

LASER EXCITED RAMAN SPECTRUM AND VIBRATIONAL ANALYSIS OF THIOPHOSPHORYL DIFLUOROCHLORIDE

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الخلاصة :

تمَّ رصد طيف (رامان) المُحرَّض لثاني فلوركلوريد الفوسفوريل باستخدام جهاز (كاري - ٨٢) للمطيافية الضوئية المُشعَّة لليزر الناتج عن غاز الأرجون . وقد تمَّ تعيين الترددات المقاسة حسب نسق الترددات المختلفة من الأساسية الى المركبة بافتراض التناظر حسب المجموعة النقطية C_s . وباستخدام الترددات المرصودة تمَّ عمل تحليل الإحداثيات المتعامدة للجزيء . والبحث يناقش النتائج بشكل موجز .

ABSTRACT

The laser Raman spectrum of thiophosphoryl difluorochloride has been recorded by using a Cary Model 82 grating spectrophotometer with an argon laser source. The observed frequencies are assigned to the various modes of vibration in terms of fundamentals and combinations, by assuming C_s point group symmetry. Using the observed frequencies a normal co-ordinate analysis has also been carried out for the molecule. The results are briefly discussed.

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INTRODUCTION

A number of workers [1-4] have studied the vibrational spectra of thiophosphoryl trichloride and trifluoride. The infrared and Raman spectra of thiophosphoryl difluorochloride have been reported by Durig and Clark [5]. But their vibrational assignments concerning PF symmetric and antisymmetric stretching, FPF bending and PS wagging vibrations are in doubt. Further descriptions of bending modes differ greatly from literature values. The present work was undertaken to reinvestigate the vibrational spectrum of SPF_2Cl through laser Raman spectroscopy and to arrive at a satisfactory vibrational assignment for this molecule.

EXPERIMENTAL DETAILS

The thiophosphoryl difluorochloride has been prepared by the method suggested by Booth and

Cassidy [6] and used in the liquid state for the present work. The polarized laser Raman spectra of the thiophosphoryl difluorochloride has been recorded using the 488 nm line of a 4W Ar^+ laser for excitation in the region $100 - 4000 \text{ cm}^{-1}$ on a Cary Model 82 grating spectrophotometer. The frequencies for all the sharp bands are accurate to $\pm 1 \text{ cm}^{-1}$ (Figure 1).

RESULTS AND DISCUSSION

Thiophosphoryl difluorochloride belongs to the point group C_s and has only one plane of symmetry. From the symmetry of the molecule, there are nine fundamentals. Out of the nine fundamentals, six vibrations are symmetric (A' species) with respect to the plane of symmetry and hence they are expected to be polarized. The rest are asymmetric vibrations (A'' species) and are depolarized. The observed frequencies of SPF_2Cl along with their relative

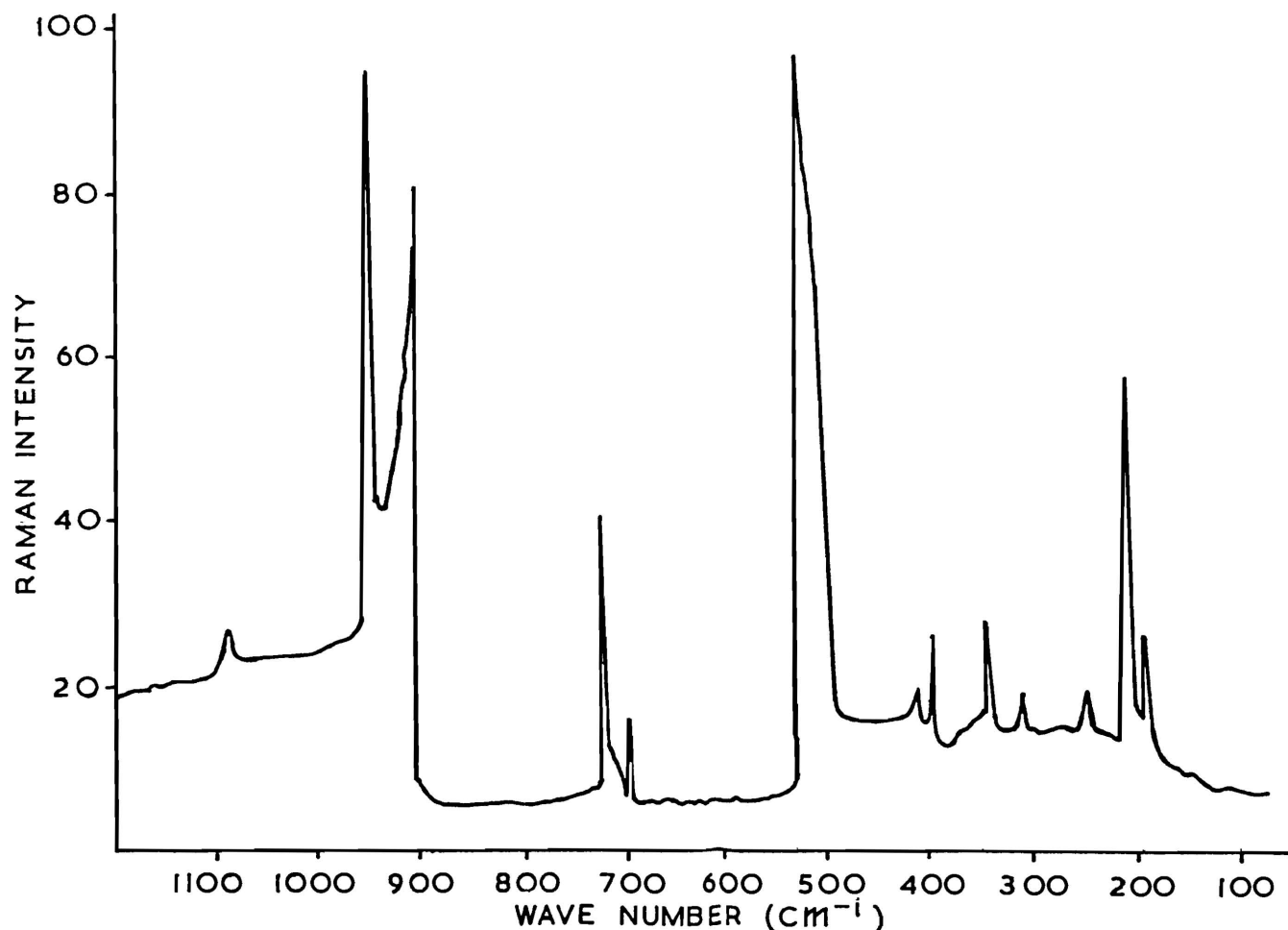


Figure 1. Laser Raman Spectrum of Thiophosphoryl Difluorochloride.

intensities and probable assignments are presented in Table 1.

With the help of thiophosphoryl halides and phosphorus halides [4, 7–9] the observed frequencies are assigned in a satisfactory manner. The strong polarized line at 917 cm^{-1} is assigned to the P–F symmetric stretch $\nu_1(A')$ and the strong line at 942 cm^{-1} is assigned to the P–F antisymmetric stretch $\nu_7(A'')$ without any doubt. The P–F stretch in phosphorus pyramidal halides adds support to this assignment. [4, 7–9].

Comparison with the PCl_3 stretching frequency in POCl_3 [10], PSCl_3 [5], PCl_3 [11] and PCl_3F_2 [12] leads to the proposal that the polarized band at 537 cm^{-1} is assigned to the P–Cl stretching, mode $\nu_2(A')$. The polarized medium band at 731 cm^{-1} is assigned to P–S stretching $\nu_3(A')$, which agree quite well with the P–S stretching frequency in PSCl_3 and PSBr_3 [4, 7]. The band centered at 394 cm^{-1} is assigned to the $\text{F}\hat{\text{P}}\text{F}$ bending $\nu_4(A')$ and this agrees quite well with the $\text{F}\hat{\text{P}}\text{F}$ bending in PSF_3 [13] and POF_3 [14]. The depolarized band at 362 cm^{-1} is assigned to the PF_2 wagging (out-of-plane) vibration $\nu_8(A'')$ in the present work. The lowest frequency between 198 cm^{-1} is assigned to the P–S wagging vibration $\nu_6(A')$ since the wagging frequency is always low. Further, it is known that P–S wagging $\nu_6(A')$ and SPCl torsion $\nu_9(A'')$ differ by more than 15 cm^{-1} . Hence the medium intensity

band at 211 cm^{-1} is assigned to the SPCl torsional mode $\nu_9(A'')$ [15]. The remaining very weak frequency at 318 cm^{-1} is assigned to the PF_2 wagging vibration $\nu_5(A')$. The rest of the observed frequencies in Table 1 may be accounted for as resulting from allowed combination and overtones of the selected nine fundamentals giving additional support to their choice.

The normal coordinate analysis of thiophosphoryl difluorochloride has been carried out using Wilson's F–G matrix method, on the basis of a C_s point group, using a general quadratic valence force field. The structural parameters employed in the present work are P–S 186.4 pm, P–F 153.5 pm, P–Cl 198.5 pm., $\text{F}\hat{\text{P}}\text{F} = 100.5^\circ$, $\text{S}\hat{\text{P}}\text{Cl} = 118^\circ$ and $\text{S}\hat{\text{P}}\text{F} = 116.2^\circ$ [16]. In Table 2 and 3 the molecular constants of the molecule under study are given. The evaluated major potential constants agree well with earlier works [17, 18].

Although electron diffraction data concerning mean amplitudes are not available for this molecule the vibrational mean amplitudes for P–F, P–S, and P–Br and for non-bonded atoms are characteristic. They also agree well with Muller's values [17, 18].

The evaluated molecular constants which are in the expected range add weight to suggested assignments for this molecule. Also, to check whether the chosen set of vibrational frequencies contributes to a maximum extent to the potential energy associated

Table 1. Assignment of Vibrational Frequencies of Thiophosphoryl Difluorochloride

Symmetry Class	No.	Description	Position of the bands (cm^{-1}) and Intensity	Depolarization $P = I_{\perp}/I_{\parallel}$	Calculated	PED %
A'	ν_1	P–F symmetric stretch	917 s (p)	0.16	926	100 S ₁
	ν_2	P–Cl stretching	537 vs (p)	0.20	539	100 S ₂
	ν_3	P–S stretching	731 m (p)	0.17	726	100 S ₃
	ν_4	F $\hat{\text{P}}\text{F}$ bending	394 w (p)	0.27	383	94 S ₄
	ν_5	PF_2 rocking	318 vw (p)	0.25	310	92 S ₅
	ν_6	P–S wagging	198 w (p)	0.40	191	89 S ₆
		$\nu_3 + \nu_6$ $2\nu_4 - \nu_2$	1096 w 255 vw			
A''	ν_7	P–F antisymmetric stretch	942 vs (dp)	0.95	938	99 S ₇
	ν_8	PF_2 wagging	362 w (dp)	3.1	355	91 S ₈
	ν_9	SPCl torsion	211 m (dp)	1.36	206	90 S ₉
		$\nu_1 - \nu_9$	699 w			
		$\nu_7 - \nu_2$	411 w			

vs – Very strong, s – Strong, m – Medium, w – Weak, vw – Very weak, p – Polarized, dp – Depolarized.

Table 2. Valence Potential Constants (10^2 Nm^{-1}) of Thiophosphoryl Difluorochloride.

$f_r(\text{P}-\text{Cl})$	2.85	f_{DR}	0.31
$f_D(\text{P}-\text{S})$	6.81	f_{Dd}	0.40
$f_d(\text{P}-\text{F})$	5.60	f_{Rd}	0.22
$f_\alpha(\text{FPF})$	0.10	f_{dd}	0.32
$f_\beta(\text{ClPS})$	0.45	$f_{d\alpha}$	0.48
$f_\gamma(\text{FPFCl})$	0.85	$f_{R\beta}$	0.21
$f_\delta(\text{FPS})$	0.52	$f_{D\beta}$	0.18
		$f_{R\gamma}$	0.20
		$f_{D\delta}$	0.30
		$f_{d\gamma}$	0.28
		$f_{d\delta}$	0.30

Table 3. Vibrational Mean Amplitudes (pm) for Thiophosphoryl Difluorochloride at 298.16 K

$l(\text{P}-\text{F})$	4.20
$l(\text{P}-\text{S})$	3.75
$l(\text{P}-\text{Cl})$	4.79
$l_p(\text{Cl} \dots \text{F})$	4.41
$l_q(\text{Cl} \dots \text{S})$	8.48
$l_r(\text{F} \dots \text{S})$	6.52
$l_s(\text{F} \dots \text{F})$	10.02

with the normal coordinates of the molecule, the potential energy distribution has been calculated using the relation,

$$\text{P.E.} = F_{ii} L_{ik}^2 / \lambda_k$$

P.E. is the contribution of the i th symmetry coordinate to the potential energy of the vibration whose frequency is ν_k . (F_{ii} = potential constants, L_{ik} = L matrix elements, and $\lambda_k = 4\pi^2 C^2 \nu_k^2$).

The calculated frequencies are also listed along with the observed frequencies in Table 1.

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