

Mean Amplitudes of Vibration of the Tetrafluorophosphate, PF_4^- , Anion

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Mean amplitudes of vibration of the pseudo-trigonal bipyramidal PF_4^- anion have been calculated from vibrational spectroscopic data in the temperature range between 0 and 1000 K. The results are briefly discussed in relation to the structural peculiarities of the anion and some comparisons with related species are made.

Key words: Tetrafluorophosphate; Mean Amplitudes of Vibration; Bond Properties.

Although salts of the PBr_4^- and PCl_4^- anions are well-known [1–3], a salt of the corresponding fluoroanion could only recently be prepared by reaction between $\text{N}(\text{CH}_3)_4\text{F}$ and PF_3 using either CH_3CN , CHF_3 or excess PF_3 as a solvent [4], and the novel PF_4^- anion is stabilized in the form of its tetramethylammonium salt, $\text{N}(\text{CH}_3)_4\text{PF}_4$. It possesses a pseudo-trigonal bipyramidal structure with two longer (1.74 Å) axial bonds and an equatorial plane containing two shorter P-F bonds (1.60 Å) and a sterically active free electron pair.

As a continuation of our studies concerning vibrational and bond properties of simple novel inorganic species, we have now calculated the mean amplitudes of vibration of this interesting anion in order to attain a wider insight into its bond characteristics and peculiarities. For comparative purposes we have also undertaken a recalculation for the isoelectronic SF_4 molecule.

The calculations were performed with the method of the characteristic vibrations of Müller and co-workers [5–7]. The necessary vibrational and structural data for PF_4^- were taken from [4]. For SF_4 , the structural parameters were taken from [8] and the vibrational data from [9].

The obtained values, in the temperature range between 0 and 1000 K, are shown in Table 1 for PF_4^- and in Table 2 for SF_4 .

A comparison of the results obtained for SF_4 with those previously calculated for this molecule [10] shows

Table 1. Calculated mean amplitudes of vibration (in Å) for the PF_4^- anion.

T (K)	$u_{\text{P-F(eq)}}$	$u_{\text{P-F(ax)}}$	$u_{\text{FF(eq)}}$	$u_{\text{FF(ax)}}$	$u_{\text{F(eq)F(ax)}}$
0	0.0431	0.0545	0.057	0.065	0.048
100	0.0431	0.0546	0.057	0.066	0.048
200	0.0433	0.0563	0.059	0.069	0.051
298.16	0.0442	0.0603	0.063	0.076	0.056
300	0.0442	0.0604	0.063	0.076	0.056
400	0.0460	0.0654	0.068	0.083	0.062
500	0.0482	0.0706	0.073	0.091	0.067
600	0.0506	0.0758	0.078	0.098	0.072
700	0.0532	0.0809	0.083	0.105	0.078
800	0.0558	0.0857	0.088	0.111	0.082
900	0.0583	0.0904	0.093	0.117	0.087
1000	0.0609	0.0948	0.097	0.123	0.091

Table 2. Calculated mean amplitudes of vibration (in Å) for SF_4 .

T (K)	$u_{\text{S-F(eq)}}$	$u_{\text{S-F(ax)}}$	$u_{\text{FF(eq)}}$	$u_{\text{FF(ax)}}$	$u_{\text{F(eq)F(ax)}}$
0	0.0401	0.0461	0.053	0.057	0.045
100	0.0401	0.0461	0.053	0.057	0.045
200	0.0402	0.0466	0.054	0.058	0.047
298.16	0.0407	0.0482	0.056	0.061	0.052
300	0.0407	0.0482	0.056	0.061	0.052
400	0.0418	0.0508	0.059	0.065	0.056
500	0.0434	0.0538	0.063	0.070	0.061
600	0.0453	0.0571	0.067	0.075	0.066
700	0.0473	0.0603	0.071	0.080	0.070
800	0.0494	0.0635	0.075	0.084	0.075
900	0.0515	0.0666	0.079	0.088	0.079
1000	0.0536	0.0697	0.083	0.093	0.083

a good agreement, especially for the mean amplitude values of the S-F bonds, whereas for the non bonded pairs some discrepancies are observed. These differences probably arise from the different set of spectroscopic data [11] used in the previous calculations. On the other hand, the present results are also in reasonable agreement with amplitude values derived from electron diffraction data [12].

A comparison of the data presented in Tables 1 and 2 shows that the mean amplitude of vibration for the bonded atoms are always higher in the PF_4^- anion than in the isoelectronic SF_4 molecule. Besides, the axial bonds present higher amplitude values than those of the equatorial bonds in both species. These results are in agreement with the respective force constants, i.e.: $f_r(\text{S-F}_{\text{eq}}) = 5.405 > f_r(\text{P-F}_{\text{eq}}) = 3.940$ and $f_r(\text{S-F}_{\text{ax}}) = 3.150 > f_r(\text{P-F}_{\text{ax}}) = 1.822 \text{ mdyn/Å}$ [4]. Moreover, the remarkable low value of $f_r(\text{P-F}_{\text{ax}})$ correlates with specially high mean amplitude values for this same bond.

The commented trends are those usually observed in pairs of isoelectronic species of this type, in which mean amplitude values of the X–F bond diminish with increasing charge of the central atom, reflecting the expected bond strengthening [13]. Consistent with its weaker bonds, also the temperature dependence is much greater for the bonds of the anion than for those of the molecule.

The analysis of these trends may be extended to other isoelectronic species. Thus, the ClF_4^+ cation shows, for the equatorial Cl–F bond, a mean amplitude value comparable to that of SF_4 (0.0417 Å, at 298 K), whereas that of the axial bonds shows clearly the expected diminution (0.0458 Å, at 298 K) [14] when compared with that of SF_4 (i.e., the bond reinforcement on going from S(IV) to Cl(V)). Interestingly, ClO_2F_2 , another isoelectronic species, also containing Cl(V), shows an unexpectedly high mean amplitude of vibration for its axial Cl–F bonds (0.0622 Å, at 298 K) [15] pointing to particularly weak axial bonds with a highly ionic character. Also in PF_4^- a similar effect is responsible for the commented weakening of the P–F axial bonds, in which a strong contribution from semi-ionic, three-center four-electron bonding is evident [4].

For the mean amplitudes of vibration of the non-bonded pairs the trends are not so straightforward. In

general, all of them show a greater temperature dependence in the case of PF_4^- . Interestingly, for SF_4^- , $u_{\text{FF}(\text{eq})}$ and $u_{\text{F}(\text{eq})\text{F}(\text{ax})}$ become comparable at increasing temperatures, whereas for PF_4^- they remain different in the full temperature range. But, on the other hand, at 298.16 K, in both isoelectronic species these non-bonded pairs show the same trends, i.e., $u_{\text{FF}(\text{ax})} > u_{\text{FF}(\text{eq})} > u_{\text{F}(\text{eq})\text{F}(\text{ax})}$.

Finally, a comparison of the mean amplitudes of PF_4^- with those of other P(III) compounds also seems interesting. At 298 K, the equatorial P–F bonds, present only slightly higher amplitude values than those calculated for PF_3 (0.041 Å) [6] and for the mixed PF_2X and PFX_2 halides, which, lie at around 0.042 Å [6, 16]. This implies that, although the bonding and vibrational properties of this anion are somewhat peculiar, the mean amplitudes of vibration of its strongest bonds are still found in the characteristic range [6].

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