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THE VIBRATIONAL SPECTRUM OF THIONYL FLUORIDE AND ITS OXYGEN-18 ISOTOPOMER[1]

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SUMMARY

The vibrational spectrum of thionyl fluoride, SOF_2, has been reinvestigated by means of high resolution infrared and Raman spectroscopy. Substitution of oxygen-16 by oxygen-18 led to a definitive identification of those modes to which sulfur-oxygen motion makes a large contribution. The band structure of the sulfur-oxygen stretching vibration, which is obscured by Fermi resonance with a combination band in $S^{16}OF_2$, has been resolved in $S^{18}OF_2$. The experimental isotopic splittings are compared with those calculated by previous investigators.

INTRODUCTION

In 1938, Yost [2] quoted a report by Best and Trampe on the Raman spectrum of thionyl fluoride in which six bands were observed and assigned to the fundamental frequencies of vibration. Goehring [3] later reported a Raman spectrum of SOF_2 which seemed to confirm the observations of Best and Trampe. In 1955, O'Loane and Wilson [4] investigated the infrared spectrum while Bender and Wood [5] examined the Raman spectrum of SOF_2. Both groups failed to observe the lowest frequency band at 326 cm^{-1} assigned to ν_4 by Best and Trampe. They concluded that a very weak feature at 940 cm^{-1} resulted from a combination band involving ν_3 and ν_4 and placed the frequency of the missing band at 410 cm^{-1}. Later, Gillespie and Robinson [6] concluded from a study of several sulfur-oxygen compounds that 326 cm^{-1} was a more reasonable frequency for ν_4 in SOF_2. In an investigation of S_2F_2, Seel and Budenz [7] had occasion to record a high resolution infrared spectrum of SOF_2 in which a complex band envelope was

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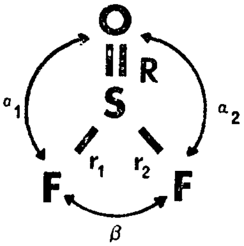
observed from 365 to 409 cm^{-1}; they assigned this complex band to ν_6 and indicated that ν_4 was probably contained within it. These results led Pace and Samuelson[8] to undertake a high resolution infrared and Raman study of SOF_2; a set of highly accurate frequencies was obtained from which an assignment was made. These workers assigned ν_4 to a sharp feature at 377.8 cm^{-1} in the complex band envelope first observed by Seel and Budenz.[7]

Normal coordinate calculations agreeing with the data of Best and Trampe,[9] O'Loane and Wilson,[10,11,12] and Pace and Samuelson[13,14] have been carried out with varying degrees of success. Because of the discrepancies in the assignment of ν_4, we thought it worthwhile to reinvestigate the vibrational spectrum of SOF_2 using the oxygen-18 isotopomer as an aid in making a positive identification of the vibrational modes involving significant oxygen motion.

RESULTS AND DISCUSSION

Thionyl fluoride belongs to point group C_s and possesses six normal modes of vibration, four of symmetry a' and two of symmetry a'', all of which are infrared and Raman active. The symmetry coordinates for SOF_2 (listed below) follow the convention of Cyvin et al.[15]; the diagram at the right shows the internal coordinates used to construct them.

$$S_1 = \Delta R$$
$$S_2 = (\tfrac{1}{2})^{\frac{1}{2}}(\Delta r_1 + \Delta r_2)$$
$$S_3 = (\tfrac{Rr}{2})^{\frac{1}{2}}(\Delta\alpha_1 + \Delta\alpha_2)$$
$$S_4 = r\Delta\beta$$
$$S_5 = (\tfrac{1}{2})^{\frac{1}{2}}(\Delta r_1 - \Delta r_2)$$
$$S_6 = (\tfrac{Rr}{2})^{\frac{1}{2}}(\Delta\alpha_1 - \Delta\alpha_2)$$



Since the mass of the central atom differs considerably from that of the terminal atoms, this set of symmetry coordinates should be a good first approximation to a description of the normal modes. The coordinates S_1, S_3, and S_6 involve significant oxygen motion and ought to be sensitive to substitution of oxygen-16 by oxygen-18. The isotopic shift, calculated using the harmonic-oscillator approximation for the diatomic molecule SO, is 0.962. This would indicate a shift of about 50 cm^{-1} at 1350 cm^{-1} and about 20 cm^{-1} at 500 cm^{-1}. Vibrational spectra are shown in Figs. I and II, and frequencies, along with their assignments, appear in Table I. The assignment, based on oxygen-18 isotopic shifts and polarization measurements, agrees very well with that proposed by Pace and Samuelson(8).

TABLE I

Raman and Infrared Spectral Data for SOF_2

Assign.	$S^{16}OF_2$ (ℓ)	$S^{16}OF_2$ (g)		$S^{18}OF_2$ (g)		$\Delta\nu$	
	R,ν (cm^{-1})	R	IR	R	IR	Exptl.	Calcd.*
		1338	1339				
ν_1 (a')	1314(s,p)	1330	1329	1285	1285	49	50.4
ν_2 (a')	801(s,p)	806	807	806	806	1†	0.9
ν_5 (a'')	724(m,b,dp)	747	747	747	746	1†	0.3
ν_3 (a')	528(s,p)	531	530	521	520	10	9.3
ν_6 (a'')	385(m,dp)	393	††	384	††	9	10.0
ν_4 (a')	366(m,b,p)	376		376		?	2.5

*Isotopic shifts estimated by Lucas and Smith, ref. 16

†Estimated from infrared data

†† Complex envelope

The doublet centered at 1334 cm^{-1} in the infrared spectrum has been ascribed to Fermi resonance of the combination mode $\nu_2 + \nu_3$ with ν_1, the sulfur-oxygen stretching mode [4, 8]. Our data for $S^{18}OF_2$ are clearly consistent with that conclusion. The SO bond lies in the AC plane[16,17] and, thus, an A/C band contour is expected for the SO stretching mode. It is not observed for $S^{16}OF_2$ because of complications introduced by Fermi resonance.

The SO stretch occurs at 1285 cm^{-1} for $S^{18}OF_2$, however, and is sufficiently removed from the combination of ν_2 and ν_3 (1327 cm^{-1}) so that Fermi resonance is not possible. The A/C band contour is clearly observed in the case of $S^{18}OF_2$. The magnitude of the isotopic shift, 49 cm^{-1}, indicates that the SO stretching mode involves very little contribution from other a' modes.

The symmetric FSO deformation, ν_3, has been previously assigned to a strong band at 530 cm^{-1} [4,5,8]. The isotopic splitting of 9 cm^{-1} observed for $S^{18}OF_2$ clearly indicates that this assignment is correct (Fig. I).

The antisymmetric FSO deformation, ν_6, is overlapped strongly by ν_4, the symmetric SF_2 deformation. The better evidence for these assignments was obtained from the Raman spectrum (Fig. I) since the corresponding region in the infrared spectrum was not resolved. Three bands can be ob-

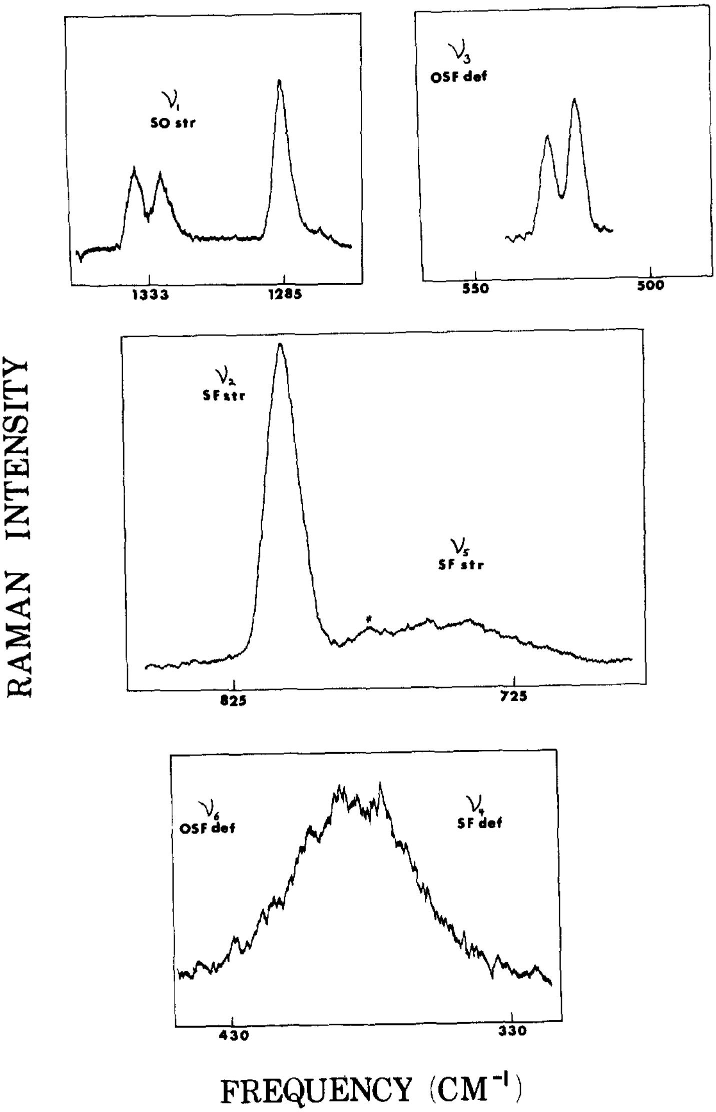


Fig. I Raman Spectrum of $S^{18}OF_2/S^{16}OF_2$ Mixture

Gas phase; power, 660 mw at 488.0 nm; sensitivity, 9500; scan rate, 4 cm^{-1}/min; slits, 8-8.5-8; time constant, auto. (changes in parameters noted below) ν_1: scan rate, 1 cm^{-1}/min. ν_3: scan rate, 0.5 cm^{-1}/min; slits 4-8.5-4. ν_2, ν_5: power, 600 mw; sensitivity, 3000. ν_6, ν_4: sensitivity, 7000; scan rate, 1 cm^{-1}/min. *indicates trace SF_6.

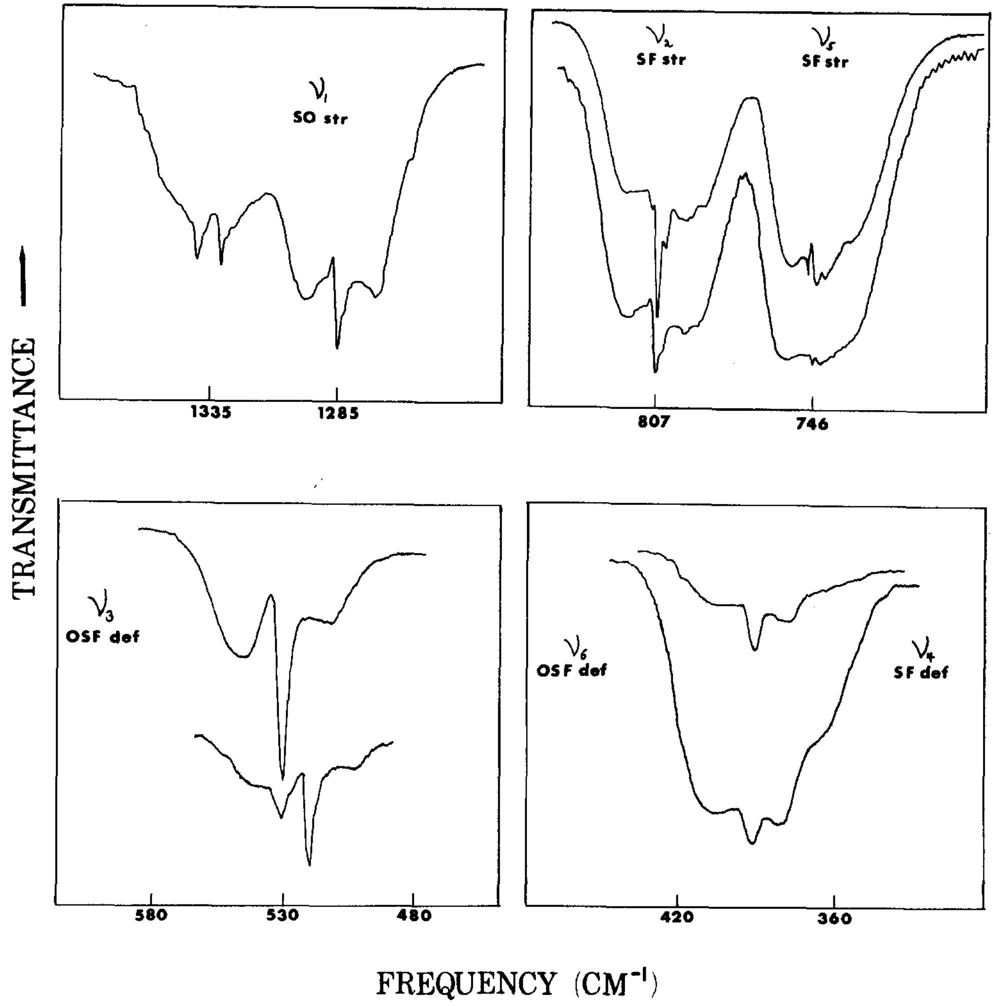


Fig. II Infrared Spectra of $S^{16}OF_2$ and $S^{18}OF_2/S^{16}OF_2$ Mixture

Gas phase, pressure, 8 torr; expansion, 5x; scan time, 1600; slit program, 1000; attenuator speed, 1100; gain, 4.6; suppression, 4 (except as noted). ν_1: mixture. ν_2, ν_5: top, $S^{16}OF_2$; attenuator speed, 526; gain, 8; bottom, mixture. ν_3: top, $S^{16}OF_2$; attenuator speed, 526; gain, 8; bottom, mixture. ν_6, ν_4: top, $S^{16}OF_2$; pressure, 36 torr; attenuator speed, 525; gain 8; bottom, $S^{16}OF_2$; pressure, 267 torr.

served in the region around 400 cm^{-1}, and, although there is considerable noise, the band complex was reproducible. The band at the highest frequency (393 cm^{-1}) was assigned to ν_8 of $S^{16}OF_2$, the next (384 cm^{-1}) to ν_8 of $S^{18}OF_2$, and the band at lowest frequency (376 cm^{-1}) to the ν_4 vibrations of both $S^{16}OF_2$ and $S^{18}OF_2$ which ought to lie close in frequency since that vibration does not involve extensive motion of oxygen.

The symmetric and antisymmetric SF stretching modes of SOF_2 are not expected to shift very much upon oxygen-18 substitution, and the infrared spectrum (Fig. II) bears this out. The top trace shows these bands for $S^{16}OF_2$ and the bottom trace for a mixture of $S^{18}OF_2$ and $S^{16}OF_2$. The bands have broadened in the mixture and the absorption maximum has shifted slightly down in frequency; we estimate the shift to be close to 1 cm^{-1}.

Lucas and Smith [16], in a microwave study of SOF_2, have obtained information on the quadratic force field from the centrifugal distortion parameters. Using their force field, they predicted the vibrational frequencies of $S^{18}OF_2$; the splittings calculated from their frequencies and our experimental data are compared in the last two columns of Table I. Their force field appears to be consistent with the experimental results. Interestingly, the force constant they calculated for the SO stretch is 11.22 mdyne/Å which is slightly higher than that resulting from most other force field calculations for SOF_2 and is slightly higher than that for SO_3 [18].

Since the rotational constants and, hence, the principal moments of inertia were available from a microwave study of $S^{16}OF_2$ and $S^{18}OF_2$ [17], it was possible to apply the Teller-Redlich product rule[19] to the sets of frequencies obtained for SOF_2 and its isotopomer. The corrected rotational constants of Lucas and Smith[16] were used. For the a' modes, the left hand side (0.9440) and the right hand side (0.9389) of the Teller-Redlich expression agreed within 0.5%. For the a'' modes, agreement (0.9758, 0.9728) was within 0.3%. These results are consistent with our assignment.

EXPERIMENTAL

Thionyl fluoride was prepared by hydrolysis of commercial SF_4 (Air Products) according to the following equation:

$$SF_4 + H_2{}^{16}O = S^{16}OF_2 + 2HF. \qquad (2)$$

The HF was removed by passing the mixture over anhydrous NaF. All operations were carried out in a Ni vacuum line with Monel and copper components. The product was subjected to gas chromatographic separation (20% OV-210 on Chromosorb WH-P DMCS 80/100) to remove SF_6 which is a common impurity in commercial SF_4. This procedure was also employed for the preparation of $S^{18}OF_2$ using 99.5 atom precent $H_2{}^{18}O$ (Bio-Rad Laboratories). Since SOF_2 is also a common contaminant of commercial SF_4, $S^{16}OF_2$ was present in the final product. Care must be taken in handling $S^{18}OF_2$ because of the possibility of exchange with ^{16}O-containing species on the walls of vacuum systems and in the gas chromatographic column. The final mixture was about 60% $S^{18}OF_2$ and 40% $S^{16}OF_2$ as judged from infrared absorption measurements; this is only a very crude estimate since the infrared intensities of oxygen-18 containing species can vary considerably from those of the normal species [20,21].

Infrared spectra were recorded on a Perkin-Elmer Model 621 infrared spectrophotometer which was purged with dry air during use. Samples were contained in 10 cm cells equipped with either KBr or CsI windows. Raman spectra were taken using a Beckman Model 700 laser-Raman spectrometer equipped with a two-watt argon-ion laser. Liquid samples were held in Pyrex capillaries, and gaseous samples were held in 7 mm Pyrex heavy walled tubing. Since SOF_2 may react slowly at room temperature with hydrated silica present in glass, spectra were taken immediately after filling the sampling tubes.

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