

Short communication

Theoretical insights into PF_6^- and its alkali metal ion pairs: geometries and vibrational frequencies

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Abstract

The structures, vibrational frequencies, infrared and Raman intensities of hexafluorophosphate anion (PF_6^-) and M^+PF_6^- ($\text{M}^+ = \text{Li}^+, \text{Na}^+, \text{K}^+, \text{Rb}^+$ and Cs^+) ion pairs have been studied by ab initio calculations. It is shown that the tridentate coordination of cation by PF_6^- is the most stable structure in gas phase. The vibrational spectroscopies of the most stable geometries were calculated and the changes in band position were used to probe the ion associations.

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The lithium salts used in liquid electrolytes for lithium battery preferably have large-sized univalent anions with a strongly delocalized charge to reduce viscosity and enhance conductivity of electrolytic solutions. The traditional inorganic (such as ClO_4^- , BF_4^- , PF_6^- , AsF_6^-), and new developed organic anions (CF_3SO_3^- and $(\text{CF}_3\text{SO}_2)_2\text{N}^-$) are most commonly considered [1]. High ionic conductivity for an appropriate lithium salt is the basic requirement. Therefore, the ion pair formation in solutions is undesirable because it reduces the number of effective carriers in the electrolyte, increases the viscosity of electrolyte and affects the ion intercalation into electrode. Unfortunately, ion association often occurs in the commercial electrolyte of lithium battery since its concentration is at least 1 M. It is believed that different types of ionic species make different contributions to the total ionic conductivity and the process of lithium electrochemical intercalation [1]. Knowledge of the extent of association of electrolyte solutions, and the type, structure and the lifetime of the ion pair in solutions used in lithium battery, are relevant information on understanding the mechanism of ion conduc-

tion at molecular level and on choice and optimization for new liquid electrolytes for electrochemists.

Experimentally, vibrational spectroscopies [2–8] and conductivity measurements [9–11] have been proved to be powerful techniques for probing ion associations. As a noted example, Raman spectra of LiClO_4 in several organic solvents have been extensively studied [2,3,7], and three bands, at 931, 938 and 945 cm^{-1} , have been used to fingerprint the free anion, contact ion pair and dimer, respectively. Ab initio calculations have also been an important tool to evaluate interactions between cation and anion [12–18]. Some authors [12,16] have studied the structures and spectral changes of $\text{Li}^+\text{ClO}_4^-$ with different geometries. The bidentate structure was found to be preferred over the monodentate or tridentate structures. Although LiPF_6 is now in practical use for lithium ion battery, little structural information is available for the Li^+PF_6^- ion pairs [15]. The reason is mainly due to the thermal instability, moisture sensitivity [19] and lower solubility of hexafluorophosphate [1]. For example, Borodin and co-workers have studied interactions between LiPF_6 and poly(ethylene-oxide) and the partial information of Li^+PF_6^- ion pairs are given. The knowledge of other M^+PF_6^- ($\text{M} = \text{Na}^+, \text{K}^+, \text{Rb}^+$ and Cs^+) ion pairs is even absent in literature, which are difficult

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to form in the solutions because of the large cation radius, and their structural parameters calculated using electron correlation methods at large basic set is acceptable. In the present paper, we perform a detailed study using ab initio calculations to characterize the structures of PF_6^- and its alkaline metal ion pairs M^+PF_6^- ($\text{M} = \text{Li}^+, \text{Na}^+, \text{K}^+, \text{Rb}^+$ and Cs^+). Furthermore, the vibrational spectra and frequency shifts for ion pairs have been calculated and discussed based on the energetically favorable structure.

1. Computational methods

All the calculations have been carried out using Gaussian98 program suite [20]. Geometry optimization, following the preliminary calculations at HF/6-31G* level, was performed using the tight convergence criterion. Symmetry constrains were applied for each desired coordination geometry in order to minimize the computational cost. Vibrational frequency was calculated at the same computational level with geometry optimization and then used to evaluate the zero-point vibrational energy (ZPVE). The HF and DFT (B3LYP) methods were used for all the systems studied, and MP2 for the selected. For Li^+PF_6^- , Na^+PF_6^- and K^+PF_6^- systems, the calculations were carried out using the following basis sets: D95+(d), D95+(2d), 6-31G(d), 6-31+G(d), 6-311G(d), 6-311+G(d), 6-311+G(2d) and 6-311+G(2df). For Rb^+PF_6^- and Cs^+PF_6^- ion pairs, the

effective core potentials (ECPs) of Hay and Wadt [21], LANL2DZ and SDD, were used for the Rb and Cs atoms, and 6-311+G(d) for others. It is found that the polarization function is very important for these calculations. Partial atomic charges are obtained from a Mulliken population analysis. The zero-point energies and vibrational frequencies were not corrected. The relative energies are defined as $\Delta E = E(\text{M}^+\text{PF}_6^-) - E(\text{M}^+) - E(\text{PF}_6^-)$.

2. Results and discussions

2.1. Free PF_6^- anion

Free PF_6^- anion has octahedral symmetry (O_h) and the bond angle formed by F–P–F is found to be exactly 90° . The optimized P–F bond lengths at different basis sets are given in Table 1. Different experimental bond lengths for P–F have been reported in literature. Wang et al. [21] cited a value of 1.568–1.592 Å arising from the X-ray crystallographic data of $(\text{CH}_3)_4\text{NPF}_6$, a less value of 1.555–1.556 Å was also obtained from $\text{P}(\text{C}_6\text{H}_5)_4\text{PF}_6$ crystal [22]. As can be seen in Table 1, the optimized P–F bond length is slightly greater than the experimental one. The best predicted value is 1.5897 Å at the HF/6-311+G(2df) level, and the optimization at B3LYP or MP2 level results in an increase in P–F bond length. The greater is the polarization function, the more reasonable is the bond length. On the other hand, the energy follows the order HF > MP2 > B3LYP at the same basis set. It must be

Table 1
Optimized bond lengths, energies and frequencies for free PF_6^- anion^a

Method	F–P length	Energy	ZPVE	Frequency (cm^{-1})					
				t_{2u}	t_{2g}	t_{1u}	e_g	a_{1g}	t_{1u}
HF/d95+(d)	1.6160	–937.7766866	0.020764	323.2	486.2	594.7	620.0	791.7	956.8
HF/d95+(2d)	1.6006	–937.8215483	0.020408	323.4	497.0	590.5	603.0	790.3	909.8
HF/6-31g(d)	1.6057	–937.6027092	0.021101	323.6	490.1	587.6	643.9	799.5	990.4
HF/6-31+g(d)	1.6092	–937.6391342	0.020807	325.1	494.9	596.7	617.2	791.8	952.4
HF/6-311g(d)	1.6005	–937.7779926	0.020989	331.4	502.4	602.6	610.1	790.6	964.5
HF/6-311+g(d)	1.6025	–937.7968325	0.020801	332.9	503.9	599.9	602.6	787.2	942.7
HF/6-311+G(2df)	1.5897	–937.8787707	0.020940	333.6	503.5	604.5	613.8	813.5	941.9
B3LYP/d95+(d)	1.6588	–940.8585456	0.018257	283.0	428.2	523.9	548.8	684.4	842.1
B3LYP/d95+(2d)	1.6393	–940.9025238	0.018187	286.9	442.7	529.6	538.9	694.2	811.2
B3LYP/6-31g(d)	1.6373	–940.6431734	0.019130	287.2	440.0	528.4	594.1	719.2	907.7
B3LYP/6-31+g(d)	1.6485	–940.7159646	0.018322	283.5	435.6	524.5	547.9	689.8	842.1
B3LYP/6-311g(d)	1.6401	–940.8657778	0.018675	291.3	443.9	534.4	553.8	693.0	862.6
B3LYP/6-311+g(d)	1.6458	–940.896614	0.018175	288.6	439.6	526.0	531.8	678.4	824.5
B3LYP/6-311+g(2df)	1.6292	–940.9635409	0.018555	295.2	447.6	539.5	544.2	706.4	834.4
MP2/d95+(2d)	1.6386	–939.1827519	0.018300	283.9	443.1	527.9	546.2	700.9	824.9
MP2/6-31g(d)	1.6365	–938.7668506	0.019647	296.3	450.2	540.4	610.6	737.9	934.8
MP2/6-31+g(d)	1.6481	–938.8412914	0.018792	289.6	445.1	538.8	562.0	708.1	865.4
MP2/6-311g(d)	1.6285	–939.1392923	0.019521	306.3	466.0	560.2	572.0	720.2	902.4
MP2/6-311+g(d)	1.6348	–939.1807623	0.018882	301.1	455.9	547.5	549.3	703.6	857.5
Expt.	1.568–1.592 ^b ; 1.555–1.556 ^c	–	–	–	470 ^d	558 ^d	567 ^d	741 ^d	838 ^d

^a Energy in a.u., bond length in Å and frequency in cm^{-1} .

^b Ref. [21].

^c Ref. [22].

^d Ref. [23].

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