Vibrational spectrum of an ionic liquid from Born-Oppenheimer molecular dynamics

Andrzej Eilmes, Piotr Kubisiak, Mateusz Brela

Jagiellonian University, Faculty of Chemistry

KUKDM 17, Zakopane, 09.03.2017

Motivation

- Vibrational spectroscopy (infrared (IR) or Raman scattering) can provide information about interactions between molecules or ions
- Harmonic frequencies for isolated species are routinely available from quantum-chemical calculations – but they correspond to gas-phase
- Chemical processes occur in solutions, therefore we need to take solvent effects into account
- Computationally cheap and very popular are continuous solvent models
- Implicit solvent models do not describe well specific interactions

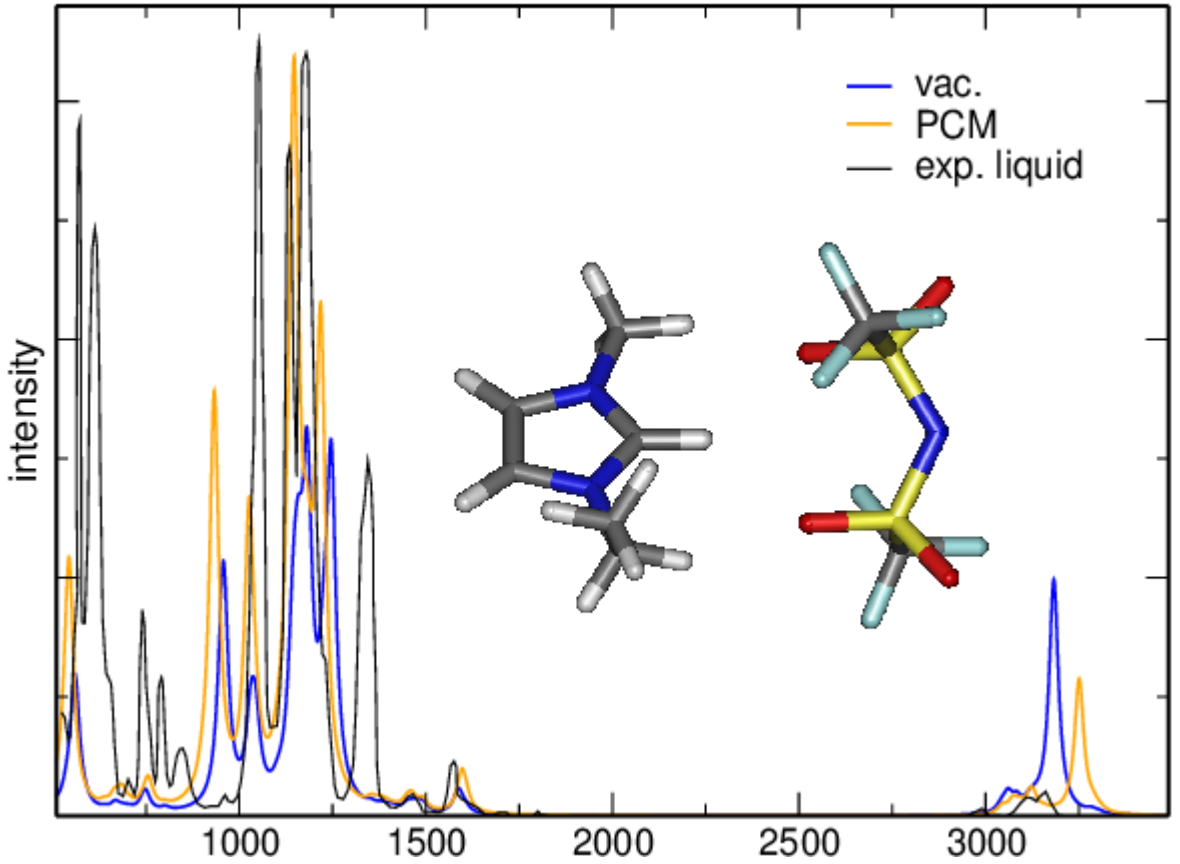
Motivation

- Room-Temperature Ionic Liquids (RTILs) – organic salts liquid at room temperatures
- Considered as prospective solvents with unique properties („green chemistry”)

- ILs are composed of ions only, therefore electrostatic interactions are crucial for the properties of an IL
- ILs are different from typical molecular liquids
- Properties of molecular liquid and ionic liquid with similar static dielectric constant usually differ

IR spectrum of a model IL

Ionic liquid: 1-ethyl-3-methylimidazolium ($EMIM^+$)
bis(trifluoromethylsulfonyl)imide ($TFSI^-$)



IR spectrum of a single EMIM-TFSi ion pair

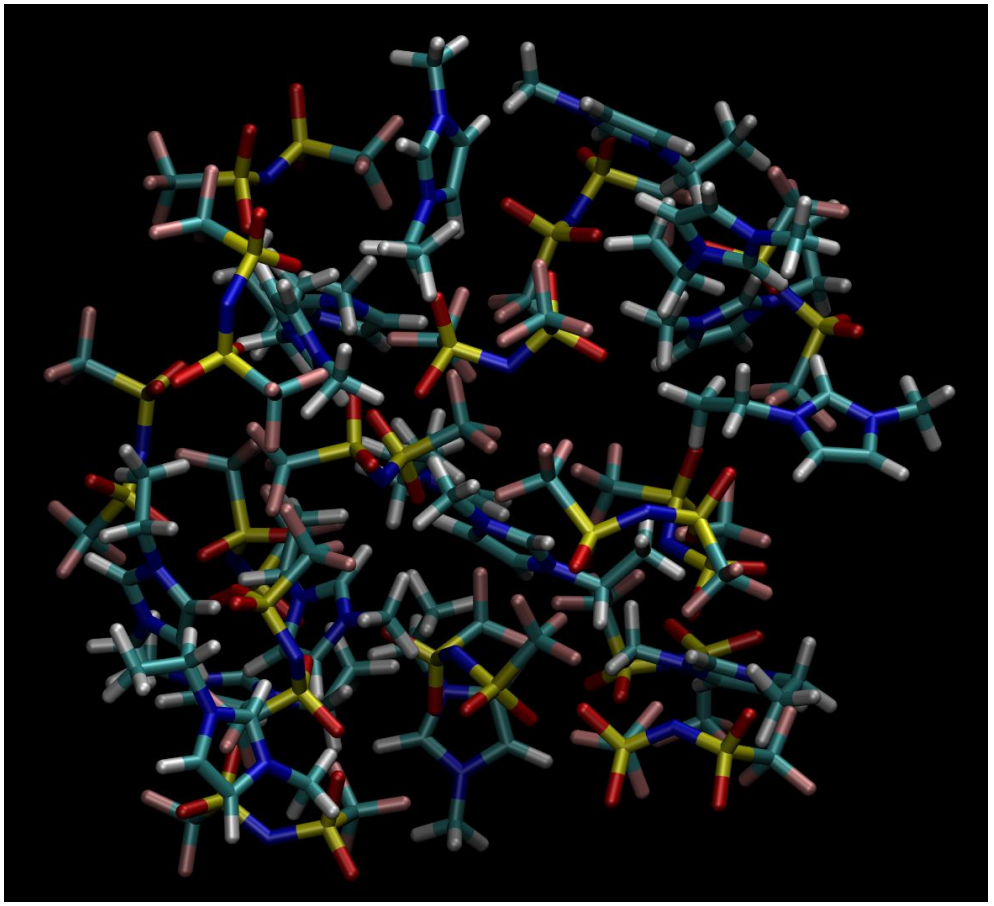
B3LYP/aug-cc-pVDZ calculations for isolated pair and in the PCM solvent

PCM model does not improve the spectrum with respect to bulk liquid

Our goal: calculation of the IR spectrum of a bulk liquid using explicit solvent

ab initio Molecular Dynamics

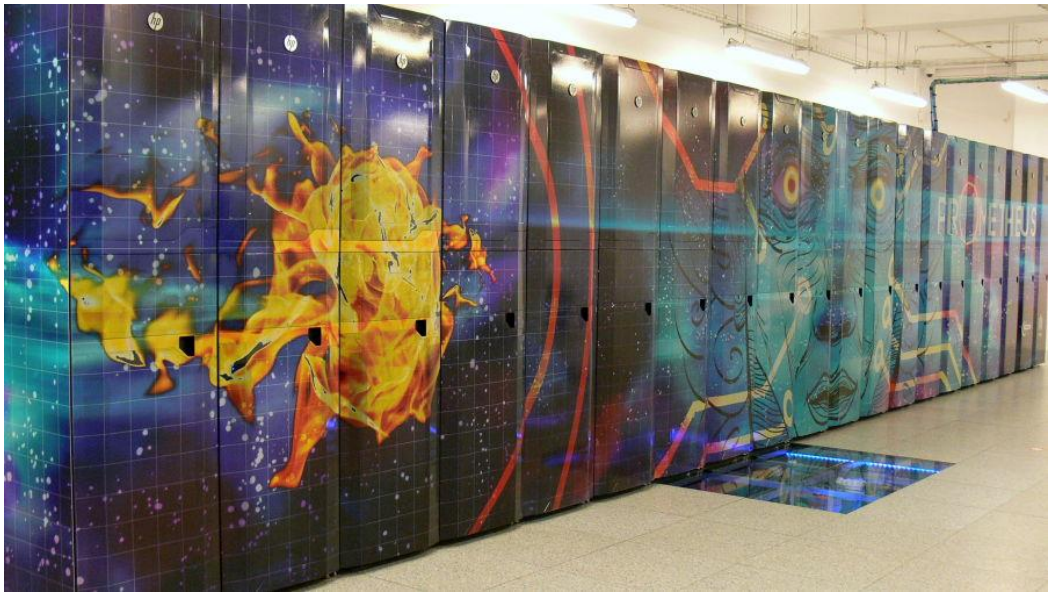
- IR spectrum may be obtained from molecular dynamics simulations as a Fourier transform of the autocorrelation function od the total dipole moment
- ab initio MD should be employed for this purpose (force-field based MD usually performs badly)
- AIMD is computationally expensive and we need a system large enough to represent the bulk liquid

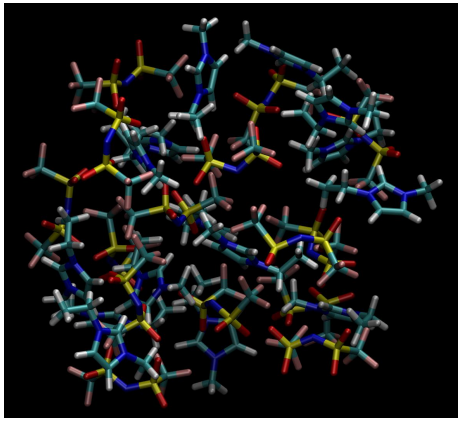


simulation box of 15 EMIM-TFSI ion pairs

ab initio Molecular Dynamics

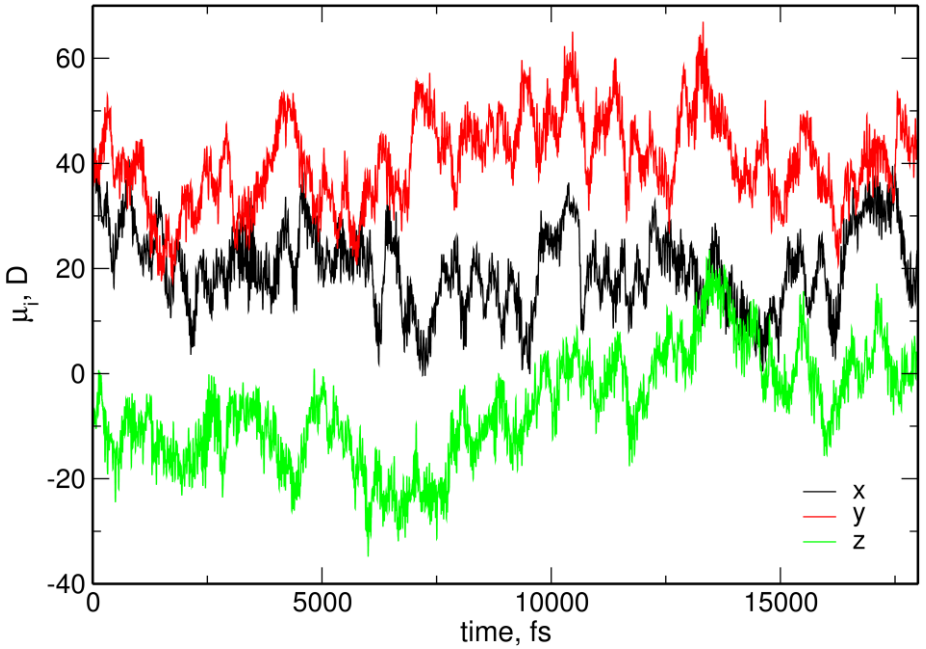
- Born-Oppenheimer MD in CP2K v. 2.6.1 package
- NVT simulations with Nose-Hoover thermostat (T=298 K) for 15 ion pairs
- LDA (Pade) functional with DZVP basis set
- 50-70 ps of the MD trajectory collected





- two Prometheus nodes (48 CPU cores) were used for each simulation
- each run produced approx. 0.75 ps trajectrory per day
- about 1M walltime hours were spent for the project

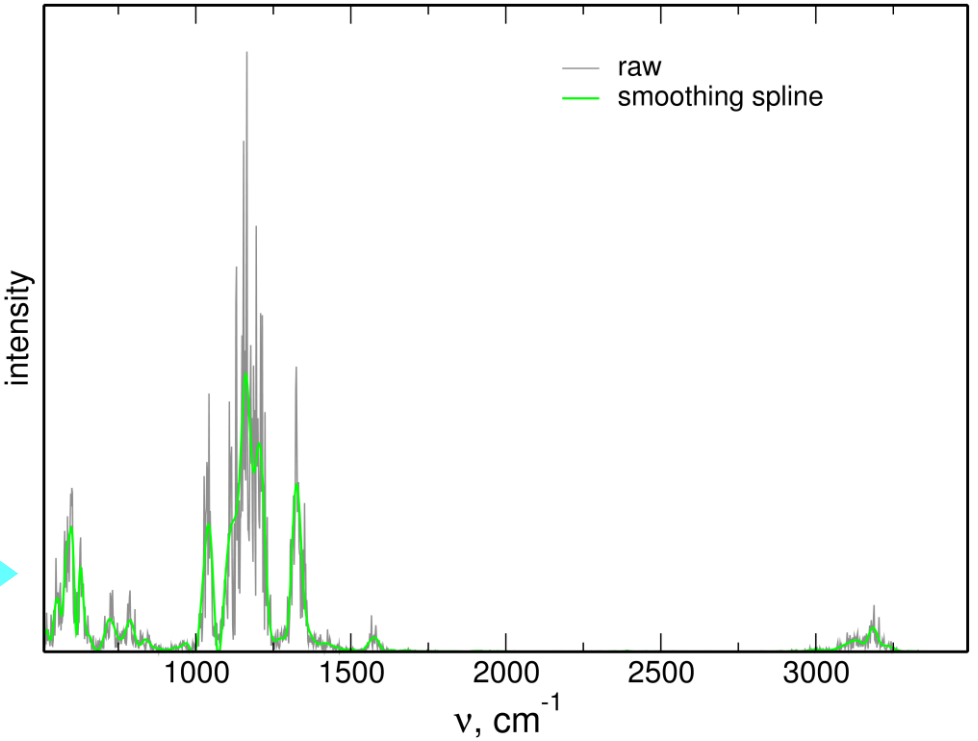
IR spectrum from BOMD



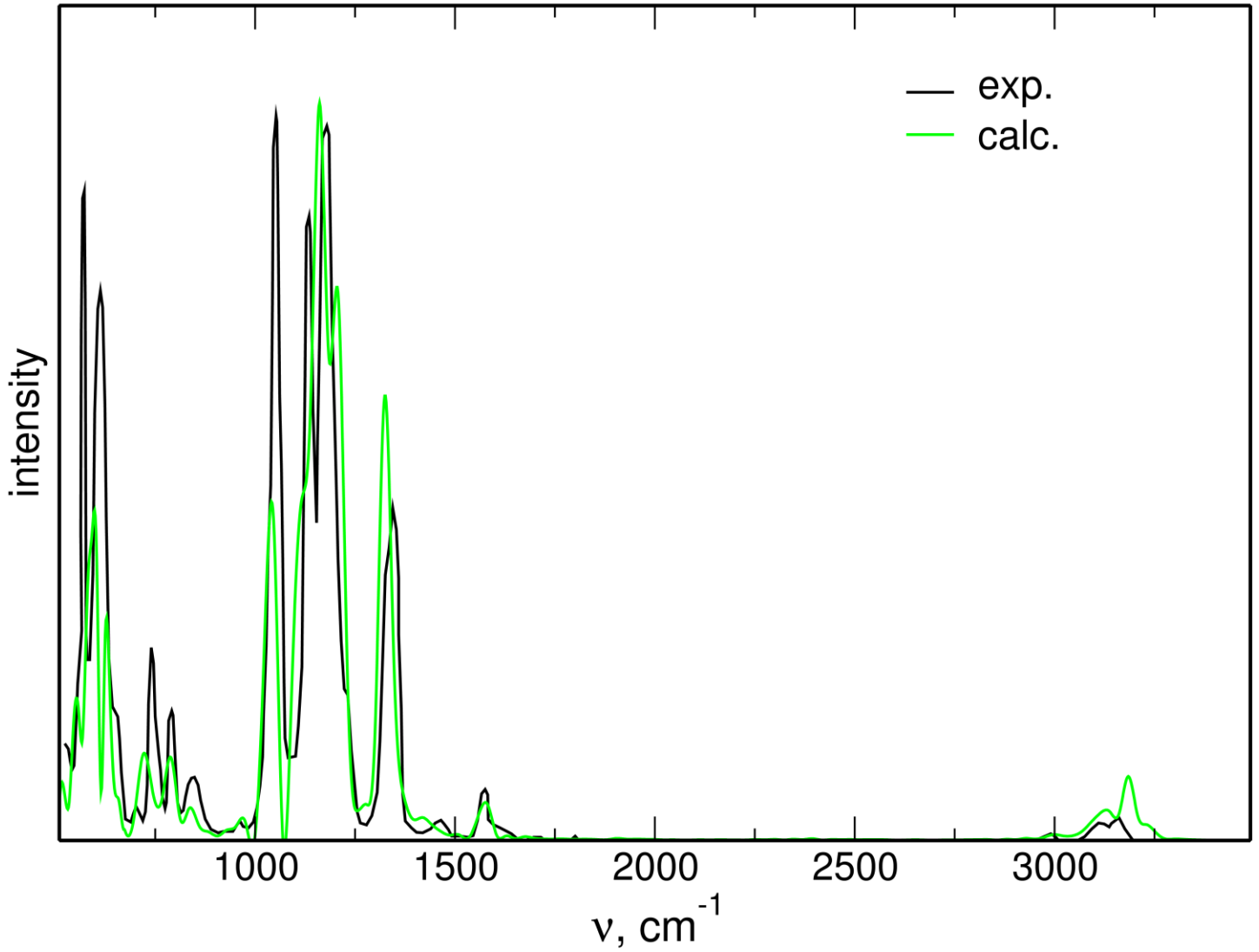
- about last 20-30 ps of the trajectory was used in the analysis
- results averaged over 3 components of the dipole moment

autocorrelation function of the dipole moment

Fourier transform

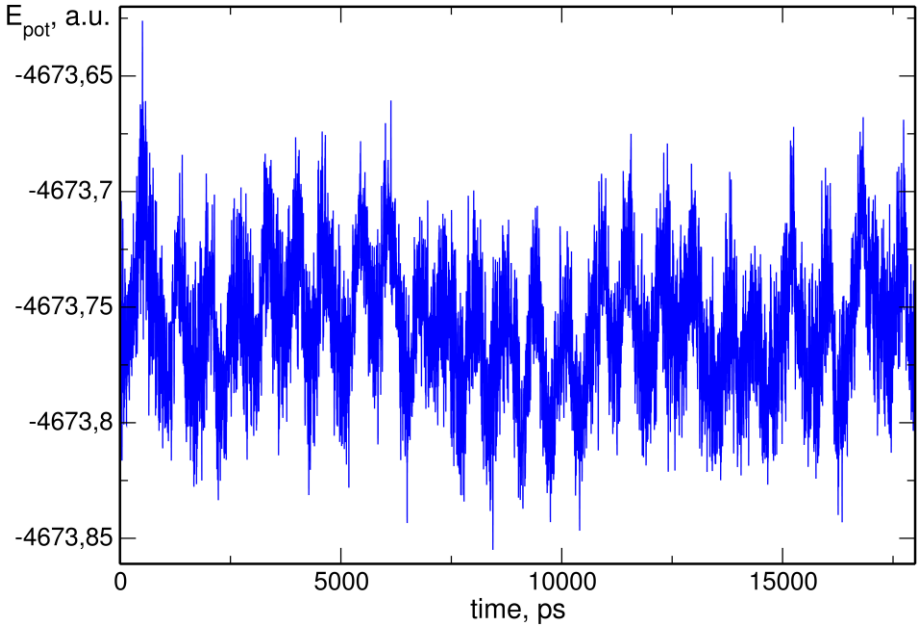


IR spectrum from BOMD



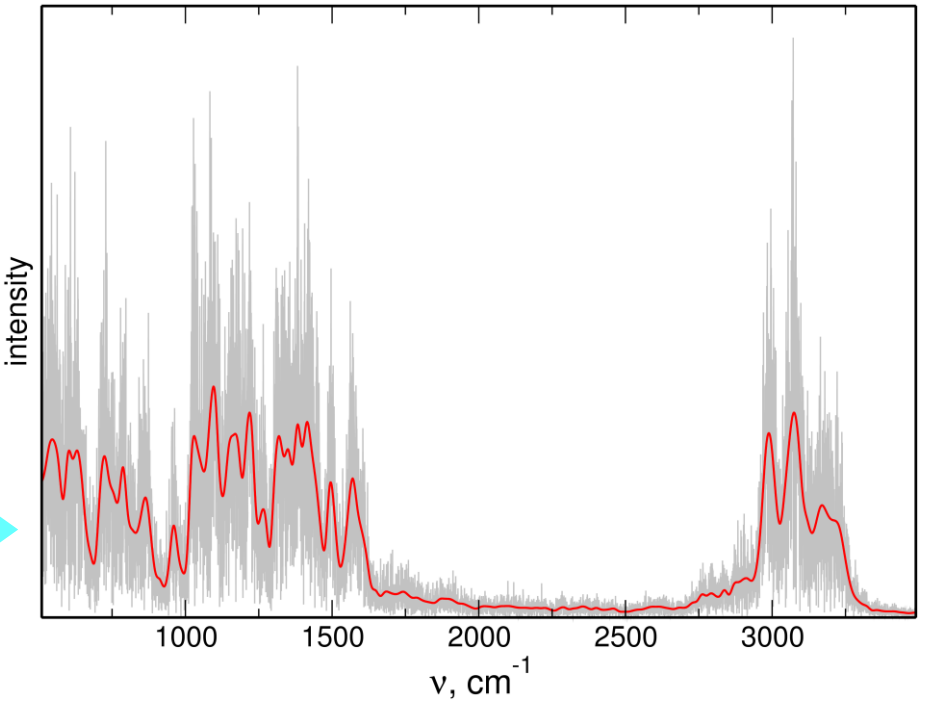
calculated spectrum agrees well with the IR spectrum of EMIM-TFSI liquid

IR spectrum from BOMD

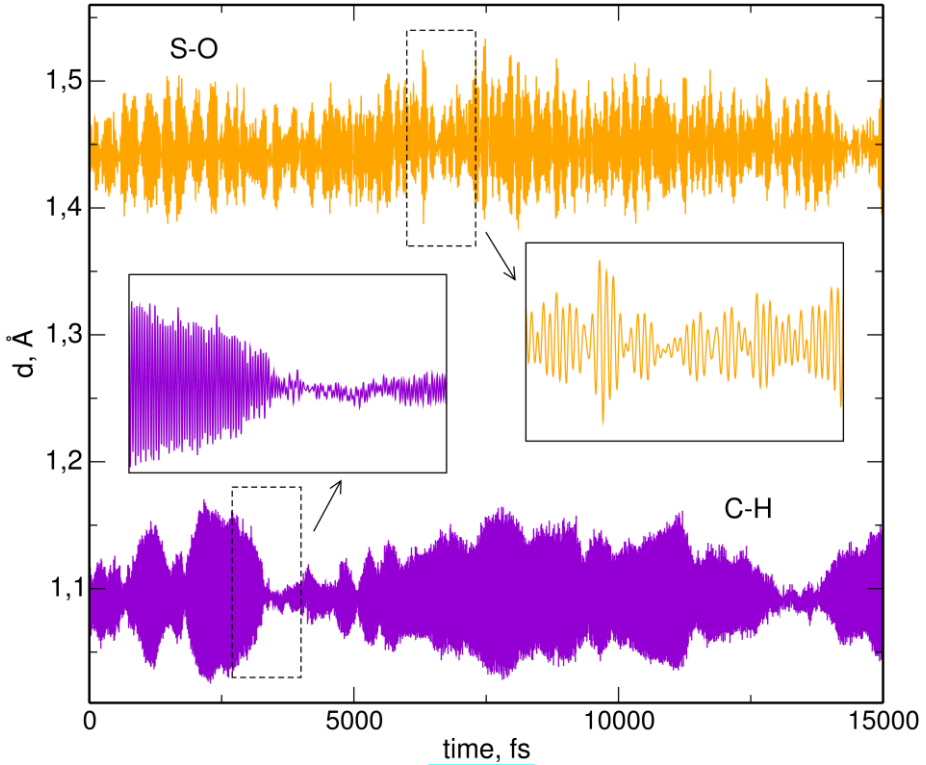


- vibrational frequencies may be obtained just from Fourier transform of the potential energy
- it is simple but information on the intensities is lost

Fourier transform of the potential energy

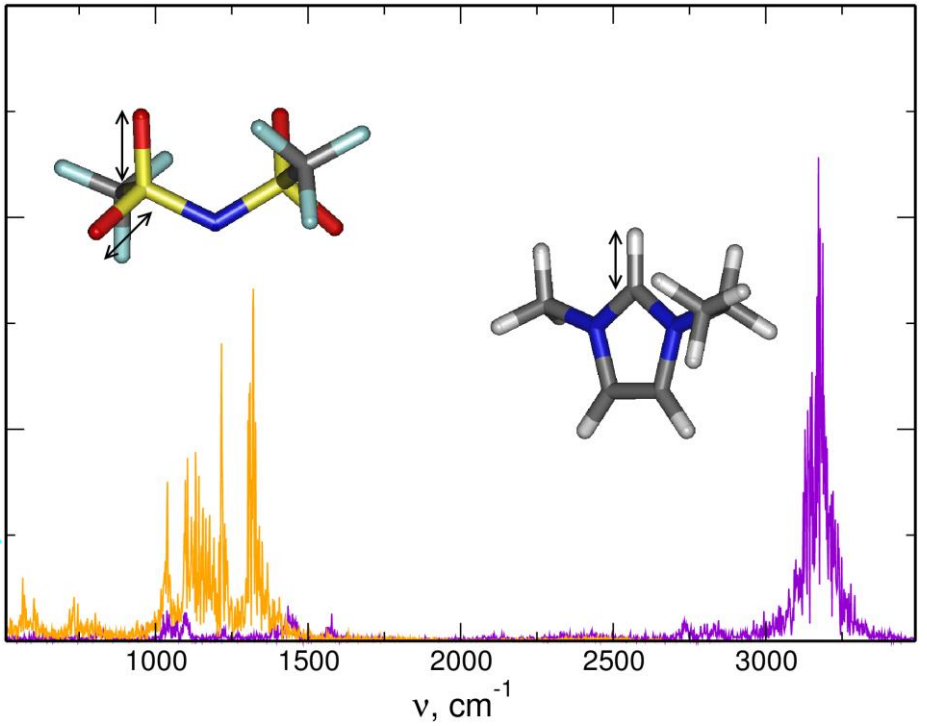


IR spectrum from BOMD

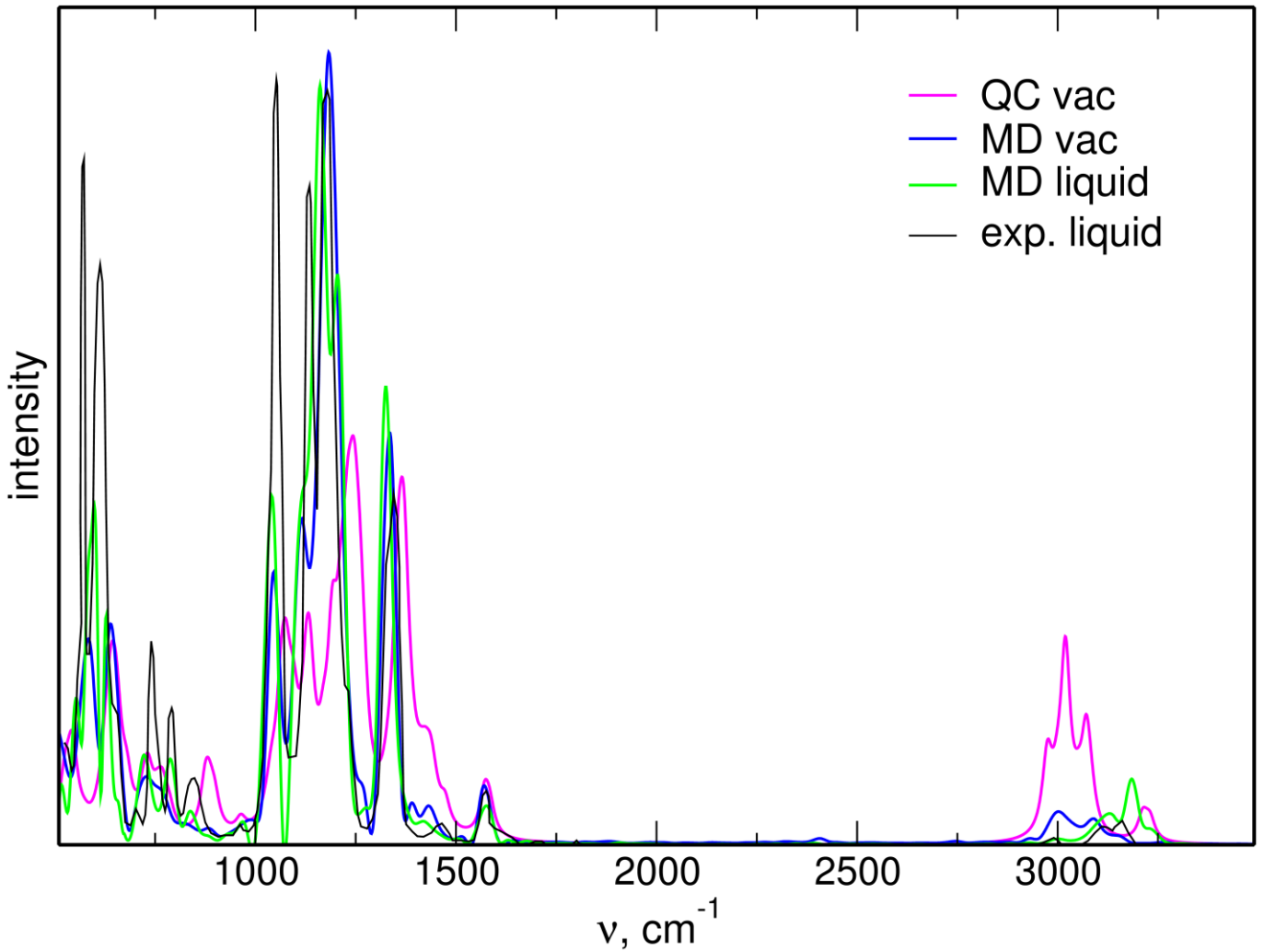


Fourier transform of the bond length

- we can analyze individual vibrations
- C-H stretch at 3165 cm^{-1} is decoupled form other modes
- C-O stretch contributes to several normal modes in the range 1000-1500 cm^{-1}



IR spectrum: gas phase vs. liquid



- BOMD improves agreement with experiment even for single ion pair
- effect of the bulk solvent is necessary to reproduce energies above 3000 cm^{-1}

Summary

- IR spectrum of bulk EMIM-TFSI ionic liquid can be satisfactorily reproduced from ab initio molecular dynamics
- a large part of the improvement seems to be related to sampling of different cation-anion configurations
- effect of the bulk solvent is pronounced mainly for IR bands above 3000 cm^{-1}
- further analysis of this spectral region will provide information on hydrogen bonds

A. Eilmes, P. Kubisiak, M. Brela: "Explicit Solvent Modeling of IR and UV−Vis Spectra of 1-Ethyl-3-methylimidazolium Bis(trifluoromethylsulfonyl)imide Ionic Liquid", J. Phys. Chem. B 2016, 120, 11026-11034.

Ackowledgments

Co-workers:

Dr Piotr Kubisiak

Dr Mateusz Brela

PL-Grid infrastructure (Prometheus) was used in calculations

INNOWACYJNA GOSPODARKA
NARODOWA STRATEGIA SPÓJNOŚCI

UNIA EUROPEJSKA
EUROPEJSKI FUNDUSZ ROZWOJU REGIONALNEGO