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VIBRATIONAL SPECTRA AND NORMAL COORDINATE ANALYSIS OF POTASSIUM FLUOROPHOSPHATE

S MOHAN, S DURAI *and* S SRINIVASAN

Division of Applied Sciences, Anna University, Madras Institute of Technology, Madras-600044, India

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This paper presents the infrared spectrum. Fourier far infrared spectrum and Laser Raman spectrum of potassium fluorophosphate from 525–4000cm^{-1}, 100–650cm^{-1} and 50 to 4000cm^{-1} respectively. The vibrational analysis has been made for fluourophosphate ion on the basis of tetrahedral C_{3v} symmetry and the general quadratic valence force field are reported. The fundamental frequencies for fluorophosphate ion are A_1 = 706, 930 and 530cm^{-1} and E = 1008, 481 and 370cm^{-1}. Further using the values of potential constants other molecular constants are also evaluated. The thermodynamic properties are presented over the temperature range 298.16 to 1000 K.

Key Words : Vibrational Spectra; Fluorosulphate Ion; Vibrational Analysis; Force Field

INTRODUCTION

IN the course of our investigation on the study of characteristic constants of tetrahedral molecules, our attention has been turned to the oxoanion, where the 'Z' is the fluorine atom (PO_3F^{--}). The vibrational frequencies of tetrahedral molecules and ions of substituted halides and oxoanions are available in the literature.[1-4] Either infrared or the laser Raman data had not been reported for potassium fluorophosphate. The present study has been initiated to find the vibrational frequencies of fluorophosphate ion and to determine whether the C_{3v} configuration may be adopted to explain the vibrations of this molecule in agreement with normal coordinate analysis. In this paper the infrared and Fourier far infrared spectra the potassium fluorophosphate have been reported. The vibration frequencies of the fluorophosphate ion have been assigned on the basis of tetrahedral C_{3v} symmetry.

EXPERIMENTAL

Potassium fluorophosphate was obtained from Ranbaxy Laboratory Chemicals, India. The infrared spectrum of potassium fluorophosphate has been recorded in Perkin Elmer IR-257 double beam grating spectrometer in the region 625–4000 cm^{-1}. The Fourier far infrared has been recorded in Polytech FIR 30 from 100–650cm^{-1}. The Laser Raman Spectrum has also been recorded on Cary model 82 spectrophotometer equipped with argon laser of power 4000mw in the region 50 to 4000cm^{-1}. The observed frequencies are listed in Table I. The frequencies of all sharp bands are expected to be accurate to $\pm$ 1cm^{-1}.

FREQUENCY ASSIGNMENT

Vibrational frequencies are assigned for fluorophosphate ion in the present investigation on the basis of C_{3v} symmetry. The molecules belonging to this symmetry give rise to six frequencies—three belonging to nondegenerate vibrations of A_1 type while the other three to doubly degenerate vibrations of E-type. The fundamentals observed for fluorophosphate ion are 1008, 930, 706, 530, 481 and 370 cm^{-1}. For non-planar molecules one expects $\nu_4(E)$ mode to be much more intense than $\nu_2(A_1)$ mode. On this basis the most intense band at 1008cm^{-1} is assigned to P–O assymmetric stretch vibration and the band at 930cm^{-1} is assigned to P–O symmetric stretching. This assignment agrees quite well with P-O vibration in PO_3S^{3-} ion.[5] The other very strong band at 706cm^{-1} assigned to P-F stretching appears to be reasonable with P–F vibration of POF_3 molecule.[6] The present assignment assumes low value in comparison with the P–F vibration of POF_3 molecule due to the ionic nature of the present compound. The band at 530cm^{-1} is the combination vibration of $O\hat{P}F$ and $O\hat{P}O$ deformation. OPF bending frequency is assigned to the band at 481cm^{-1}. This assignment also agrees favourably with the corresponding bending vibration in POF_3 molecules.[6] The remaining frequency 370cm^{-1} is assigned to $O\hat{P}O$ bending. This assignment agrees quite well with $O\hat{P}O$ vibration in PO_3S ion.[7] The rest of the frequencies in Table I, may be accounted for, as

TABLE I

Infrared, Fourier far infrared and laser Raman frequencies (cm^{-1}) *of fluorophosphate ion in potassium fluorophosphate*

Frequency Far Infrared	Intensity*	Assignment	Intensity	Frequency Raman
122	M	$\nu_5 - \nu_6$		
370	W	ν_6		
481	M	ν_5	M	480
530	VS	ν_3	M	536
Infrared				
706	VS	ν_1	S	711
812	W	$2\nu_2 - 2\nu_3$		
905	W	$2\nu_2 - 2\nu_5$		
930	S	ν_2	S	934
1008	VS	ν_1	VS	1010
1162	S	$2\nu_2 - \nu_4$	S	1160
1541	W	$2\nu_3 + \nu_5$		
1655	W	$2\nu_4 - \nu_6$		
1995	W	$2\nu_3 + \nu_2$	M	2006
2020	M	$2\nu_4$	M	2020
2220	M	$2\nu_2 + \nu_6$		

*VS : Very strong S : Strong
M : Medium W : Weak

resulting from allowed combinations and overtones of the selected six fundamentals which give additional support to their choice.

Normal Coordinate Analysis

A normal coordinate analysis of fluorophosphate ion has been carried out using Wilson's F–G matrix method using General quadratic valence force field and molecular kinetic constants on the basis of C_{3v} symmetry and a set of force constants has been reported. The symmetry coordinates and details of procedure are given in earlier papers.[8]

The kinetic constants, force constants, the compliance constants and the mean square amplitudes are given in Table II.

Table II

Values of kinetic constants (10^{-23}g), *force constants* (10^5 dynes/cm) *compliance constants* (*A*/*mdyne*) *and vibrational mean square amplitudes* (10^{-3}Å^2) *both bonded and non-bonded at* 298.16 *K*

	D d Dd	dd α β	D d'_α d''_α	$d\theta'$ θ' $\alpha\alpha$
Kinetic constants	2.5428 1.1296 0.1717	0.6908 0.1646 0.1775	− 0.1188 − 0.1070 0.1036	− 0.1100 − 0.0175 − 0.0374
Valence force constants	4.1496 6.6422 0.2803	0.3747 0.0954 0.1943	− 0.1185 − 0.0349 0.0674	− 0.0930 − 0.0725 − 0.0682
Compliance constants	0.2771 0.1644 − 0.0162	− 0.0099 2.0037 1.2877	0.0939 0.0485 − 0.0883	0.0757 − 0.3593 − 0.6154
Bonded mean square amplitudes	2.0559 1.6836 − 0.3538	− 0.0965 10.8194 4.9083	0.7901 0.4649 − 0.5601	0.5569 − 2.6250 − 2.8874
Non-bonded mean square amplitudes		σ_p 6.5563	σ_q 6.6154	

The stretching force constants P–F and P–O are in the expected range. The P–O stretching force 6.4215 × 10^{+5} dynes/cm agrees quite well with P–O stretching force constant of PO_4^{3-} ion (6.8241 × 10^5 dynes/cm).[9] The present value of P–F stretching force constants agrees quite well with P–F stretching force constants in POF_3 molecule.[8]

The interaction force constants $f_{D\alpha}$ and $f'_{d\alpha}$ are negative for this ion as expected. Also the case of bond angle interaction is negative for the kinetic constants. All the individual potential constants are given in Phosphorofluoridate ion.

The compliance constants which is a measure of bond strength and interaction show a trend opposite to that of force constants.

The vibrational mean square amplitude and the mean amplitudes for the bonded and non-bonded distances are in the expected range and exhibit characteristic values for the P–F and P–O bonds.

The Coriolis coupling constants and the centrifugal distortion constants are given in Table III. The Coriolis coupling constants obtained in the present investigation are found to obey the linear and quadratic sum rules derived by Boyd and Longuet Higgins[10] respectively. The high values of the Coriolis constants ζ_{15}, ζ_{34}, ζ_5 and ζ_6 in the PO_3F ion suggest that the coupling between the vibration concerned is more significant than others.

TABLE III

Vibrational mean amplitudes (10^{-2}A) at 298.16 K; *Coriolis coupling constants and centrifugal distortion constants* (MHz)

Mean amplitudes	Coriolis coupling constants						Centrifugal distortion constants
	$(E \times E)^z$ type		$(A_1 \times E)^{xy}$ type		$(E \times E)^{xy}$ type		
l_D	ζ_4	ζ_{45}	ζ_{14}	ζ_{15}	ζ_{16}	ζ_{45}	D_J
l_d	ζ_5	ζ_{46}	ζ_{24}	ζ_{25}	ζ_{26}	ζ_{46}	D_{JK}
l_p	ζ_6	ζ_{56}	ζ_{34}	ζ_{35}	ζ_{36}	ζ_{56}	L_K
l_q							
4.5342	0.4097	− 0.2520	0.4260	− 0.8149	0.1773	0.2245	1.8198
4.1032	0.5497	0.8216	− 0.0254	0.1180	− 0.0039	0.2321	− 6.1171
8.0971	− 0.5074	− 0.0024	0.7230	0.3101	0.4635	0.4119	2.6928
8.1335							

The rotational distortion constants for fluorophosphate ion are also in the expected range. As expected the D_{JK} value is negative for this ion.

The thermodynamic fuuctions for PO_3F ion have been evaluated for the ideal gas state at 1 atm. assuming the rigid rotor harmonic oscillator model. The influence of spin contribution, anharmonicity and non-rigidity are neglected. The contribution to the vibrational part of these thermodynamic functions have been calculated from tables given by Johnson *et al.*[11] The values are presented in Table IV. These constants are useful to interpret the exprimental results of thermodynamic properties.

TABLE IV

Heat content, free energy, heat capacity (in cale deg^{-1} mole^{-1}) and entropy of potassium fluorophosphate ion for the ideal gaseous state at 1 atmospheric pressure

T (K)	$\frac{(H_0 - E_0)}{T}$	$\frac{(F_0 - E_0)}{T}$	C_p^0	S^0
298.16	9.9948	322.7639	13.6010	332.7631
300	10.0217	323.2629	13.6362	334.3895
400	11.1750	326.2976	15.4568	337.4727
500	12.1555	328.8989	16.6788	341.0543
600	12.9887	331.2033	17.4878	344.1927
700	13.6729	333.2575	18.0362	346·9307
800	14.2472	335.1253	18.4235	349.3726
900	14.7194	336.8229	18.6979	351.5422
1000	15.1331	338.4095	18.9054	353.5367

CONCLUSIONS

A complete vibrational analysis of PO_3F ion using frequencies obtained from infrared, Fourier far infrared and laser Raman spectra is available on the basis of C_{3v} symmetry in the present study.

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