

Infrared Spectra of NaFSI/EMIM-FSI Electrolyte from *Ab Initio* Molecular Dynamics Simulations

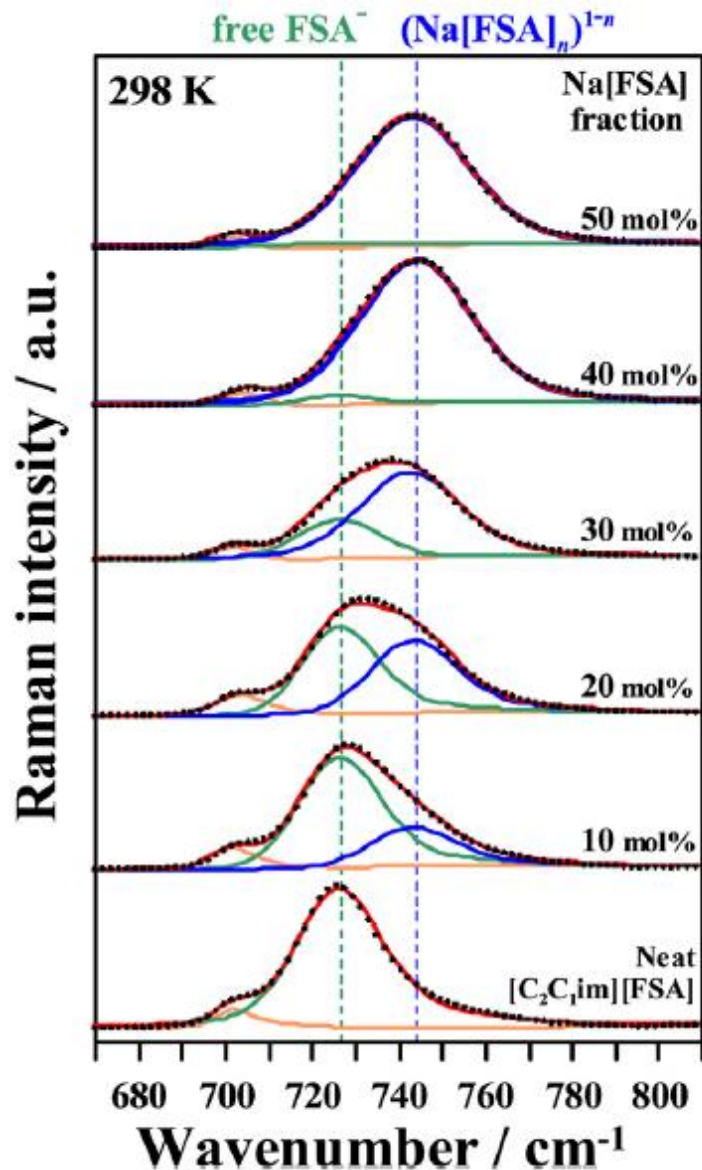
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Problem

- 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
- Our aim: to check how MD can help us to understand the vibrational spectra and relate them to the interactions in condensed phase

Experimental vibrational spectra of Na/EMIM/FSI electrolytes



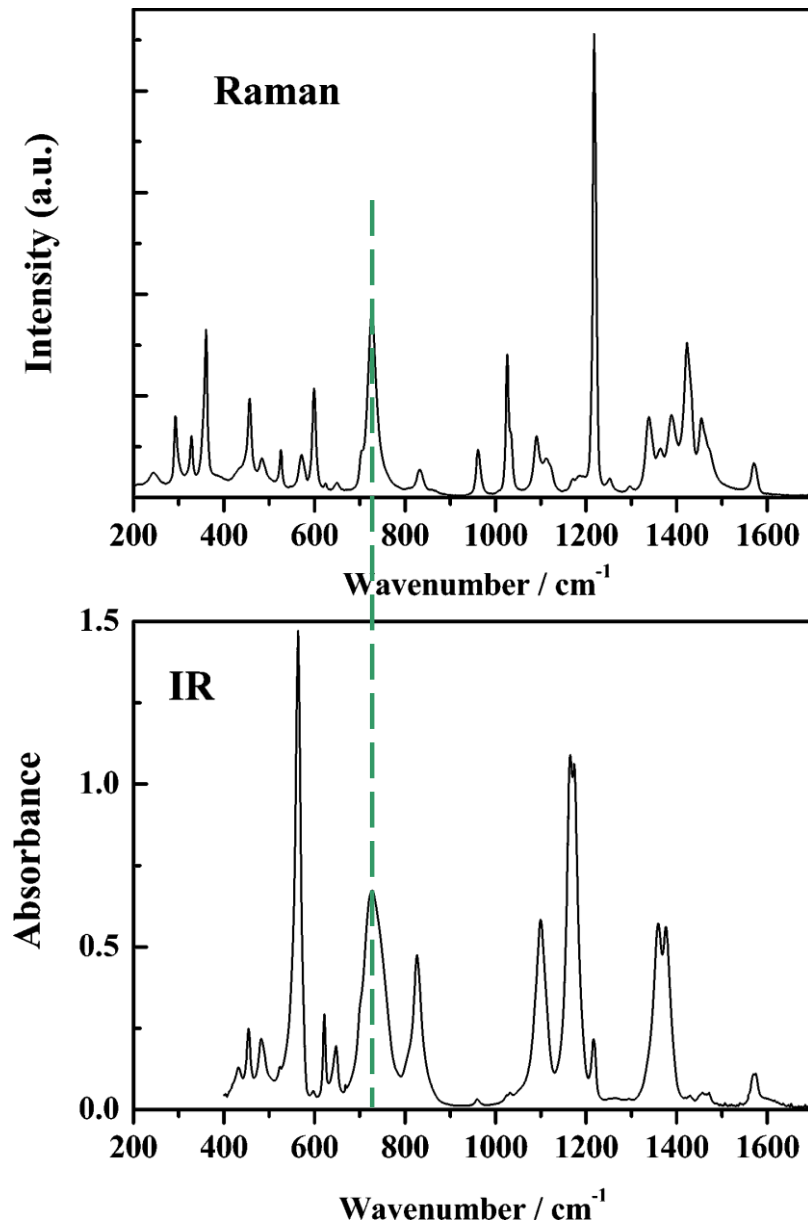
Vibrational spectroscopies are often used to study ion-ion interactions in electrolytes

Experimental study on the 1-ethyl-3-methylimidazolium (EMIM) bis(fluorosulfonyl)imide (FSI) ionic liquid based electrolytes [*J. Power Sources*, 332 (2016) 51]

Electrolytes EMIM-FSI with increasing content of dissolved NaFSI salt

In Raman spectrum the band at 726 cm⁻¹ shifts to higher frequencies when the salt fraction increases – the effect is attributed to Na-FSI interactions

Experimental vibrational spectra of Na/EMIM/FSI electrolytes



IR and Raman spectra of neat EMIM-FSI liquid

The band at $\sim 730 \text{ cm}^{-1}$ is active both in IR and Raman spectrum

We can therefore study the IR spectrum to reduce the cost of computations

IR spectra of Na⁺ - FSI⁻ ion pairs

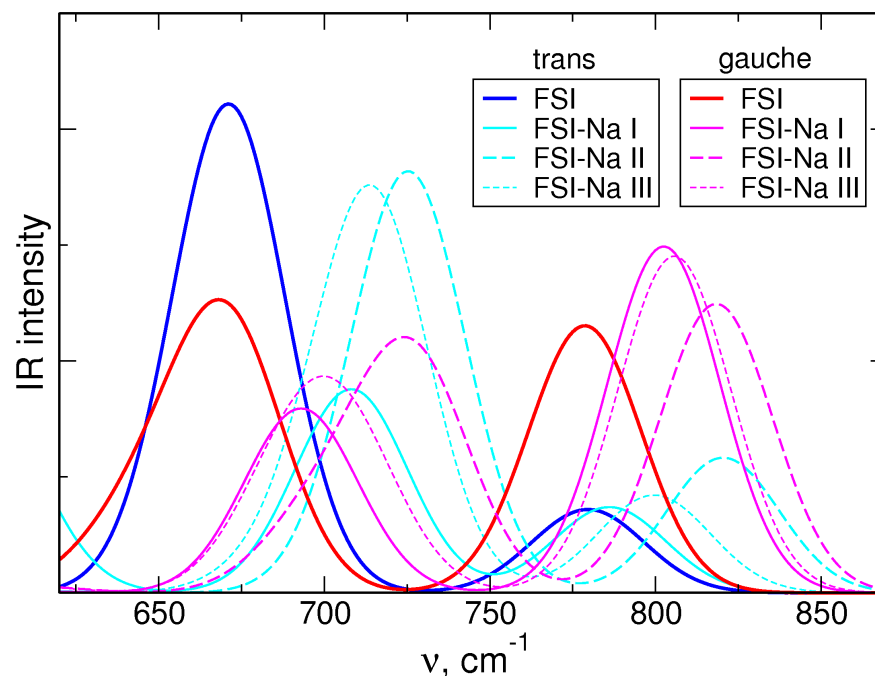
The vibrational band of our interest shifts to higher frequencies in the Na-FSI ion pair

But:

- the reference should be EMIM-FSI pair, not the free anion
- in the liquid there are interactions with many EMIM⁺, FSI⁻ and Na⁺ ions
- there is a population of FSI conformers
- conformations of anions and their solvation shells change dynamically

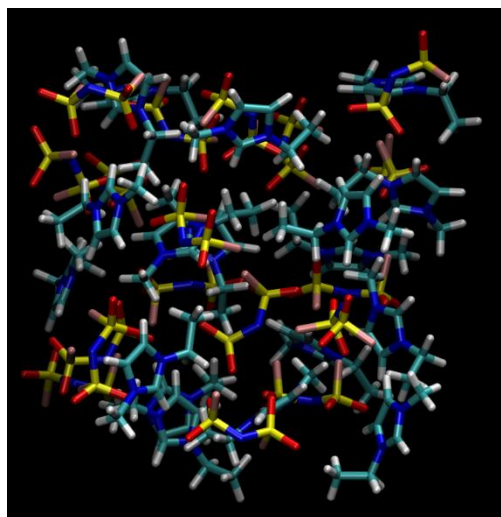
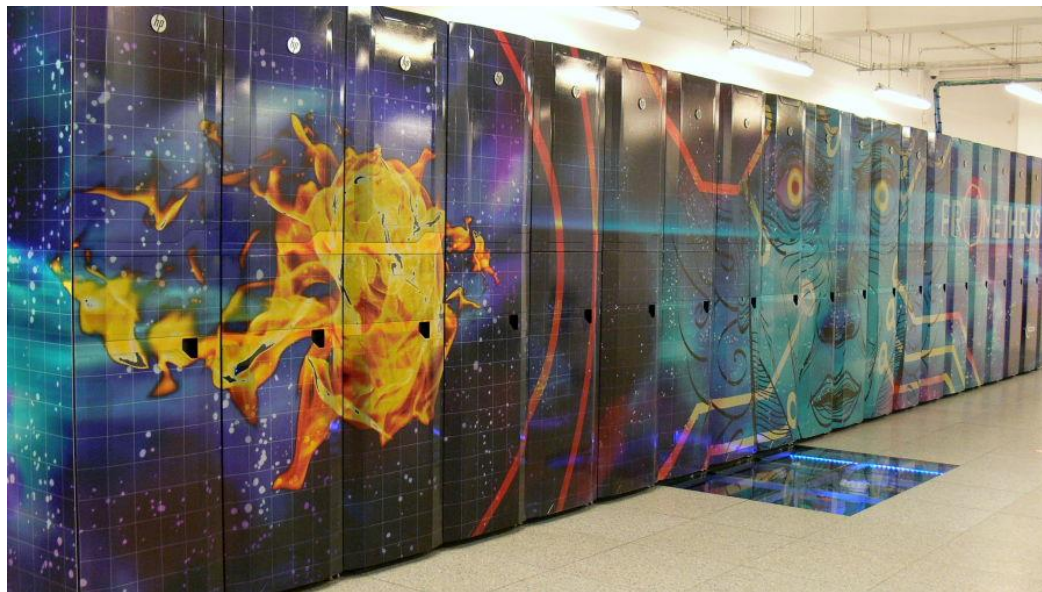
Gas phase QC may give some clues, but we need molecular dynamics to account for the structure of the electrolyte and interactions

Ab initio MD is necessary to study the vibrational spectrum

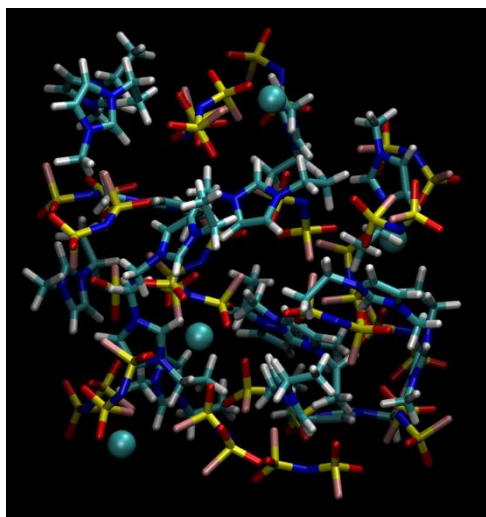


ab initio Molecular Dynamics

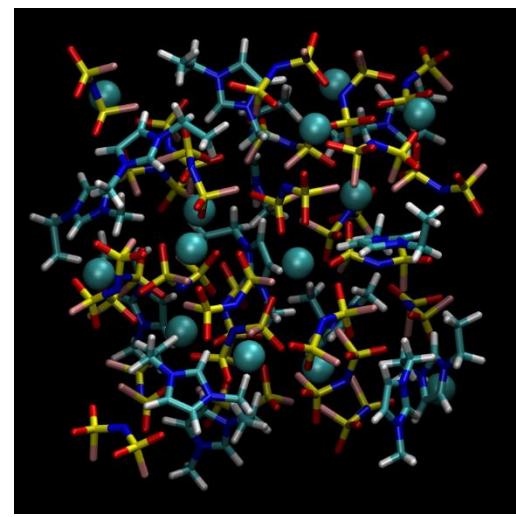
- Born-Oppenheimer MD in CP2K v. 2.6.1 package
- NVT simulations with Nose-Hoover thermostat ($T=298$ K) for ~ 500 atoms
- PBE with DZVP basis set + Grimme's dispersion
- 30 ps of the MD trajectory collected for each system
- initial MD simulations in a classical polarizable FF



$c = 0$



$c = 0.2$

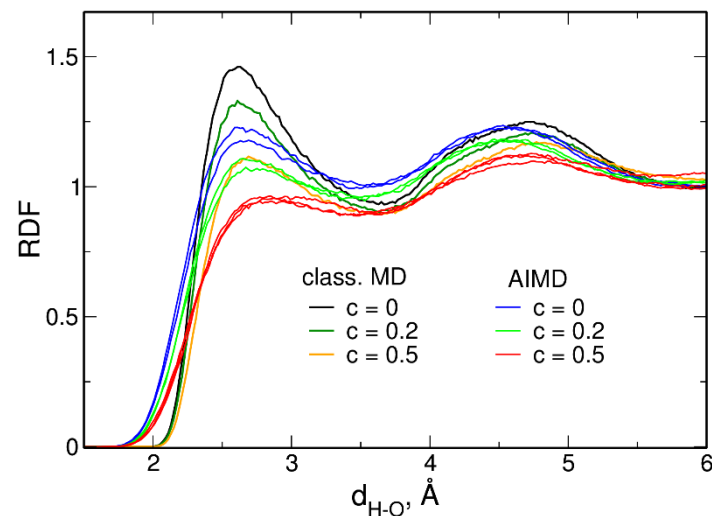


$c = 0.5$

Classical vs. *ab initio* simulations

Structure of electrolytes from *ab initio* and classical MD simulations

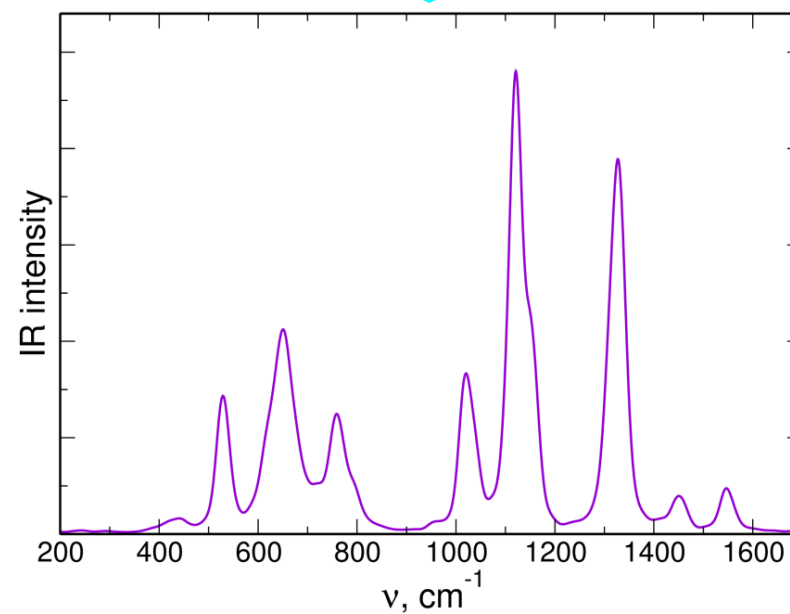
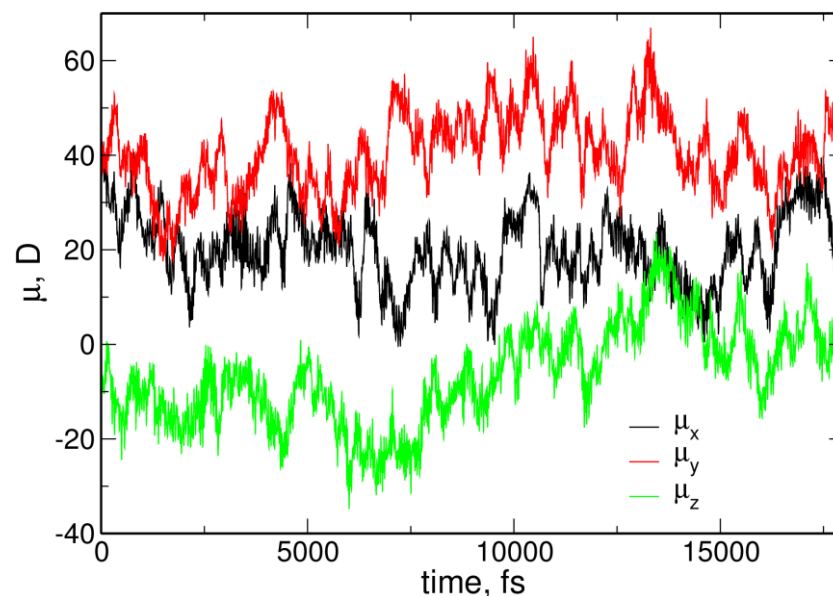
Viscosity and conductivity estimated from classical MD



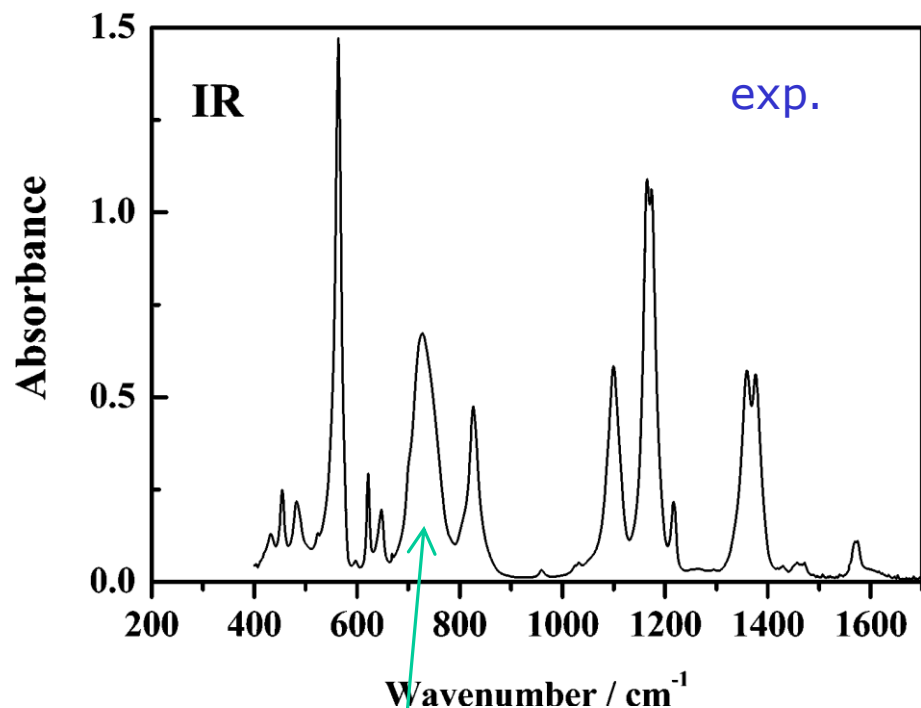
Poster #1: P. Wróbel, P. Kubisiak, A. Eilmes, „Classical and Ab Initio Molecular Dynamics of NaFSI/EMIM-FSI Electrolytes”

IR spectrum from MD simulations

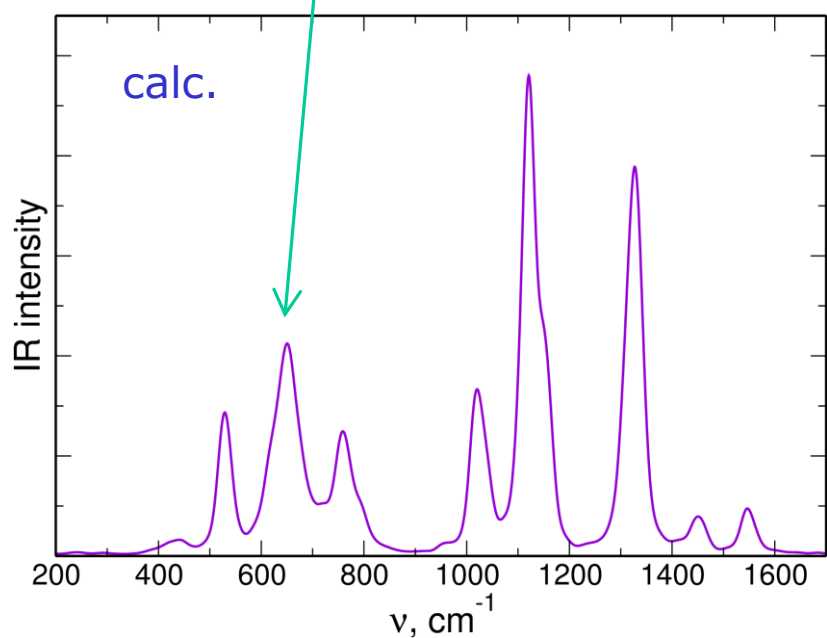
- vibrational spectrum can be obtained from MD trajectories as Fourier Transform of the autocorrelation function of the dipole moment (IR spectrum) or of the polarizability (Raman spectrum)
- calculations of the polarizability are expensive, therefore we calculated only the dipole moment of the system and the IR spectrum, accordingly
- the band we are interested in is active both in IR and in the Raman spectrum



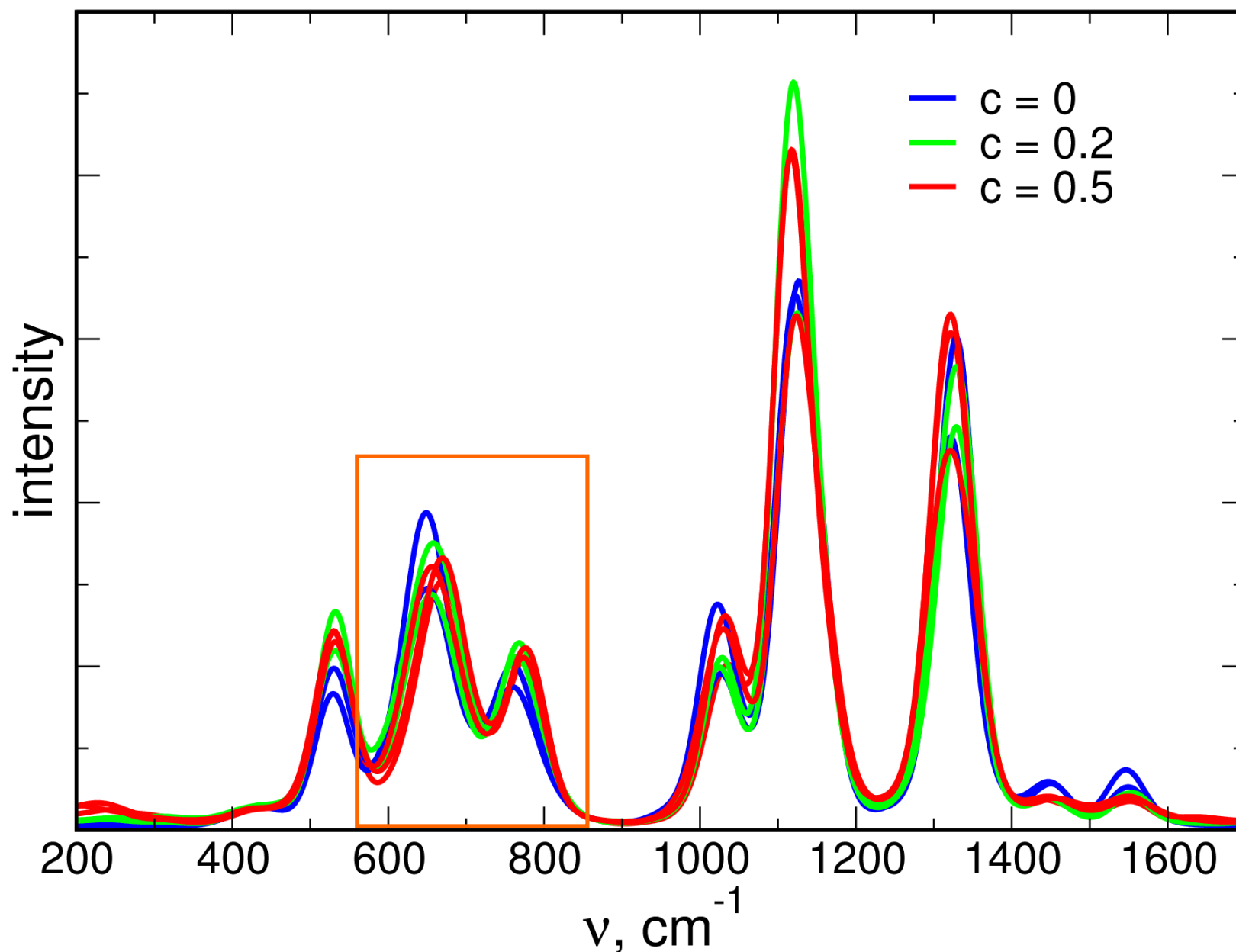
IR spectrum from MD simulations



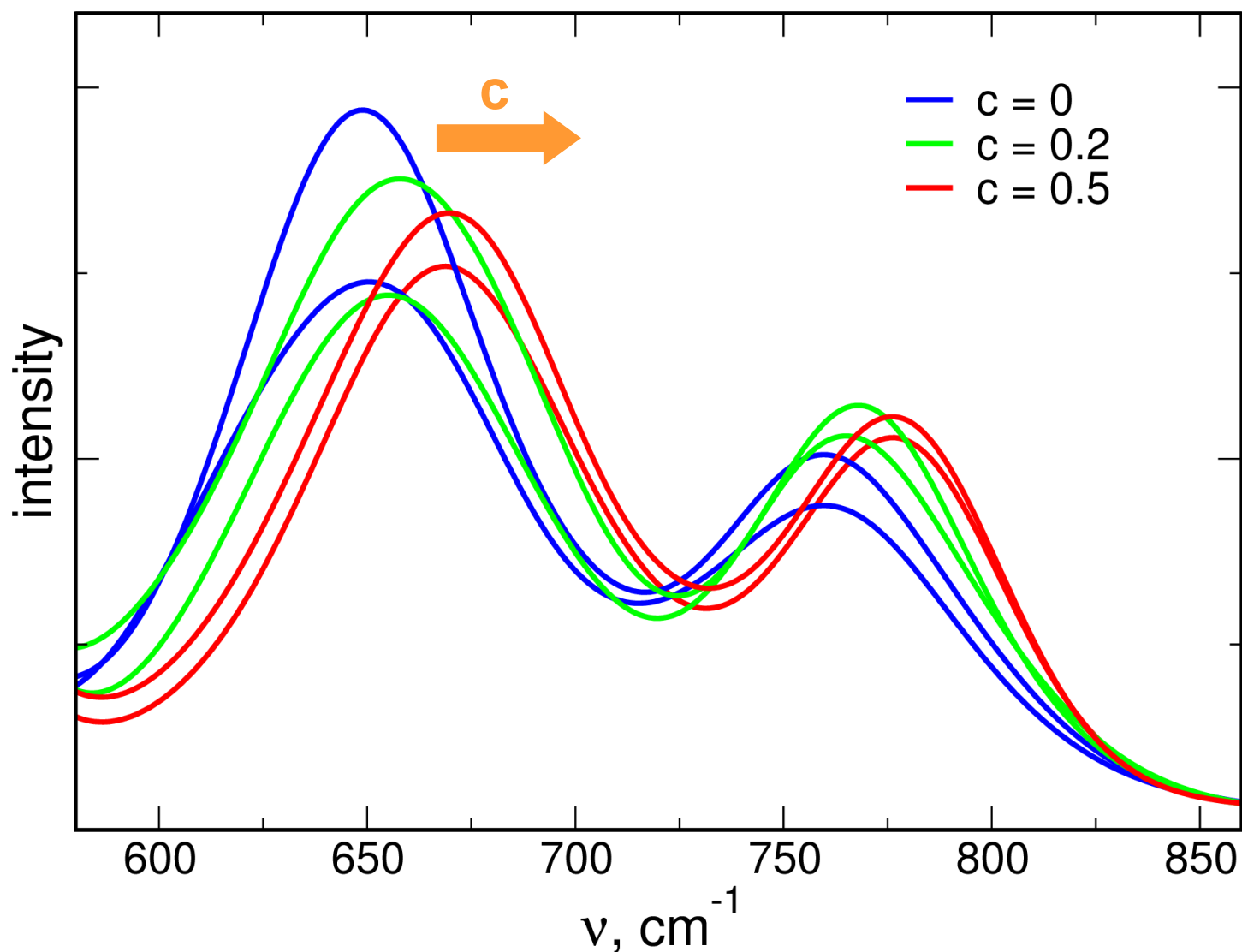
- agreement between experimental and calculated spectrum is quite satisfactory
- calculated spectrum is red-shifted by about 80 cm^{-1}
- the experimental band at 730 cm^{-1} corresponds therefore to the band at 650 cm^{-1} in the spectrum from AIMD



Changes in the IR spectrum with increasing c

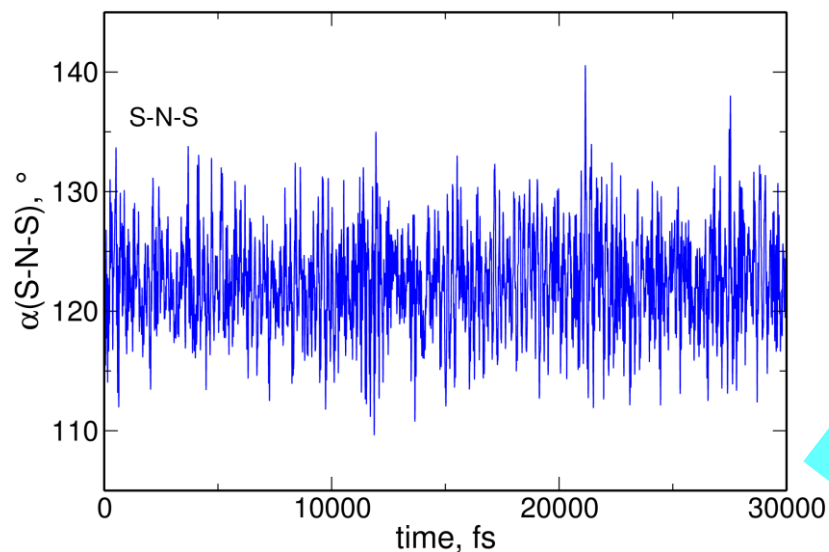


Changes in the IR spectrum with increasing c

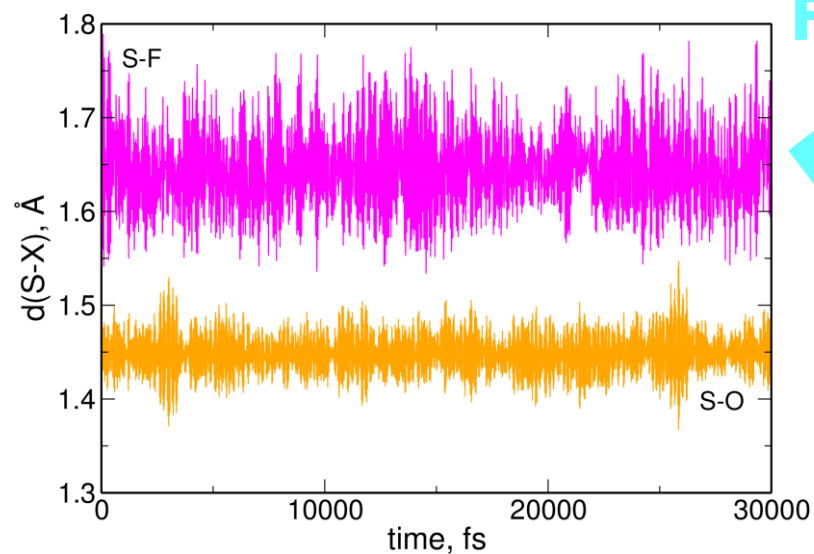


Maximum blue shift of about 20 cm^{-1} observed for $c=0.5 \text{ M}$ agrees well with experimental data

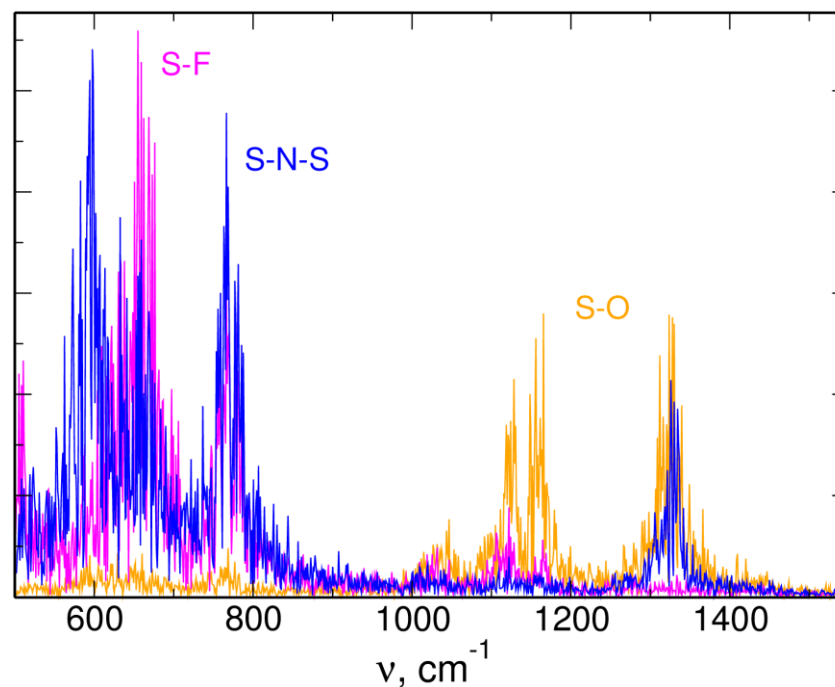
FT of geometrical parameters of anions



Fourier transform of the bond length or of the valence angle helps to find normal modes related to the changes of selected geometrical parameter

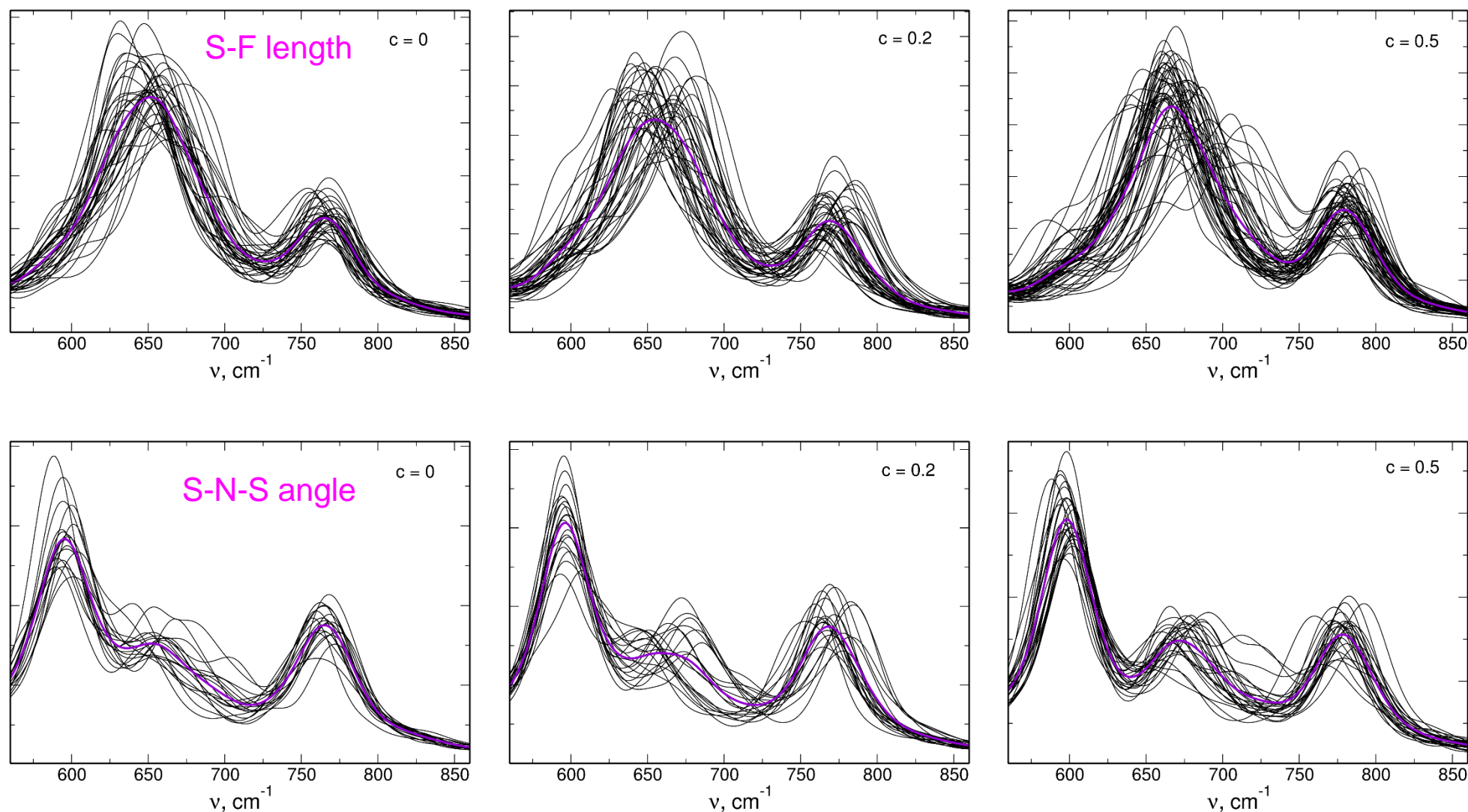


FT



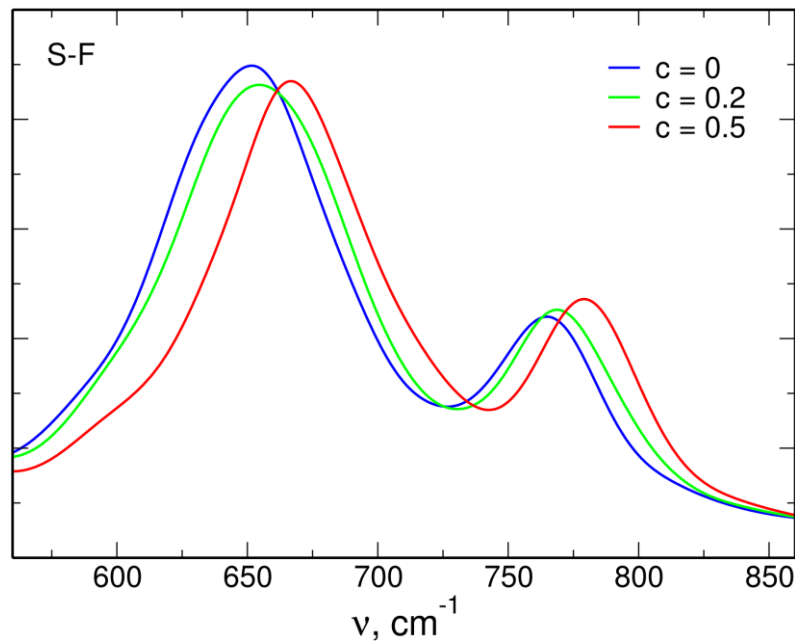
the band at 650 cm^{-1} originates from S-F stretches and S-N-S bending

FT of geometrical parameters of anions



Frequencies of vibrational modes differ significantly between FSI ions and the spread increases with salt concentration

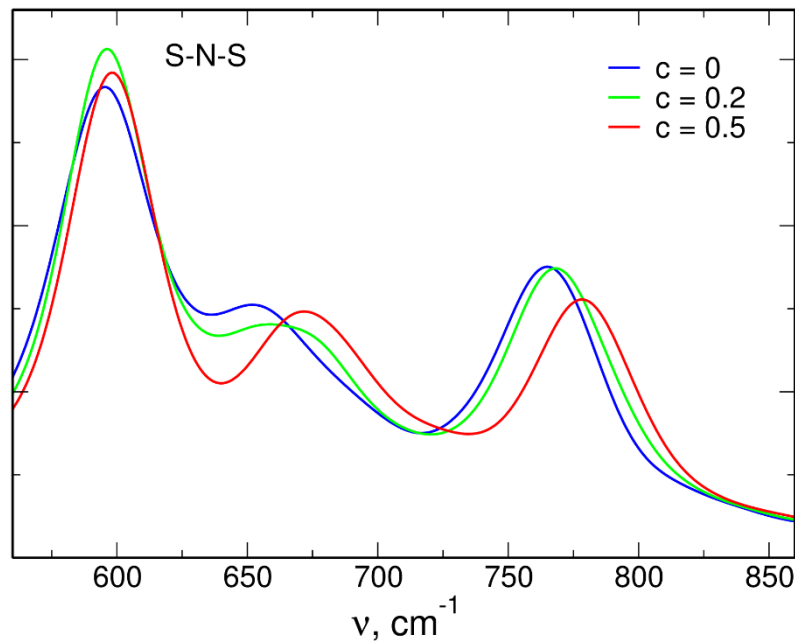
FT of geometrical parameters of anions



Frequencies of vibrational modes averaged over all FSI ions clearly shift to higher energies for increasing Na⁺ concentration

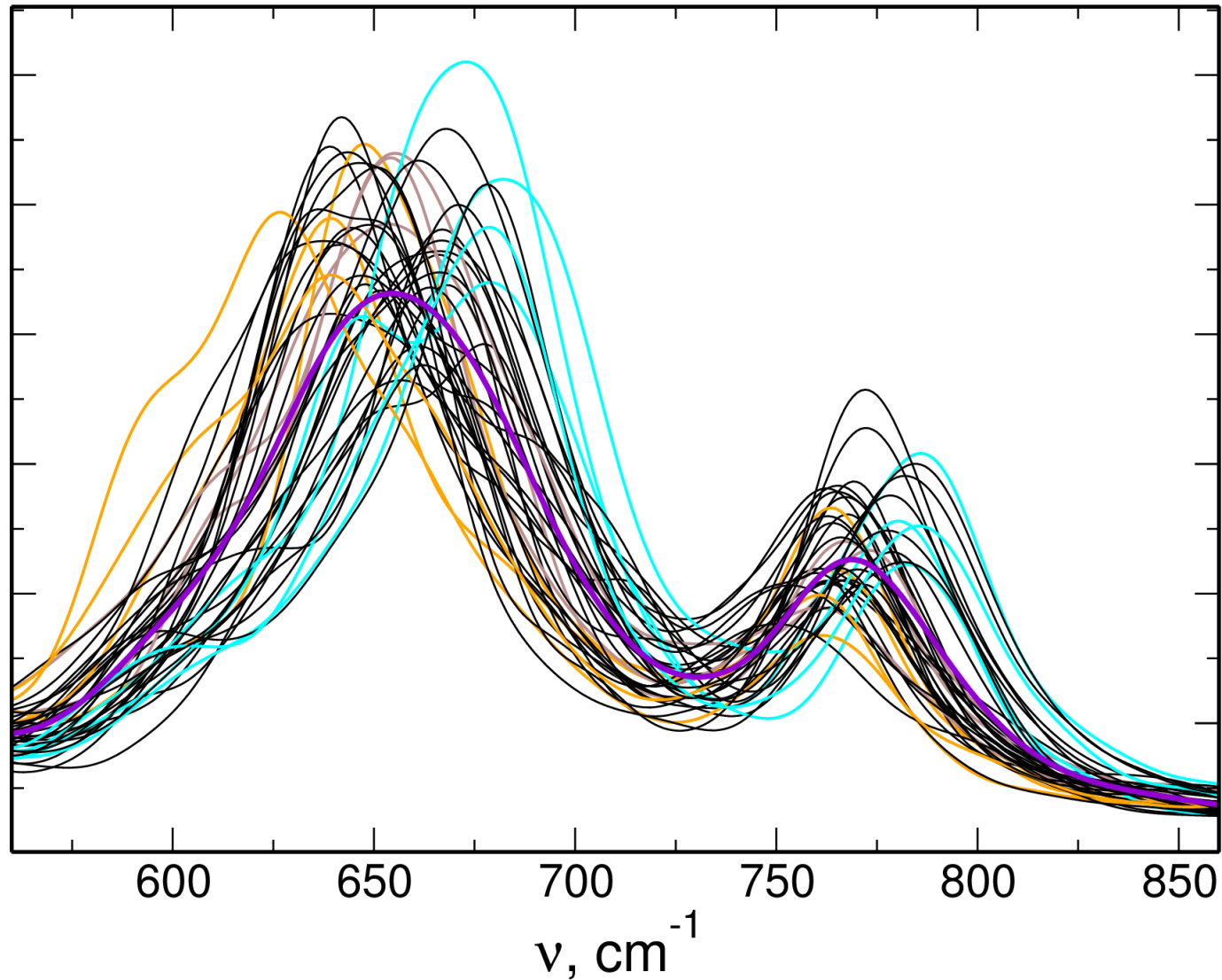
Shifts are comparable to those observed in calculated IR spectrum

Can we relate the frequency of S-F stretch or S-N-S bending extracted for given anion to its solvation shell?



An insight into the local structure

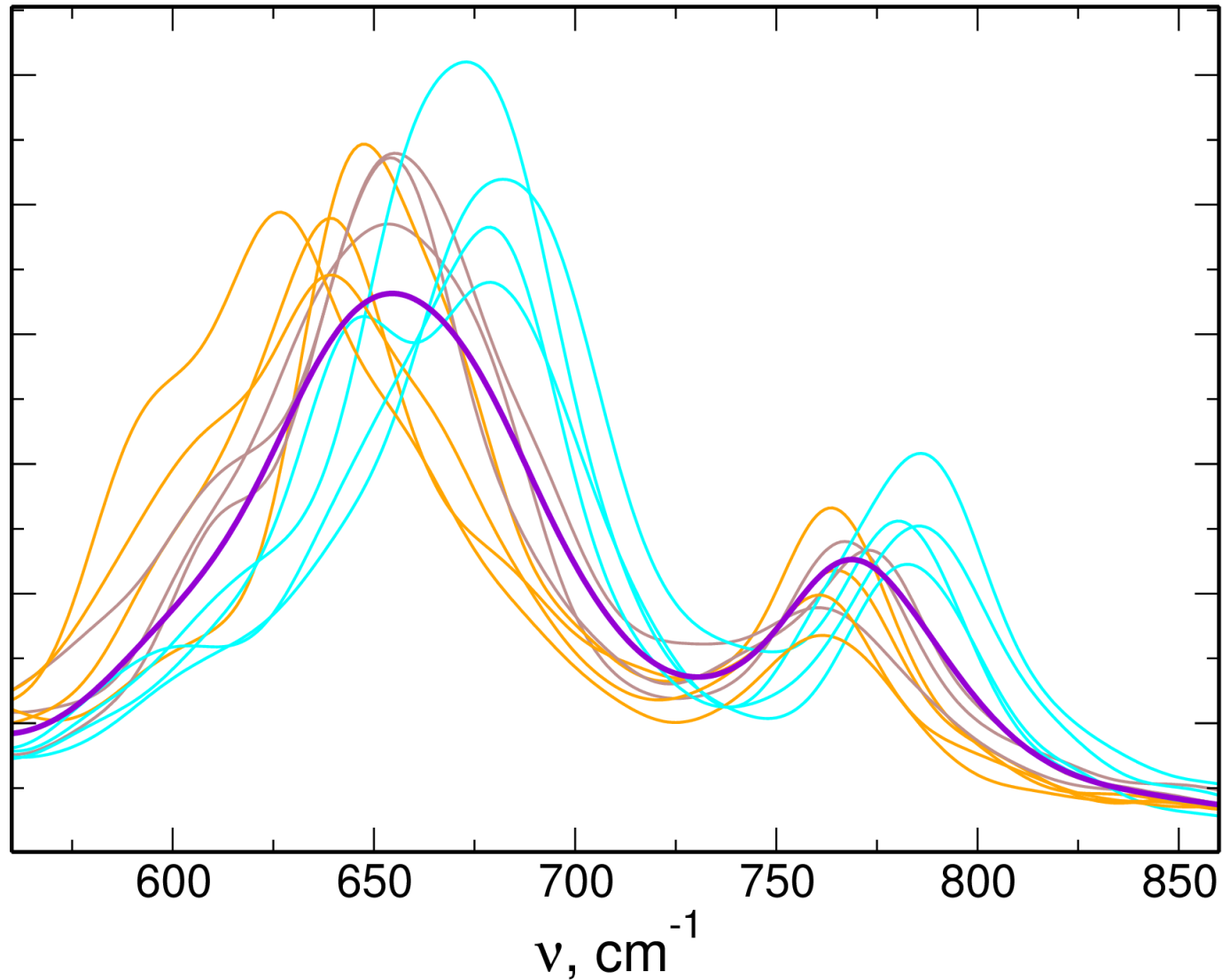
S-F
length
 $c = 0.2$



From all modes we can select some close to average, blue- or redshifted

An insight into the local structure

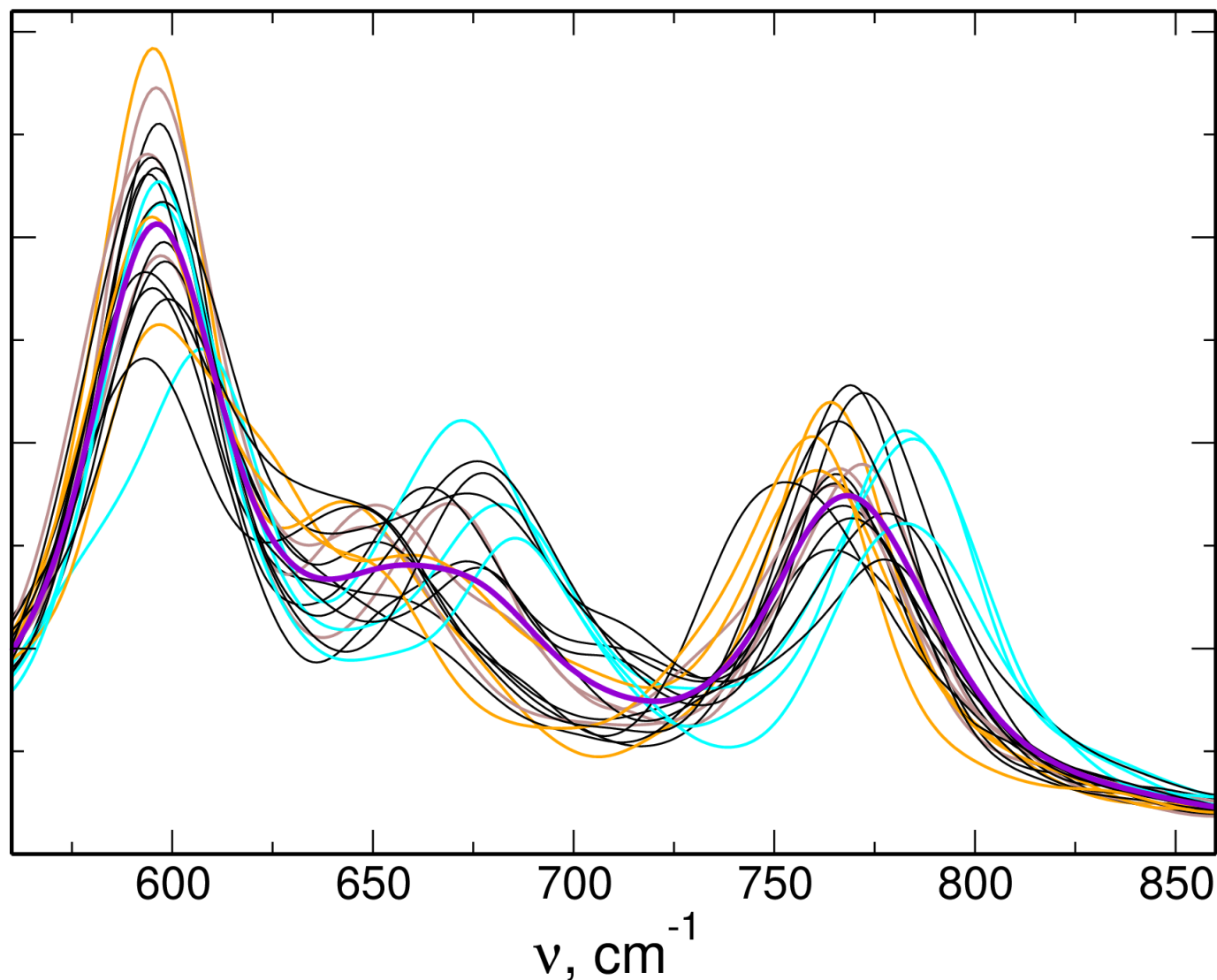
S-F
length



From all modes we can select some close to average, blue- or redshifted

An insight into the local structure

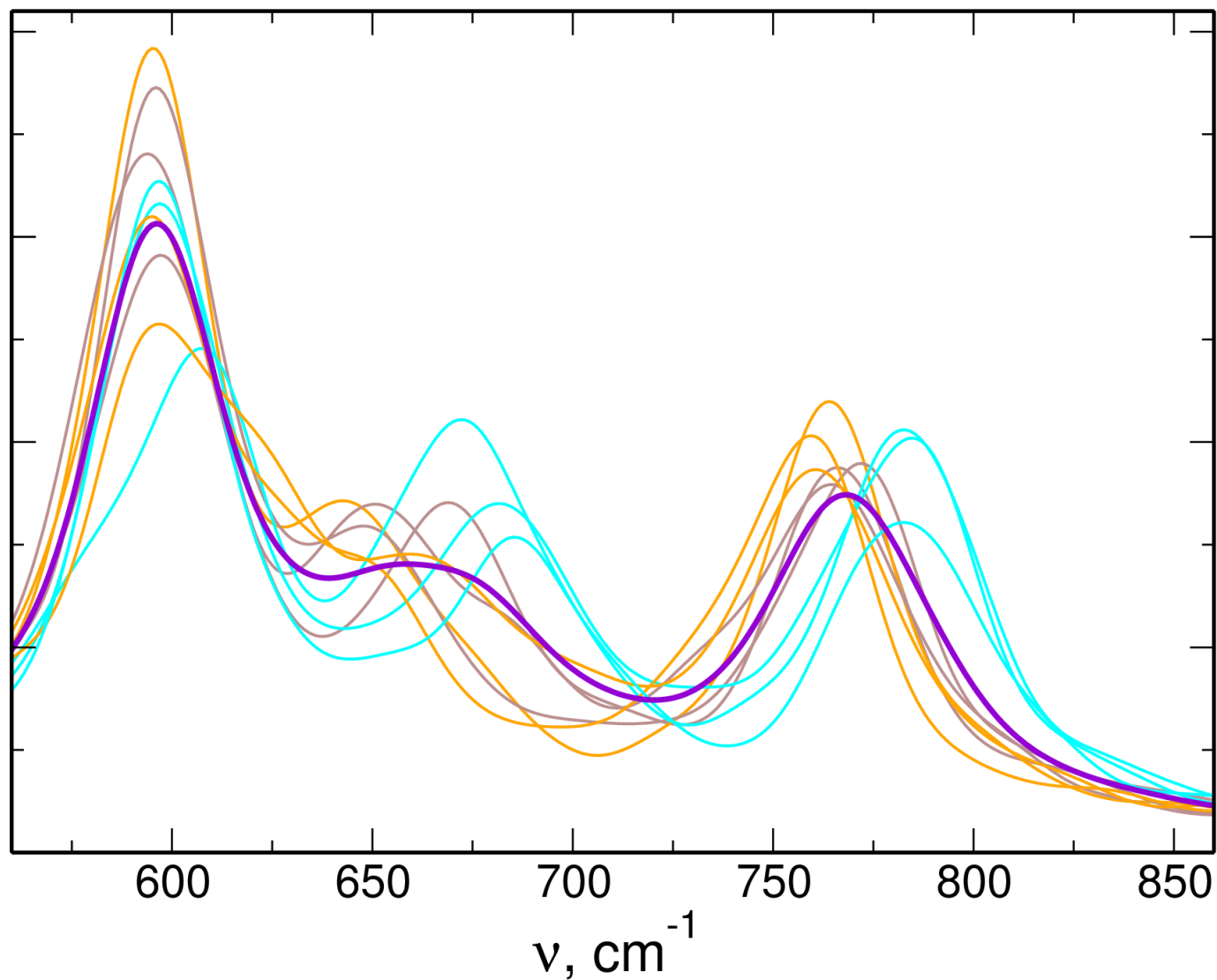
S-N-S
angle



Then we can do the same for S-N-S bending mode using the same colors for the same FSI ions

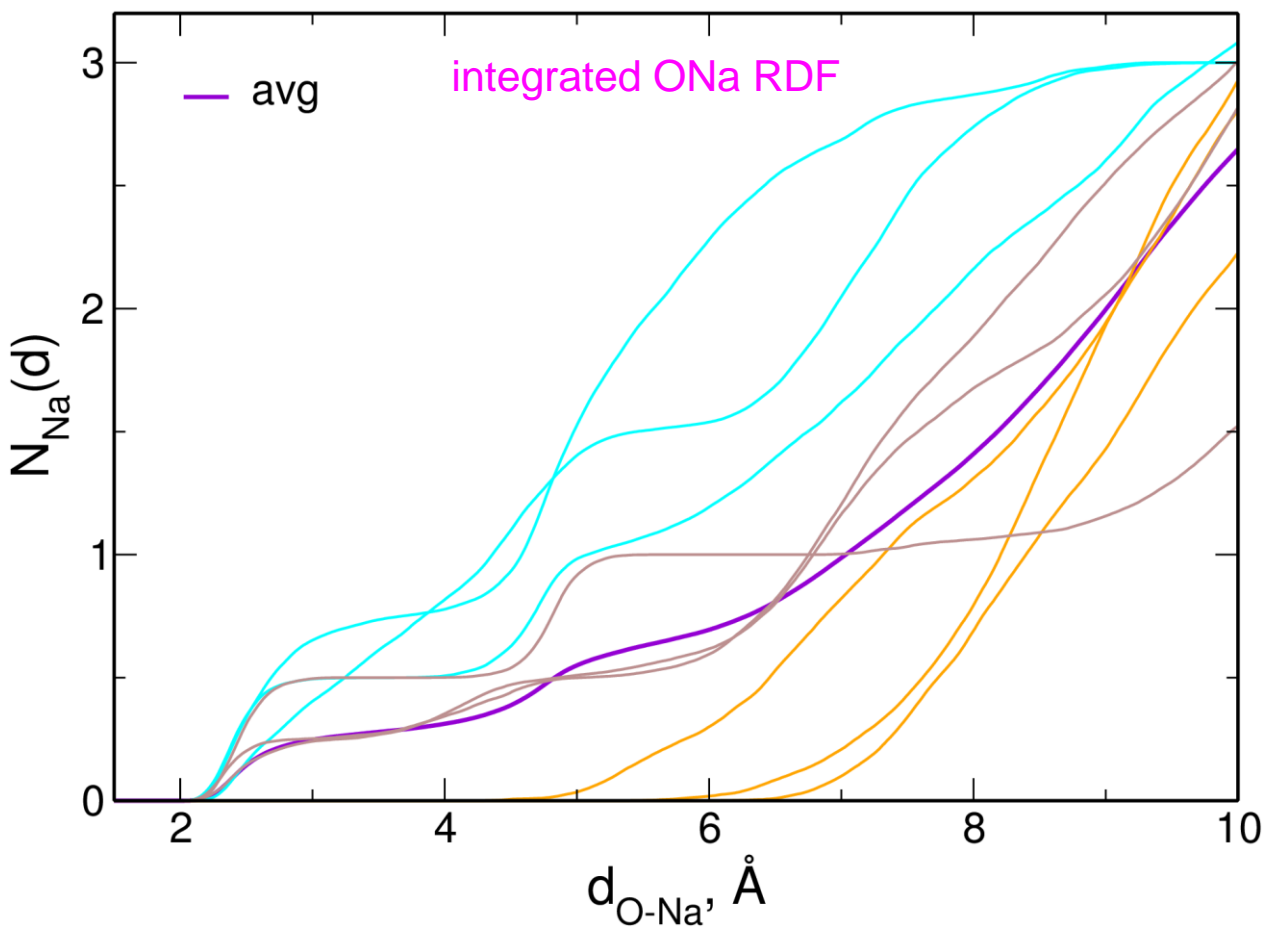
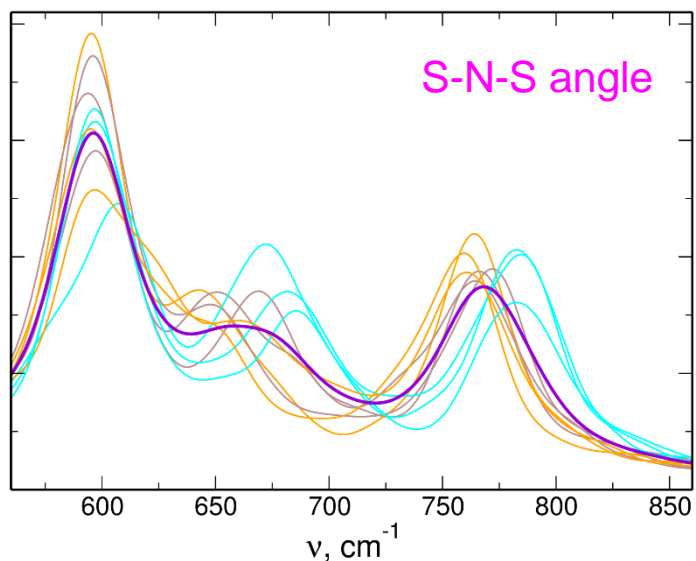
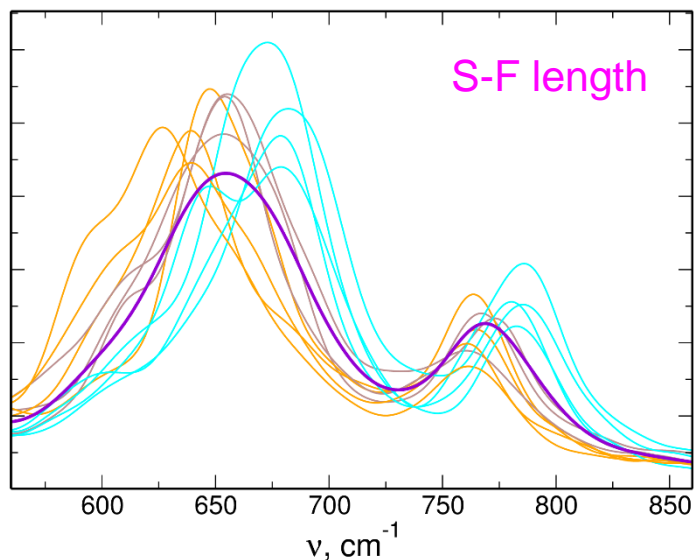
An insight into the local structure

S-N-S
angle



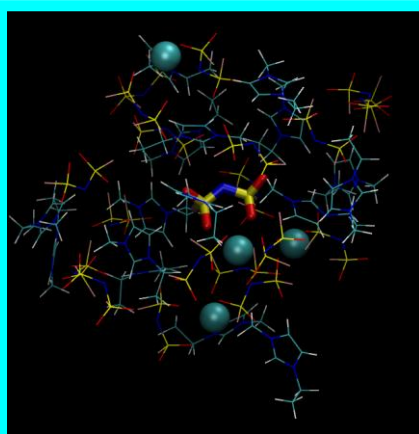
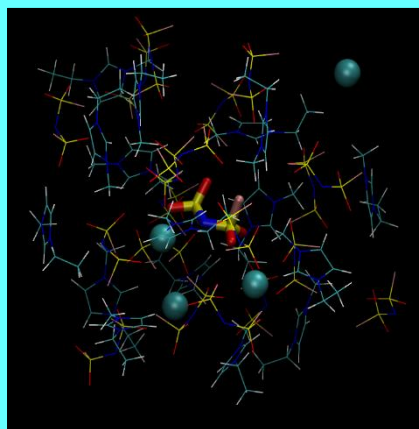
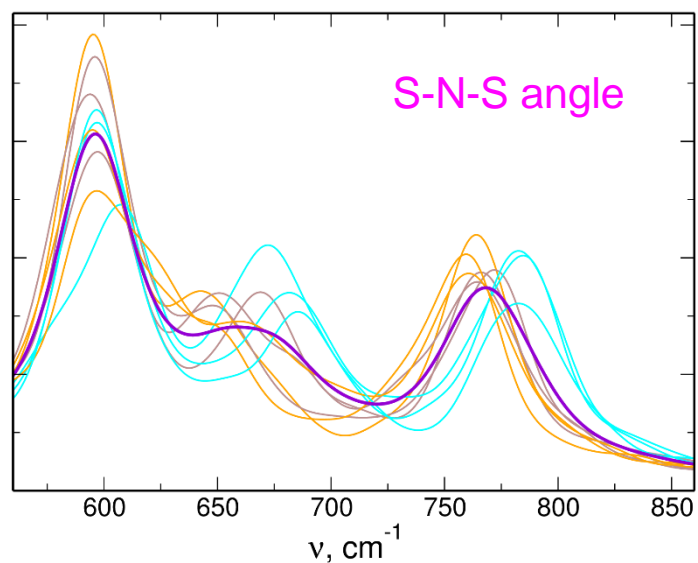
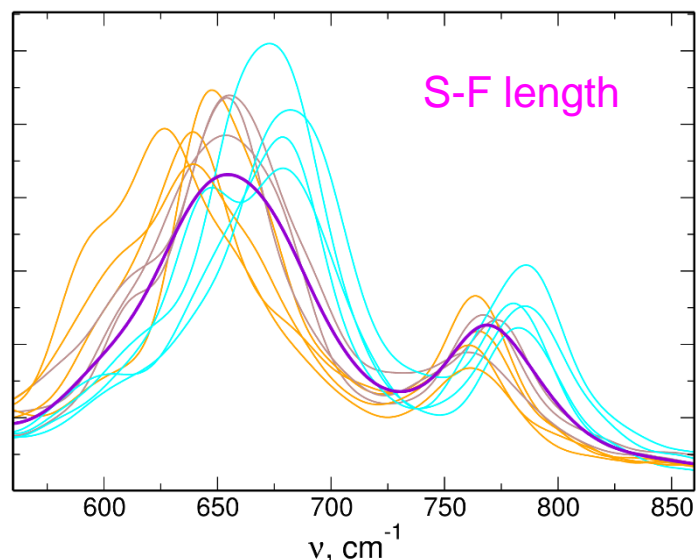
...and the result is quite similar

An insight into the local structure

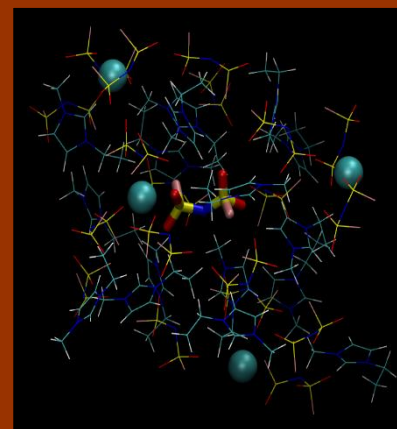


Frequency of the vibrational mode is apparently correlated with the number of Na cations close to the FSI anion

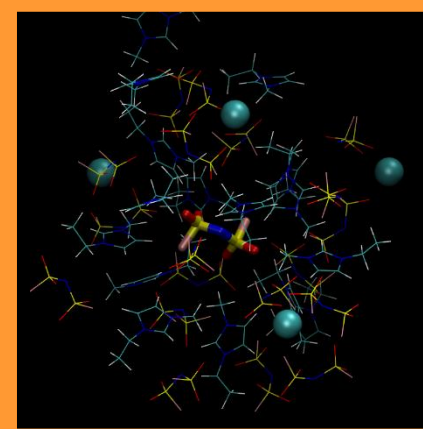
An insight into the local structure



**strong Na-FSI
coordination**



**weak Na-FSI
coordination**



**no Na-FSI
interaction**

Frequency of the vibrational mode correlates with local environment of the anion

Conclusions

- *Ab initio* molecular dynamics is able to provide correct reproduction of IR spectra in liquids and interaction-induced shifts
- Shifts of the vibrational frequencies may be related to local environment of interacting molecules/ions
- Fourier transform of selected geometrical parameters is helpful in the analysis of local interactions

Acknowledgments

Co-workers:

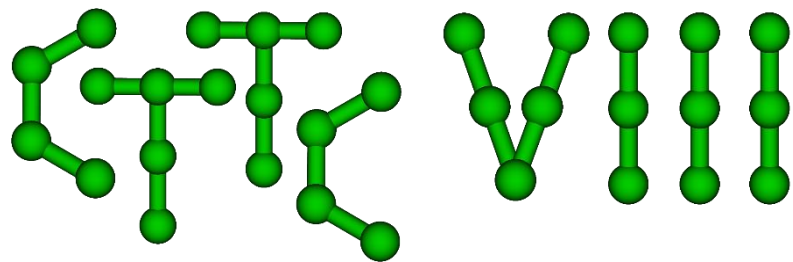
Dr. Piotr Kubisiak

Piotr Wróbel, M.Sc.

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