The Anion Effect on Li⁺ Ion Coordination Structure in Ethylene Carbonate Solutions

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Ⓢ *Supporting Information*

ABSTRACT: Rechargeable lithium ion batteries are an attractive alternative power source for a wide variety of applications. To optimize their performances, a complete description of the solvation properties of the ion in the electrolyte is crucial. A comprehensive understanding at the nanoscale of the solvation structure of lithium ions in nonaqueous carbonate electrolytes is, however, still unclear. We have measured by femtosecond vibrational spectroscopy the orientational correlation time of the CO stretching mode of Li⁺-bound and Li⁺-unbound ethylene carbonate molecules, in LiBF₄, LiPF₆, and LiClO₄ ethylene carbonate solutions with different concentrations. Surprisingly, we have found that the coordination number of ethylene carbonate in the first solvation shell of Li⁺ is only two, in all solutions with concentrations higher than 0.5 M. Density functional theory calculations indicate that the presence of anions in the first coordination shell modifies the generally accepted tetrahedral structure of the complex, allowing only two EC molecules to coordinate to Li⁺ directly. Our results demonstrate for the first time, to the best of our knowledge, the anion influence on the overall structure of the first solvation shell of the Li⁺ ion. The formation of such a cation/solvent/anion complex provides a rational explanation for the ionic conductivity drop of lithium/carbonate electrolyte solutions at high concentrations.
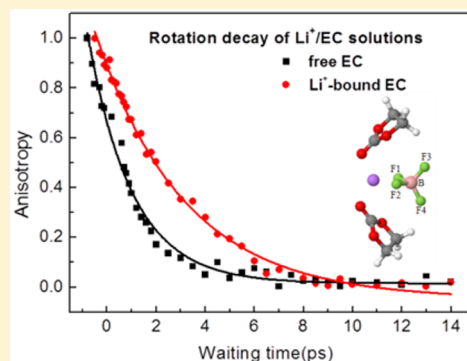
Lithium ion batteries (LIBs) are extensively used in small electronic devices such as cell phones and notebook computers. They are also growing in popularity for automotive applications, in order to decrease the greenhouse gas emissions and air pollution. The typical lithium-ion battery is composed by two electrodes that intercalate lithium materials, and a layer of a nonaqueous electrolyte solution, which directly determines the conductivity of the device.[1−3] The dynamics of Li⁺ through the electrolyte controls the rate of the energy transfer. It is generally accepted that transport of Li⁺ ions can be described as a complex mechanism, involving first solvation of the ions by the solvent molecules, followed by the migration of the solvated ions.[4] The ionic conductivity in a solution is, as a consequence, the overall result of these two steps.

In the last two decades, an impressive amount of theoretical and experimental work has focused on the interactions of Li⁺ with carbonate-based electrolytes that are applied in batteries. In particular, spectroscopy techniques, such as nuclear magnetic resonance (NMR), Raman spectroscopy, and electrospray ionization mass spectrometry (ESI-MS), have been employed to determine the coordination numbers corresponding to the first solvation shell of the ion. The details of the solvation structure and of the dynamics of lithium ions in these solvents are, however, still a subject of lively debate. NMR measurements indicate that up to six ethylene carbonate molecules can coexist in the Li⁺ solvation shell.[5−7] Raman spectroscopy measurements[8] concluded similarly as the NMR results. Intriguingly, MS measurements point in the opposite direction, suggesting much lower coordination numbers.[9] We add that none of these techniques has been able to provide detailed information about the modifications induced by the presence of the anions, or on the solvation structure under conditions sufficiently similar to those of the actual environments found in batteries. In the MS experiments, the solvated Li⁺ ion was studied in the gaseous state, and probably already experienced partial dissociation before being observed. In the NMR
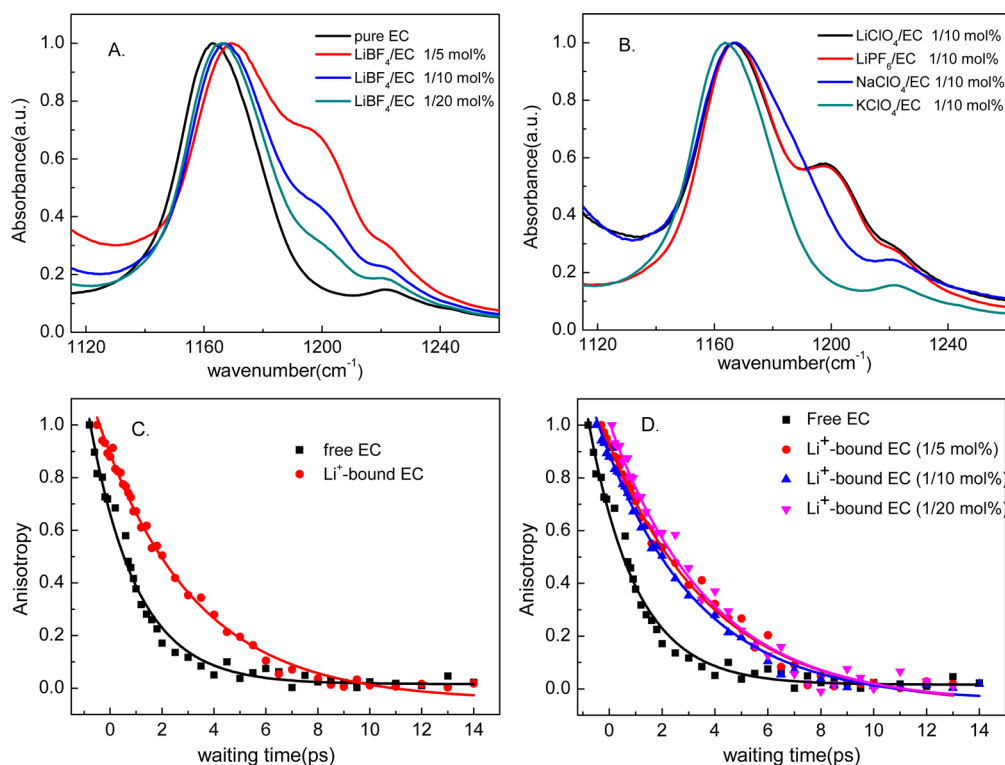
Figure 1. (A) FTIR spectra of EC: 1/5 mol %, 1/10 mol %, and 1/20 mol % LiBF$_4$/EC. (B) FTIR spectra of EC: 1/10 mol % LiClO$_4$/EC, 1/10 mol % LiPF$_4$/EC, 1/10 mol % NaClO$_4$/EC, and 1/10 mol % KClO$_4$/EC. (C) Time-dependent anisotropies of CO stretch of free EC (1165 cm^{-1}) and Li$^+$-bound EC (1203 cm^{-1}) in a 1/10 mol % LiBF$_4$/EC solution. (D) Time-dependent anisotropies of CO stretch of Li$^+$-bound EC (1203 cm^{-1}) with the concentration of 1/5, 1/10, 1/20 mol % LiBF$_4$/EC solution.

experiments, the ^{13}C or ^{17}O nuclei of the solvent molecules provide only an indirect probe of Li$^+$ solvation, and it is therefore difficult to derive quantitative information from the associated chemical shifts. In linear vibrational spectroscopy measurements, the derivation of coordination number suffers from the unknown ratio of transition dipole moments of Li$^+$-bound and unbound solvent molecules and the unknown salt dissociation constant.[10]

Numerical studies were not conclusive either. Both ab initio calculations and molecular dynamics (MD) simulations suggest that the small ionic radius of lithium cannot directly bind more than five organic solvent molecules, and the complex with a (total) coordination number of four is the most stable.[11−16] Unfortunately, both techniques also appear problematic in the present case. On one side, the relevance of DFT-stable finite-size clusters for the bulk electrolyte is not obvious. On the other, one must emphasize that the validity of the force fields used in MD simulations can only be scrutinized by a direct comparison with experimental data. The development of experimental methods proving a *direct* determination of the coordination number therefore becomes indispensable, for obtaining from simulation an unambiguous picture of the solvation properties of lithium ion solutions.

Here, we propose an integrated experimental spectroscopy/ab initio calculations investigation (with some reference to our previous MD work[17]), in order to minimize the limitations of the two approaches when used separately. We have employed a combination of nonlinear vibrational spectroscopy and DFT calculations to provide deeper insight on the solvation structure of lithium in solutions of high concentrations similar to those in Li$^+$ batteries. Our studies suggest a surprising Li$^+$ solvation structure sensibly different from the generally accepted

tetrahedral coordination of the carbonyl oxygen atoms around Li$^+$.

We have focused on the solvation structure of different Li$^+$ ion solutions, and measured the orientational correlation time of Li$^+$-bound and Li$^+$-unbound (free) solvent molecules for different salt solutions, by using infrared femtosecond spectroscopy. All details of the methodology are described in our previous publication[10] and also given in the Supporting Information (SI). Here we only recall that with this method we can observe the dynamical behavior of the different solvent chemical species on time scales shorter than the typical time associated with the exchange mechanism(s) between the solvation shells and the bulk liquid. According to the Stokes−Einstein equation, $D_r = \frac{kT}{8\pi \cdot \eta \cdot r^3}$, the rotational diffusion time constant is proportional to the volume of the molecule.[18] Here, D_r is the rotational diffusion time constant, η is the viscosity, r is the particle radius, T is the temperature, and k is the Boltzmann constant. As a consequence, the heavier the considered molecule, the slower the associated orientational decay time is. Here, we want to emphasize that the equation is rigorously valid only for ideal conditions, which a real system can hardly achieve. In order to evaluate the applicability of the equation in determining molecular volumes in liquids, we measured three different systems: (1) a series of flexible molecules with different alkyl lengths; (2) rigid molecules with different numbers of benzene rings; and (3) Li$^+$ salts in CH$_3$CN of which the crystalline structures of the Li$^+$−CH$_3$CN complexes have been identified by X-ray diffraction (XRD). Experimental results show that the method works well for all three different systems.[10] Details of the experimental methods are provided in the SI.

We show in Figure 1A the absorption spectra of ethylene carbonate (EC) and $LiBF_4$/EC solutions at 1/5, 1/10, and 1/20 mol % concentration, in the frequency region of the O−C−O stretching mode. The main peak for the pure ethylene carbonate (black line) centered at 1165 cm^{-1} is assigned to the O−C−O mode mentioned above. The secondary peak of small intensity at ∼1222 cm^{-1} is assigned to a combination band. With the addition of $LiBF_4$, the stretching and combination band features keep the same position, increasing in intensity. Interestingly, a third attribute develops at ∼1203 cm^{-1}, and its intensity grows by increasing the concentration of $LiBF_4$. We associate this observation to the binding of either Li$^+$ or BF_4^- with EC, causing the frequency blue shifts.

To unambiguously identify the ion responsible of this latter phenomenon, FTIR spectra of $LiClO_4$, $LiPF_6$, $NaClO_4$, and $KClO_4$, dissolved in EC at the indicated fixed concentration, are shown in Figure 1B. From these data it is clear that a change in the nature of the anions (from BF_4^- to PF_6^- or ClO_4^-) does not influence the frequency position of the peak. By contrast, modifications of the cation (from Li$^+$ to Na$^+$ or K$^+$) even completely destroy the peak at 1203 cm^{-1}.

This conclusion has an important implication: the orientational dynamics of (free) bulk-like solvent molecules, and that of solvent molecules bound to the Li$^+$ ion can be studied separately. In Figure 1C we show the measured time decay of the anisotropy parameter R, for the 1/10 mol % $LiBF_4$/EC solution. The decay time of parameter $R = \frac{(P_\parallel - P_\perp)}{(P_\parallel + 2P_\perp)}$ represents the orientational correlation time of the solvent molecules (where $P_\parallel$ and $P_\parallel$ are the parallel and perpendicular signals, respectively). In these measurements, the O−C−O stretch band of the free EC (1165 cm^{-1}) and of the Li$^+$- bound EC (1203 cm^{-1}) was excited and detected at the 0 → 1 transition. Based on our previous work,[10] the anisotropy decay is mainly controlled by the molecular rotation, since both resonant and nonresonant energy transfers are much slower than the molecular rotation in EC solutions (see the SI). Interestingly, for the Li$^+$-bound EC, the anisotropy decay is 3.7 ± 0.2 ps, which is twice that of unbound EC (1.8 ± 0.1 ps). We will discuss the implications of this finding in what follows.

Next, in Figure 1D we show the anisotropy decay curves of the stretch mode of Li$^+$-bound EC, in 1/5 mol %, 1/10 mol %, and 1/20 mol % $LiBF_4$/EC solutions. The time constants extracted from the data are now 3.7 ± 0.2 ps, 3.6 ± 0.2 ps and 3.7 ± 0.2 ps, respectively, in the three cases. The decay of R therefore turns out to be independent of the salt concentration, implying that the probability for multiple anions to strongly bind to the cation or EC is very small. The results seem to be consistent with the conclusion from recent work[19] that "anions exist relatively free with little solvation". Indeed, further experimental evidence on additional solutions, including $LiPF_6$/EC and $LiClO_4$/EC, support the conclusion that the measured anisotropy decays are determined by the rotational time scale of complexes without any binding to multiple anions (see Table 1 and Figures S2−6). We have performed a similar analysis for all investigated lithium salts, obtaining the rotational time ratios for the Li$^+$/EC complex over the free EC molecule (in the same solutions to remove the overall viscosity effect) listed in Table 1, at the indicated concentrations. In all solutions, the values of the rotation ratio are comprised in the range 2.0 to 2.3. Here an issue is worth noting. In our previous work,[10] we developed a method to quantitatively measure the dissociation constants of Li$^+$ salts in

Table 1. Time Constants of Anisotropy Decay of Free EC and Li$^+$-Bound EC in Lithium Salts/EC Solutions with Different Concentrations[a]

rotation time constant	free EC (ps)	Li+-bound EC (ps)	rotation ratio
$LiBF_4$/EC (1/5 mol %)	1.8 ± 0.1	3.7 ± 0.2	2.1
(1/10 mol %)	1.8 ± 0.1	3.6 ± 0.2	2.0
(1/20 mol %)	1.8 ± 0.1	3.7 ± 0.2	2.1
$LiPF_6$/EC (1/10 mol %)	1.9 ± 0.1	4.3 ± 0.2	2.3
(1/20 mol %)	2.0 ± 0.1	4.4 ± 0.2	2.2
$LiClO_4$/EC (1/5 mol %)	1.9 ± 0.1	4.1 ± 0.2	2.1
(1/10 mol %)	1.9 ± 0.1	4.3 ± 0.2	2.3
(1/20 mol %)	1.8 ± 0.1	4.0 ± 0.2	2.2

[a]All measurements were performed at 40 °C.

organic solvents. Our results are consistent with the well-known knowledge that $LiPF_6$ has a larger dissociation constant than $LiBF_4$ in CH_3CN or EC and with increasing salt concentration more cation−anion ion pairs form. However, what our experiments measure here is the Li$^+$-bound EC. With the increase of salt concentration, the salt dissociation/association equilibrium may shift to more cation/anion ion pair from EC solvated Li$^+$, but such an equilibrium shift does not necessarily change the solvation structure of Li$^+$. We believe that this is the intrinsic reason for that our results are insensitive to anion and salt concentrations.

Interestingly, we are now in the position to directly associate these (dynamical) results to the detailed (structural) composition of the detected rotating units. Indeed, based on the Stokes−Einstein equation introduced above, this finding indicates that the volume of the Li$^+$/EC complex is about 2 times bigger than that pertaining to one free EC molecule. Excluding the negligible volume occupied by Li$^+$, we can therefore immediately conclude that two EC molecules bind to Li$^+$ in the observed complexes, a value sensibly lower than the total coordination number of four reported by previous experimental and theoretical studies on solutions.[14] We also note that, using the same method above, a coordination number of four was determined for Li$^+$ in CH_3CN solutions, which is in agreement with X-ray diffraction measurements.[10]

To further explore the above surprising experimental results, we have performed DFT numerical calculations. We have used the Amsterdam Density Functional (ADF) software,[20] and considered the PBE GGA functional and a TZP (core double-ζ, valence triple-ζ, polarized) slater type orbital (STO) basis set for the geometry optimization. Additional calculations for a few representative clusters have confirmed that the basis set superposition error (BSSE) corrections are negligibly small, a conclusion corroborated by our recent DFT studies.[17] Frequency analysis has been performed for each structure, ensuring the absence of negative eigenvalues to confirm them as true minima of the potential energy surface. Zero-point energy (ZPE) corrections have been also taken into account. Thermodynamic potentials associated with the investigated clusters have been determined in the gas-phase approximation and at temperature T = 298.15 K. The calculation temperature is slightly different from the experimental temperature (40 °C). However, since the free energy difference caused by the small temperature difference is much smaller than 2 kcal/mol and the binding energy of the Li$^+$ complex with two EC molecules is

higher than other complexes for at least 2 kcal/mol, the calculation/experiment temperature difference does not affect our conclusion. Additional details can be found in the SI.

We first performed the gas-phase DFT energy optimizations for the $Li^+(EC)_{1-3}(Anion^-)$ clusters. Following the methods employed in our previous study,[17] enthalpy, entropy, and Gibbs free-energy were also calculated, in order to estimate the preferential structure of the first coordination shell around the lithium cation, in the presence of the counteranion. More in details, we calculated the free energy changes for clusters of the form $Li^+(S)_n(Anion^-) + mS$ (here S is the solvent species, $n + m = 3$, and $Anion^-$ is the counteranion, ClO_4^-, BF_4^- or PF_6^-). Subsequently, we have determined the free energy differences associated with the transitions:

$$Li^+(S)_k Anion^- + l \cdot S \rightarrow Li^+(S)_n Anion^- + m \cdot S,$$
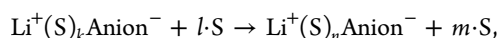
$$k + l = n + m, \quad k, l, n, m = 0 - 3$$

In cases where the above transitions exhibit negative free energy changes, this approach provides a clear indication that the formation of the $Li^+(S)_n(Anion^-)$ cluster is favorable. The obtained free energy changes, shown in Table 2, reveal that

Table 2. Gibbs Free Energy of Clusters $Li^+(EC)_{0-3}Anion^-$ (where $Anion^- = ClO_4^-$, BF_4^-, PF_6^-) (kcal/mol)

	G		
fragments	$Anion^- = ClO_4^-$	$Anion^- = BF_4^-$	$Anion^- = PF_6^-$
$Li(Anion^-) + 3\ EC$	−4738.3	−4911.1	−5052.6
$Li^+(EC)Anion^- + 2\ EC$	−4750.1	−4926.0	−5062.0
$Li^+(EC)_2Anion^- + EC$	−4752.2	−4929.2	−5067.0
$Li^+(EC)_3Anion^-$	−4749.1	−4926.5	−5064.2

clusters including two solvent molecules and one counterion around the Li^+ ion are the most thermodynamically stable. The optimized most stable structures are presented in Figure 2, for
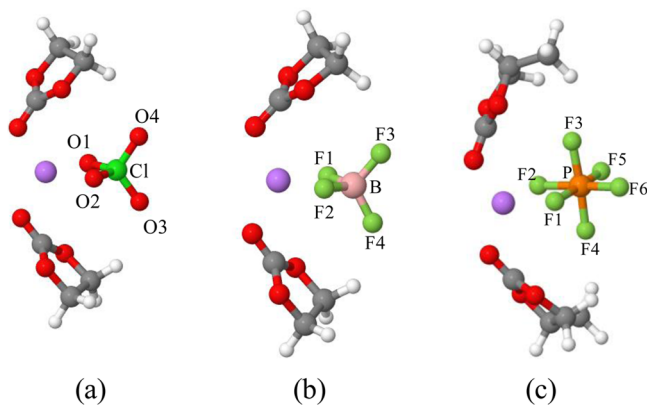
Figure 2. Optimized geometries of the most stable clusters: (a) $Li^+(EC)_2ClO_4^-$, (b) $Li^+(EC)_2BF_4^-$, and (c) $Li^+(EC)_2PF_6^-$.

each case. In order to also test whether the trends observed for gas-phase calculations change upon the addition of a dielectric continuum, we used the COSMO (COnductor-like Screening Model) model[21] to approximate solvent effects. Our tests, using the dielectric constant of EC for the continuum, have shown that the clusters containing one anion and two EC molecules around lithium are the most thermodynamically stable, even when a dielectric continuum is added (see Table S1 in the SI).

Two important observations are now in order. First, in our earlier DFT study, we have demonstrated that the most stable clusters in diluted conditions contain four solvent molecules around the Li^+ ion,[17] organized with a strong tetrahedral symmetry. Here, in contrast, we find that the addition of the counteranion both modifies the overall coordination number, which now is three instead of four, and destroys the local (tetrahedral) symmetry.

Second, the conclusions based on the DFT calculations are in full agreement with the experimental results, where we have observed that each Li^+ ion binds to 2.1 ± 0.2 EC molecules, on average. The anion influence is also evident from our experimental data sets. Indeed, the average rotation decay time of the Li^+-bound EC complexes slows down with the anion volume sequence, $BF_4^- < ClO_4^- \leq PF_6^-$. The decay time ratio, in contrast, is only slightly larger than two, implying that the effect of the anion on the rotational decay of the complex is only mild, without any evident correlation with the nature of the anion. This behavior is simple to rationalize, by observing that the anion binding energy to the complex is much weaker than that associated with the binding of the cation. The structure of solvated cation/anion weak complexes in Figure 2 lies between those of the contact ion pair and the solvent separated ion pair. The formation of such complexes provides a rational explanation for the ionic conductivity drop of lithium/carbonate electrolyte solutions at high concentrations that is not well correlated with the solution viscosity change.[22,23] Because of the complexation, the charge of solvated Li^+ is neutralized by the anion and its mobilty under applied potential can be significantly reduced. At the same time, the weak binding between the solvated cation and anion does not increase the viscosity much, as observed by the rotational dynamics measurements.

Our DFT calculations also show that a bidentate coordination is obtained in the cases of the $Li^+(EC)(Anion^-)$ and $Li^+(EC)_2(Anion^-)$ clusters. This is at variance with the case of the $Li^+(EC)_3(Anion^-)$ complex, where the steric repulsion between the anion and the solvent molecules increases substantially, and a monodentate linkage is therefore observed (see Figures S8−S10 in the SI).

We conclude this section by describing additional insight based on the DFT vibrational frequency analysis that we have used to extract the vibrational IR spectra. We have considered the clusters indicated in Figure 3, and compared them with the case of the isolated EC molecule. Focusing on the O−C−O stretch band, the experimental absorption frequency peak is located at 1165 cm^{-1} in the case of isolated EC, while the value calculated by DFT is 1074 cm^{-1}. In the case of the $(Li^+(EC)_2Anion^-)$ clusters, in the DFT calculation the O−C−O frequency is blue-shifted in all cases, and the peaks are located around 1150 cm^{-1}, with a shift of about 76 cm^{-1}. The corresponding blue-shift in the experiments is about 2 times smaller (around 38 cm^{-1}). We note that these discrepancies can be certainly also attributed to the fact that the DFT calculations are performed with (isolated) clusters in the gas phase, while experiments are made in solution (bulk) phases. As a result, the DFT calculations only take into account interactions within the first solvation shell around Li^+ ion, disregarding longer-range intermolecular interactions with the condensed bulk phase. These have been demonstrated to be crucial in ref 17. Notwithstanding these differences, however, the overall trend in both the experiments and DFT calculations is very similar,
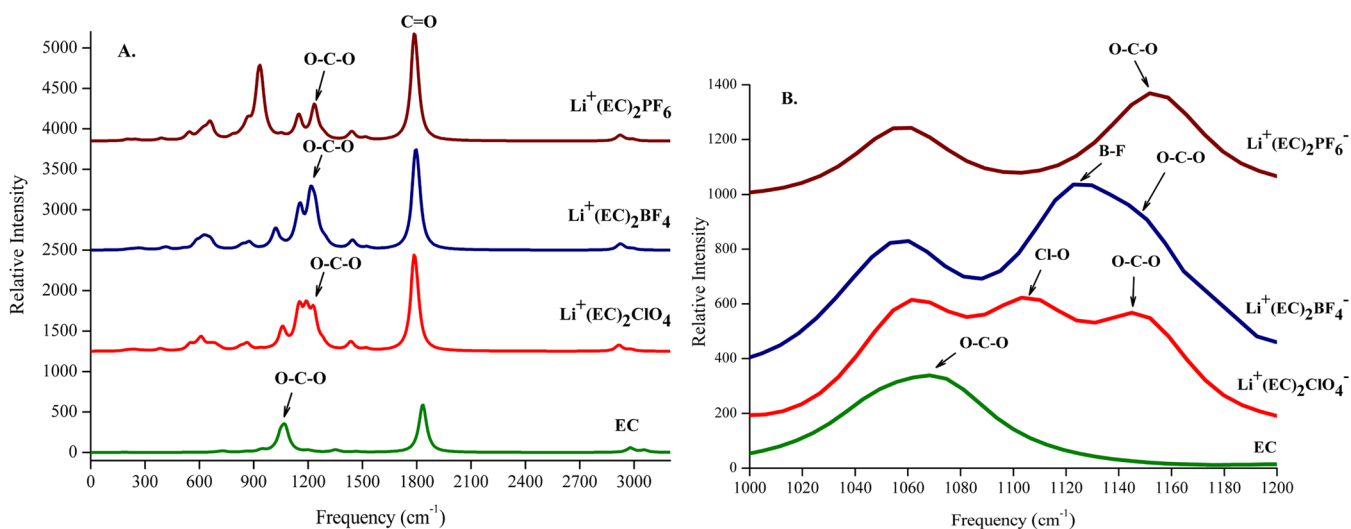
Figure 3. Calculated vibrational IR spectra of isolated EC and of $(Li^+(EC)_2(Anion^-))$ optimized clusters (A) and corresponding O−C−O stretching frequency regions (B).

further confirming the relevance of the DFT calculations for a full rationalization of the experimental data.

In summary, dynamical spectroscopy methods have been employed to clarify the solvation structure of lithium-salts in EC, a popular Li-ion batteries electrolyte, and provide a *direct* determination of the solvent coordination number around the Li⁺ ions by measuring the orientational correlation dynamics of the solvent molecules. The presence of the anions, and the salt concentration itself, both have a strong effect on the solvation structure. In particular, we have demonstrated that the local tetrahedral structure around Li⁺, widely accepted in dilute conditions, is strongly modified in concentrated solutions, leading to a first coordination shell of Li⁺ comprising two EC molecules only. We have also clarified the elusive role played by the anion, by employing systematic DFT calculations performed for numerous clusters of the type $Li^+(EC)_{1-3}(Anion^-)$, with ClO_4^-, BF_4^- and PF_6^- being the considered anions. On the basis of a detailed analysis of the changes in free energy associated with the transitions between different types of clusters, we have concluded that the formation of complexes of the type $Li^+(EC)_2(Anion^-)$ is the most favorable. These results demonstrate for the first time, to the best of our knowledge, the anion influence on the overall structure of the first solvation shell of the Li⁺ ion. This information provides deep insight on the solvation structure of nondilute Lithium salt solutions in organic electrolytes, providing a rational explanation for the ionic conductivity drop of lithium/carbonate electrolyte solutions at high concentrations. It also is, we believe, an important contribution in view of the rational design of electrolytes for battery applications with optimized properties.

ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpclett.6b01664.

Experimental methods, anisotropy decay of CO stretch in Li salt EC solutions, 2D IR chemical exchange measurements, and theoretical results (PDF)

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Notes
The authors declare no competing financial interest.

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