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Studies of Lithium Polymer Electrolytes***

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Density Functional and Neutron Studies of Lithium Polymer Electrolytes

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The structure of PEO doped with lithium perchlorate has been determined using neutron diffraction on protonated and deuterated samples. The experiments were done in the liquid state. Preliminary analysis indicates the Li-O distance is about 2.0 Å. The geometries of a series of gas phase lithium salts [LiCF_3SO_3 , $\text{Li}(\text{CF}_3\text{SO}_2)_2\text{N}$, $\text{Li}(\text{CF}_3\text{SO}_2)_2\text{CH}$, LiClO_4 , LiPF_6 , LiAsF_6] used in polymer electrolytes have been optimized at B3LYP/6-31G(d) density functional level of theory. All local minima have been identified. For the triflate, imide, methanide, and perchlorate anions, the lithium cation is coordinated to two oxygens and have binding energies of ca. 141 kcal/mol at the B3LYP/6-311+G(3df,2p)//B3LYP/6-31G* level of theory. For the hexafluoroarsenate and hexafluorophosphate the lithium cation is coordinated to three oxygens and have binding energies of ca. 136 kcal/mol.

INTRODUCTION

This work is part of a fundamental study on lithium polymer electrolytes used in lithium battery systems. Ionically conducting polymers were first discovered about 20 years ago and have subsequently been used as electrolytes in solid-state batteries.^{1,2} Ion-conducting polymers are solutions of salts in polymers. The polymer electrolytes are generally composites of a polyethylene oxide (PEO) and a salt, such as lithium triflate [$\text{Li}(\text{CF}_3\text{SO}_2)$, *LiTf*], lithium bis(trifluoromethanesulfonyl)imide [$\text{Li}(\text{CF}_3\text{SO}_2)_2\text{N}$, *LiTFSI*], lithium bis(trifluoromethanesulfonyl)methanide [$\text{Li}(\text{CF}_3\text{SO}_2)_2\text{CH}$, *LiTFSM*], LiAsF_6 , LiPF_6 , LiClO_4 , etc. It is generally believed that ionic conduction is a property of the amorphous phase and that ion association, ion-polymer interactions, and local relaxations of the polymer strongly influence the ionic mobility. However, much about the nature of the ion association processes, the ion-polymer interactions, and the role that they play in ionic conductivity of the electrolytes remains unknown.

In the neutron diffraction studies we are investigating the structure of PEO doped with LiClO_4 . In the theoretical effort we are investigating the ion-ion interactions in lithium polymer electrolytes by carrying out electronic structure calculations of the structures and binding energies of the gas phase salts *LiTf*, *LiTFSI*, *LiTFSM*, LiAsF_6 , LiPF_6 , and

LiClO₄. In addition, we calculated the LiClO₄-PEO interaction using dyglyme as a model for PEO.

THEORETICAL METHODS

The geometries of the gas phase lithium salts were optimized using the B3LYP/6-31G(d) density functional method. Vibrational frequencies were calculated for the optimized structures at this level. In order to obtain accurate binding energies, single point calculations were carried out at the B3LYP/6-311+G(3df,2p) level of theory using the B3LYP/6-31G* geometries. The density functional method³ is based on one-electron density functionals. The B3LYP density functional^{4,6} is a hybrid method that is a linear combination of Hartree-Fock exchange, Becke exchange and LYP correlation. The B3LYP/6-31G* method generally yields very good structures and binding energies. All calculations were performed with the GAUSSIAN 94⁷ series of programs.

EXPERIMENTAL

Neutron diffraction measurements were performed at the GLAD time-of-flight facility at the Intense Pulsed Neutron Source (IPNS), and at the D4 two-axis diffractometer at the Institut Laue Langevin (ILL), following procedure used previously for a structural study of neat PEO.⁸ Runs were carried out for 24 hours at background, and a vanadium standard rod for intensity calibration. Lithium perchlorate salts containing ⁶Li and ⁷Li isotopes were mixed with hydrogenated and deuterated PEO and heated above the melting point (65 °C) for the diffraction experiments. The containers were cylindrical vanadium tubes sealed under helium atmosphere. The difference between the diffraction intensities of samples with ⁶Li and ⁷Li gives information about the Li environment.

DENSITY FUNCTIONAL RESULTS

The optimized structures of gas phase lithium salts and their corresponding anions are shown in Fig 1. The optimized structure of the dyglyme with lithium perchlorate is shown in Fig 2. The total energies and Li cation binding energies are contained in Table I and the relative binding energies are contained in Table II.

Structures of LiTf, LiTFSM, LiTFSI, LiAsF₆, LiPF₆, and LiClO₄

We investigated lithium triflate structures having Li coordinated with up to three oxygens and up to three fluorine atoms. The bidentate lithium triflate structure with Li coordinated to two oxygens was found to be the most stable structure. This is in good accord with previous results.⁹⁻¹¹ At the B3LYP/6-31G* level of theory, the Li-O, and S-O bonds are 1.887 and 1.514 Å, respectively. The S-O bond is slightly longer than the average bond distances reported by Termayne et al in their experimental x-ray powder diffraction studies.¹² The theoretical Li-O bond distance lies within the range of the measured bond distances of 1.82 – 2.02 Å. At the B3LYP/6-31G* level the Li-O bond distance in the lithium triflate is longer by 0.03 Å than the distance in the triflate "free" anion in the gas phase. The same trend has been observed by other groups.⁹⁻¹¹

The structures of lithium imide and lithium carbide with lithium coordinated to two oxygen atoms have been optimized at the B3LYP/6-31G* levels. Arnaud et al¹¹ found these structures to be the most stable structures at the HF/3-21+G* level of theory. At the

B3LYP/6-31G* level the S-O bond length in the lithium imide and lithium carbide salts are longer than the corresponding "free" anion by 0.036 and 0.034 Å, respectively. The Li-O bond distance is shorter than the measured range of 1.95 – 1.97 Å of bond distance in the x-ray powder diffraction studied reported by Nowinski et al.¹³

Our studies were extended to include the LiClO₄ salt and the ClO₄⁻ anion in the gas phase using the same level of theory. The bidentate structure was found to be the most stable one. Similar to the other complexes the Cl-O bond in the LiClO₄ structure is longer by 0.05 Å than the Cl-O bond in the "free" anion, and the ∠O-Cl-O angle facing the lithium atom is slightly narrower in the LiClO₄ salt. The Li-O bond distance at B3LYP/6-31G* level of theory is about the same as the bond distance optimized at MP2/6-311+G* level of theory by Klassen and Nazri.¹³

Optimization of a dyglyme-LiClO₄ complex was done with Li⁺ cation coordinated to two oxygens from the dyglyme and two oxygens from the anion at the HF/3-21G* level of theory. The Li-O bond distances are in the range of 1.96 – 1.98 Å. (see Fig 2): The optimized structure contains two distinct Cl-O bond distances of 1.48 Å for the Cl-O bonds facing the lithium cation, and 1.43 Å for the bonds unattached to the lithium cation.

The lithium hexafluoroarsenate structures with lithium coordinated to one, two, and three fluorine atoms have been investigated using the B3LYP/6-31G* level of theory. Unlike the lithium triflate structure, the tridentate structure of LiPF₆ is lower in energy than the bidentate structure by 4.6 kcal/mol. The P-F bond is longer in the lithium complex than the "free" anion by 0.07 Å.

A similar search of structures for lithium hexafluoroarsenate structures was carried out with lithium cation coordinated to one, two, and three fluorine atoms at the B3LYP/6-31G* level. Similar to LiPF₆, the tridentate structure of LiAsF₆ was found to be more stable than the bidentate structure by 3.8 kcal/mol. Similar to the LiPF₆, the As-F bond distance is longer than the "free" anion by 0.07 Å in the gas phase.

Binding Energies

The binding energy for lithium perchlorate obtained using the B3LYP/6-31G* level of theory is more by 13 kcal/mol than the G2(MP2, SVP) result.¹⁴ Single point calculations at the B3LYP/6-311+G(3df,2p)//B3LYP/6-31G* yields a much better binding energy within a few kcal/mol of the G2(MP2, SVP) result.

The binding energies for lithium triflate, lithium imide and lithium carbide at the B3LYP/6-31+G(3df,2p)//6-31G* level of theory are ca. 141 kcal/mol. These calculations show that the two bulky groups do not effect the binding energy. Even though the gas phase binding energies for all these salts are about the same, the ionic conductivity of the lithium triflate salt is poor relative to the excellent ionic conductivity of lithium imide and lithium carbide. For the LiAsF₆ and LiPF₆ salts the binding energy is ca. 136 kcal/mol in the gas phase, which is lower by ca. 5 kcal/mol from the binding energy of the lithium triflates, imide and methanide.

NEUTRON DIFFRACTION RESULTS

The diffraction intensities of the samples in the ⁷Li and ⁶Li salts gave somewhat noisy but structurally plausible difference functions. The Li-difference structure factor $\Delta_{\text{Li}} S(Q)$ is shown in Fig. 3. The difference pair distribution function $\Delta_{\text{Li}} G(r)$, obtained by smoothing and Fourier transforming the structure factor is shown in Fig 4. It has a main

peak at ~ 2.0 Å due to Li-O correlations and a shoulder at ~ 3.2 Å. Further analysis is expected to resolve the second feature and provide an estimate of the Li-O coordination from the first peak. In future work, it is hoped that a comparison of the Li-difference function from the protonated and deuterated doped polymer will provide an estimate of the Li-H correlation, enabling a more detailed comparison with the theoretically derived structure discussed below.

CONCLUSIONS

Comparison of the neutron diffraction intensities from the LiClO_4 salts with ^6Li and ^7Li isotopes showed a pronounced Li-O correlation at a separation of ~ 2.0 Å. The geometries of a series of gas phase lithium salts [LiTf , LiTFSI , LiTFSM , LiClO_4 , LiPF_6 , LiAsF_6] have been optimized at B3LYP/6-31G* level of theory using density functional methods. The S-O bond in all these optimized structures tends to become longer when interacting with the Li cation, and the Li-O bond average distance lies in the range of 1.81-1.89 Å. For the triflate, imide, methanide, and perchlorate anions, the lithium cation is coordinated to two oxygens and has a binding energy of ca. 141 kcal/mol at the B3LYP/6-311+G(3df,2p)//B3LYP/6-31G* level. The two bulky electron withdrawing groups did not effect the binding energies. For the LiAsF_6 and LiPF_6 the lithium is coordinated to three oxygens and have binding energies of ca 136 kcal/mol. It is hoped that a more careful analysis of the neutron diffraction data for the LiClO_4 doped PEO will enable a more detailed comparison with the calculated structure.

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Table I. Total Energies (a. u.)

structure	B3LYP/	B3LYP/
	6-31G*	6-311+G(3df,2p)// B3LYP/6-31G*
Li ⁺	-7.28454	-7.28492
TF ⁻	-961.49795	-961.82545
TFSi ⁻	-1827.20408	-1827.78405
TFSM ⁻	-1811.13952	-1811.70862
ClO ₄ ⁻	-760.79844	-761.04148
AsF ₆ ⁻	-2833.00618	-2835.39697
PF ₆ ⁻	-940.64339	-940.97660
LiTf	-969.03055	-969.33782
LiTFSi	-1834.73266	
LiTFSM	-1818.67289	-1819.21982
LiClO ₄	-768.32702	-768.55391
LiAsF ₆	-2840.55101	-2842.89986
LiPF ₆	-948.17877	-948.48308

Table II. Binding energies (kcal/mol).

Reaction				B3LYP/	B3LYP/
				6-31G*	6-311+G(3df,2p)// B3LYP/6-31G*
LiTF	→	Li ⁺	+ Tf ⁻	155.7	142.7
LiTFSi	→	Li ⁺	+ TFSi ⁻	153.1	141.4 ^a
LiTFSM	→	Li ⁺	+ TFSM ⁻	156.1	142.0
LiAsF ₆	→	Li ⁺	+ AsF ₆ ⁻	158.4	134.8
LiPF ₆	→	Li ⁺	+ PF ₆ ⁻	153.7	136.4
LiClO ₄	→	Li ⁺	+ ClO ₄ ⁻	153.1	142.8

^a The binding energy for the LiTF was calculated at the at B3LYP/6-31+G*/B3LYP/6-31G*.

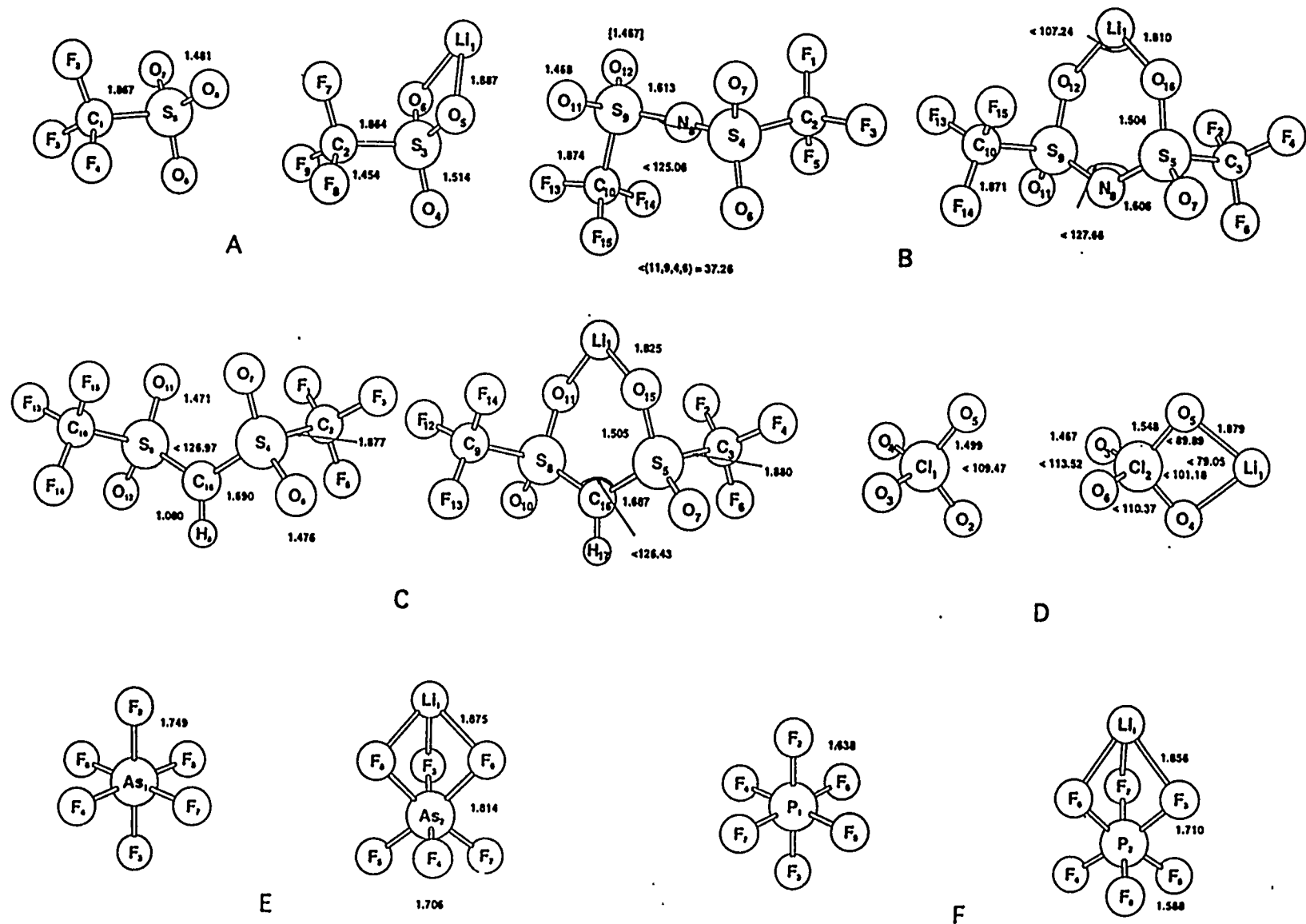


Figure 1. Optimized structures of (A) LiCF_3SO_3 , (B) $\text{Li}(\text{CF}_3\text{SO}_3)_2\text{N}$, (C) $\text{Li}(\text{CF}_3\text{SO}_2)_2\text{CH}$, (D) LiClO_4 , (E) LiAsF_6 , (F) LiPF_6 lithium salts and their "free" anions in the gas phase at the B3LYP/6-31G* level of theory.

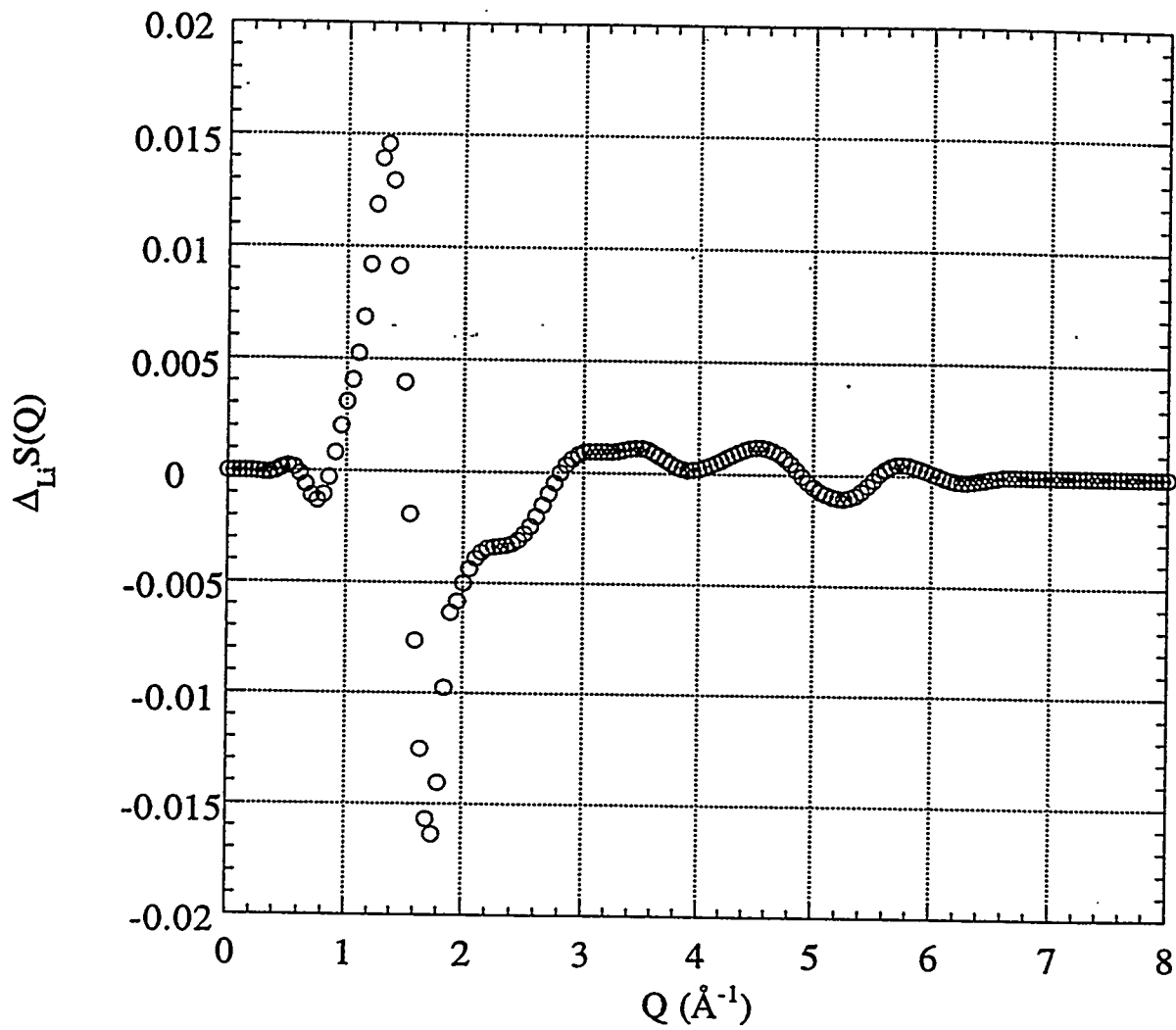


Figure 3. Lithium difference structure factor for LiClO_4 doped PEO.

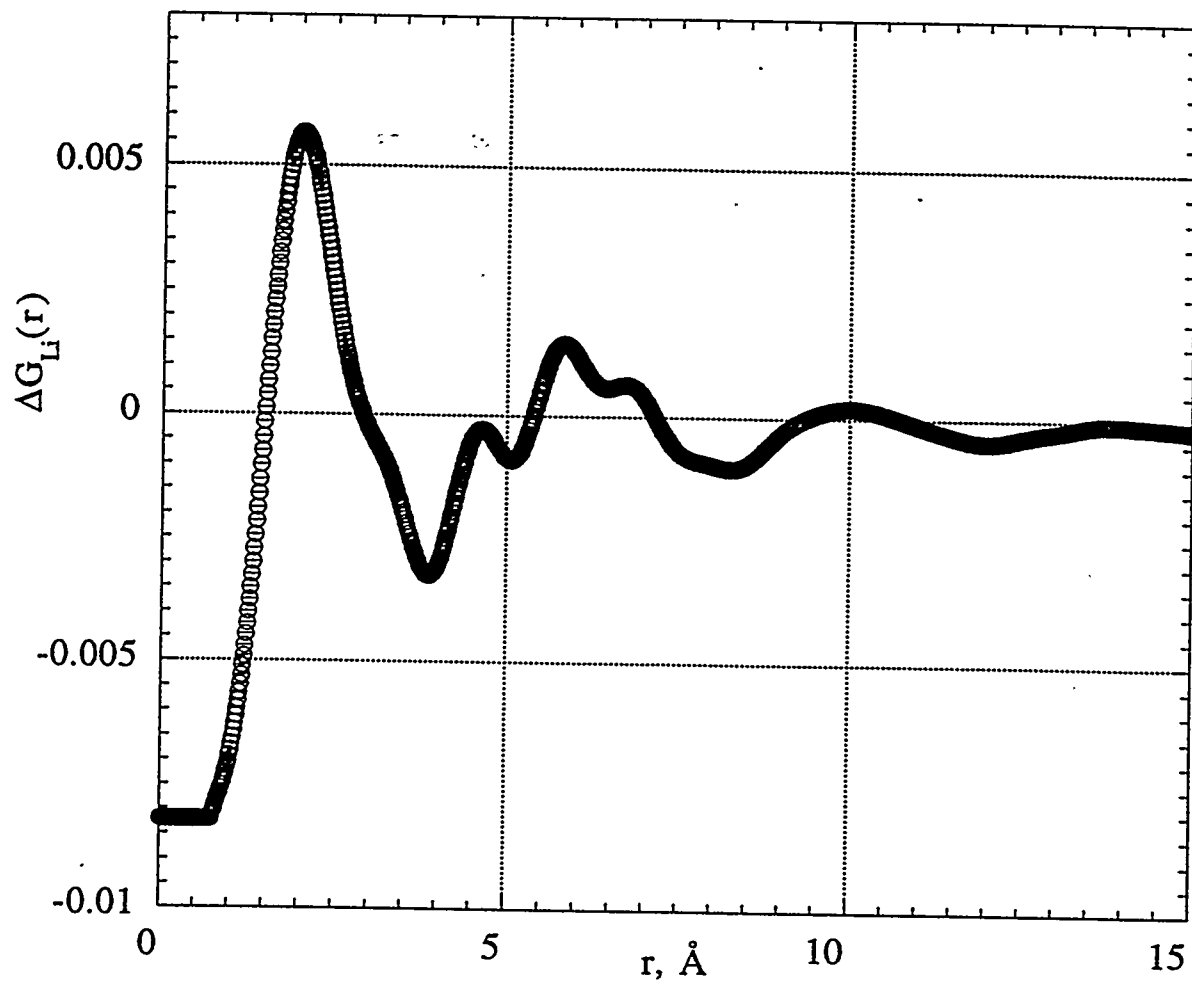


Figure 4. Lithium difference pair correlation function for LiClO_4 doped PEO.