Comparative Computational Study of Isomeric TFSI and FPFSI Anions in Li-Ion Electrolytes

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Motivation

- Rechargeable lithium-ion batteries have become very successful devices (Nobel Prize in chemistry 2019!)
- A significant effort is invested in research on metal-ion batteries

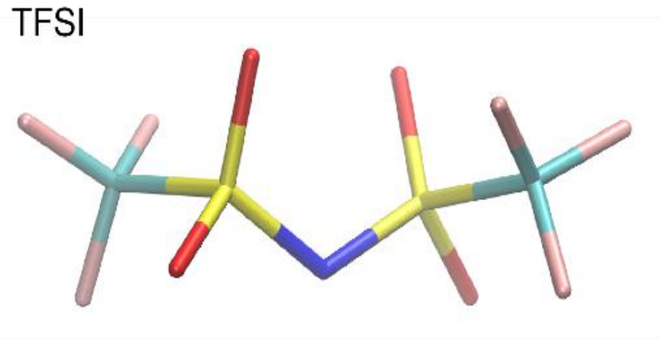
- Ion conducting electrolyte is an important component of the device
- Search for new, safer and environment-friendly electrolytes continues

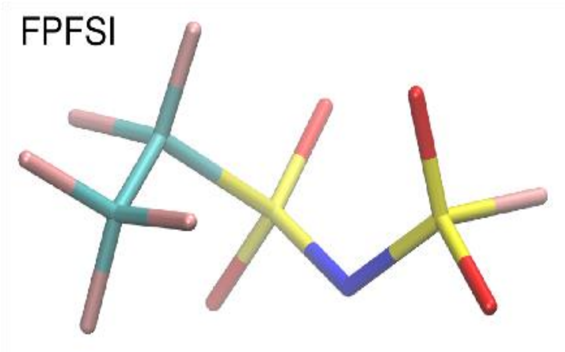
Interactions studied via vibrational spectra

- Vibrational spectroscopies are commonly used to detect interactions between molecules or ions – interactions induce frequency shifts
- Calculations of vibrational frequencies and IR intensities or Raman activities for molecules or complexes in gas phase are routine tasks in quantum chemistry
- Even for isolated species the problem may become complicated because of multiple possible conformations and geometries of complexes
- Modeling of vibrational spectra in solution is even more challenging – we have to account for the solvent effects
- Molecular Dynamics simulations provide information on the structure and dynamics of the system
- Vibrational spectra can be obtained from MD simulations as Fourier transforms of the dipole moment (IR) or the polarizability (Raman)

Weakly coordinating anions

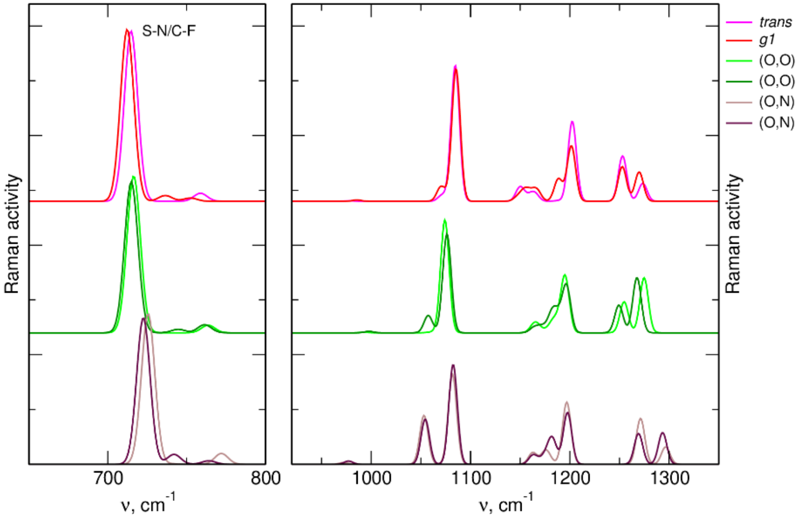
- In commercial Li-ion batteries $LiPF_6$ in organic carbonates is commonly used as an electrolyte
- Several promising salts are investigated experimentally, e.g. salts with weakly coordinating anions, such as lithium bis(trifluoromethanesulfonyl)imide (LiTFSI)
- Recently, several asymmetric perfluorinated sulfonimide anions were studied experimentally, including the TFSI isomer, (fluorosulfonyl)(pentafluoroethanesulfonyl)imide (FPFSI)
- Some computational studies on FPFSI are available, but none of them systematically compares different approaches and the vibrational spectra have not been discussed

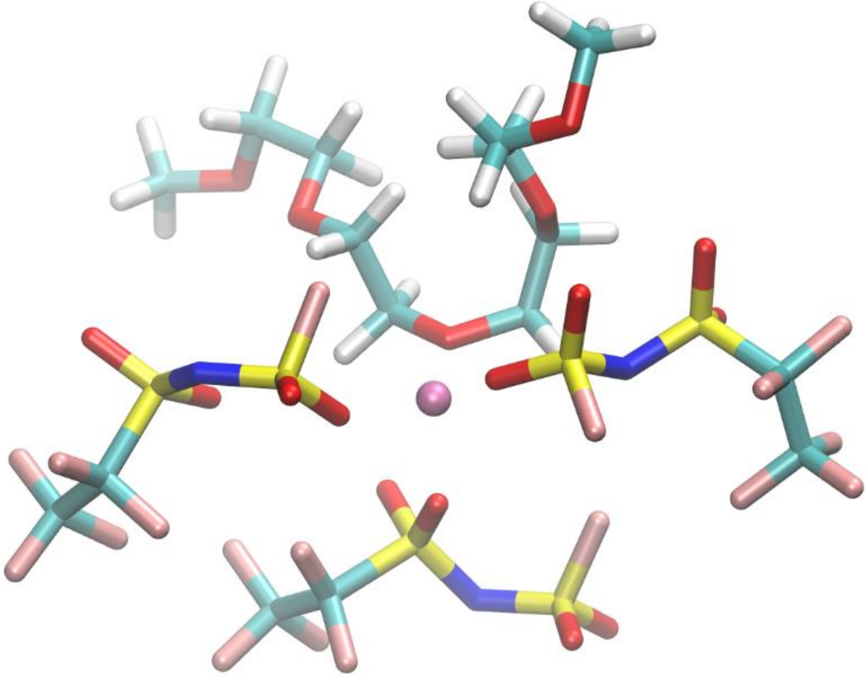




Quantum-chemical calculations

- QC calculations for TFSI, FPFSI anions and complexes with Li^+
- Gaussian 09
- MP2 methodology or B3LYP, PBE and M062X functionals
- aug-cc-pVDZ basis set

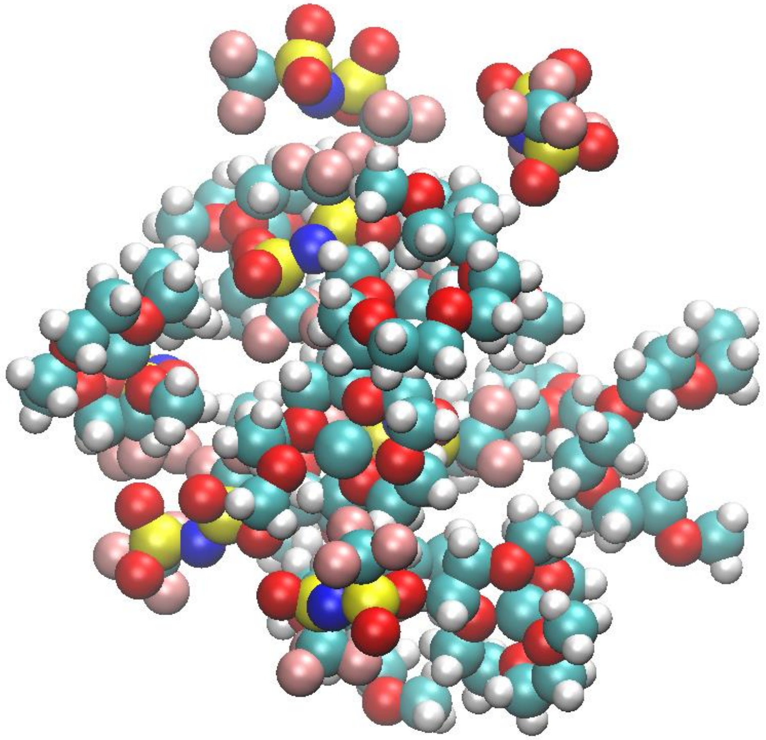




- structure, energies and vibrational frequencies in vacuum and in the solvent (PCM, ε = 5)

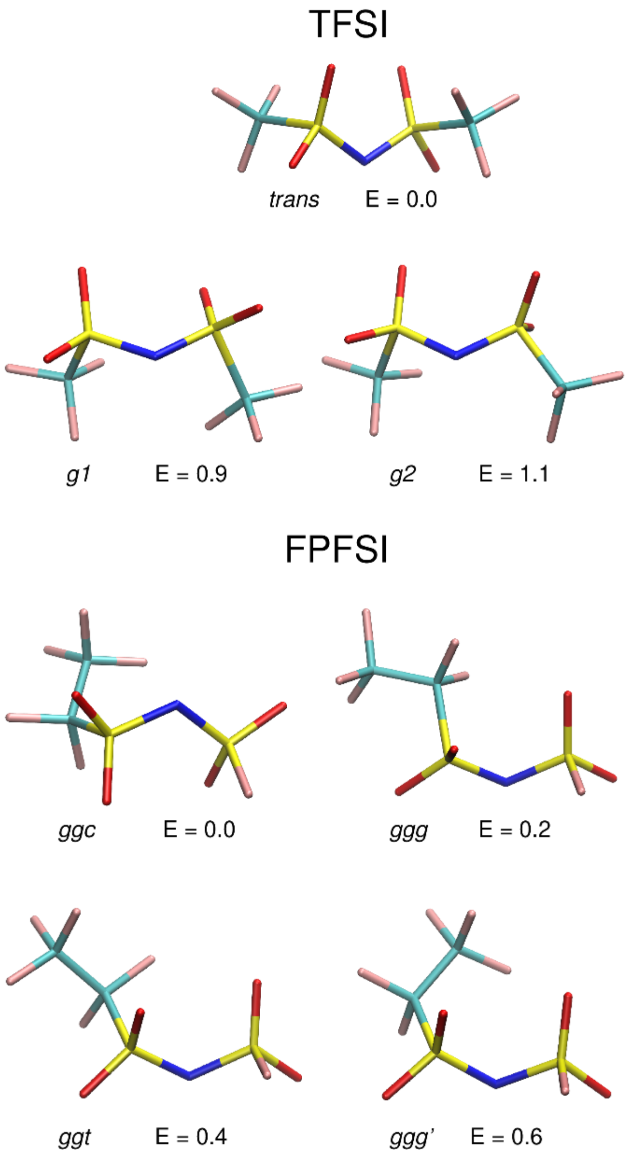
MD simulations

- ab initio Molecular Dynamics for LiTFSI/LiFPFSI in tetraglyme (G4)
- $\mathrm{Li{:}O_g}$ ratios 1:20 and 1:8
- CP2K used for simulations
- PBE functional with DZVP basis set



- 50 ps of trajectory collected in the NVT ensemble at T = 303 K
- calculations consumed about 420 k CPU hours on Ares

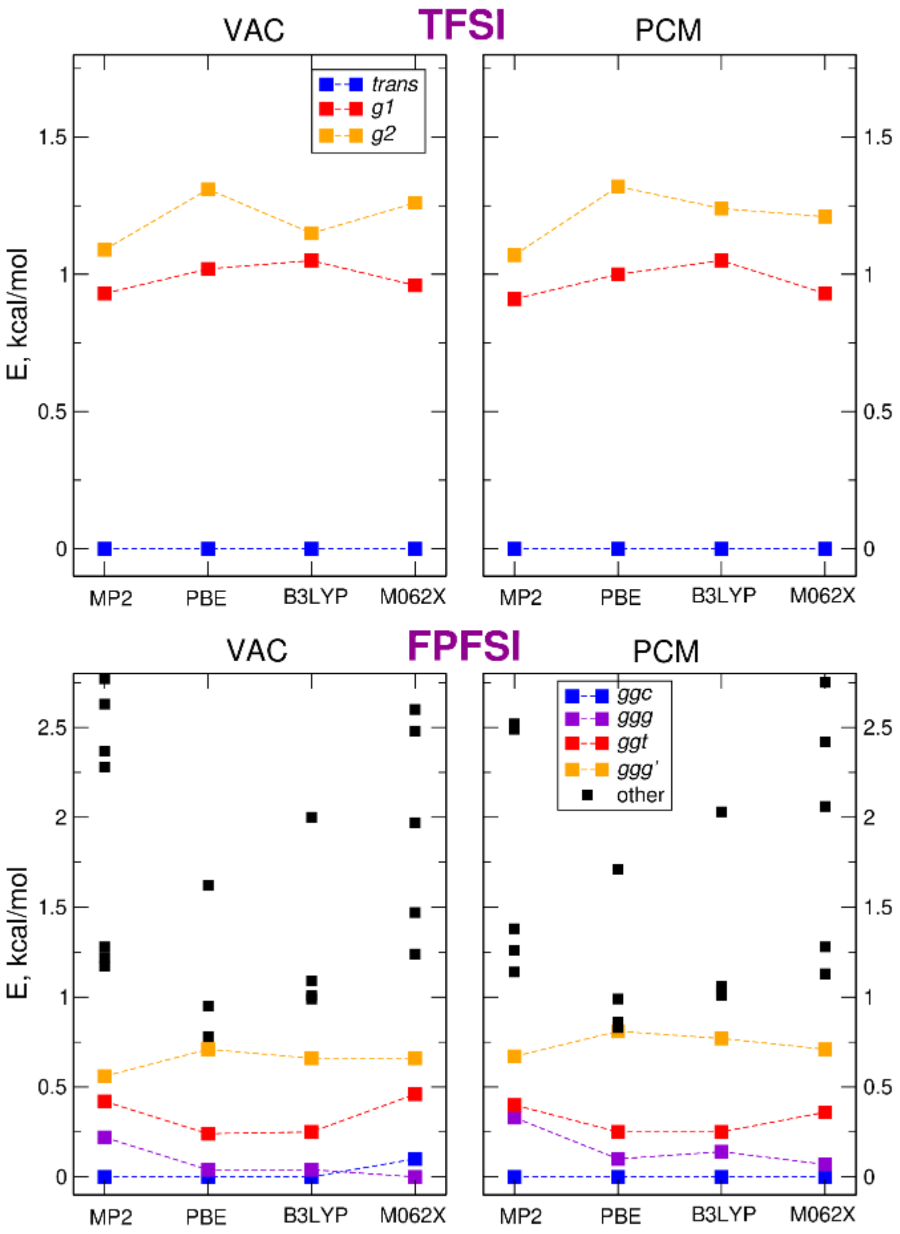
Free anions – conformations and energies



- The lowest conformation of TFSI is the *trans* structure
- Surprisingly, two *gauche* conformers were found at the energies ~ 1 kcal/mol
- More low-energy conformations are possible for FPFSI in a quite narrow energy interval

original figures from https://doi.org/10.1021/acs.jpcb.4c08414

Free anions – conformations and energies



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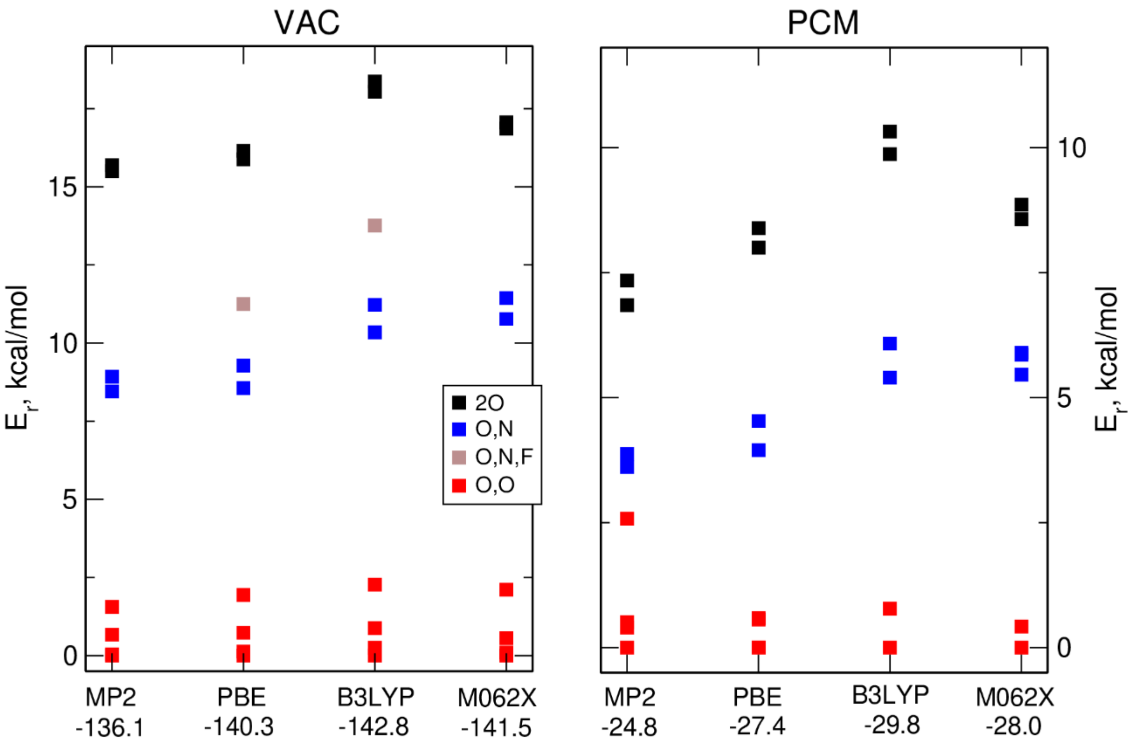
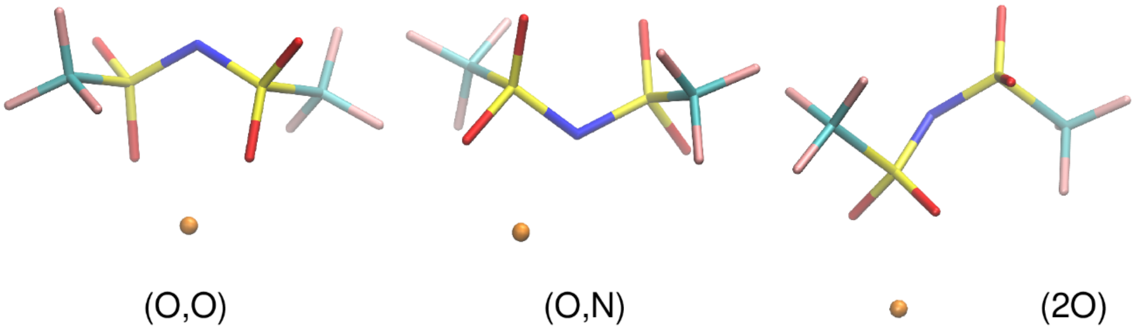
- Surprisingly, two *gauche* conformers were found at the energies ~ 1 kcal/mol
- More low-energy conformations are possible for FPFSI in a quite narrow energy interval
- There is an overall agreement between methods

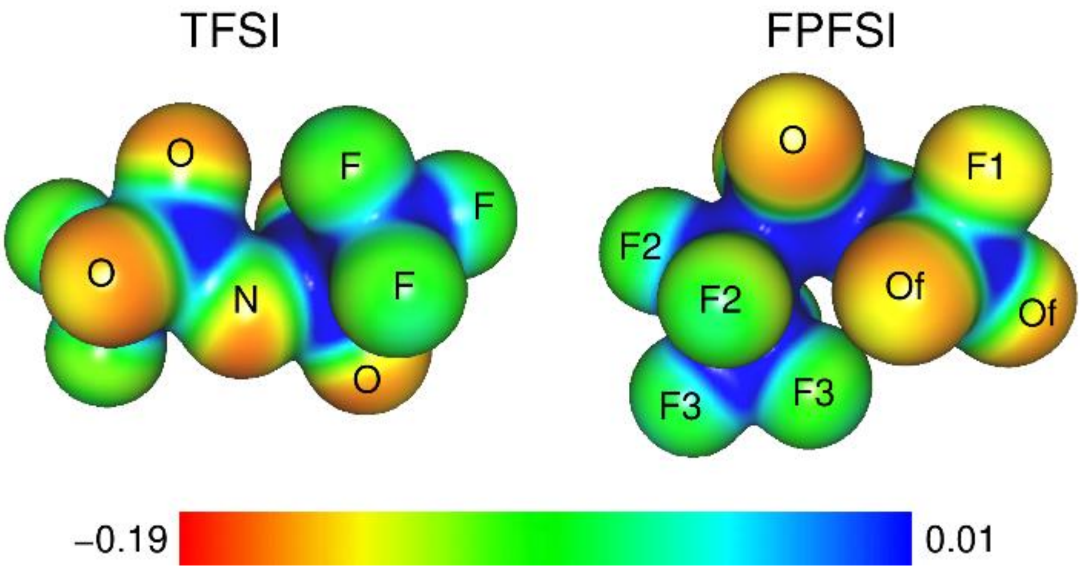
Li-anion complexes: TFSI





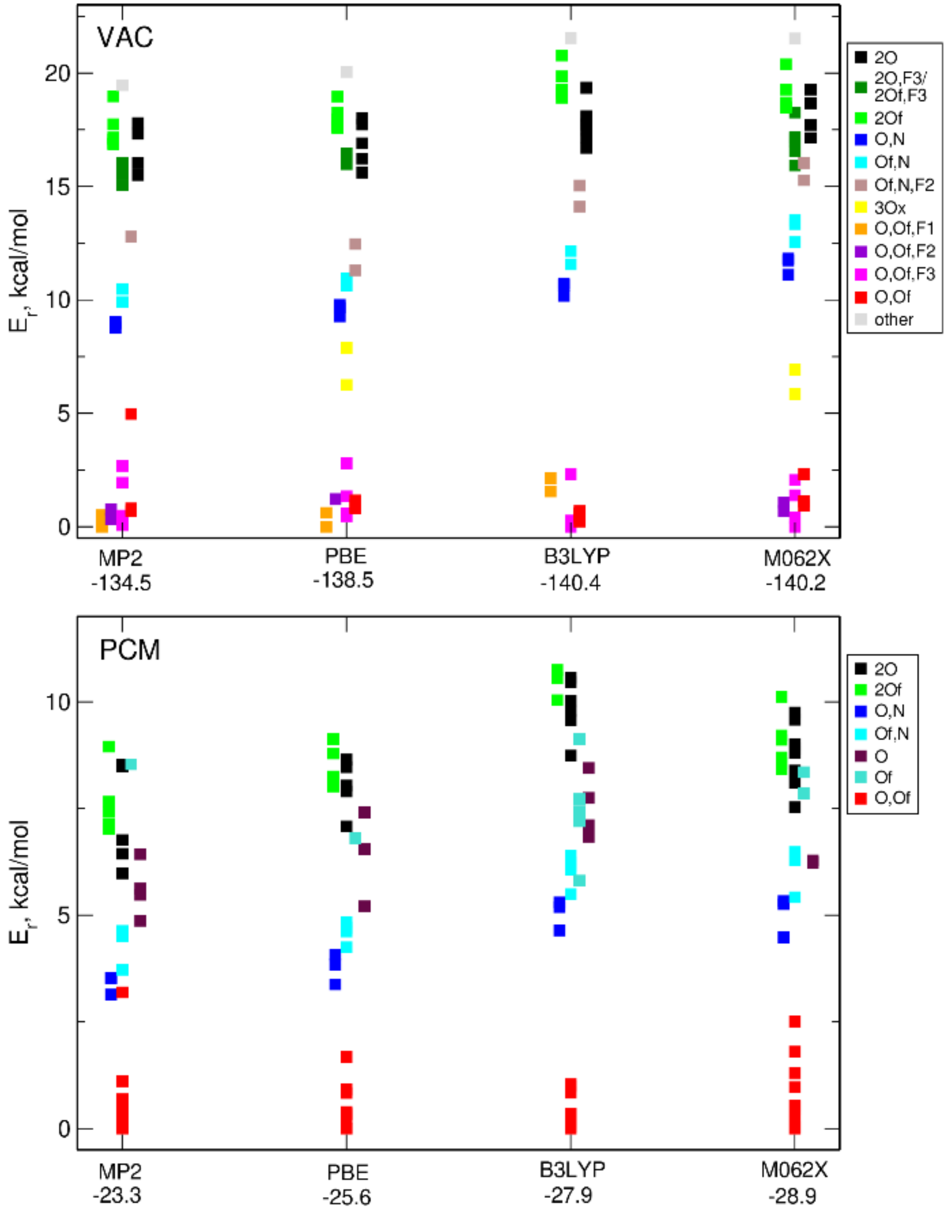
- The strongest binding of the cation is through two oxygen atoms in a bidentate coordination
- This effect does not depend on the method or the solvent (though the medium reduces the binding energies)

Li-anion complexes: FPFSI



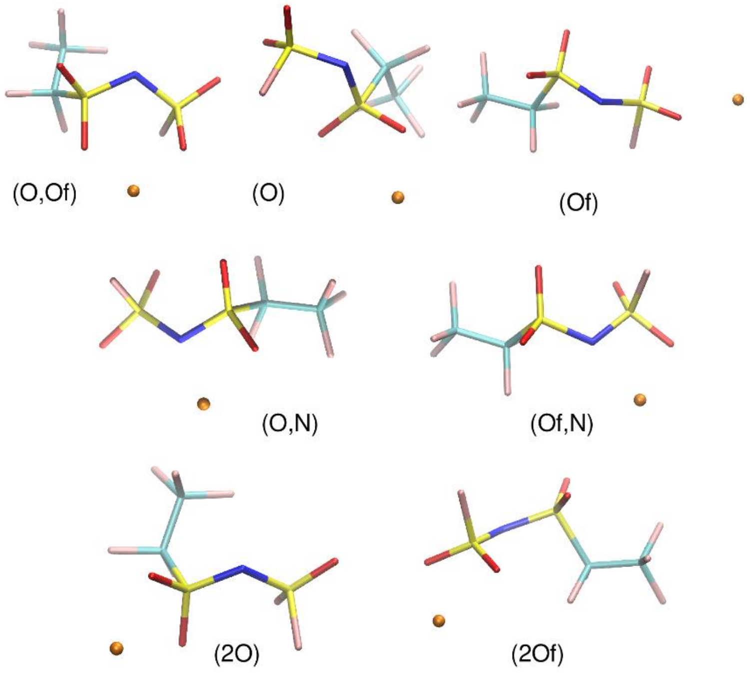
- Electrostatic potential is similar for both anions
- There is a region of negative potential at F1 atom of FPFSI – possible coordination site for the Li^+ cation?

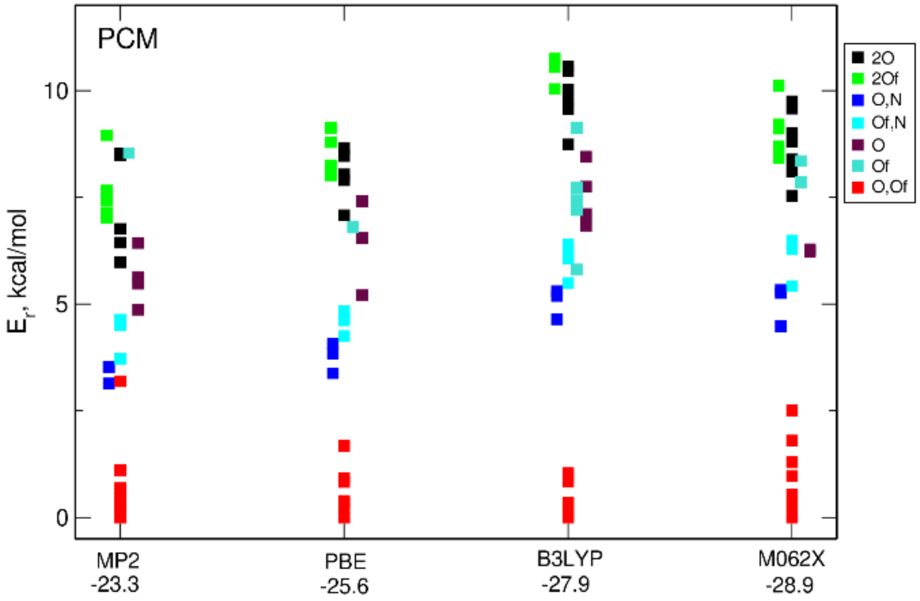
Li-anion complexes: FPFSI



- There is a region of negative potential at F1 atom of FPFSI – possible coordination site for the Li$^+$ cation?
- Indeed, several coordination modes involving F1 atom (in addition to oxygen atoms) were found – but only in vacuum
- In the solvent, the preferred coordination is bidentate to O and Of atoms

Li-anion complexes: FPFSI





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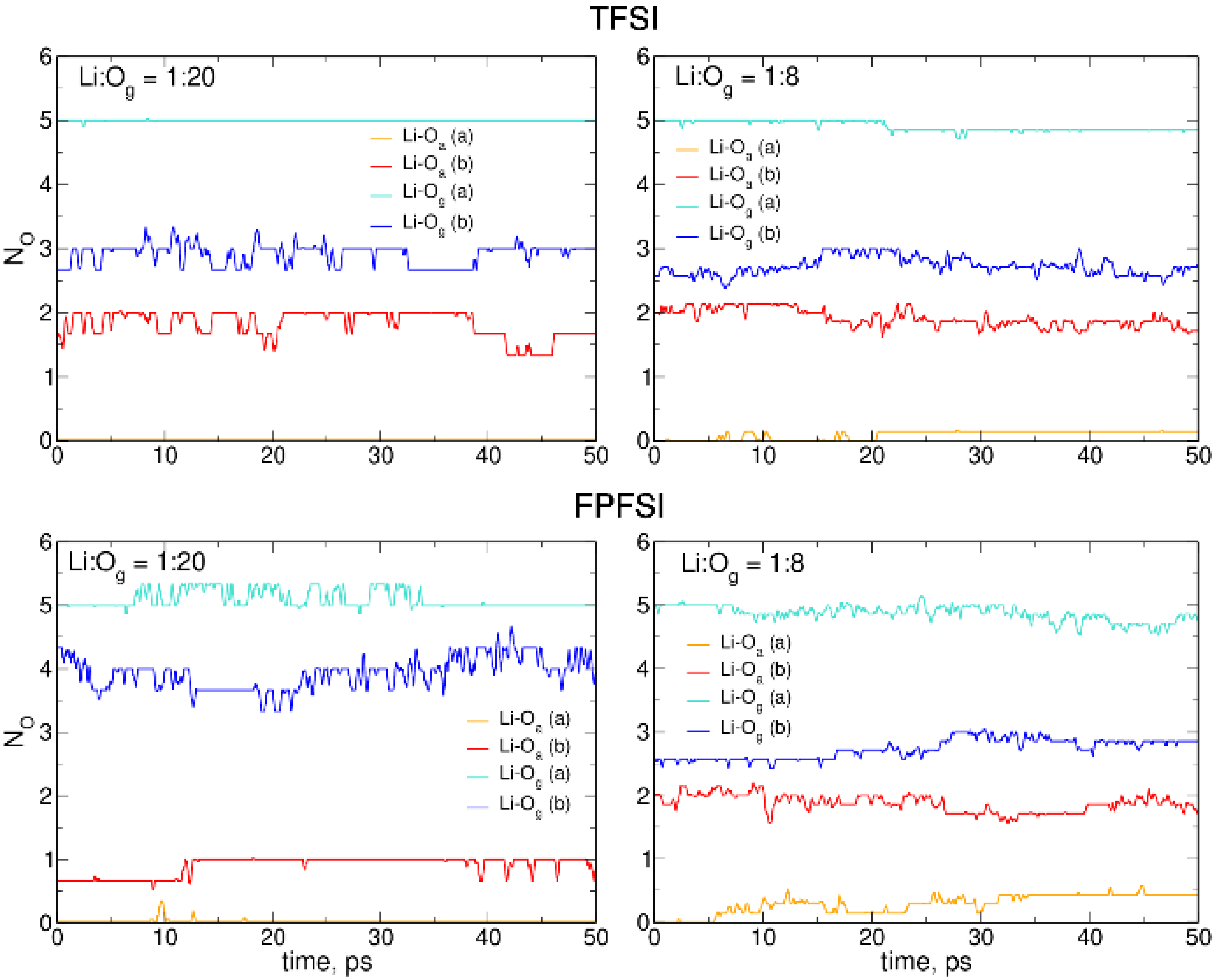
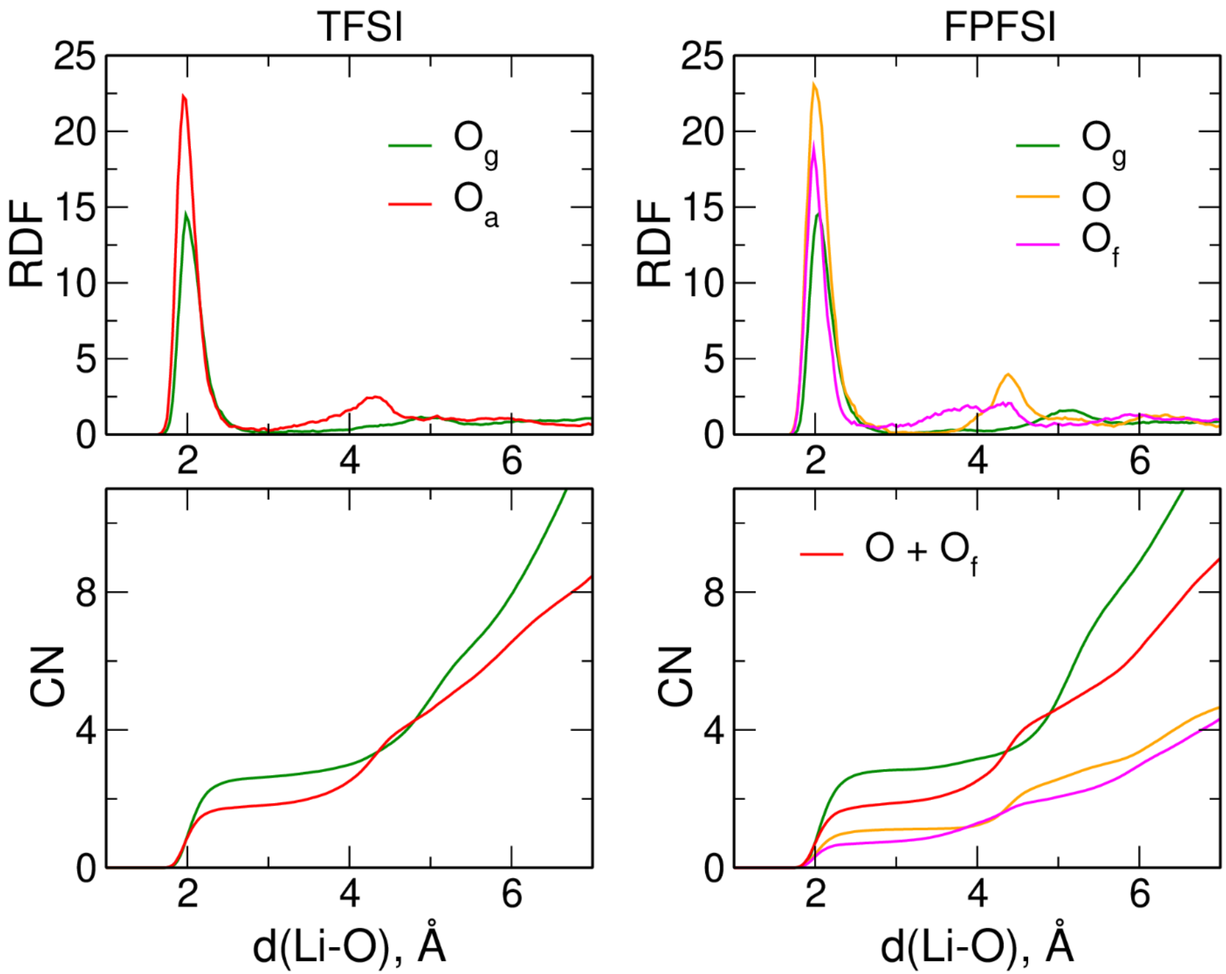
- Indeed, several coordination modes involving F1 atom (in addition to oxygen atoms) were found – but only in vacuum
- In the solvent, the preferred coordination is bidentate to O and Of atoms
- The PBE results are the most close to MP2
- Li^+ binding to FPFSI is a little weaker than interactions with TFSI

MD simulations of electrolytes

- Changes in ion coordination are very slow (large viscosity) – but the Li^+ coordination to anions apparently increases in the LiFPFSI-G4 electrolyte

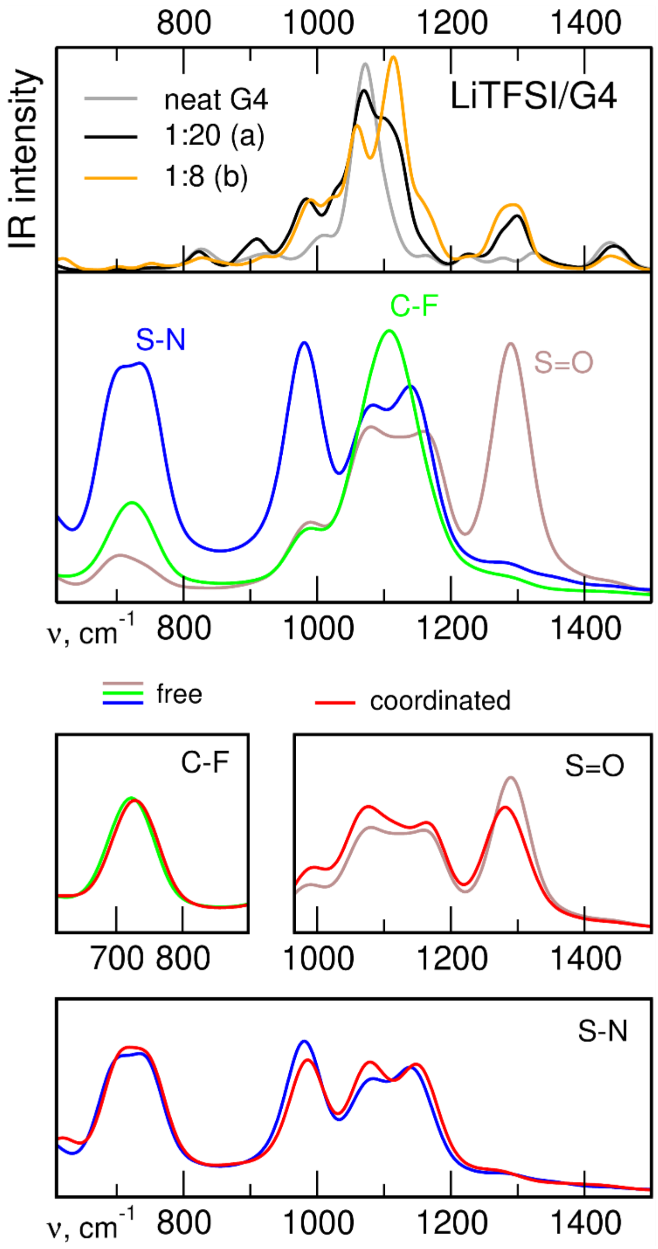


MD simulations of electrolytes



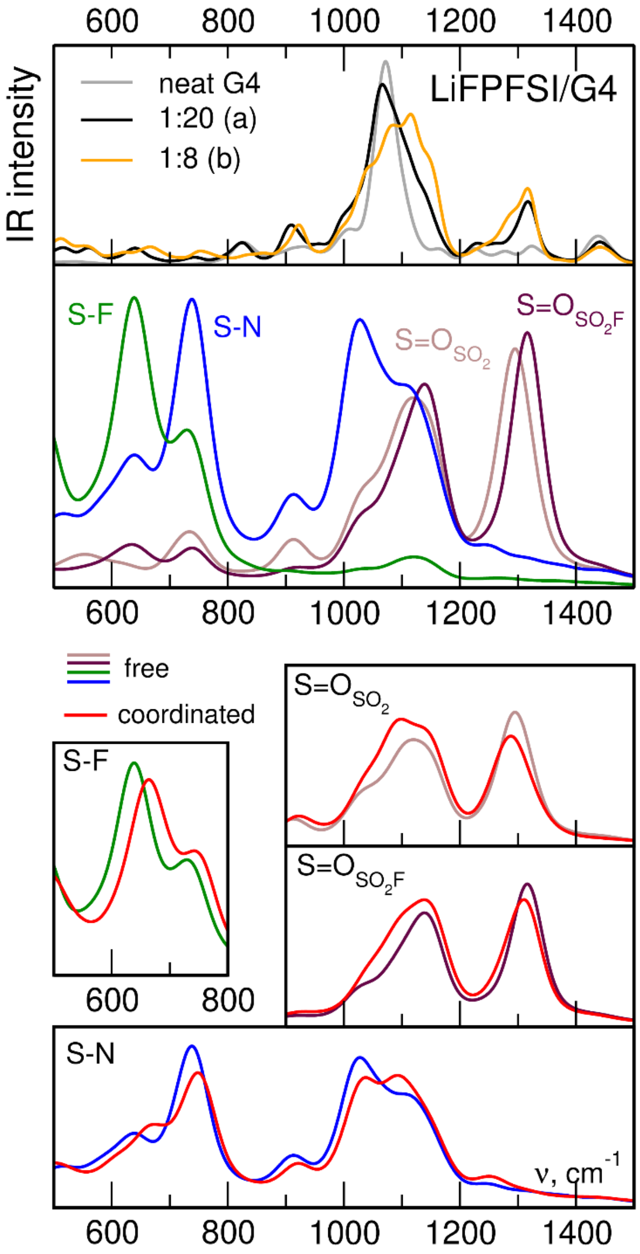
- Li-O_{an} distances are slightly larger in the LiFPFSI electrolyte
- accordingly, coordination to G4 molecules increases in LiFPFSI-G4 with a decrease of Li-O_{an} CN

IR spectra of electrolytes: LiTFSI-G4



- Changes mainly in the regions of S=O and S-N vibrations
- Fourier transforms of bond lengths allow us to correlate frequency shifts with the coordination of the TFSI anion
- An upshift of ~7 cm^{-1} of the 740 cm^{-1} band (IR inactive, but observable in Raman spectra) agrees well with the experimental data

IR spectra of electrolytes: LiFPFSI-G4



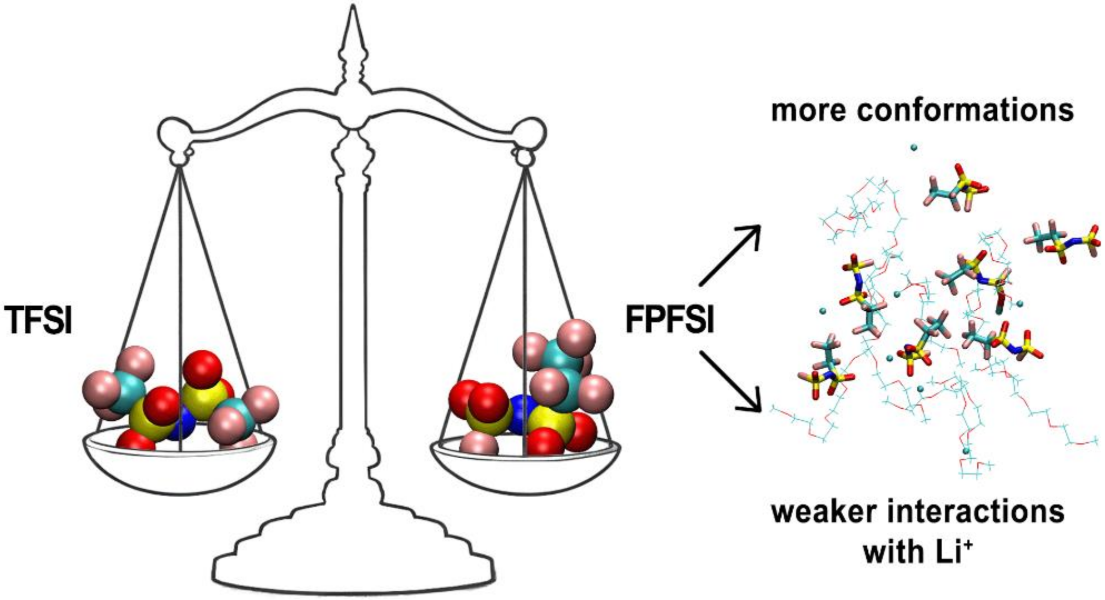
- Frequency shifts in the regions of S=O, S-N and S-F vibrations

- There is a clear coordination-induced upshift (~25 cm^{-1}) of the 640 cm^{-1} mode, corresponding to S-F stretching

- The 640 cm^{-1} band is IR and Raman active, therefore it should be well suited to monitor the coordination of FPFSI anions

Conclusions

- Asymmetry and flexibility of FPFSI anion leads to an increased number of low-energy conformers
- Li^+ binding to FPFSI is slightly weaker compared to TFSI
- The S-F vibration in the range 600-700 cm^{-1} is a good candidate to monitor anion complexation in FPFSI electrolytes



P. Kubisiak, D. Narkevičius, C. Nicotri, A. Eilmes, Comparative Study of Isomeric TFSI and FPFSI Anions in Li-Ion Electrolytes Using Quantum Chemistry and Ab Initio Molecular Dynamics, *J. Phys. Chem. B* **2025**, *129*, 2560; https://doi.org/10.1021/acs.jpcb.4c08414.

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