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Quantum-Chemical Study of Ion Association in Electrolyte Systems Containing $LiAsF_6$

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The possibility that ion clusters of different species are formed during dissolution of $LiAsF_6$ in a low- or high-molecular-weight solvent has been studied. The Hessian matrix of clusters has been calculated by the numerical and analytical differentiation of their full energy in the MO LCAO approximation using the Roothaan−Hartree−Fock method and the PC GAMESS software package. It was found that stable ion clusters are represented by ion pairs $Li^+[AsF_6]^-$ with the bi- or tridentate coordination of the cation relative to the octahedral anion, triple ions $[AsF_6]^-Li^+[AsF_6]^-$ and $Li^+[AsF_6]^-Li^+$ with the bi- or tridentate coordination, ion dimers $\{Li^+[AsF_6]^-\}_2$ with the bidentate coordination, and also ion trimers $\{Li^+[AsF_6]^-\}_3$ and ion tetramers $\{Li^+[AsF_6]^-\}_4$ shaped as symmetric ring structures with the unidentate coordination. The frequencies and intensities of IR absorption bands of different species of ion clusters in the gaseous phase and nonaqueous solutions (acetone, ethanol, nitromethane, and tetrahydrofurane) have been calculated. This presents a basis for identification of ion particles during IR spectroscopic measurements in electrolyte solutions containing $LiAsF_6$.

Introduction

Information about the ionic structure of electrolyte solutions over a wide interval of salt concentrations is required both for a correct theoretical description of their properties and further advancement of the theory of electrolyte solutions and for the improvement of transport properties of electrolyte systems used in power sources. The method of vibrational spectroscopy is used frequently to determine the structure and the spatial configuration of ion particles, which are formed in low- and high-molecular-weight electrolyte systems.

Solutions of complex lithium fluorides in dipolar aprotic and/or macromolecular solvents are characterized by high transport characteristics. They are widely used as electrolytes in lithium cells and rechargeable lithium-ion batteries.[1,2] The $LiAsF_6$ salt presents a special interest among these compounds. Processes of ion solvation and association in electrolyte systems containing lithium hexafluoroarsenate have been dealt with in a number of papers.[3−12] It was found that $LiAsF_6$ dissolves thanks to the formation of a donor−acceptor bond between a lithium cation and a donor atom of the coordinating group in the solvent. The coordination between solvent molecules and Li^+ cations gives rise to new absorption bands in their vibrational spectra.[3−6] At the same time, the spectrum of the polyatomic anion $[AsF_6]^-$ in the solution is almost insensitive to ion−molecular interactions and, therefore, effects of ion−ion interactions can be clearly seen.[7]

The vibrational spectrum of the anion $[AsF_6]^-$ in the $CsAsF_6$ crystalline salt has been described in ref 13. According to ref 13, the anion $[AsF_6]^-$ has the octahedral symmetry O_h. It corresponds to three Raman vibrations: $\nu_1(A_g)$ at 685 cm^{-1}, $\nu_2(E_g)$ at 576 cm^{-1} (double degenerate), and $\nu_5(T_{2g})$ at 372 cm^{-1}. Also, there are two vibrations, which are active in the IR spectrum, namely, $\nu_3(T_{1u})$ at 699 cm^{-1} and $\nu_4(T_{1u})$ at 392 cm^{-1} (both triple degenerate). The coordination between the anion $[AsF_6]^-$ and the Li^+ cation during the formation of ion aggregates decreases the anion symmetry, which should be reflected in the anion vibrational spectrum.[7]

Experimental vibrational spectroscopic studies of the ion association in $LiAsF_6$ solutions in dipolar aprotic solvents and polymer electrolyte systems were performed by a number of researchers.[3,4,7−11] IR spectra of dilute solutions in solvents having a high dielectric constant exhibit a single absorption band of the triple degenerate vibration ν_3 of the "spectroscopically free" $[AsF_6]^-$ anion near 700−706 cm^{-1} depending on the origin of the solvent. The appearance of a high-frequency component at 708−720 cm^{-1} and a low-frequency shoulder near 680 cm^{-1} in the IR spectrum is generally acknowledged as an indication of the formation of contact ion pairs $Li^+[AsF_6]^-$.[3,4,7−11] Different researchers uniquely relate the high-frequency component to ion pairs $Li^+[AsF_6]^-$. However, opinions vary as to the ≈680 cm^{-1} band. Some researchers attribute it to the combination of valence vibrations $\nu_5 + \nu_6$.[8,11] One more opinion exists. Researchers[7,12] noted that the octahedral anion $[AsF_6]^-$ may have three coordinations with the lithium cation:

1. *The unidentate coordination*: The Li^+ ion is located at the 4-fold axis of the $[AsF_6]^-$ octahedron. Thus, it interacts only with one fluorine atom.
2. *The bidentate coordination*: The Li^+ ion is located at the 2-fold axis of the $[AsF_6]^-$ octahedron, which coincides with the bisector of the angle formed by the As atom and two nearest F atoms. In this case, the Li^+ cation interacts with the octahedron via two fluorine atoms.
3. *The tridentate coordination*: The Li^+ ion is located at the 3-fold axis of the $[AsF_6]^-$ octahedron. Here the anion coupling is realized via three fluorine atoms.

The semiempirical quantum-chemical calculation[12] showed that two configurations of the ion pair $Li^+[AsF_6]^-$ corresponding to the bi- and tridentate coordinations of the cation by the anion are stable and energy equivalent. Considering these data,

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researchers[7,12] related the two absorption bands at 708−720 and 680 cm^{-1} to a contact ion pair and explained their appearance by splitting of the triple degenerate vibration ν_3 into two vibrations ($A_1 + E$) after the symmetry of the anion in the ion pair decreased to C_{3v} (the tridentate coordination). However, the authors[12] and other researchers did not calculate vibrational spectra of the anion $[\mathrm{AsF_6}]^-$ in the contact ion pair having different coordinations of the anion and the cation. Therefore, the choice of the tridentate coordination seems to be insufficiently substantiated. Thus, the question of the spatial configuration of ion pairs in $\mathrm{LiAsF_6}$ solutions and their manifestations in vibrational spectra is still open.

Additional high-frequency components at 703−711 and 725−733 cm^{-1}, which are observed experimentally in spectra of some solutions (for example, acetone, tetrahydrofurane, ethyl acetate, and diethyl ester) with high concentrations of $\mathrm{LiAsF_6}$, were related[7] to the formation of triple ions such as $\mathrm{Li^+[AsF_6]^-Li^+}$. However, the authors[7] did not substantiate their interpretation.

The aforementioned information nearly exhausts the knowledge about spectroscopic manifestations of the ion association in $\mathrm{LiAsF_6}$ solutions. The literature does not report any data on spectroscopic manifestations of ion aggregates, which are more complicated than ion pairs or triple ions. Obviously, the available data are insufficient for the unique identification of the composition and the spatial structure of ion clusters formed in electrolyte solutions containing $\mathrm{LiAsF_6}$. In this connection, it is necessary to perform a quantum-chemical study of the structure and stability of different species of ion particles comprising a $\mathrm{Li^+}$ cation and a $[\mathrm{AsF_6}]^-$ complex anion and calculate their vibration spectra. The present study just deals with these problems.

Computation Details

The objective of the study was to analyze the possibility of formation of the following ion aggregates: ion pairs $\mathrm{Li^+[AsF_6]^-}$; two types of triple ions ($\mathrm{[AsF_6]^-Li^+[AsF_6]^-}$ and $\mathrm{Li^+[AsF_6]^-Li^+}$); dimers (quadruples) $\{\mathrm{Li^+[AsF_6]^-}\}_2$; trimers $\{\mathrm{Li^+[AsF_6]^-}\}_3$; and tetramers $\{\mathrm{Li^+[AsF_6]^-}\}_4$. Since the $\mathrm{Li^+}$ ion can be located differently relative to the $[\mathrm{AsF_6}]^-$ octahedron,[7,12] several possible spatial configurations were considered for each type of ion aggregate.

The stability of an arbitrary $\mathrm{Li}_m^+[\mathrm{AsF_6}]_n^-$ ion cluster was determined by locating the minimum of the full energy of the cluster $E_{\mathrm{Li}_m^+[\mathrm{AsF_6}]_n^-}$ in the assigned symmetry group and calculating vibrational frequencies of a cluster with an equilibrium (corresponding to the minimum of the full energy) structure. A cluster was assumed to be stable if its equilibrium structure had no imaginary vibrational frequencies, that is, all eigenvalues of the Hessian of the cluster were not negative. The stability of the ion cluster was determined only in terms of the Roothaan−Hartree−Fock (RHF) approximation on the assumption that structures that are unstable according to these calculations will also be unstable if correlation corrections MP2 are introduced. Given in Table 1 for all unstable structures are Cartesian coordinates of symmetry-nonequivalent atoms, which correspond to the minimum of the cluster energy. Coordinates of other atoms can be obtained by symmetry operations.

The formation energy of an ion aggregate containing n complex anions $[\mathrm{AsF_6}]^-$ and m cations $\mathrm{Li^+}$ can be determined from

$$E = E_{\mathrm{Li}_m^+[\mathrm{AsF_6}]_n^-} - nE_{[\mathrm{AsF_6}]^-} - mE_{\mathrm{Li^+}} \qquad (1)$$

where $E_{[\mathrm{AsF_6}]^-}$ is the full energy of a free anion $[\mathrm{AsF_6}]^-$ in the equilibrium configuration, $E_{\mathrm{Li^+}}$ is the full energy of a free cation $\mathrm{Li^+}$, and $E_{\mathrm{Li}_m^+[\mathrm{AsF_6}]_n^-}$ is the full energy of an ion aggregate in an equilibrium configuration.

TABLE 1: Coordinates of Symmetry-Unique Atoms

structure number	symmetry group	atom	coordinates		
			X	Y	Z
II	C_{2v}	As	0	0	0
		F	0.13	1.78	0
		F	0.08	0.08	−1.68
		F	0.09	−1.66	0
		Li	1.90	1.90	0
III	C_{3v}	As	0	0	0
		F	1.74	0.11	0.11
		F	−1.66	0.07	0.07
		Li	1.43	1.43	1.43
V	D_{2h}	As	0	0	0
		F	0	0	1.67
		F	1.72	0.07	0
		Li	1.96	1.96	0
VI	D_{3d}	As	0	0	0
		F	1.70	0.05	0.05
		Li	1.51	1.51	1.51
VIII	C_{4v}	As	0	0	2.83
		F	−1.17	0	1.53
		F	−1.23	0	3.98
		F	0	1.69	2.78
		Li	0	0	0
X	D_{3d}	As	1.55	1.55	1.55
		F	3.23	1.51	1.51
		F	−0.18	1.47	1.47
		Li	0	0	0
XIV	C_{2h}	As	0.31	2.52	0
		F	−0.61	3.89	0
		F	1.10	0.91	0
		F	1.35	3.01	−1.21
		F	−0.70	1.76	1.21
		Li	0	0	1.41
XV	D_{3h}	As	3.89	0	0
		F	3.78	0	1.68
		F	2.59	1.21	0
		F	5.02	1.23	0
		Li	−2.97	0	0
XVI	D_{4h}	As	4.79	0	0
		F	1.21	3.49	0
		F	5.91	1.24	0
		F	4.67	0	1.68
		Li	2.85	2.85	0

Optical properties of the solution containing the ion aggregates under study can be described by the following relationship for the dielectric constant:

$$\epsilon(\omega) = \epsilon_\omega + \sum_s \frac{f_s}{{\omega_s}^2 - \omega^2 + i\omega\Gamma_s} \qquad (2)$$

where s numbers the vibrational frequencies of the particles, ω_s is the frequency of the corresponding vibration, f_s is the oscillator strength, and Γ_s is the line width in the vibrational spectrum.

The “oscillator strength” means the value that is determined together with vibrational frequencies via the dipole moment derivatives of the ion cluster from displacements of its atoms.[15,16]

The line width was not calculated. The Γ_s value was fixed at 30 cm^{-1} for all the spectra.

In this case, the absorption $A(\omega)$ is proportional to

$$A_e(\omega) \propto -\omega\, \mathrm{Im}(\sqrt{\epsilon(\omega)}) \qquad (3)$$

The calculation of the full energy of ion clusters (for determination of both the equilibrium structure and the Hessian matrix)

TABLE 2: Vibrational Frequencies and Structure Parameters of the Complex Anion $[AsF_6]^-$

As−F distance, Å	ν_1 (A_g)	ν_2 (E_g)	ν_5 (T_{2g})	ν_4 (T_{1u})	ν_3 (T_{1u})	T_{2u}
1.82[a]	685[a]	576[a]	372[a]	392[a]	699[a]	
1.71[b]	746[b]	608[b]	403[b]	442[b]	763[b]	261[b]
1.75[c]	653[c]	555[c]	359[c]	396[c]	686[c]	233[c]

[a] Experimental data (ref 13). [b] Calculated values (RHF method). [c] Calculated values (RHF with MP2).

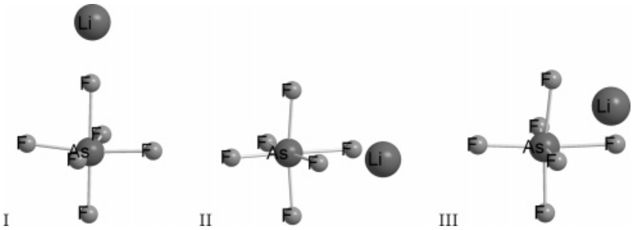

Figure 1. The possible structures of ionic pairs $Li^+[AsF_6]^-$.

was made using the RHF nonempirical MO LCAO SCF method[14] and the PC GAMESS version[15] of the GAMESS(US) package of quantum-chemical programs.[16] All the ion aggregates were calculated using the same atomic basis GTO: 6-311G* for As,[17] TZV for F with three polarizing *d* functions (with exponents 5.12, 1.28 and 0.32),[16] and cc-pVDZ for Li.[18]

Results and Discussion

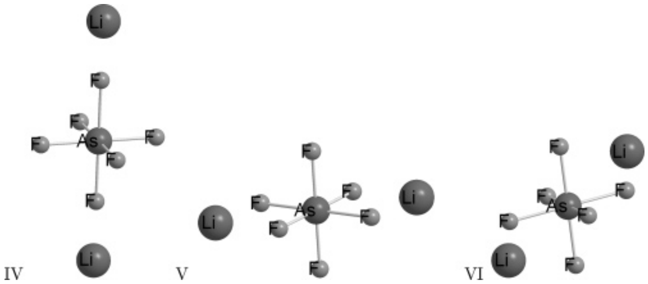

Figure 2. The possible structures of ionic triples $Li^+[AsF_6]^-Li^+$.

Structure and Stability of $Li_m^+[AsF_6]_n^-$ Aggregates in the Gaseous Phase. *Anion $[AsF_6]^-$*. Calculated parameters of the structure and vibrational frequencies of the free octahedron $[AsF_6]^-$ are given in Table 2 where they are compared with the literature data for $CsAsF_6$.[13] Since Cs^+ cations and $[AsF_6]^-$ complex anions are bound much weaker in the crystal than in the $[AsF_6]^-$ complex, this comparison is correct. The calculation of the optimal structure of the complex showed that the equilibrium state As−F, which was obtained using the RHF scheme, was 1.71 Å. This value is smaller than the experimental value (1.82 Å[13]). If correlation corrections are introduced in terms of the MP2 method, the equilibrium state equals 1.75 Å, which is closer to the experimental value. Vibrational frequencies of the $[AsF_6]^-$ complex, which were calculated using the RHF method, proved to be a little higher than the observed frequencies (Table 2). Nevertheless, as seen from Table 2, the characteristics of the calculated and experimental spectra are in good mutual agreement, a fact which points to correctness of the calculation methods used.

Ion Pairs $Li^+[AsF_6]^-$. Ion pairs can have three spatial configurations corresponding to uni-, bi-, and tridentate coordinations of Li^+ relative to the $[AsF_6]^-$ octahedron (Figure 1 and Table 3). The calculation showed that the unidentate configuration I is unstable with respect to the movement of a Li^+ ion corresponding to the transition to the bidentate configuration (II) or the tridentate configuration (III), which are stable as follows from the calculation of the Hessian matrix (Table 3).

Triple Ions $Li^+[AsF_6]^-Li^+$. Three possible spatial structures (Figure 2) were considered for positive triple ions: both cations Li^+ were unidentate, bidentate, or tridentate relative to the $[AsF_6]^-$ octahedron (the configurations IV, V, and VI in Table 3, respectively). In all these configurations, the lithium cations hit a straight line passing through the As atoms. According to the calculation, similarly to the ion pairs, the unidentate configuration IV proved to be unstable with respect to the movement of Li^+ in the direction of the unstable bi- and tridentate configurations V and VI.

Triple Ions $[AsF_6]^-Li^+[AsF_6]^-$. One tridentate configuration (X), two bidentate configurations (VIII and IX), and one unidentate configuration (VII) (Table 3) were considered for negative triple ions $[AsF_6]^-Li^+[AsF_6]^-$. The calculation showed that the tridentate configuration X was stable. It could be pictured as follows (Figure 3): the Li^+ ion and the As atoms were located on a single axis, while the $[AsF_6]^-$ octahedrons were turned such that the lithium cation was surrounded by an octahedron of the nearest fluorine atoms. Of the two bidentate configurations studied, only configuration VIII proved to be stable (Figure 3): the lithium ion and the As atoms hit a single straight line, which coincided with the 2-fold axis of the $[AsF_6]^-$ octahedrons. Note that one $[AsF_6]^-$ octahedron can be obtained

TABLE 3: Structure and Formation Energy for the $Li_m^+[AsF_6]_n^-$ Ion Aggregates

associate type	Li^+ coordination with respect to $[AsF_6]^-$	structure number	symmetry group	Is structure stable?	$\langle r_{As-F}\rangle$, Å	$\langle r_{As-Li}\rangle$, Å	$\langle r_{As-F}\rangle$, Å (MP2)	$\langle r_{As-Li}\rangle$, Å (MP2)	formation energy, kJ/mol	formation energy (MP2), kJ/mol
$Li^+[AsF_6]^-$	monodentate	I	C_{4v}	no						
	bidentate	II	C_{2v}	yes	1.71	2.69	1.75	2.75	−591	−550
	tridentate	III	C_{3v}	yes	1.71	2.48	1.75	2.55	−597	−562
$Li^+[AsF_6]^-Li^+$	monodentate	IV	D_{4h}	no						
	bidentate	V	D_{2h}	yes	1.71	2.78	1.75	2.82	−735	−736
	tridentate	VI	D_{3d}	yes	1.71	2.61	1.75	2.66	−719	−727
$[AsF_6]^-Li^+[AsF_6]^-$	monodentate	VII	D_{4h}	no						
	bidentate	VIII	C_{4v}	yes	1.71	2.83	1.75	2.86	−734	−748
	bidentate	IX	D_{2h}	no						
	tridentate	X	D_{3d}	yes	1.71	2.68	1.75	2.71	−747	−752
$\{Li^+[AsF_6]^-\}_2$	bi- and tridentate	XI	C_{2v}	no						
	monodentate	XII	D_{2h}	no						
	tridentate	XIII	C_{2v}	no						
	bidenatate	XIV	C_{2h}	yes	1.71	2.90			−1267	
$\{Li^+[AsF_6]^-\}_3$	monodentate	XV	D_{3h}	yes	1.71	3.52			−1826	
$\{Li^+[AsF_6]^-\}_4$	monodentate	XVI	D_{4h}	yes	1.71	3.44			−2455	

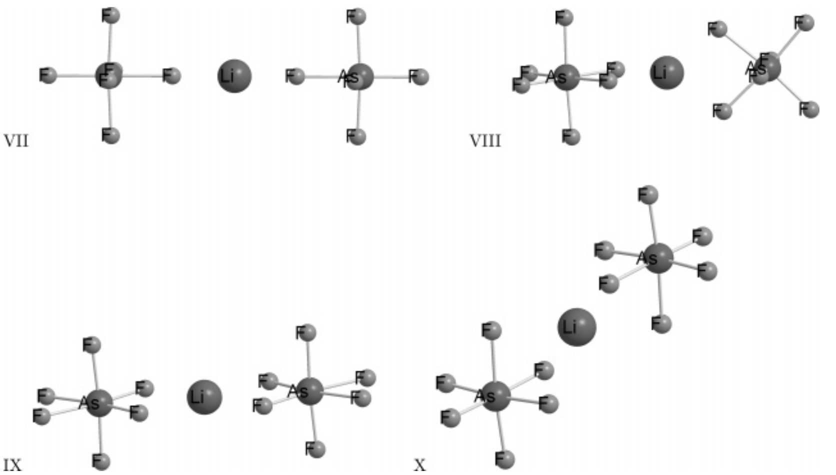

Figure 3. The possible structures of ionic triples $[AsF_6]^{-}Li^{+}[AsF_6]^{-}$.

from another octahedron by turning it around the axis connecting the As atoms and Li^+ through the angle $\pi/2$ and the parallel shift along the turning axis. This case corresponds to the space group C_{4v}. Thus, the Li^+ cation in structure VIII has the tetrahedral environment of the nearest fluorine atoms.

It is remarkable that the first coordination sphere of the lithium cation is saturated in the two stable configurations of triple ions $[AsF_6]^{-}Li^{+}[AsF_6]^{-}$ (configurations VIII and X). Therefore, one may expect that particles having this structure will not be involved in the donor−acceptor interaction with the solvent molecules, that is, will not be solvated.

Dimers (Quadruples) $\{Li^+[AsF_6]^-\}_2$. The calculation of the structure and the check of the stability of dimers $\{Li^+[AsF_6]^-\}_2$ with a linear arrangement of the ions and the bi- and tridentate coordinations of the anions $[AsF_6]^-$ showed that a cluster of the $Li^+[AsF_6]^-Li^+[AsF_6]^-$ type was unstable. This was caused probably by the saturation of $Li^+-[AsF_6]^-$ bonds in this configuration.

In addition to the linear spatial configuration, three more possible spatial configurations XI, XII, and XIII (Table 3 and Figure 4) were considered for the dimers. In all the dimers studied, both As atoms and four F atoms of each complex anion $[AsF_6]^-$ lie in a single plane. One dimer differs from another dimer by the relative orientation of the $[AsF_6]^-$ octahedrons. In one case, the anions $[AsF_6]^-$ are "parallel" one to the other (Figure 4, configuration XII), while in the other case they are turned through $\pi/2$ (Figure 4, configuration XI). These two configurations proved to be unstable. The third nonlinear configuration (Figure 4, configuration XIII) was unstable also.

The relaxing of the symmetry of each of the nonlinear configurations XI, XII, and XIII relative to unstable vibrations brings all these clusters to a single common stable structure with the bidentate coordination of lithium ions (Figure 4, configuration XIV). The straight lines connecting Li^+ ions and As atoms in this structure are mutually perpendicular. In this case, the octahedrons $[AsF_6]^-$ are located such that the As−As axis is their 3-fold axis (C_3). Moreover, the octahedrons are rotated relative to one another through the angle π around this axis. Each Li^+ ion in this structure is surrounded by four F atoms (two of them are bridge atoms belonging simultaneously to both Li^+ ions), which form an octahedron with two vacant sites. Thus, dimers $\{Li^+[AsF_6]^-\}_2$ have the only stable configuration XIV with the bidentate coordination of Li^+ ions corresponding to the C_{2h} symmetry.

Trimers $\{Li^+[AsF_6]^-\}_3$ *and Tetramers* $\{Li^+[AsF_6]^-\}_4$. Since the linear structure of the dimers $\{Li^+[AsF_6]^-\}_2$ proved to be unstable, these configurations were neglected in more complex ion aggregates $\{Li^+[AsF_6]^-\}_3$ and $\{Li^+[AsF_6]^-\}_4$.

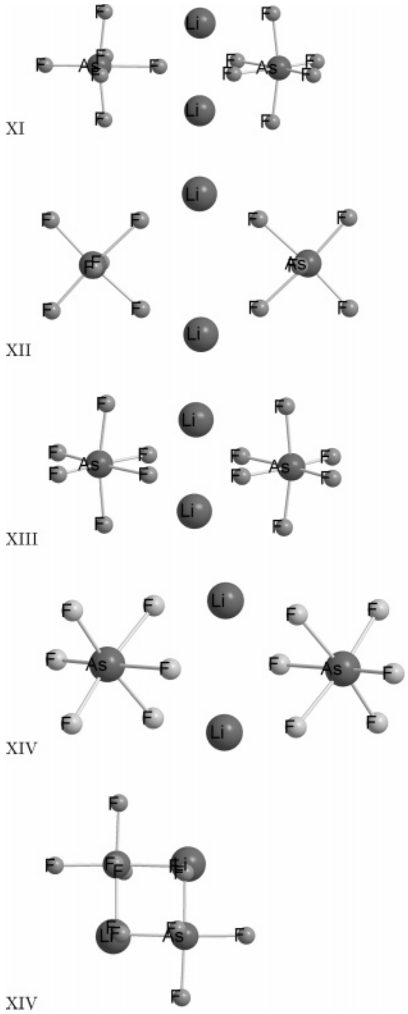

Figure 4. The possible structures of ionic dimers (quadruples) $\{[AsF_6]^{-}Li^{+}\}_2$.

One nonlinear configuration corresponding to the unidentate coordination was considered for tri- and tetramers (Table 3). In these configurations (Figure 5, configurations XV and XVI), one 2-fold axis of each octahedron $[AsF_6]^-$ intersects in a common center and the axes lie in a single plane. One octahedron $[AsF_6]^-$ can be obtained from another octahedron by turning it around the axis, which is perpendicular to the plane

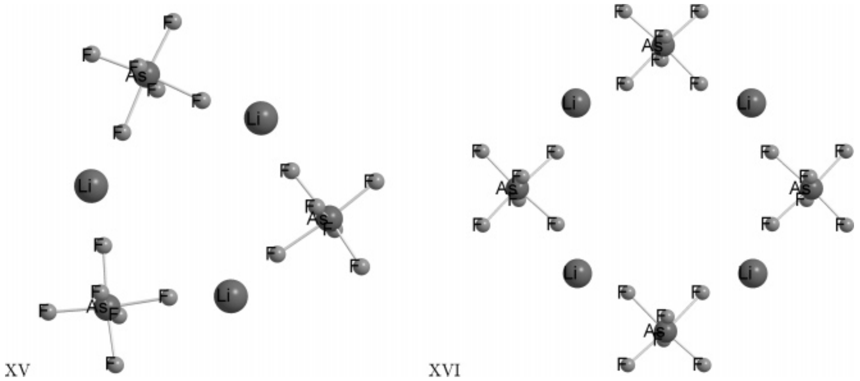

Figure 5. The possible structures of ionic trimers $\{Li^+[AsF_6]^-\}_3$ (left) and tetramers $\{Li^+[AsF_6]^-\}_4$ (right).

formed by the preferred 2-fold axes, through the angle $2\pi/3$ for the trimer XV and $\pi/2$ for the tetramer XVI. Thus, in structures XV and XVI four F atoms of each octahedron $[AsF_6]^-$ lie in a single plane common for all the atoms. Li^+ atoms are located in the same plane. According to the calculation, these ring structures are quite stable.

From the calculation, it is seen (Table 3) that in almost all the types of ion aggregates, except ring trimers and tetramers, the unidentate coordination of the Li^+ cation relative to the $[AsF_6]^-$ octahedron leads to unstable spatial configurations. This situation can be explained qualitatively if one considers that the Li^+ cation with the unidentate coordination in ion pairs and triple ions neighbors on one fluorine atom only and a continuous transition is available to more stable bi- and tridentate coordinations, when the Li^+ ion interacts with more fluorine atoms. In ring trimers and tetramers, the Li^+ cation is surrounded by two F atoms and these particles do not have stable modifications with another coordination means.

The first coordination sphere of Li^+ cations is not saturated in all stable configurations of the ion aggregates, except triple ions $[AsF_6]^-Li^+[AsF_6]^-$ (structures VIII and X). It has vacant coordination sites, which can be occupied by solvent molecules.

Formation Energies of $Li_m^+[AsF_6]_n^-$ Ion Aggregates. The energy of formation of an ion aggregate of individual Li^+ ions and $[AsF_6]^-$ in the gaseous phase or, in other words, the energy of binding of complex anions $[AsF_6]^-$ and lithium cations was calculated from eq 1 using the RHF approximation. The energy of formation of ion aggregates was estimated for all the structures at hand (configurations I−XVI). Table 3 gives formation energy values for stable configurations only.

The correlation energy makes some contribution to the formation energy. Correlation corrections were introduced in the calculation made in terms of the Moller−Plesset second-order perturbation theory (MP2).[16] The binding energy was calculated taking into account MP2 correlation corrections so as to determine the new structure of ion aggregates $Li_m^+[AsF_6]_n^-$ corresponding to the minimum of the full energy with MP2 corrections, and then the structure of the free complex anion $[AsF_6]^-$ was optimized a second time. The overall accuracy of the calculation was evaluated by calculating MP4 corrections[15] without optimization of the ion aggregate structure. The maximum error, that is, the value of the correction MP2 to the full energy of a complex anion $[AsF_6]^-$ was about 20 kJ/mol. The correction to the full energy of complexes $Li_m^+[AsF_6]_n^-$ had the same value. The minimum error, which was estimated from the correction MP4 to the energy of a complex anion $[AsF_6]^-$, was about 0.3 kJ/mol. The calculation of the formation energy of ion aggregates $Li_m^+[AsF_6]_n^-$, which takes into account correlation corrections, provides more accurate values, but it is very awkward. Therefore, only several structures (see Table 3) were calculated taking into account MP2 correlation corrections.

From Table 3, it is seen that dimers $\{Li^+[AsF_6]^-\}_2$, trimers $\{Li^+[AsF_6]^-\}_3$, and tetramers $\{Li^+[AsF_6]^-\}_4$ are most favorable configurations from the energy viewpoint. However, if the total formation energy of an ion aggregate is referred to the number of $Li^+-[AsF_6]^-$ "bonds", the largest energy corresponds to bonds in ion pairs: it is ≈200 kJ/mol higher than in triple ions and ≈280 kJ/mol larger than in trimers. The formation energy of dimers, trimers, and tetramers can also be compared with the formation energy of ion pairs if the formation energy of $\{Li^+[AsF_6]^-\}_k$ is referred to the number of ion pairs k in a neutral aggregate. The comparison of these quantities shows that the formation of dimers provides the largest (40 kJ/mol) energy gain. The energy gain from the formation of trimers and tetramers is 20 kJ/mol.

Thus, the cluster formation energy rises with the growing number of particles in the ion aggregate $Li_m^+[AsF_6]_n^-$. However, the analysis of experimental data should take into account that the probability of formation of a particular aggregate depends not only on the energy of ion−ion interactions but also on the concentration fluctuations in the solution. Therefore, one should expect that different concentration intervals will correspond to different species of dominating ion particles.

Vibrational Frequencies of Ion Aggregates: IR Spectrum. Vibrational frequencies of stable clusters $Li_m^+[AsF_6]_n^-$ in the gaseous phase (Table 3) were calculated in terms of the RHF method. The Hessian matrix was calculated analytically for all ion aggregates, except the dimer, the trimer, and the tetramer. The calculated vibrational frequencies are given in Table 4.

The introduction of the lithium ion caused the following qualitative changes in the IR spectrum of the complex ion $[AsF_6]^-$: (1) the appearance of new lines related to Li^+ vibrations; (2) the appearance of new lines caused by the decrease in the local symmetry of the $[AsF_6]^-$ octahedron; (3) the shift of the lines of the complex anion $[AsF_6]^-$, which was connected with the interaction between Li^+ vibrations and $[AsF_6]^-$ vibrations.

The shift and splitting of odd vibrations of the anion $[AsF_6]^-$, which are active in the IR spectrum, depend on frequencies connected with vibrations of the Li^+ cation. The frequency of these vibrations is determined by two factors, namely, the mass of the Li^+ cation and the strength of its interaction with other atoms in ion aggregates. Since Li^+ has a small mass, positions of the spectrum lines will considerably depend on the strength of the $[AsF_6]^--Li^+$ bond. It should be expected that positions of Li^+ lines will be determined mainly by the coordination (uni-, bi-, or tridentate) of the cation.

TABLE 4: Calculated Vibrational Frequencies for the Stable Ion Aggregates $Li_m^+[AsF_6]_n^-$

structure number	symmetry group		frequencies, cm^{-1}
II	C_{2v}	A_1	829 731 610 578 459 375 269
		A_2	403 206
		B_1	827 440 410 60
		B_2	821 549 499 362 224
III	C_{3v}	A_1	840 711 528 488 393
		A_2	240
		E	826 579 449 410 290 208
V	D_{2h}	A_{1g}	776 649 484 372
		B_{1g}	400
		B_{2g}	420 101
		B_{3g}	602 297
		A_{1u}	276
		B_{1u}	755 484 436 289
		B_{2u}	720 468 278 170
		B_{3u}	869 442 90
VI	D_{3d}	A_{1g}	768 434 392
		E_g	643 407 94
		A_{1u}	221
		A_{2u}	818 510 358
		E_u	777 442 294 71
VIII	C_{4v}	A_1	796 737 621 472 411 275 78
		A_2	402 267
		B_1	403 268 15
		B_2	620 571 454 391 270
		E	807 780 581 461 438 408 295 226 71 27
X	D_{3d}	A_{1g}	805 744 476 407 76
		A_{2g}	245
		E_g	783 604 435 404 273 39
		A_{1u}	246 14
		A_{2u}	800 740 522 430 399
		E_u	791 618 449 405 276 136 34
XIV	C_{2h}	A_g	838 818 712 546 493 441 412 406 332 273 124 98
		B_g	815 603 512 437 376 278 261 182 88
		A_u	820 599 464 425 289 272 257 84 49
		B_u	833 824 706 577 541 461 441 405 384 274 213 57
XV	D_{3h}	A_1'	813 756 630 450 381 268 238 56
		A_2'	798 695 485 414 254 36
		E'	814 805 774 688 613 509 436 419 379 261 250 238 26 22
		A_1''	405 265
		A_2''	836 436 403 89 33 25
		E''	832 431 405 403 266 49 29 25
XVI	D_{4h}	A_{1g}	810 755 614 464 398 267 203 87
		A_{2g}	794 668 503 419 257 46
		B_{1g}	810 769 677 534 414 379 244 8
		B_{2g}	804 604 440 303 239 30 29
		E_g	832 434 406 403 266 73 26 19
		A_{1u}	404 266 31
		A_{2u}	836 442 404 90 67
		B_{1u}	406 267 61 20
		B_{2u}	830 431 403 28 8
		E_u	808 800 761 677 619 518 441 425 389 283 252 227 36 30

New lines associated with the decrease in the anion symmetry may emerge for two reasons: removal of the inversion on the As atom and splitting of the lines, which are active in the IR spectrum of the undistorted free anion $[AsF_6]^-$. The first situation is not realized only in triple ions $Li^+[AsF_6]^-Li^+$. The IR spectra of all the other structures should contain additional lines whose frequencies approach those of the combination scattering of the undistorted octahedron $[AsF_6]^-$.

A group-theoretical analysis was performed to determine possible splittings of vibrations of the octahedron $[AsF_6]^-$ resulting from the decrease in the octahedron symmetry after the formation of ion aggregates. The analysis results are given in Table 5.

Partial densities of vibrational states were plotted (Figure 6) to picture the distribution of vibrational degrees of freedom. Considering that ion aggregates comprising a small number of ions have little vibrational states, the density of states may be presented as Gaussians:

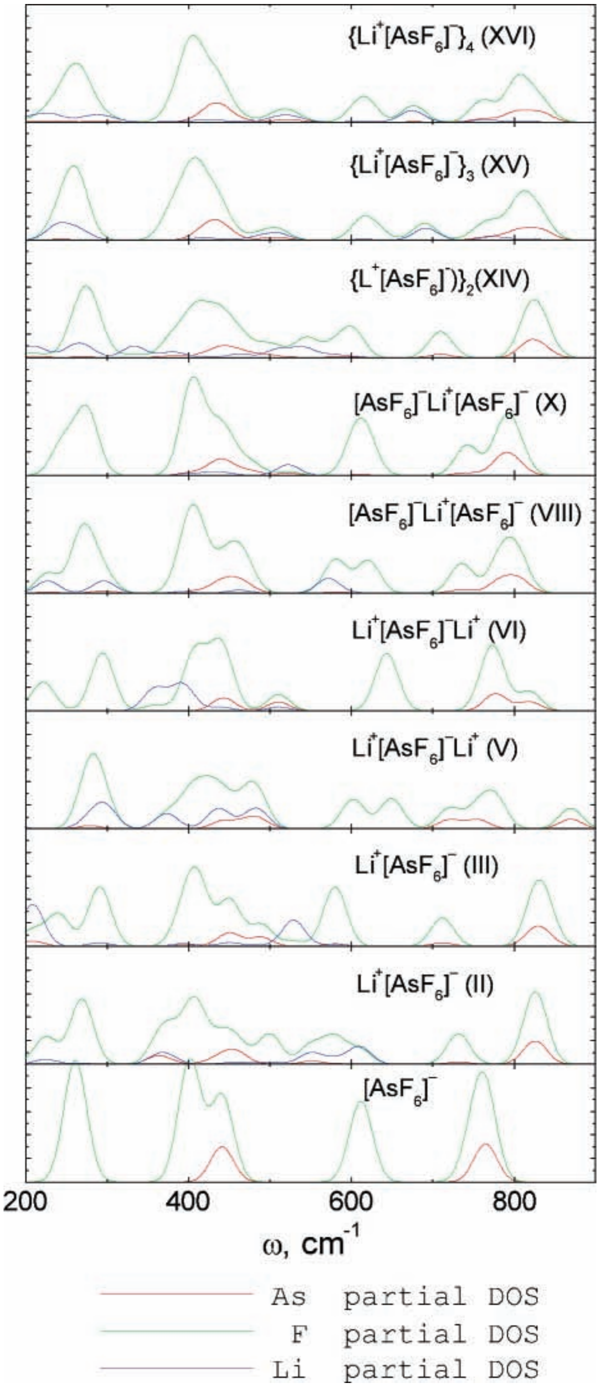

Figure 6. The partial vibrational densities of states of stable ionic associates.

$$g_i(\omega) = \frac{\sum_{k\alpha} e(i\alpha|k)e^*(i\alpha|k) \exp(-(\omega - \omega_k)^2/\sigma^2)}{\int_0^\infty g(\omega)\, d\omega} \tag{4}$$

where i numbers the aggregate ions; $g(\omega)$ is the total density of vibrational states (the integral in the denominator means normalization of the densities to unity); $e(i\alpha|k)$ is the component of the vibrational vector numbered k. Thus, the partial density of vibrational states for each ion species is the sum of densities

TABLE 5: Results of Group Theory Analysis of $[AsF_6]^-$ Vibration Splitting Caused by Formation of $Li_m^+[AsF_6]_n^-$ Ion Associates

structure number	irreducible representations of $[AsF_6]^-$ complex					
	A_g	E_g	T_{2g}	T_{2u}	T_{1g}	T_{1u}
II	A_1	$A_1 + B_2$	$A_1 + B_1 + A_2$	$A_1 + A_2 + B_1$	$A_2 + B_1 + B_2$	$A_1 + B_2 + B_1$
III	A_1	E	$A_1 + E$	$A_2 + E$	$A_2 + E$	$A_1 + E$
V	A_g	$A_g + B_{3g}$	$A_g + B_{1g} + B_{2g}$	$A_u + B_{1u} + B_{2u}$	$B_{1g} + B_{2g} + B_{3g}$	$B_{1u} + B_{2u} + B_{3u}$
VI	A_g	E_g	$A_g + E_g$	$A_{1u} + E_u$	$A_{2g} + E_g$	$A_{2u} + E_u$
VIII	$A_1 + B_2$	$A_1 + B_2 + E$	$A_1 + A_2 + B_1 + B_2 + E$	$A_1 + A_2 + B_1 + B_2 + E$	$A_2 + B_1 + 2E$	$A_1 + B_2 + 2E$
X	$A_g + A_{2u}$	$E_g + E_u$	$A_g + A_{2u} + E_g + E_u$	$A_{1u} + A_{2g} + E_g + E_u$	$A_{1u} + A_{2g} + E_g + E_u$	$A_g + A_{2u} + E_g + E_u$
XIV	$A_g + B_u$	$A_g + B_g + A_u + B_u$	$2A_g + B_g + A_u + 2B_u$	$A_g + 2B_g + 2A_u + B_u$	$A_g + 2B_g + 2A_u + B_u$	$2A_g + B_g + A_u + 2B_u$
XV	$A_1' + E'$	$A_1' + A_2' + 2E'$	$A_1' + A_1'' + A_2'' + E' + 2E''$	$A_1' + A_2' + A_1'' + 2E' + E''$	$A_2' + A_1'' + A_2'' + E' + 2E''$	$A_1' + A_2' + A_2'' + 2E' + E''$
XVI	$A_g + B_{1g} + E_u$	$A_g + A_{2g} + B_{1g} + B_{2g} + 2E_u$	$A_g + A_u + A_{2u} + B_{1g} + B_{1u} + B_{2u} + 2E_g + E_u$	$A_g + A_u + A_{2g} + B_{1g} + B_{1u} + B_{2g} + E_g + 2E_u$	$A_u + A_{2g} + A_2 + B_{1u} + B_{2g} + B_{2u} + 2E_g + E_u$	$A_{1g} + A_{2g} + A_{2u} + B_{1g} + B_{2g} + B_{2u} + E_g + 2E_u$

$g_i(\omega)$, where i numbers fluorine ions for the partial density of fluorine vibrations and As ions for the density of As vibrations.

The line width was arbitrarily taken as equal to 20 cm^{-1} in the calculation for all densities of vibrational states. From Figure 6, it is seen that vibrational frequencies associated with the Li^+ movement are not higher than the upper vibrational frequencies of the F atom in nearly all the ion aggregates under study. Their maximum corresponds to 700 cm^{-1}.

The vibrational frequency characterizes rigidity of Li^+ cation binding in an ion aggregate. The higher the vibrational frequency, the more rigid the bond. The presence of several maxima of the density of vibrational states of lithium in Figure 6 corresponds to different spatial directions of vibrations. Their different frequencies reflect different rigidity of bonds. An examination of Figure 6 shows that the Li^+ cation in the ion pair III with the tridentate coordination is bound less rigidly than in the ion pair II with the bidentate coordination. Li^+ cations proved to be most mobile in triple ions $Li^+[AsF_6]^-Li^+$ (configurations V and VI) and least mobile in triple ions $[AsF_6]^-Li^+[AsF_6]^-$ (configurations VIII and X) where the first coordination sphere of the lithium cation is fully occupied with fluorine atoms. Lithium ions may vibrate in several directions in neutral ion aggregates $\{Li^+[AsF_6]^-\}_n$. Cations are bound more rigidly in some directions (high-frequency maxima in Figure 6) and less rigidly in other directions (low-frequency maxima). It may be thought therefore that lithium cations in neutral ion aggregates will be mobile in directions beyond the limits of their plane. This information may be useful for identification of mechanisms of the transport of lithium cations in real electrolyte solutions.

From Table 2, it is seen that the calculated vibrational frequencies of the free anion $[AsF_6]^-$ are nearly 10% higher than the experimental frequencies,[13] which is typical for RHF calculations. One may assume therefore that the calculated vibrational frequencies of the ion aggregates $Li_m^+[AsF_6]_n^-$ are slightly overestimated as compared with the experimental frequencies. Therefore, it is difficult to compare the calculated absorption spectra in Table 4 with the experimental spectra.

The correction factor of 0.92 was introduced, and the spectrum lines were calculated from formula 3 for convenient comparison of the calculated IR spectra of stable ion aggregates and the experimental spectra. Since the line widths Γ_s were unknown, they were arbitrarily taken as equal to 30 cm^{-1} for all the lines. The IR spectra, which were calculated for all stable ion aggregates after the aforementioned transformations, are shown in Figure 7. To render the analysis of the experimental data convenient, Figure 7 presents the spectrum of the free anion $[AsF_6]^-$. From this figure, it is seen that each type of ion aggregates gives its own specific IR spectrum in the gaseous phase and, therefore, the IR spectroscopic method can be used in principle for identification of ion particles in solutions and determination of their spatial configuration. One should analyze the whole frequency interval from 200 to 850 cm^{-1}, rather than limiting the analysis to a fragment of the spectrum near the

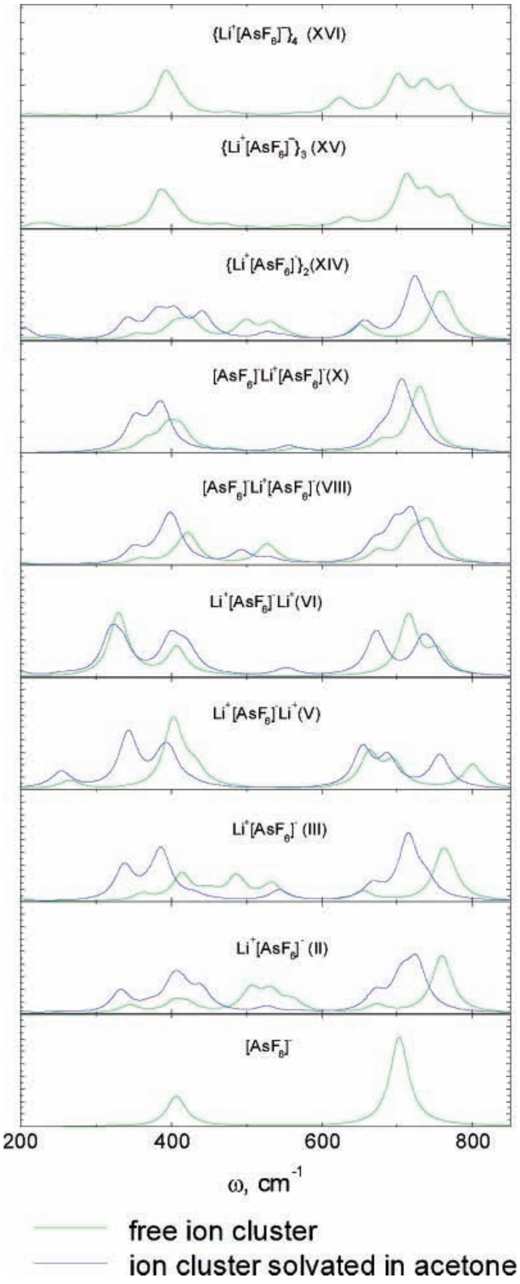

Figure 7. The calculated IR spectra of free anion $[AsF_6]^-$ and stable associates $Li_m^+[AsF_6]_n^-$. (The frequencies for this figure were multiplied by a factor of 0.92.)

absorption band at 700 cm^{-1}, which has been a common practice so far.[3,4,6−11]

The spectra of all stable particles (configurations II, III, V, VI, VIII, X, and XIV), except the trimer (configuration XV) and the tetramer (configuration XVI) were calculated to analyze how the solvent affects the shape of the IR spectra of the ion aggregates. The model of a continuous polarized medium[19] was used for the calculations. Therefore, it was possible not to preset the spatial configuration of the solvated ion aggregate and disregard the geometry of solvent molecules. The solvents were acetone, ethanol, and nitromethane, which have nearly equal dielectric constants (20.5, 24.3, and 38.6, respectively[20]), as well as tetrahydrofurane ($\epsilon = 7.4$[20]). The calculations showed that the spectra of the particles in the solution differed slightly from the corresponding spectra in the gaseous phase. However, each particle had its own inherent shape of the spectrum. The effect of the solvent led to a monotonic shift of (polar) vibrations, which were active in the IR spectra, to the low-frequency region. The shift value depended on the polarity of the medium. In the case of solvents with similar characteristics (acetone, ethanol, and nitromethane), the shift value was the same and the calculated spectra were almost identical. Figure 7 presents spectra of the ion aggregates II, III, V, VI, VIII, X, and XIV in acetone.

The comparison of the spectra in Figure 7 with those reported in the literature shows that the researchers[7−11] were right in relating the high-frequency component at 708−720 cm^{-1} and the low-frequency shoulder near 680 cm^{-1} to the formation of contact ion pairs $Li^+[AsF_6]^-$. However, the analysis of a narrow section of the spectrum near the absorption band $\nu_3([AsF_6]^-)$ is insufficient for establishment of the spatial configuration of ion pairs and the conclusion[7] about the tridentate coordination of the cation has not been substantiated. The observed increase[8] in the relative intensity of the absorption band at 676 cm^{-1} with growing concentration of the salt in the poly(ethylene oxide)−$LiAsF_6$ system may be due not to the increase in the fraction of ion pairs in the electrolyte, as the authors[8] think, but to the replacement of the species of dominating ion particles. The increase in the intensity and the appearance of additional high-frequency components of the complex absorption band at $\nu_3([AsF_6]^-)$, which were noted by researchers[7] in IR spectra of strong solutions in dipolar aprotic solvents with a small dielectric constant and by us in strong polymer solid electrolytes,[9,10] may be due to the formation of ion dimers, trimers, or tetramers, rather than the appearance of triple ions of the $Li^+[AsF_6]^-Li^+$ type along with ion pairs and free anions.

The comparison of our calculation results with experimental data obtained by different authors demonstrated their good mutual agreement. Therefore, IR spectra of real electrolyte solutions can be interpreted more accurately.

Conclusion

It was found that stable ion clusters are ion pairs $Li^+[AsF_6]^-$ with the bi- or tridentate coordination of the cation relative to the octahedral anion, triple ions $[AsF_6]^-Li^+[AsF_6]^-$ and $Li^+[AsF_6]^-Li^+$ with the bi- or tridentate coordination, dimers $\{Li^+[AsF_6]^-\}_2$ with the bidentate coordination, and ion trimers $\{Li^+[AsF_6]^-\}_3$ and tetramers $\{Li^+[AsF_6]^-\}_4$ in the form of symmetric ring structures having the unidentate coordination.

The formation energy of the clusters $E_{Li_m^+[AsF_6]_n^-}$ rises as the number of aggregate ions grows. The difference between the energies of stable bi- and tridentate configurations of a single species of ion particles is insignificant, and these configurations can be formed equiprobably.

The calculations of the frequency and the intensity of IR absorption bands of ion clusters showed that each stable ion particle has a special spectral pattern over the interval of 200−850 cm^{-1}. Therefore, the ion clusters are rendered spectroscopically discernible. The calculated spectra may serve as a basis for identification of the composition and the structure of ion aggregates during experimental studies of particular electrolyte systems.

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References and Notes

(1) *Lithium battery technology*; Venkatasetty, H. V., Ed.; John Wiley & Sons: New York, 1984.

(2) Aurbach, D. *J. Power Sources* **2003**, *119−121*, 497−503.

(3) Deng, Z.; Irish, D. E. *Can. J. Chem.* **1991**, *69*, 1766−1773.

(4) Deng, Z.; Irish, D. E. *J. Chem. Soc., Faraday Trans.* **1992**, *88* (19), 2891−2896.

(5) Eschmann, J.; Strasser, J.; Xu, M.; Okamoto, Y.; Eyring, E. M.; Petrucci, S. *J. Phys. Chem.* **1990**, *94*, 3908−3916.

(6) Bushkova, O. V.; Lirova, B. I.; Zhukovskii, V. M. *Russ. J. Phys. Chem.* **1999**, *73* (5), 735−738.

(7) Pereligyn, I. S.; Klimchuk, M. A. *Koord. Khim.* **1990**, *16* (8), 1042−1046.

(8) Laik, B.; Legrand, L.; Chausse, A.; Messina, R. *Electrochim. Acta* **1998**, *44*, 773−780.

(9) Zhukovsky, V. M.; Bushkova, O. V.; Lirova, B. I.; Krugliashov, A. L. *Electrochim. Energetica* **2001**, *1* (1−2), 43−49.

(10) Bushkova, O. V.; Lirova, B. I.; Zhukovsky, V. M. *Russ. J. Electrochem.* **2003**, *39* (5), 519−528.

(11) Inoue, N.; Xu, M.; Petrucci, S. *J. Phys. Chem.* **1987**, *91*, 4628−4635.

(12) Perelygin, I. S.; Shatochin, S. A.; Kononenko, A. B. *J. Struct. Chem.* **1992**, *33* (1), 163−166.

(13) Begun, G. M.; Rutenberg, A. C. *Inorg. Chem.* **1967**, *6* (12), 2212−2216.

(14) Roothaan, C. C. J. *Rev. Mod. Phys.* **1951** *23*, 69−89.

(15) Granovsky, A. A. http://classic.chem.msu.su/gran/gamess/index.html.

(16) Schmidt, M. W.; Baldridge, K. K.; Boatz, J. A.; Elbert, S. T.; Gordon, M. S.; Jensen, J. J.; Koseki, S.; Matsunada, N.; Nguyen, K. A.; Su, S.; Windus, T. L.; Dupuis, M.; Montgomery, J. A. *J. Comput. Chem.* **1993**, *14*, 1347.

(17) Curtiss, L. A.; McGrath, M. P.; Blandeau, J.-P.; Davis, N. E.; Binning, R. C.; Radom, L., Jr. *J. Chem. Phys.* **1995**, *103*, 6104.

(18) Dunning, T. H. *J. Chem. Phys.* **1989**, *90*, 1007.

(19) Miertus, S.; Scrocco, E.; Tomasi, J. *Chem. Phys.* **1981**, *55*, 117.

(20) Burgess, J. *Metal Ions in Solutions*; Ellis Horwood: Chichester, U.K., 1978.