

Solid state vibrational spectroscopy of anhydrous lithium hexafluorophosphate (LiPF₆)

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Abstract

Raman and Infrared studies of solid anhydrous lithium hexafluorophosphate (LiPF₆) have been carried out. The studies were complemented by X-ray powder diffraction (XRD) and Thermogravimetric (TG) analysis techniques. The results indicate that when solid LiPF₆ is studied in a strictly anhydrous environment, more consistent thermal stability data can be obtained. TG analysis, using a scan rate of 10 °C min⁻¹, indicate the onset of thermal decomposition of the anhydrous LiPF₆ occurring at about 134.84 °C while partially hydrolysed compound starts at 114.46 °C. The Raman spectra of anhydrous MPF₆ (M = Li⁺, Na⁺ and K⁺) are best interpreted in terms of a cubic space group F_{m3m} (O_h⁵), (Z^B = 1), giving rise to twenty one vibrational modes (A_{1g}^(R) + E_g^(R) + T_{1g} + T_{2g}^(R) + 3T_{1u}^(IR) + T_{2u}) and as such, LiPF₆ may be considered isostructural with NaPF₆ and KPF₆. Crystal symmetry distortions in the anhydrous LiPF₆ give rise additional bands in the Raman spectrum due to T_{1u} infrared active modes and the ν₁ (A_{1g}) Raman band appears in the infrared spectrum in violation of the mutual exclusion selection rule for centro-symmetric sites. When these observations are considered, the Raman spectrum of LiPF₆ is similar to those of NaPF₆ and KPF₆, with observations of the expected shifts due to cation size and/or electronegativity effects.

Key words: Anhydrous lithium hexafluorophosphate, Raman, FTIR, XRD, TGA

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1. Introduction

Lithium hexafluorophosphate (LiPF_6) is the most widely used salt in electrolytes for commercial lithium ion cells, due to its high conductivity and low viscosity.^[1-2] Studies on the bulk properties of LiPF_6 in solution have been carried out primarily to understand and describe properties such as conductivity, viscosity and the mobility of electrolyte and ion transport in solution.^[2-4] Studies have also been carried out in order to understand the solution behavior of LiPF_6 in electrolyte solutions.^[5-8] The theoretical calculations on LiPF_6 ^[2] and experimental vibrational spectroscopy techniques have been used in other studies to further understand the cation-anion interactions.^[2,9-14] This salt is also known to decompose to LiF and PF_5 in air and ambient temperature, with additional decomposition of the PF_5 in the presence of water.^[15] It is for this reason that it is sometimes kept as the more stable and easier to handle $\text{Li}(\text{C}_5\text{H}_5\text{N})\text{PF}_6$ complex^[16]. Apart from being stable in this form, high purity (99.8%) LiPF_6 can also easily be recovered from $\text{Li}(\text{C}_5\text{H}_5\text{N})\text{PF}_6$ complex.^[17] Results from Ab-initio studies of a series of M^+PF_6^- salts (where $\text{M}^+ = \text{Li}^+, \text{Na}^+, \text{K}^+, \text{Rb}^+$ and Cs^+) have determined the most stable vapor phase geometry (C_{3v}), based on changes in the Raman and infrared band positions.^[2] Vapor phase geometries of the Li^+PF_6^- ion pairs were used in these studies. Liu-Jian Wen et al studied the solid LiPF_6 ^[18]. However, it is evident that hydrolysis processes could not be ruled out in that study, as their infrared spectrum also showed the presence of water^[18]. As the most important industrial salt in electrolyte mixtures, LiPF_6 is usually also mixed with solvents, for example, ethylene carbonate, diethyl carbonate or dimethyl carbonate^[19], amongst others. It is for this reason that most studies have concentrated on the vibrational analysis of the PF_6^- in solution. However, the possibility of handling the pure salt can also not be overlooked. In this paper we report the vibrational spectroscopy of anhydrous lithium hexafluorophosphate in the solid state and discuss the effect of change in electronegativity within the group I (Li^+, Na^+ and K^+) hexafluorophosphate series and its influence on the obtained Raman and infrared spectra. Studies by Burba and Frech^[6] for instance have indicated that $\nu_1(\text{A}_{1g})$ Raman band has shown simultaneous Infrared and Raman activity, and this phenomenon was used to probe ionic interactions in solution.^[6] We further examine this phenomenon in the solid state as it relates to electronegativity and cation sizes to explain changes in the vibrational spectra of the solid

MPF₆ (M = Li⁺, Na⁺ and K⁺) compounds. We further clarify the apparent literature disagreements on the onset of thermal decomposition of LiPF₆, an important salt used extensively in the portable power industry.

2. Experimental method and materials

2.1 Materials and handling

The pure (99.9 %) hexafluorophosphate salts (MPF₆ (Li⁺, Na⁺ and K⁺)) were purchased from Sigma-Aldrich and used as received. The salts were kept dry in a glove box under inert gas until use. When ready for use, they were loaded into a new ATR sample cell designed for hygroscopic samples ^[20] to prevent contact with moisture. The loading of the sample occurred inside a glove box under dry inert atmosphere and the sample holder was then transferred to the FTIR spectrometer and inserted as a drop-in replacement for the HarrickTM Mvp-pro FTIR-Attenuated Total Reflectance (ATR) accessory ^[20]. Similar precautions were taken with all the salts that were used for the XRD, Raman and TG analysis studies in order to retain anhydrous conditions for the hygroscopic MPF₆ (Li⁺, Na⁺ and K⁺) salts.

2.2 Raman and infrared spectroscopy

The Raman spectra were acquired with a Ram II (FT-Raman) spectrometer (Bruker) fitted with a liquid nitrogen cooled Germanium detector. The 1064 nm wavelength radiation was used with 50 mW laser power setting. The spectral resolution on the instrument was set at 4 cm⁻¹. The infrared reflectance spectra were acquired with Bruker's Tensor 70 FTIR spectrometer fitted with a Harick Mvp-pro ATR cell and a hygroscopic in-house developed ATR sample holder ^[20] and handled as described above. The reflectance spectra were recorded and averaged over 32 scans using the total internal reflectance configuration with a diamond crystal.

2.3 X-ray powder diffraction and thermal analysis

The X-ray powder diffraction (XRD) studies were carried out with an AXS D8 Advanced spectrometer (Bruker). The 2θ values were set between 15 and 120 ° with a step size of

0.03 °. The sample was packed in an air-tight sample holder fitted with special air tight seals under anhydrous inert atmosphere for XRD studies. The thermogravimetric analysis of the pure compound was carried out in a Perkin Elmer TGS-2 thermogravimetric analyzer under dry inert gas. A scan rate of 10 °C min⁻¹, using sample mass of between 20 and 22 mg over dry N₂ gas was used in the study. The details of how the thermo-balance is protected against environmental moisture has been reported and described.^[21]

3. Results and discussion

The onset of thermal decomposition of the anhydrous LiPF₆ has been studied and reported in the literature.^[1,22-24] Disagreements among researchers have emerged, especially on results from studies using the DSC methods as compared to those from TGA methods, where results have been known to differ by almost 130 °C,^[1,18,22-24] as noted also by Yang, Zhuang and Ross.^[1] In the absence of water, pure anhydrous LiPF₆ is expected to decompose via a one step process ($\text{LiPF}_{6(s)} \rightarrow \text{LiF}_{(s)} + \text{PF}_{5(g)}$), while in the presence of water, the decomposition will include an additional step ($\text{PF}_{5(g)} + \text{H}_2\text{O} \rightarrow \text{POF}_{3(s)} + 2\text{HF}_{(g)}$).^[1] H. Yang et al, discussed the decomposition of LiPF₆ products in the presence of water.^[1] In their studies that were complemented by Molecular Orbital (MO) calculations, they readily assigned a band at 473 cm⁻¹ to the P=O (1018 cm⁻¹) and O=PF₃ (483 cm⁻¹) modes. It is also known that infrared bands between 1200 cm⁻¹ and 1350 cm⁻¹ are characteristic of P=O and P-O hydrolysis products^[25]. These modes have neither been observed in our dry LiPF₆ nor the atmospheric-moisture exposed LiPF₆ infrared spectra (**Figure 1**), except one small broad band at about 1267 cm⁻¹. What we do observe are bands associated with crystal water especially the band at 1649 cm⁻¹. This could mean that even our “wet” LiPF₆ is not wet enough to produce hydrolysis products but does have crystal water within the crystal.

Results from DSC studies using neat LiPF₆ at ambient pressure has reported the onset of thermal decomposition of LiPF₆ to be 177 °C,^[18] while results from TG Analysis studies give a value of 107 °C^[1] and 78.33 °C^[18] in a dry inert atmosphere and ambient pressure at the same scan rate (10 °C min⁻¹). Ella Zinigrad et al, have also obtained a value of

Figure 1

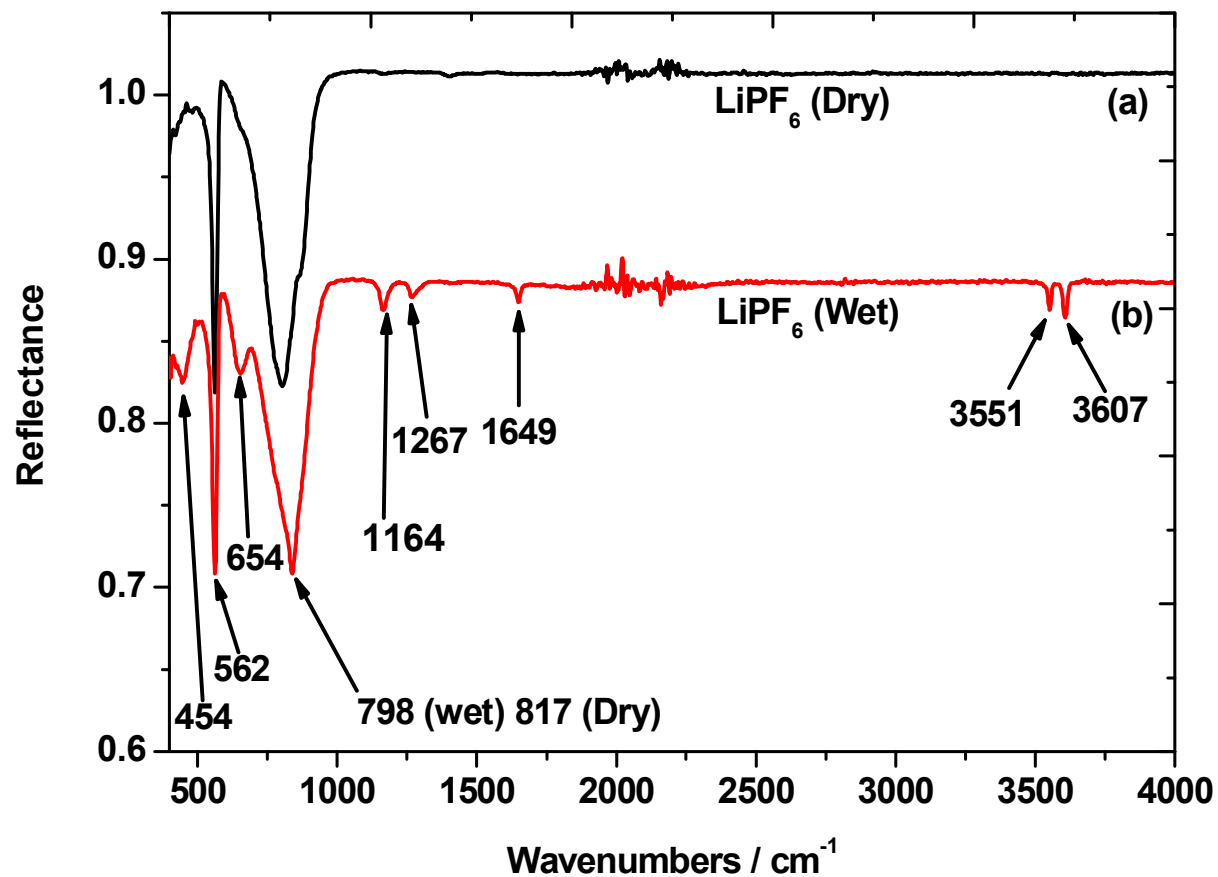


Figure 1. The ATR-IR reflectance spectra of (a) anhydrous LiPF₆ and (b) LiPF₆ exposed to moisture at ambient temperature and pressure. We particularly notice the appearance of crystal water band around 1649 cm⁻¹ (Figure 5(b)). The band at 798 cm⁻¹ (wet sample) is found to shift to 817 cm⁻¹ in the dry sample.

467K (194 °C) for the temperature at which LiPF_6 melts reversibly^[26]. Results from our own TG Analysis studies at ambient pressure under a dry inert atmosphere and a scan rate of 10 °C min^{-1} , indicate the onset of thermal decomposition at 134.84 °C (**Figure 2**) for the anhydrous lithium salt and 114.46 °C (**Figure 3**) for the lithium salt that was exposed to atmospheric moisture. X.G. Teng et al pointed out that their previous studies showed three decomposition peaks^[27], while subsequent studies only showed only one decomposition peak instead of the three showed in their previous studies^[28]. It is this ambiguity in results that lead us to exercise extreme care in keeping our samples as anhydrous and as possible. Our own studies show one decomposition peak (**Figure 2**). On careful inspection of X.G. Teng et al's data (Figure 1 of reference [28]), their onset of thermal decomposition, as determined by the same DTG inspection method used for our data, (see **Figures 2 and 3**), shows the onset of thermal decomposition at about 137 °C which is very close to our own value of 134.84 °C for the anhydrous LiPF_6 . The maximum change at 212.48 °C is also relatively consistent with our own 216.90 °C, differing by only about 4.4 °C. We postulate that the peak observed at 65.53 °C in their study may be the result of minute amounts of crystal water still present in the sample. Our own wet sample (Figure 3) shows a small but discernible peak on the DTG curve at around 68 °C, which we also attribute to crystal water as exemplified in our ATR-IR results (**Figure 1(b)**).

Yang et al^[1] observed a decrease of ca. 27 °C in the onset of thermal decomposition of LiPF_6 in the presence of 300 ppm water vapor in the carrier gas compared to that with 10 ppm, which is consistent with observations in this study (see **Figure 2 and 3**). It is clear that to develop consistent thermal data, a strict anhydrous environment is required and similar conditions are also maintained in this study in order to obtain consistent vibrational information from these hygroscopic solids (MPF_6 (Li^+ , Na^+ and K^+)).

The crystal structure of some cubic hexafluorophosphates (MPF_6 , $\text{M} = \text{Na}, \text{K}, \text{Rb}, \text{Cs}$) at ambient temperatures have been studied by K. Kitashita et al^[29], and the vibrational spectroscopy of these hexafluorophosphates have also received considerable attention,^[29-32] but not so for the anhydrous solid LiPF_6 . It has been reported that

Figure 2

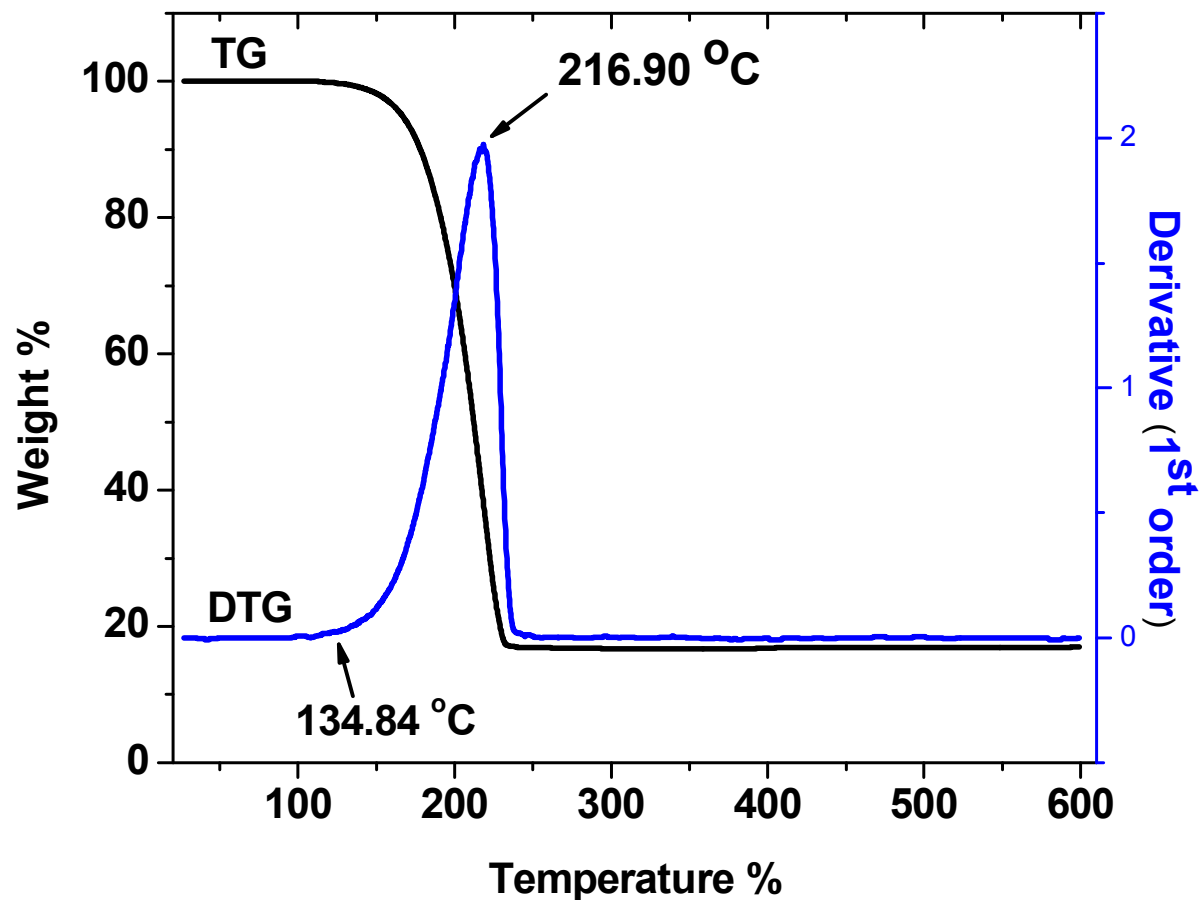


Figure 2. The figure shows a thermogravimetric curve of anhydrous pure LiPF_6 under dry N_2 gas. Initial mass used was 20 mg and the mass loss during thermal decomposition at a rate of $10\text{ }^\circ\text{C min}^{-1}$, indicate the onset of thermal decomposition at $134.84\text{ }^\circ\text{C}$, the blue curve shows the 1^{st} derivative.

Figure 3

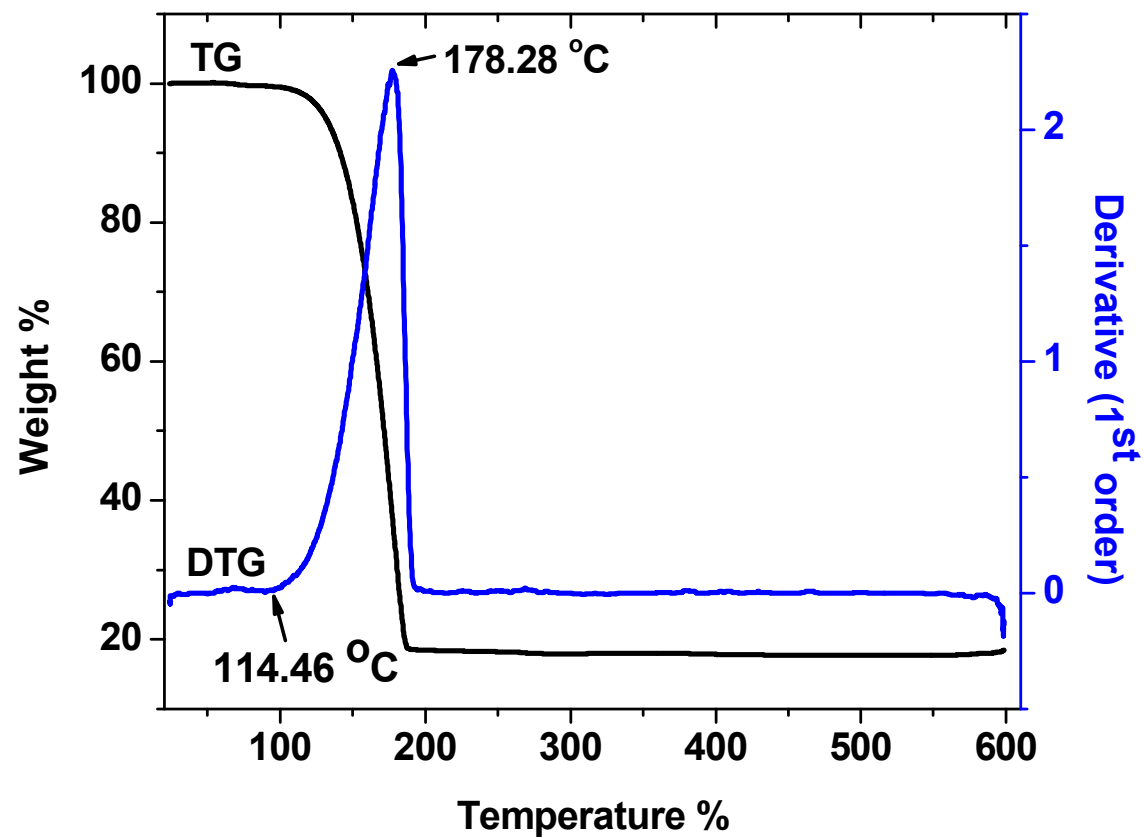


Figure 3. The figure shows a thermogravimetric curve for partially hydrolysed LiPF_6 . Initial mass used was 22 mg and mass loss during thermal decomposition at a rate of $10\text{ }^\circ\text{C min}^{-1}$, indicate the onset of thermal decomposition at $114.46\text{ }^\circ\text{C}$, the blue curve shows the 1st derivative curve.

hexafluorophosphates of univalent metals (MPF₆ (M = Na, K, Rb, Cs) except lithium, have cubic lattices at ambient temperatures, [29] it is therefore expected that the vibrational spectra of these hexafluorophosphates should differ from that of the lithium salt. Indeed, the Raman spectrum of solid anhydrous LiPF₆ seems to differ from that of NaPF₆ and KPF₆ as shown in **Figure 4**. Also shown in **Figure 5** is the infrared spectra of the anhydrous salts (MPF₆, M = Li⁺, Na⁺, K⁺).

Figure 6 shows the X-ray powder diffraction (XRD) patterns of the pure anhydrous MPF₆ (M = Li, Na and K) salts that were used. Assuming a *Fm3m* (225) space group, and $Z^B = 1$, which has already been verified for NaPF₆ and KPF₆ [29], from group theoretical considerations using the correlation method outlined by Fatelly et al [33], total irreducible representation is determined to be;

$$\Gamma_{\text{vib}}^{\text{MPF}_6} = A_{1g}^{(R)} + E_g^{(R)} + T_{1g} + T_{2g}^{(R)} + 3T_{1u}^{(IR)} + T_{2u} \quad (1)$$

where the superscripts R and IR indicate Raman and Infrared activity respectively, while the rest ($T_{1g} + T_{2u}$) are silent in both Raman and the infrared.

Equation 1 lists all the 21 predicted modes ($3N-3 = 3(8)-3$ for the solid) including the Raman active modes ($A_{1g}^{(R)}$, one doubly degenerate $E_g^{(R)}$ and one triply degenerate $T_{2g}^{(R)}$ modes). The Raman spectrum of lithium hexafluorophosphate shown in **Figure 4** (see also **Table 1**) shows Raman band assignments of lithium hexafluorophosphate compared to those of the other two group I (Na⁺ and K⁺) hexafluorophosphates. The wavenumber of the ν_1 (A_{1g}) Raman band of this series including that of the lithium salt at 771 cm⁻¹, decreases systematically with increasing cation size, a fact pointed out by Kitashita et al [29] in studies which excluded the lithium salt. In solution studies of LiPF₆, the $\nu_1(A_{1g})$ Raman active band from PF₆⁻ has also been observed in the infrared transmission spectrum of LiPF₆⁻ based electrolyte solutions [6], and was attributed to ion – ion (Li⁺ and PF₆⁻) interactions that may distort the symmetry of the anion resulting in a violation of the mutual exclusion selection rule for centro-symmetric octahedral specie. In this study, a

Figure 4

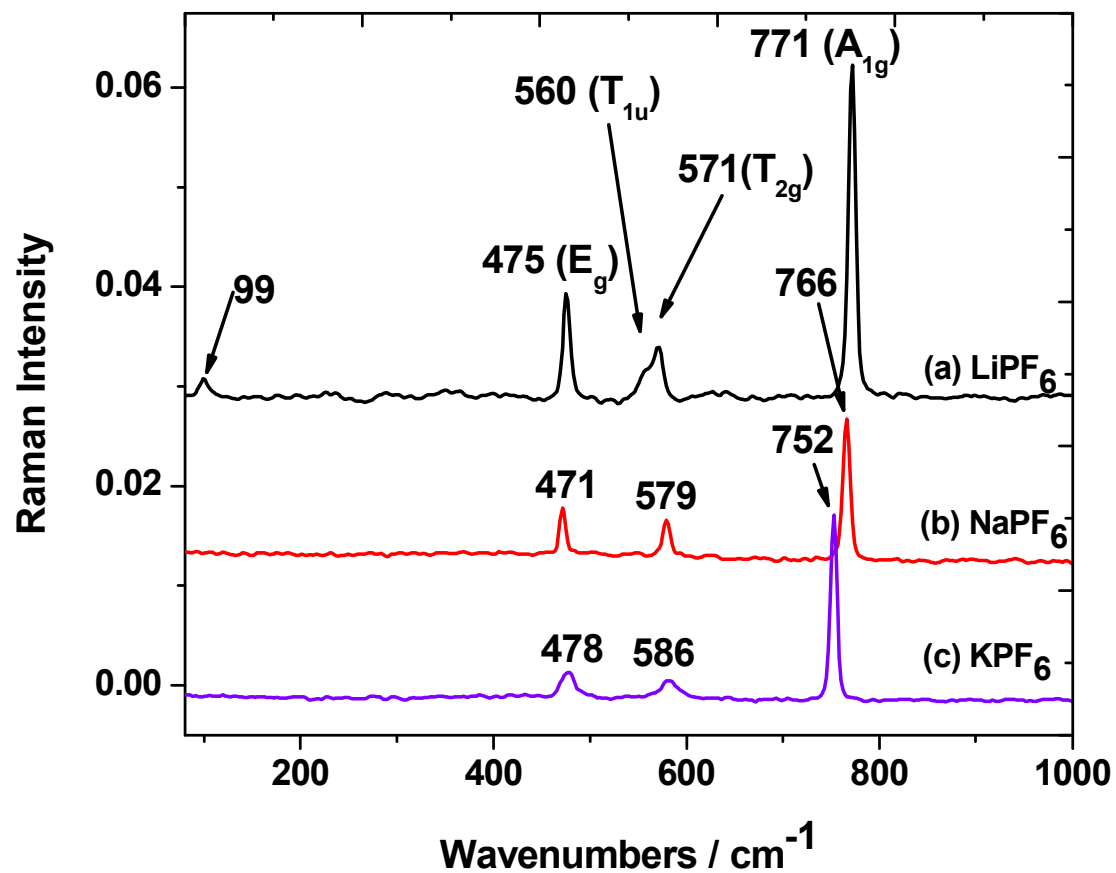


Figure 4. The Raman spectra of anhydrous MPF₆ (M = Li⁺, Na⁺ and K⁺) with the assignments. The shoulder at 560 cm⁻¹ is attributed to the infrared active ν_4 (T_{1u}) band that becomes Raman active due to crystal distortions, that are less prominent in less electronegative NaPF₆ (b) and KPF₆ (c).

Figure 5

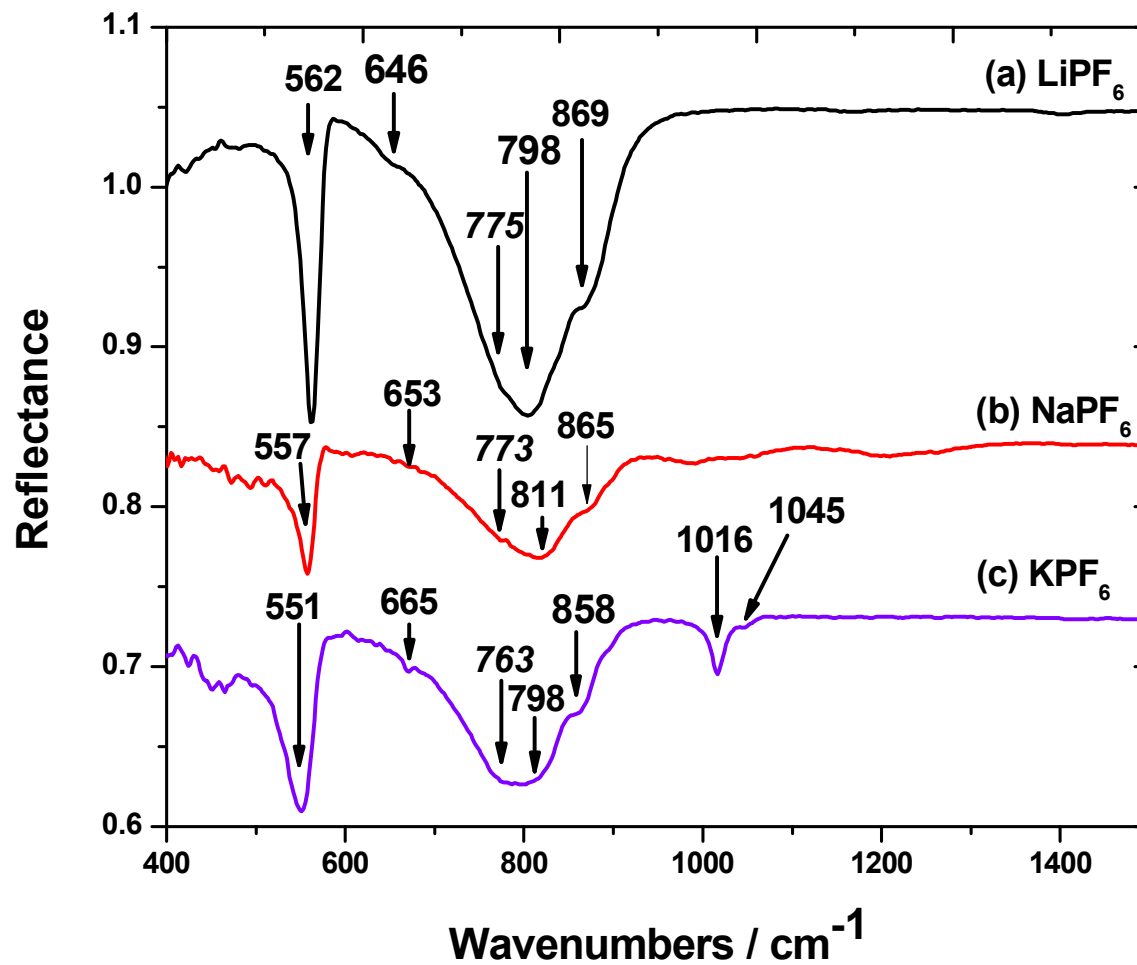


Figure 5. The ATR-IR reflectance spectra of anhydrous MPF₆ (M = Li⁺, Na⁺ and K⁺) is presented. There are no discernible hydrolysis products such as O=PF₃ usually observed between 1250 and 1300 cm⁻¹.

Figure 6

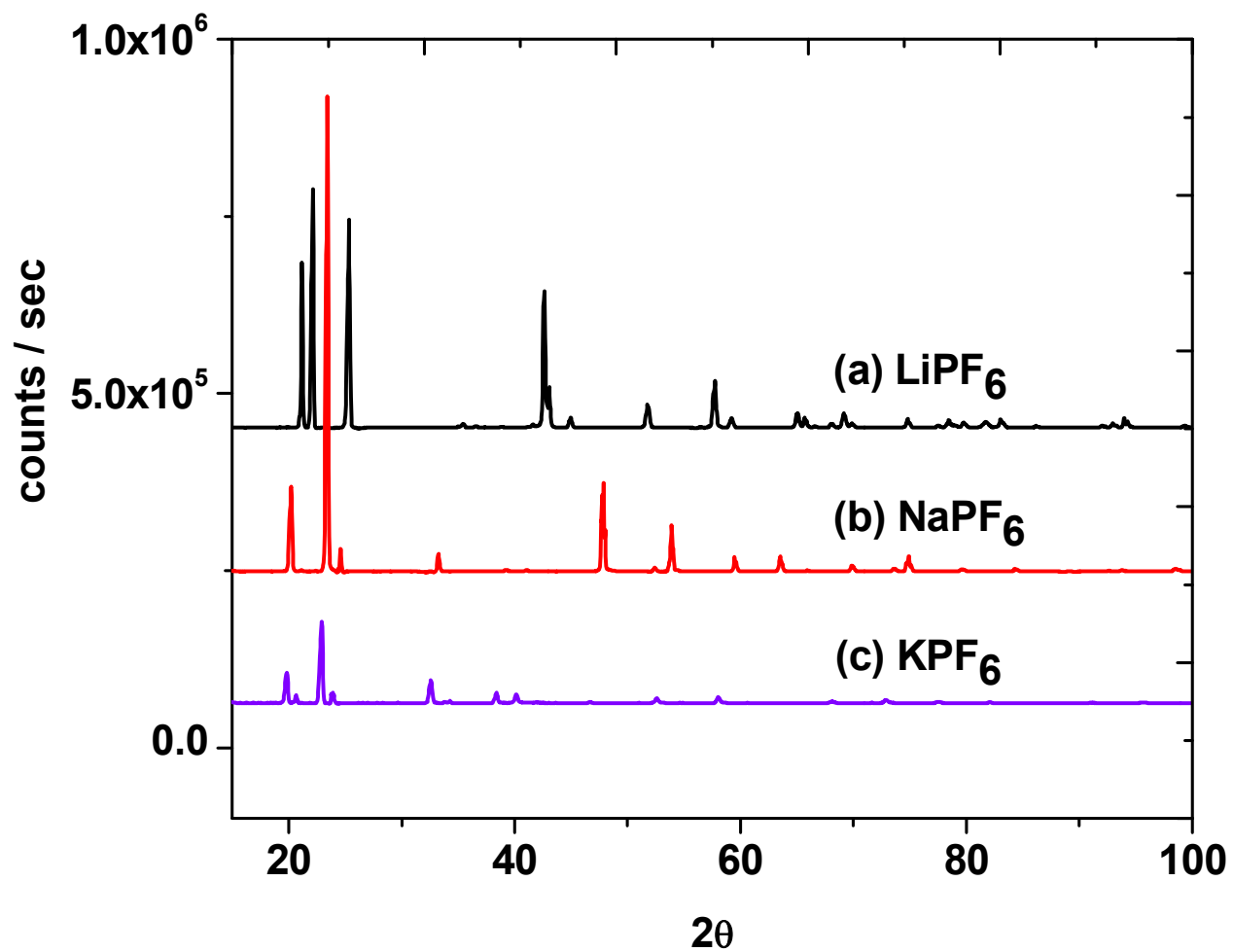


Figure 6. The XRD patterns for the anhydrous MPF₆ (M = Li⁺, Na⁺ and K⁺) salts are presented and confirms the pure samples in our study.

shoulder at 771 cm^{-1} in the infrared spectrum of the solid anhydrous LiPF_6 (**Figure 5**), attributed to the Raman active mode ν_1 (A_{1g}), is observed while the ν_4 (T_{1u}) infrared active band (560 cm^{-1}) is also observed in the Raman spectrum (**Figure 4**) due to crystal symmetry distortions which may be attributed to the higher electronegativity and size of the lithium ion. The ν_2 (E_g) Raman band is found at 475 cm^{-1} for lithium hexafluorophosphate and ranges from 469 , 476 and 480 cm^{-1} for the NaPF_6 , KPF_6 , and CsPF_6 respectively (**Table 1**, CsPF_6 data is from K. Kitashita et al^[29]).

A 560 cm^{-1} in the Raman spectrum is seen appearing as a shoulder on the ν_5 (T_{2g}) = 571 cm^{-1} Raman band and is assigned as the F-P-F bending mode^[30]. The 560 cm^{-1} band also appears as an intense band in the infrared spectrum (**Figure 5**) and it is assigned as the ν_4 (T_{1u}) infrared active band^[31]. The ν_4 (T_{1u}) decreases slightly in intensity as it shifts from higher to lower wavenumbers from LiPF_6 to KPF_6 as observed in the infrared reflectance spectra. This is consistent with its disappearance in the Raman spectra of NaPF_6 and KPF_6 . The appearance of this band in the Raman spectrum is also in violation of the mutual exclusion selection rule for centro-symmetric sites, due to distortions in the crystal lattice. Following on this argument, the less electronegative and slightly larger (but not large enough to be as effective in distorting the crystal from electronegativity and ionic size) Na^+ and K^+ should neither show the ν_4 (T_{1u}) shoulder in their Raman spectra, nor the intense ν_1 (A_{1g}) band in their infrared spectra. Close inspection of **Figure 4** reveals that this is indeed so, for the Raman spectra. The fact that NaPF_6 still shows a small shoulder due to ν_1 (A_{1g}) in its infrared spectrum (**Figure 5**), may be attributed to differences in sensitivity of the two techniques. These results combine to show that indeed the three hygroscopic salts (MPF_6 , $M = \text{Li}^+$, Na^+ , K^+) may be considered as isostructural (average F_{m3m} space group) with minor differences contributed by crystal lattice distortions emanating from differences in the electronegativity of the respective cations. Table 2 also shows a summary of the infrared reflectance bands.

T_{1u} symmetry translational mode under F_{m3m} space group for CsPF_6 was observed at 76 cm^{-1} .^[34] A band at 99 cm^{-1} in the Raman spectrum of LiPF_6 may be assigned to this mode. Similar Raman bands for NaPF_6 and KPF_6 that (if present) may be expected to

Table 1. Raman band positions (cm^{-1}) and intensities (Raman Intensities)* of LiPF_6 compared to literature values of group I metal hexafluorophosphates (MPF_6 , $M = \text{Na, K, Rb, Cs}$).				
Anhydrous LiPF_6 (This work)	NaPF_6	KPF_6	CsPF_6	Assignment
771 ^b (s) -	766 ^b (s) 765 ^a (s)	752 ^b (s) 750 ^a (s)	- 743 ^a (s)	$\nu_1 (\text{A}_{1g})$
475 (m) -	471 ^b (m) 469 ^a (m)	478 ^b (m) 476 ^a (m)	- 480 ^a (m)	$\nu_2 (\text{E}_g)$
571b (m) -	578 ^b (m) 576 ^a (m)	581b(m) 582a(m)	- -	$\nu_5 (\text{T}_{2g})$
560 99 w	n.o. n.o.	n.o. n.o.	- 76 ^c (w)	$\nu_4 (\text{T}_{1u})$
a = K. Kitashita et al. [29]. b = This work. *s = strong, m = medium, w = weak. c = A.M. Heyns et al [34]. n.o. = Not observed in the Raman spectra for this study.				

appear at lower wavenumbers than that for LiPF_6 but higher than that for CsPF_6 are not observed due to limitations in our instrument.

4. Conclusion

The vibrational spectroscopy of anhydrous LiPF_6 has been investigated. The results indicate that, when anhydrous LiPF_6 is analysed in a strict anhydrous environment, results show that it may be considered as isostructural with the other univalent hexafluorophosphate (MPF_6 , $M = \text{Na}, \text{K}, \text{Rb}$ and Cs) salts. More consistent thermal stability data is also obtained in this dry environment and indicates the onset of thermal decomposition at $134.84\text{ }^\circ\text{C}$ using a scan rate of $10\text{ }^\circ\text{C min}^{-1}$ and a mass of 20 mg. A vibrational band that is observed at 560 cm^{-1} ($\nu_4(\text{T}_{1u})$) in the Raman spectrum and another at 771 cm^{-1} ($\nu_1(\text{A}_{1g})$) in the infrared spectrum appear in violation of the mutual exclusion selection rule for centro-symmetric sites due to crystal symmetry distortions arising from the higher electronegativity of the lithium cation in comparison to the others (Na^+ and K^+). Infrared bands that are observed between 1200 cm^{-1} and 1350 cm^{-1} are due to O=P and O-P bonds from hydrolysis products such as, for example O=PF_3 and not due to anhydrous LiPF_6 . Previous studies of LiPF_6 that have observed these bands in the Raman spectra of LiPF_6 may have been affected by the presence of large amounts of moisture owing to the hygroscopic nature of these compounds.

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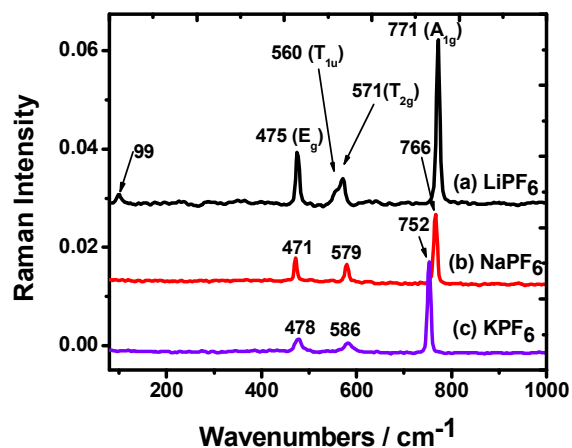
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Graphical Abstract

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Raman and infrared studies complemented by XRD and TG analysis indicate that anhydrous solid LiPF_6 is best interpreted as isostructural with other anhydrous NaPF_6 and KPF_6 salts, when crystal distortions due to cation size and/or electronegativity effects are taken into account. The onset of thermal decomposition of the anhydrous LiPF_6 is recorded at $134.84\text{ }^\circ\text{C}$ compared to the atmospheric moisture exposed LiPF_6 salt at $114.46\text{ }^\circ\text{C}$.



Highlights

Solid state vibrational spectroscopy of anhydrous lithium hexafluorophosphate (LiPF₆)

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- Is LiPF₆ isostructural with NaPF₆ and KPF₆? Raman agrees despite slight differences.
- Disagreements on the onset of thermal decomposition of dry and wet LiPF₆ is resolved to be 134.84 °C and 114.46 °C respectively.
- Violation of selection rules dominated by electronegativity/size effects contribute to Crystal symmetry distortions.