

## Molecular constants of $\text{PSF}_3$ and $\text{NSF}_3$

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**Abstract.** A complete vibrational analysis of  $\text{PSF}_3$  and  $\text{NSF}_3$  molecules is described in this paper. Urey-Bradley and General valence Force Fields have been computed for these molecules, belonging to  $C_{3v}$  symmetry using the fundamental frequencies obtained from infrared spectra. The mean square amplitudes, Coriolis coupling coefficients and centrifugal distortion constants have also been calculated and presented here.

**Keywords.** Symmetry; vibrational frequencies; normal coordinate analysis; molecular constants.

### 1. Introduction

The molecules  $\text{PSF}_3$  and  $\text{NSF}_3$  possess  $C_{3v}$  symmetry. Their fundamental frequencies are distributed accordingly as  $3a_1 + 3e_1$ .

Considerable amount of work has been done on the spectra of  $\text{PSF}_3$ . Normal coordinate analysis has been carried out by Shurvell (1969) and Koniger and Muller (1977). Recently fresh vibrational assignments have been made for  $\text{PSF}_3$  and  $\text{NSF}_3$  by Koniger *et al* (1979) and they are used for the present work. The internal coordinates, numbering of atoms and the orientation of Cartesian coordinate axes of these molecules are shown in figure 1.

Normal coordinate analysis has been performed by Koniger *et al* (1979) using the general valence force field (GVFF). However, the GVFF has been repeated and in addition Urey-Bradley force field (UBFF) has also been worked out. The mean square amplitudes of vibration, the generalized mean square amplitudes of vibrations, shrinkage constants, Coriolis coupling coefficients and centrifugal distortion constants have been computed and reported here.

### 2. Theoretical considerations

#### 2.1. Molecular force field

UBFF and GVFF are used to obtain the force constants. A reliable set of force constants has been obtained by Wilson's (1939) *F-G* matrix formalism.

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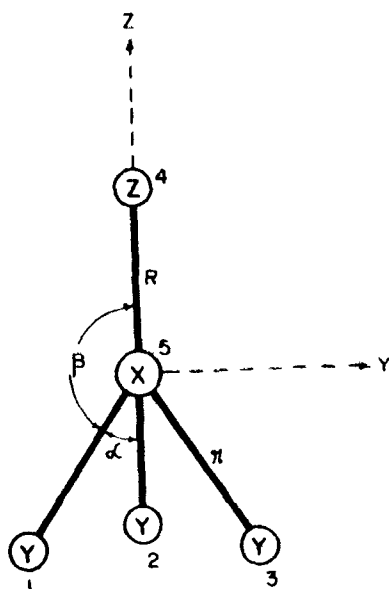


Figure 1. The orientation of Cartesian coordinate axes, the numbering of atom and the internal coordinates of  $XY_3Z$  (pyramidal) type of molecules.

## 2.2. Mean square amplitudes of vibration

The symmetrised mean square amplitude matrix  $\Sigma$  has been evaluated using the relation (Cyvin 1960)

$$\Sigma = L \Delta L',$$

where the  $L$ 's are the characteristic vectors and  $\Delta$  is a diagonal matrix consisting of the mean square values of the normal coordinates given by Block (1932). The generalised mean square amplitudes (Morino and Hirota 1955)  $\langle(\Delta Z)^2\rangle$ ,  $\langle(\Delta X)^2\rangle$  and  $\langle(\Delta Y)^2\rangle$  have been evaluated using the  $\Sigma$  matrix from the relation

$$X = AS,$$

where

$$A = M^{-1} B' G^{-1}.$$

## 2.3. Coriolis coupling coefficients

The active couplings for these molecules are  $a_1 \times e$  and  $e \times e$  belonging to  $\zeta^a$  and  $\zeta^e$  respectively. The Coriolis coupling coefficients have been calculated from the relation given by Meal and Polo (1956)

$$\zeta^a = L^{-1} C^a (L')^{-1},$$

where  $C^a$  matrix is obtained from the geometry and atomic masses.

## 2.4. Centrifugal distortion constants

The centrifugal distortion constants have been computed using the relations given by Kivelson and Wilson (1952, 1953) and by Cyvin *et al* (1968).

### 2.5. Potential energy distribution

To check whether the chosen set of symmetry coordinates contributes maximum to the potential energy associated with the normal coordinates of the molecule, the P.E.D. was calculated using the relation

$$V_{iK} = \frac{100 \cdot F_{ii} L_{iK}^2}{\lambda_K}$$

It is found (table 1) that the contributions to the main diagonal elements are predominant which confirms that the chosen coordinates form a normal mode representation.

### 3. Results and discussion

The molecular parameters, the observed and calculated frequencies of the fundamentals are given in table 1. The valence force constants in GVFF and the Urey-Bradley force constants are presented in table 2. The values agree very well with those calculated by Koniger *et al* (1979). The N-S force constant in  $\text{NSF}_3$  molecule is found to be 12.683 m dyne/Å in general valence and 12.369 in UBFF. This indicates the double bond nature of the N-S bond.

It is slightly larger than  $f_{\text{N-S}}$  in other molecules such as NSCl [ $f_{\text{N-S}}$ : 10.57 m dyne/Å, Namasivayam and Nair 1978; 10.15 m dyne/Å, Peacock *et al* 1969; 10.41 m dyne/Å, Nagarajan *et al* 1967]. This may be due to the delocalisation of electrons in the N-S bond region and consequently enhancement of nitrogen-sulphur back donation of electron density. This results in the reduction of such back donation from fluorine to sulphur. Hence the  $f_{\text{S-F}}$  is comparatively small.

The mean square amplitude quantities at 300 K calculated using  $\Sigma$  matrix elements are presented in table 3. The mean amplitudes of vibration at 300 K for bonded and non-bonded distances are given in table 4, and the generalised mean square amplitudes (both parallel and perpendicular) of vibration along with the shrinkage constants are given in table 5. The mean amplitudes of vibration for non-bonded distances are larger than those for bonded distances. The Coriolis coupling coefficients of  $\text{PSF}_3$  and  $\text{NSF}_3$  molecules are listed in table 6. The Coriolis coupling between the two degenerate modes of the fundamentals  $\nu_4$  and  $\nu_5$  are fairly strong for rotation about the  $Z$  axis. The Coriolis coupling coefficients satisfy the sum rule

$$\sum_{i=4}^6 \zeta_{ii}^2 = \frac{I_A}{2I_B}$$

where  $I_A$  and  $I_B$  are the principal moments of inertia whose calculated values are also given in table 1. The calculated values of  $\zeta_{44}^2$ ,  $\zeta_{55}^2$  and  $\zeta_{66}^2$  agree very well with the experimental values obtained by Koniger *et al* (1979) in the band contour analysis of the spectra and also with the experimental values investigated in the microwave analysis by Small and Smith (1976). These values are also given in table 6 for comparison. The coupling between  $\nu_1$  and  $\nu_4$  is very strong in  $\text{PSF}_3$  while the coupling between  $\nu_2$  and  $\nu_5$  is strong in  $\text{NSF}_3$ .

**Table 1.** Observed and calculated frequencies (cm<sup>-1</sup>), molecular parameters and PED of NSF<sub>3</sub> and PSF<sub>3</sub>.

		NSF <sub>3</sub>		PSF <sub>3</sub>		PED	
	Obs.	Cal.		Obs.	Cal.		
<i>a</i> <sub>1</sub>	<i>v</i> <sub>1</sub>	1522.7	1521.8	93.52 S <sub>1</sub> + 6.48 S <sub>3</sub>	695.5	695.3	73.91 S <sub>1</sub> + 24.46 S <sub>2</sub> + 1.63 S <sub>3</sub>
	<i>v</i> <sub>2</sub>	772.0	771.6	0.40 S <sub>1</sub> + 98.50 S <sub>2</sub> + 1.10 S <sub>3</sub>	985.0	984.8	4.77 S <sub>1</sub> + 93.99 S <sub>2</sub> + 1.24 S <sub>3</sub>
	<i>v</i> <sub>3</sub>	522.9	522.6	0.10 S <sub>1</sub> + 0.70 S <sub>2</sub> + 99.20 S <sub>3</sub>	441.8	441.2	14.87 S <sub>1</sub> + 2.17 S <sub>2</sub> + 82.96 S <sub>3</sub>
<i>e</i> <sub>1</sub>	<i>v</i> <sub>4</sub>	817.4	817.0	98.03 S <sub>4</sub> + 1.16 S <sub>5</sub> + 0.81 S <sub>6</sub>	947.0	947.3	80.08 S <sub>4</sub> + 18.02 S <sub>5</sub> + 1.90 S <sub>6</sub>
	<i>v</i> <sub>5</sub>	429.8	429.0	1.59 S <sub>4</sub> + 91.28 S <sub>5</sub> + 7.13 S <sub>6</sub>	404.7	404.2	1.09 S <sub>4</sub> + 92.56 S <sub>5</sub> + 6.35 S <sub>6</sub>
	<i>v</i> <sub>6</sub>	342.2	342.0	3.50 S <sub>4</sub> + 0.84 S <sub>5</sub> + 95.66 S <sub>6</sub>	274.8	274.3	0.70 S <sub>4</sub> + 1.54 S <sub>5</sub> + 97.76 S <sub>6</sub>
<i>R</i> (X-Z)		1.416 Å			1.86 Å		
<i>r</i> (X-Y)		1.552 Å			1.43 Å		
<i>a</i> (YX <sup>∧</sup> Y)		94.03°			100.3°		
<i>β</i> (YZ)		122.36°			117.2°		
<i>I</i> <sub>a</sub> amu Å		97.98			104.9		
<i>I</i> <sub>b</sub> = <i>I</i> <sub>c</sub> amu Å		16.39			196.1		

Table 2. Valence and Urey-Bradley force constants of  $\text{PSF}_3$  and  $\text{NSF}_3$  in m dyne/Å.

	Valence force constants			Urey-Bradley force constants	
	$\text{PSF}_3$	$\text{NSF}_3$		$\text{PSF}_3$	$\text{NSF}_3$
$f_R$	5.8521	12.6830	$K_R$	5.8269	12.3692
$f_r$	6.2036	4.8850	$K_r$	6.2181	4.5541
$f_{rr}$	0.3410	0.2620	$H_\alpha$	0.6759	0.6043
$f_{rt}$	0.4363	0.1218	$H_\beta$	0.4287	0.2532
$f_\alpha - f_{\alpha\alpha}$	0.5390	0.7210	$f_{\gamma\gamma}$	0.2349	0.2252
$f_\beta - f_{\beta\beta}$	0.7338	0.3190	$f_{\gamma\delta}$	0.1762	0.1410
$f_{R\beta}$	0.7243	0.3372			
$f_{r\beta}$	0.6362	0.4131			
$f_{r\alpha}$	0.0411	0.1862			
$f_{\alpha\beta}$	-0.0237	-0.0460			

Table 3. Mean square amplitudes of vibration of  $\text{PSF}_3$  and  $\text{NSF}_3$  at 300 K ( $10^{-4} \text{ \AA}^2$ ).

	$\text{PSF}_3$	$\text{NSF}_3$
$\sigma_R$	16.0720	11.5866
$\sigma_r$	12.9593	17.9935
$\sigma_{rr}$	-0.7306	-0.4385
$\sigma_{rt}$	-1.2124	-1.2126
$\sigma_\alpha - \sigma_{\alpha\alpha}$	94.3682	119.6820
$\sigma_\beta - \sigma_{\beta\beta}$	81.3021	131.1066
$\sigma_{r\alpha}$	-8.1070	-3.3928
$\sigma_{r\beta}$	-5.2334	-7.9621
$\sigma_{R\beta}$	-2.3510	-5.9198
$\sigma_{\alpha\beta}$	17.6240	8.7983

Table 4. Mean amplitudes of vibration (Å) of bonded and nonbonded distances of  $\text{PSF}_3$  and  $\text{NSF}_3$  at 300 K.

	$\text{PSF}_3$	$\text{NSF}_3$
$l_{x-y}$	0.0401	0.0340
$l_{x-z}$	0.0360	0.0424
$l_{y\dots z}$	0.0723	0.0764
$l_{y\dots z}$	0.0427	0.0716

Table 5. Generalised mean square amplitudes of vibration ( $10^{-4}\text{\AA}^2$ ) and shrinkage constant ( $\text{\AA}$ ) of  $\text{PSF}_3$  and  $\text{NSF}_3$ .

Molecule	Atom Pair	Parallel $\langle (\Delta z)^2 \rangle$	Perpendicular		Shrinkage
			$\langle (\Delta x)^2 \rangle$	$\langle (\Delta y)^2 \rangle$	
$\text{PSF}_3$	P—S	16.0712	27.3312	27.3312	..
	P—F	12.9521	29.6321	41.2213	..
	F...F	52.2830	16.3217	37.9424	0.0026
	S...F	18.2137	23.1522	36.5628	0.0082
$\text{NSF}_3$	N—S	11.5832	21.7372	15.4000	..
	S—F	17.9922	53.5862	68.2162	..
	F...F	58.3631	134.6021	154.2133	0.0052
	N...F	51.2216	72.1325	83.2165	0.0093

Table 6. Coriolis coupling coefficients of  $\text{PSF}_3$  and  $\text{NSF}_3$  molecules.

Coupling $a_1 \times e :$	$\text{PSF}_3$	$\text{NSF}_3$
$\zeta_{14}$	0.6724	0.3453
$\zeta_{15}$	-0.6631	-0.3112
$\zeta_{16}$	0.0492	0.5138
$\zeta_{24}$	-0.2961	-0.2191
$\zeta_{25}$	0.1276	0.8465
$\zeta_{26}$	0.3149	0.1049
$\zeta_{34}$	0.3911	0.1739
$\zeta_{35}$	0.3462	0.0332
$\zeta_{36}$	-0.5228	-0.5082
Coupling $e \times e$		
$\zeta_{44}^e$	0.5813	0.5612
	(0.57)*	(0.5)*
	(0.59)**	
$\zeta_{55}^e$	-0.5891	-0.2330
	(-0.56)*	(-0.2)*
	(-0.49)**	(-0.2256)*
$\zeta_{66}^e$	0.2592	0.1482
	(0.26)*	(0.15)*
	(0.16)**	(0.1567)†
$\zeta_{45}^e$	-0.6525	0.4070
$\zeta_{46}^e$	0.5441	0.6066
$\zeta_{56}^e$	0.4631	-0.0177

\* band contour analysis ; Koniger *et al* (1979), \*\* spectral analysis ; Clark and Ellestad (1976)

† microwave analysis ; Small and Smith (1976)

Table 7. Centrifugal distortion constants of  $PSF_3$  and  $NSF_3$  molecules (kHz).

	$PSF_3$	$NSF_3$
$D_J$	1.0678 (1.082)*	0.2971 (0.2742)*
$D_K$	-1.4735	-1.1863
$D_{JK}$	1.9763 (1.9047)*	1.9363 (1.961)*

\* Band contour analysis: Koniger *et al* (1979)

The centrifugal distortion constants are presented in table 7. Since these molecules are symmetric tops, the centrifugal stretching coefficients  $R_5$ ,  $R_6$  and  $\delta_J$  vanish. The other coefficients  $D_J$ ,  $D_K$  and  $D_{JK}$  have been evaluated. These values agree very well with those obtained by Koniger *et al* (1979) in the band contour analysis.

#### 4. Conclusion

It is expected that the analysis presented here would help us in knowing the spectroscopic properties of these molecules. The mean amplitude calculations are useful in the interpretation of electron diffraction studies in the molecular structure determinations and the shrinkage constants are helpful in the refinement of bond lengths obtained experimentally. The Coriolis constants are used in the interpretation of vibration-rotation spectra of these molecules. The centrifugal distortion constants calculated here for  $NSF_3$  will be useful in the study of microwave spectra of the molecule.

#### References

- Block F 1932 *Z. Phys.* **74** 295  
 Clark J H and Ellestad O H 1975 *J. Mol. Spectrosc.* **56** 386  
 Cyvin S J 1960 *Acta Polytech. Scand.* Ph **6** 279  
 Cyvin S J, Cyvin B N and Hagen G 1968 *Z. Naturforsch.* **A23** 1649  
 Kivelson D and Wilson Jr E B 1952 *J. Chem. Phys.* **20** 1575  
 Kivelson D and Wilson Jr E B 1953 *J. Chem. Phys.* **21** 1229  
 Koniger F and Muller A 1977 *Spectrosc. Chim. Acta* **A33** 971  
 Koniger F, Muller A and Blom C E 1979 *J. Mol. Spectrosc.* **77** 76  
 Meal J H and Polo S R 1956 *J. Chem. Phys.* **24** 1119  
 Morino Y and Hirota E 1955 *J. Chem. Phys.* **23** 737  
 Nagarajan G, Muller A, Glemser O and Cyvin S J 1967 *Spectrosc. Chim. Acta* **A23** 2863  
 Namasiyayam R and Viswanatha Nair 1978 *Z. Phys. Chem. Leipzig* **259** 1117  
 Peacock C J, Heidborn U and Muller A 1969 *J. Mol. Spectrosc.* **30** 338  
 Shurvell H F 1969 *Spectrosc. Chim. Acta* **A25** 973  
 Small C E and Smith J G 1976 *Mol. Phys.* **32** 1247  
 Wilson Jr E B 1939 *J. Chem. Phys.* **7** 1047