{3,3} = f_R + f_R'$

$\boldsymbol{F}_{3,5} = r^{1/2}D^{1/2}f_{R\gamma} - r^{1/2}R^{1/2}f_{R\delta}$

$\boldsymbol{F}_{3,6} = 2^{1/2}N_2^{-1}[-rBf_{R\alpha} + RDC(f_{r\beta} + f_{r\beta}') - 2(rDf_{R\gamma} + rRf_{R\delta})]$

$\boldsymbol{F}_{3,7} = 2^{1/2}Rf_{R\Phi}$

$\boldsymbol{F}_{4,4} = 4N_1^{-2}[2^{-1}r^2A^2f_\alpha + rD(f_\gamma + f_\gamma') + rR(f_\delta + f_\delta')]$

$\boldsymbol{F}_{5,5} = 2^{-1}[rD(f_\gamma + f_\gamma') + rR(f_\delta + f_\delta')]$

$\boldsymbol{F}_{5,6} = -2^{1/2}N_2^{-1}[rD(f_\gamma + f_\gamma') - rR(f_\delta + f_\delta')]$

$\boldsymbol{F}_{5,7} = 2^{1/2}(rDf_{\Phi\gamma} - rRf_{\Phi\delta})$

$\boldsymbol{F}_{6,6} = 4N_2^{-2}[2^{-1}r^2B^2f_\alpha + 2^{-1}rDC^2f_\beta + rD(f_\gamma + f_\gamma') + rR(f_\delta + f_\delta')]$

$\boldsymbol{F}_{7,7} = R^2f_\Phi$

A_2

$\boldsymbol{F}_{1,1} = f_r - f_r' - f_r'' + f_r'''$

$\boldsymbol{F}_{2,2} = rD(f_\gamma - f_\gamma')$

$\boldsymbol{F}_{3,3} = rR(f_\delta - f_\delta')$

$\boldsymbol{F}_{4,4} = R^2f_\tau$

B_1

$\boldsymbol{F}_{1,1} = f_r + f_r' - f_r'' - f_r'''$

$\boldsymbol{F}_{2,2} = f_D - f_D'$

$\boldsymbol{F}_{3,3} = f_R - f_R'$

$\boldsymbol{F}_{3,5} = r^{1/2}D^{1/2}f_{R\gamma} - r^{1/2}R^{1/2}f_{R\delta}$

$\boldsymbol{F}_{3,6} = 2^{1/2}N_2^{-1}[-rBf_{R\alpha} + RDC(f_{r\beta} + f_{r\beta}') - 2(rDf_{R\gamma} + rRf_{R\delta})]$

$\boldsymbol{F}_{4,4} = 4N_1^{-2}[2^{-1}r^2A^2f_\alpha + rD(f_\gamma + f_\gamma') + rR(f_\delta + f_\delta')]$

$\boldsymbol{F}_{5,5} = 2^{-1}[rD(f_\gamma + f_\gamma') + rR(f_\delta + f_\delta')]$

$\boldsymbol{F}_{5,6} = -2^{1/2}N_2^{-1}[rD(f_\gamma + f_\gamma') - rR(f_\delta + f_\delta')]$

$\boldsymbol{F}_{6,6} = 4N_1^{-2}[2^{-1}r^2B^2f_\alpha + 2^{-1}rDC^2f_\beta + rD(f_\gamma + f_\gamma') + rR(f_\delta + f_\delta')]$

B_2

$\boldsymbol{F}_{1,1} = f_r - f_r' + f_r'' - f_r'''$

$\boldsymbol{F}_{2,2} = rD(f_\gamma - f_\gamma')$

$\boldsymbol{F}_{3,3} = rR(f_\delta - f_\delta')$

$\boldsymbol{F}_{4,4} = R^2f_\tau$

As to the assignment of the bending vibrations, this problem was not dealt in detail by Simon and Lehmann[6]; the conclusions of ref.[5] are corrected particularly in that the wavenumber of the $\omega'(SO_2)$ vibration (denoted as SO_2 rock, ||, o) is decreased from 733 to 463 cm^{-1} and the τ and $\tau'(SO_2F)$ frequencies are shifted from 366 and 290 cm^{-1} to 152 and 77 cm^{-1}, respectively. The assignment of these and of all the remaining bending vibrations agrees well with the recent assignment of spectra of the covalent bonded $-OSO_2F$ groups (refs[22,23]).

Table VI contains two solutions for $Se_2O_5F_2$, which differ only in the assignment of the bands at 711 and 674 cm^{-1} to the $\nu'(SeF)$ and $\nu'(SeOSe)$ vibrations. The interpretation of the Raman spectrum of $Se_2O_5F_2$ given in Table VII corresponds to set *A*. For set *B* the potential energy distribution changes to $30\nu_{13} + 55\nu_{14}$ for the band at 711 cm^{-1}, and to $66\nu_{13} + 24\nu_{14}$ for the band at 674 cm^{-1}, respectively. The changes of the remai-

TABLE VI
Quadratic potential constants (QPC, in N m^{-1}) of $S_2O_5F_2$ and $Se_2O_5F_2$

QPC	$S_2O_5F_2$	$Se_2O_5F_2$	
		A	*B*
f_r	1 139.33	791.26	791.31
f_r'	23.27	-18.08	-18.03
f_r''	2.60	4.51	4.48
f_r'''	-13.80	-0.56	-0.58
f_R	358.54	234.14	255.64
f_R'	90.86	19.52	26.75
f_D	482.34	432.99	426.47
f_D'	-23.66	-5.35	1.97
f_α	67.12	40.25	40.13
f_β	83.77	46.21	43.89
f_γ	77.40	43.42	43.79
f_γ'	6.48	-1.67	-1.30
f_δ	57.47	26.84	26.75
f_δ'	11.00	2.04	1.94
f_Φ	43.46	40.00	37.26
f_τ	12.46	7.89	7.89
$f_{R\Phi}$	1.45	5.04	7.71
$F^{A_1}_{3,5} = F^{B_1}_{3,5}$	-84.41	-14.37	-18.61
$F^{A_1}_{3,6} = F^{B_1}_{3,6}$	86.95	47.76	44.81
$F^{A_1}_{5,7}$	-7.62	-11.69	-12.40

ning bands being insignificant. Comparison of the wavenumbers of the bridge stretching vibrations in the spectra of $Se_2O_7^{2-}$ (ref.[24]), $H_2Se_2O_7$ (ref.[25]) and $(CH_3O)_2Se_2O_5$ (ref.[26]) demonstrates a remarkable wavenumber stability of the ν and ν′ vibrations of the SeOSe bridge, both occuring in the narrow regions of 560 – 555 and 690

TABLE VII
Fundamental frequencies of $X_2O_5F_2$ (X = S, Se)

No.	Interpretation	$S_2O_5F_2$		$Se_2O_5F_2$	
		frequency	PE distribution, %[a]	frequency	PE distribution, %[a,b]
			A_1		
1	$\nu_s XO_2$	1 258	$87\nu_1$	969	$96\nu_1$
2	νXF	867	$62\nu_2$	693	$93\nu_2$
3	νXOX	732	$52\nu_3 + 25\nu_6$	558	$39\nu_3 + 28\nu_6 + 30\nu_7$
4	δXO_2	552	$66\nu_4 + 30\nu_5$	365	$97\nu_4$
5	$\omega' XO_2$	463	$50\nu_5 + 22\nu_4$	322	$83\nu_5$
6	$\delta O{-}XF$	323	$58\nu_6 + 37\nu_3$	222	$61\nu_6 + 38\nu_3$
7	δXOX	157	$71\nu_7$	117	$57\nu_7 + 20\nu_6$
			A_2		
8	$\nu_a' XO_2$	1 480	$95\nu_8$	1 054	$99\nu_8$
9	$\rho' XO_2$	502	$88\nu_9$	372	$94\nu_9$
10	τXO_2	300	$94\nu_{10}$	202	$96\nu_{10}$
11	$\tau' XO_2F$	(77)	$91\nu_{11}$	(57)	$91\nu_{11}$
			B_1		
12	$\nu_s' XO_2$	1 254	$92\nu_{12}$	962	$97\nu_{12}$
13	$\nu' XF$	875	$76\nu_{13}$	711	$59\nu_{13} + 32\nu_{14}$
14	$\nu' XOX$	810	$71\nu_{14}$	674	$48\nu_{14} + 41\nu_{13}$
15	$\delta' XO_2$	516	$80\nu_{15}$	365	$68\nu_{15}$
16	ωXO_2	452	$66\nu_{16}$	310	$71\nu_{16}$
17	$\delta' O{-}XF$	316	$68\nu_{17} + 30\nu_{14}$	202	$64\nu_{17} + 20\nu_{14}$
			B_2		
18	$\nu_a XO_2$	1 498	$96\nu_{18}$	1 060	$99\nu_{18}$
19	ρXO_2	539	$78\nu_{20} + 21\nu_{21}$	390	$58\nu_{20} + 20\nu_{19} + 22\nu_{21}$
20	$\tau' XO_2$	488	$95\nu_{19}$	360	$78\nu_{19} + 20\nu_{20}$
21	τXO_2F	152	$77\nu_{21} + 20\nu_{20}$	112	$76\nu_{21} + 22\nu_{20}$

[a] Only contributions higher than 20% are given, rounded to integers; [b] for QPC set *A* in Table VI.

– 668 cm^{-1}, respectively. Obviously, this can be ascribed to the fact that the structure and effective weight of the ligands X are very close to each other in the $Se_2O_5X_2$ molecules considered (X = F, O, OH, OCH_3), so that, with the comparable wavenumbers of the other coupled vibrations, the resulting $\tilde{\nu}$(SeOSe) and $\tilde{\nu}'$(SeOSe) frequencies remain nearly constant. Therefore we assume that the set *A* approaches the reality better than the set *B*. Similarly stable are the wavenumbers of the Se–O–Se bridge bending vibration, to which the intense Raman line near 230 cm^{-1} has been assigned in refs[24 – 26]. An NCA, however, revealed[19] that in the spectra of the isoelectronic anions $Se_2O_7^{2-}$ and $N(SeO_3)_2^{3-}$ this vibration appears at 106 and 130 cm^{-1}, respectively, which agrees well with the value of 117 cm^{-1} found for $Se_2O_5F_2$.

REFERENCES

1. Muetterties E. L., Coffman D. D.: J. Am. Chem. Soc. *80*, 5914 (1958).
2. Clark H. C., Emeleus H. J.: J. Chem. Soc. *1958*, 190.
3. Hayek E., Koller W.: Monatsh. Chem. *82*, 942 (1951).
4. Gerding H., Linden A. C.: Rec. Trav. Chim. *61*, 735 (1942).
5. Gillespie R. J., Robinson E. A.: Can. J. Chem. *39*, 2179 (1961).
6. Simon A., Lehmann R.: Z. Anorg. Allg. Chem. *311*, 224 (1961).
7. Hencher J. L., Bauer S. H.: Can. J. Chem. *51*, 2047 (1973).
8. Dostál K.: Folia Fac. Sci. Nat. Univ. Purkynianae Brun. *18*, 1 (1977).
9. Černík M.: Z. Anor. Allg. Chem., submitted.
10. Dove M. F. A., Hallett J. G.: Chem. Ind. *1966*, 2051.
11. Schmitt W.: Monatsh. Chem. *85*, 452 (1954).
12. Gillespie R. J., Schrobilgen G. J.: Inorg. Chem. *13*, 1694 (1974).
13. Paetzold R., Ziegenbalg K.-H.: Z. Chem. *4*, 461 (1964).
14. Špirko V., Klíma P., Hájek B.: Sb. Vys. Sk. Chem.-Technol. Praze, Anorg. Chem., Chem. Technol., B *15*, 15 (1972).
15. Adámek P., Hájek B.: Sb. Vys. Sk. Chem.-Technol. Praze, Anorg. Chem., Chem. Technol., B *18*, 69 (1974).
16. Horák M., Vítek A.: *Interpretation and Processing of Vibrational Spectra*. Wiley, Chichester 1978.
17. Blake A. J., Žák Z.: Acta Crystallogr., in press.
18. Hagen K., Cross V. R., Hedberg K.: J. Mol. Struct. *44*, 187 (1978).
19. Toužín J., Růžička A.: Collect. Czech. Chem. Commun. *46*, 2620 (1981).
20. Gillespie R. J., Robinson E. A.: Can. J. Chem. *42*, 2496 (1964).
21. Brown R. G., Ross S. D.: Spectrochim. Acta, A *28*, 1263 (1972).
22. Wilson W. W., Winfield J. M., Aubke F.: J. Fluor. Chem. *7*, 245 (1976).
23. Qureshi A. M., Levchuk L. E., Aubke F.: Can. J. Chem. *49*, 2544 (1971).
24. Paetzold R., Amoulong H., Růžička A.: Z. Anorg. Allg. Chem. *336*, 278 (1965).
25. Paetzold R., Amoulong H.: Z. Anorg. Allg. Chem. *343*, 70 (1966).
26. Paetzold R., Amoulong H.: Z. Chem. *6*, 29 (1966).

Translated by P. Adámek.