Probing intermolecular interactions in water/ionic liquid mixtures by THz spectroscopy

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Outline

Introduction / Motivation

- Ionic Liquids – molten salts at room temperature
- Flow Injection System – to generate spectra
- Data Analysis Techniques
  - MCR
  - 2DCoS

Results

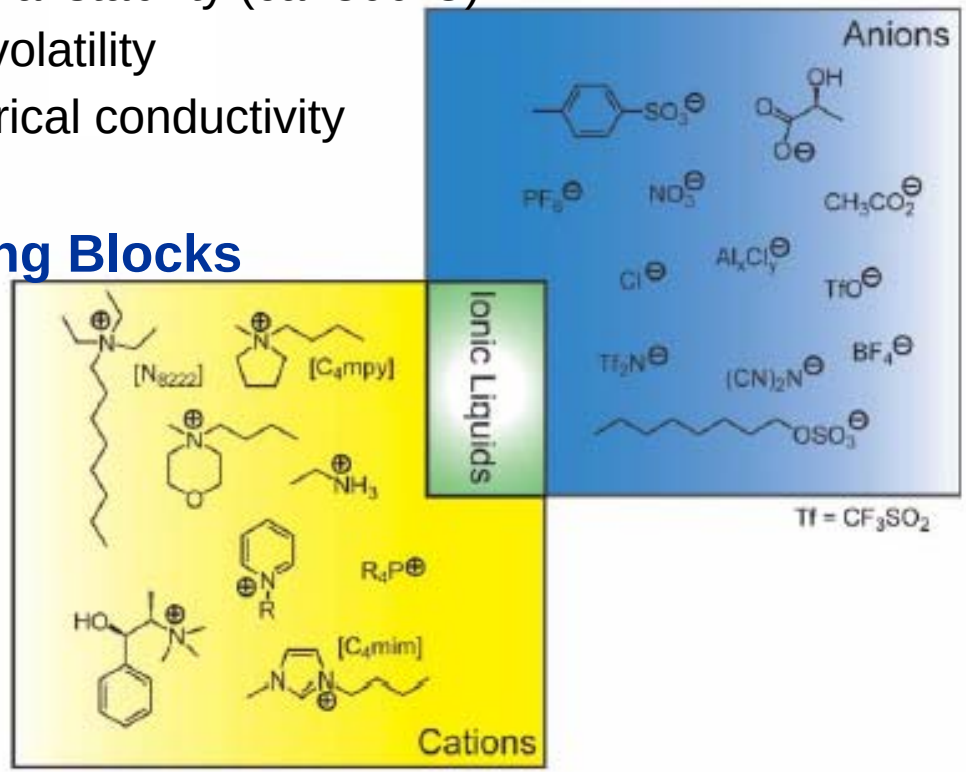
- MIR Studies
- THz (FIR) Studies

Ionic Liquids

Properties of Ionic Liquids

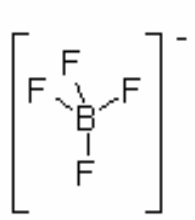
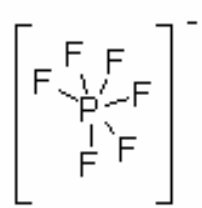
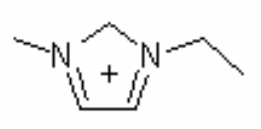
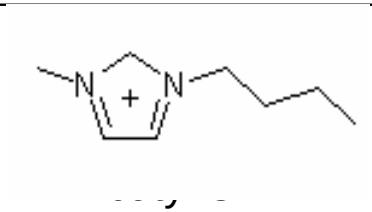
- Salts containing organic cations and inorg. or organic anions
- Molten salts at or slightly above room temperature (max. 100°C)
- Good solvation power
- Good thermal stability (ca. 300ºC)
- Negligible volatility
- Good electrical conductivity

Typical Building Blocks



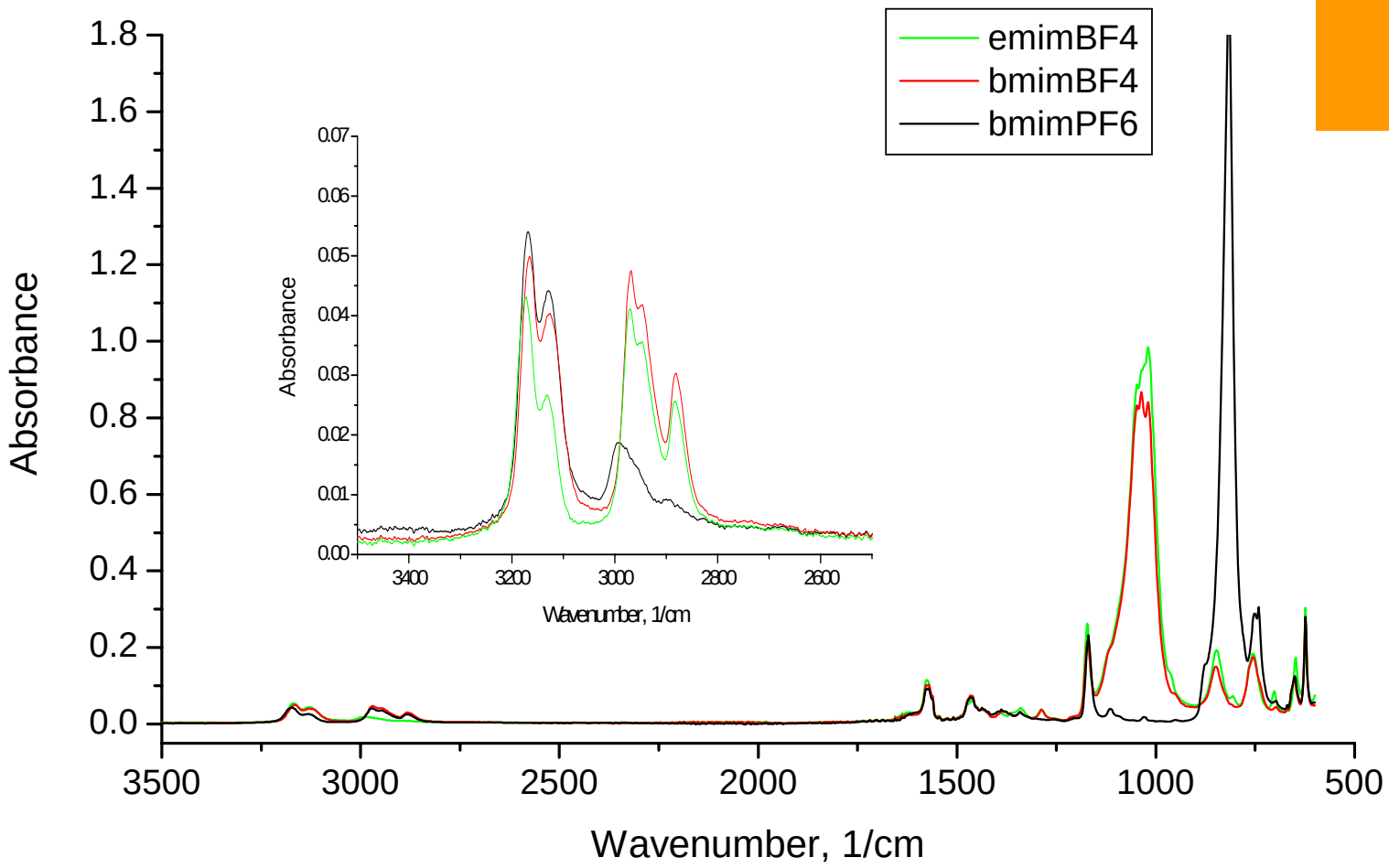
Ionic Liquids Under Study

Selected Ionic Liquids

	 tetrafluoroborate	 hexafluorophosphate
 1-ethyl-3-methylimidazolium *"emim$^+$"*	Liquid at room temperature	Solid at room temperature
 methylimidazolium *"bmim$^+$"*	Liquid at room temperature	Liquid at room temperature

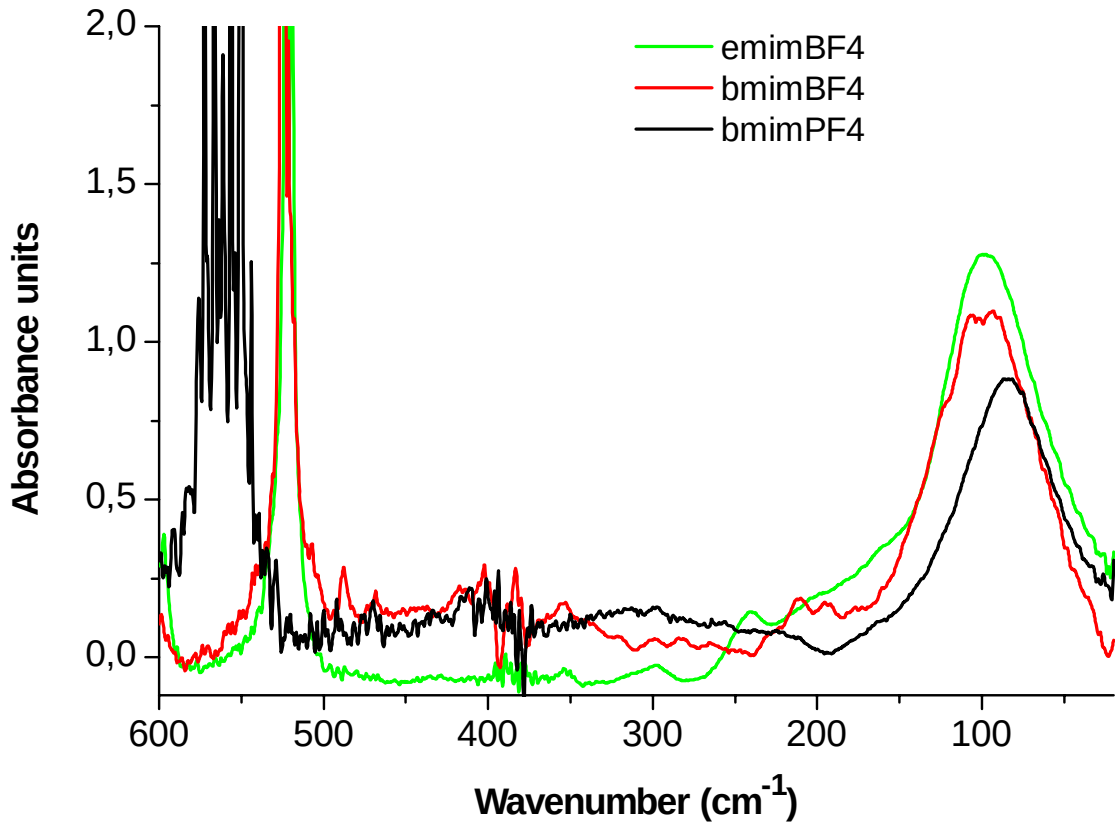
MIR Spectra of Ionic Liquids Under Study

- **ATR (1 bounce) spectra of dry Ionic Liquids**



FIR Spectra of Ionic Liquids Under Study

- **25 µm transmission cell (PE windows)**



Water - Ionic Liquid Interaction

Motivation

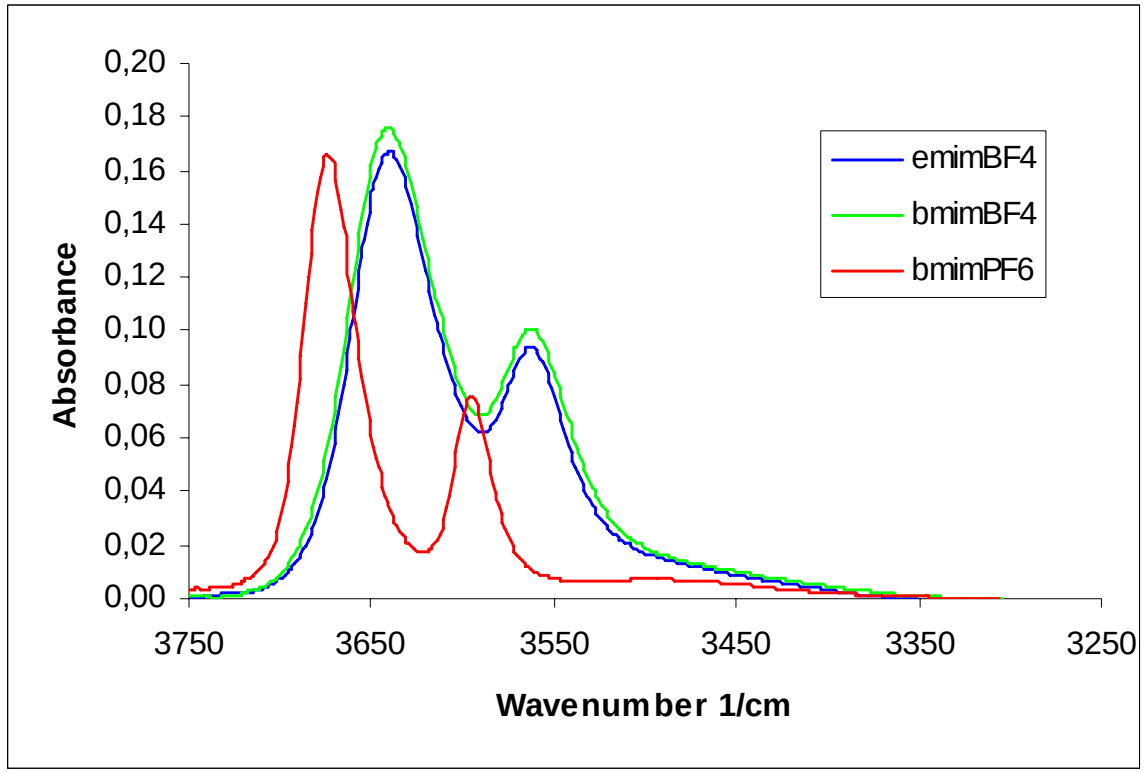
- Traces of co-solvents change properties of ionic liquids
- Get fundamental understanding on formation of small water clusters
- Fun

Results

- MIR Studies
- THz (FIR) Studies

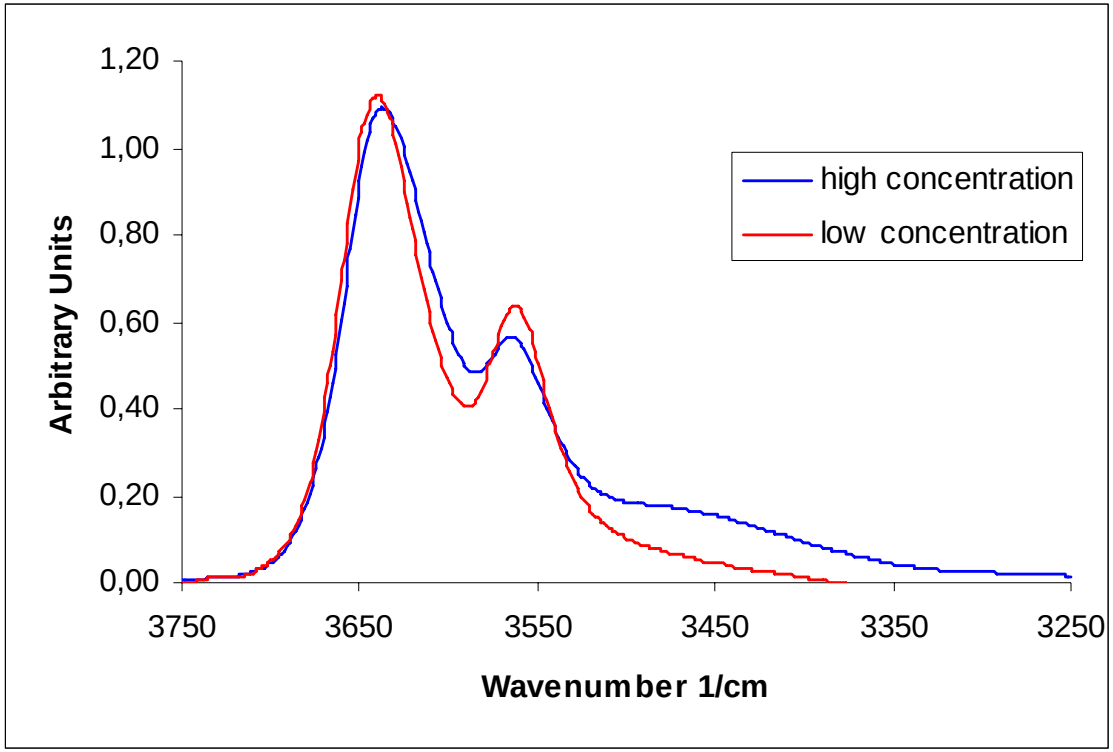
Water - Ionic Liquid Interaction

- **Type of anion influence position of OH-stretch vibrations**

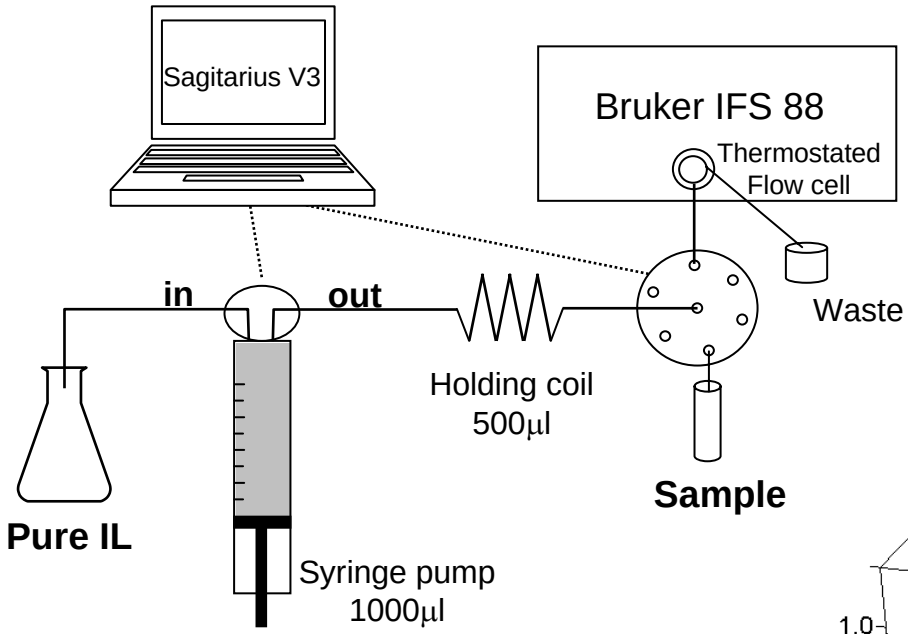


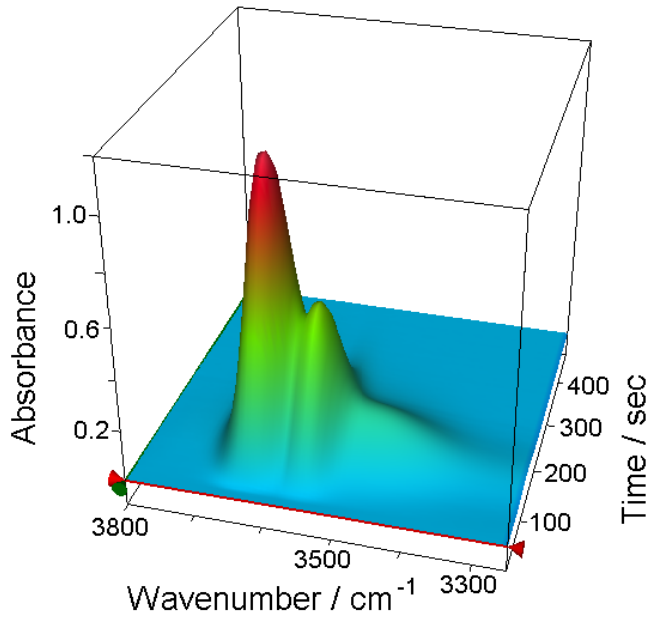
Water - Ionic Liquid Interaction

- **Change in ν-OH-stretch region as function of water concentration**



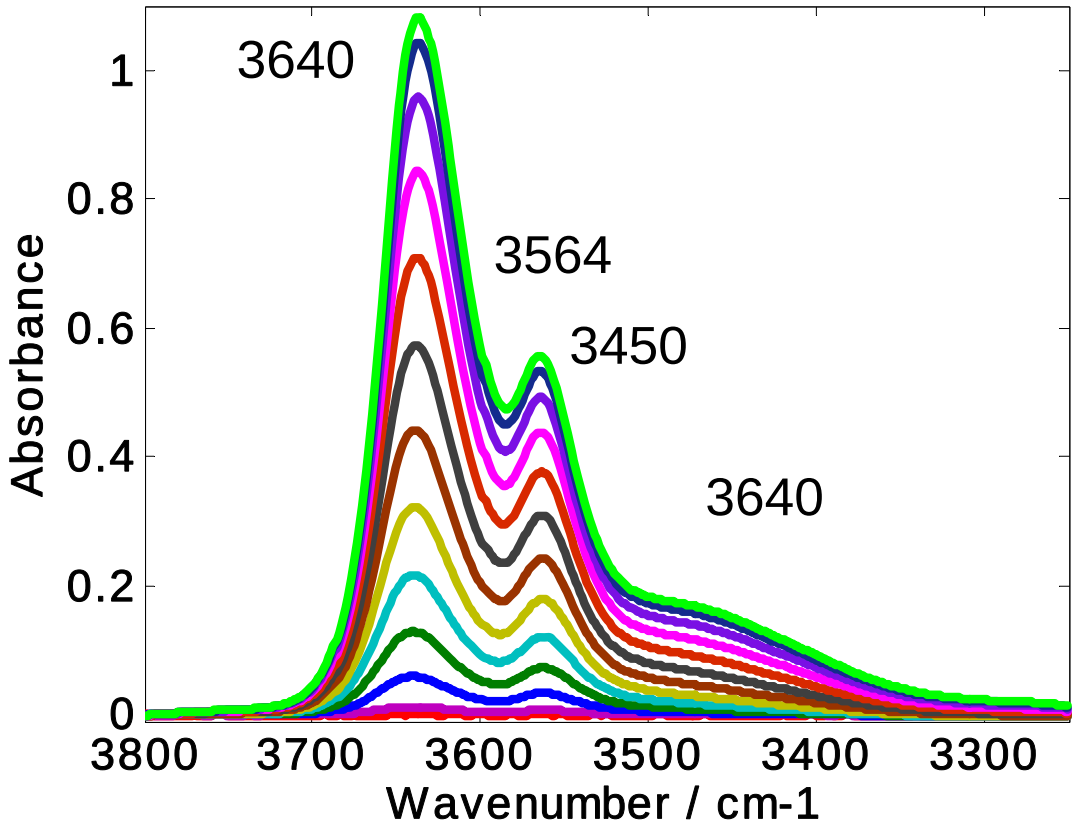
Water - Ionic Liquid Interaction





H_2O in $emim^+[BF_4]^-$ and $bmim^+[BF_4]^-$

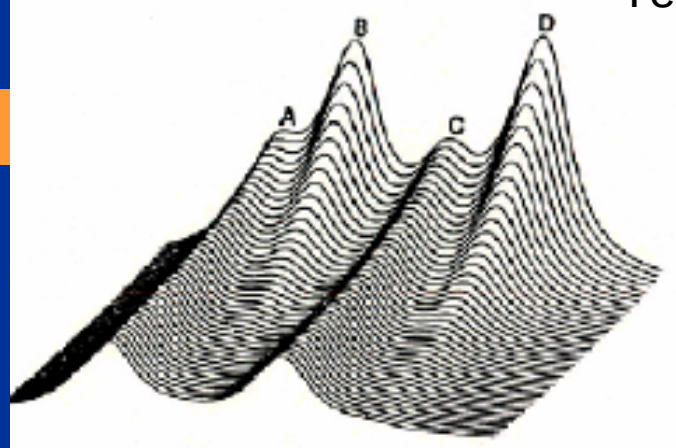
- Set of spectra covering 0-5% m/m of H_2O in $[BF_4]^-$ based ionic liquids



2DCoS - Concept

Looking for correlation in the experimental output *D*

Time resolved spectra



Spectral Variable

Time/pressure/
Temperature,..

Correlation analysis

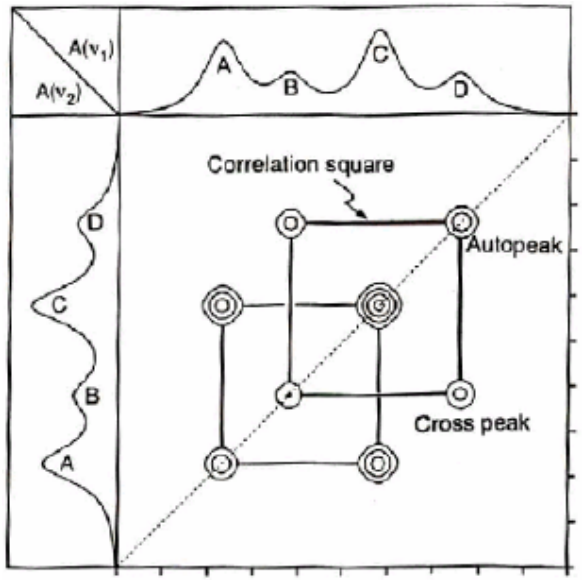
$$\Theta(\nu_1,\nu_2)+i\Psi(\nu_1,\nu_2)$$

$$=\frac{1}{\pi T}\int_0^\infty \bar{Y}_1(\omega)+i\bar{Y}_2(\omega)$$

2DCoS - Output

Correlation Maps

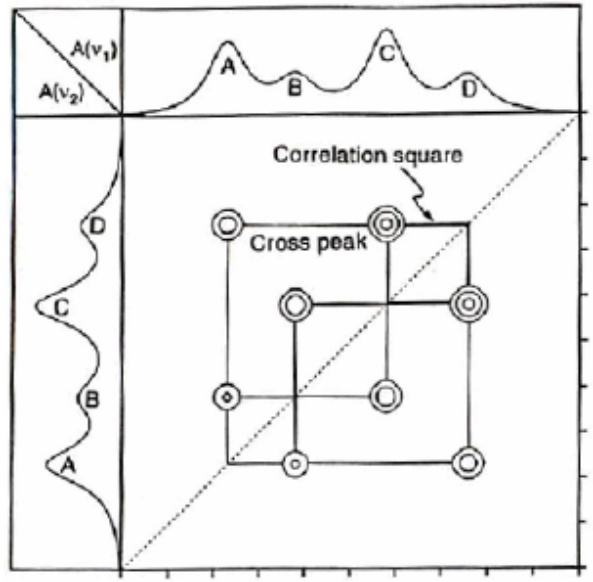
Synchronous map



Spectral variable, ν_2

Spectral variable, ν_1

Asynchronous map

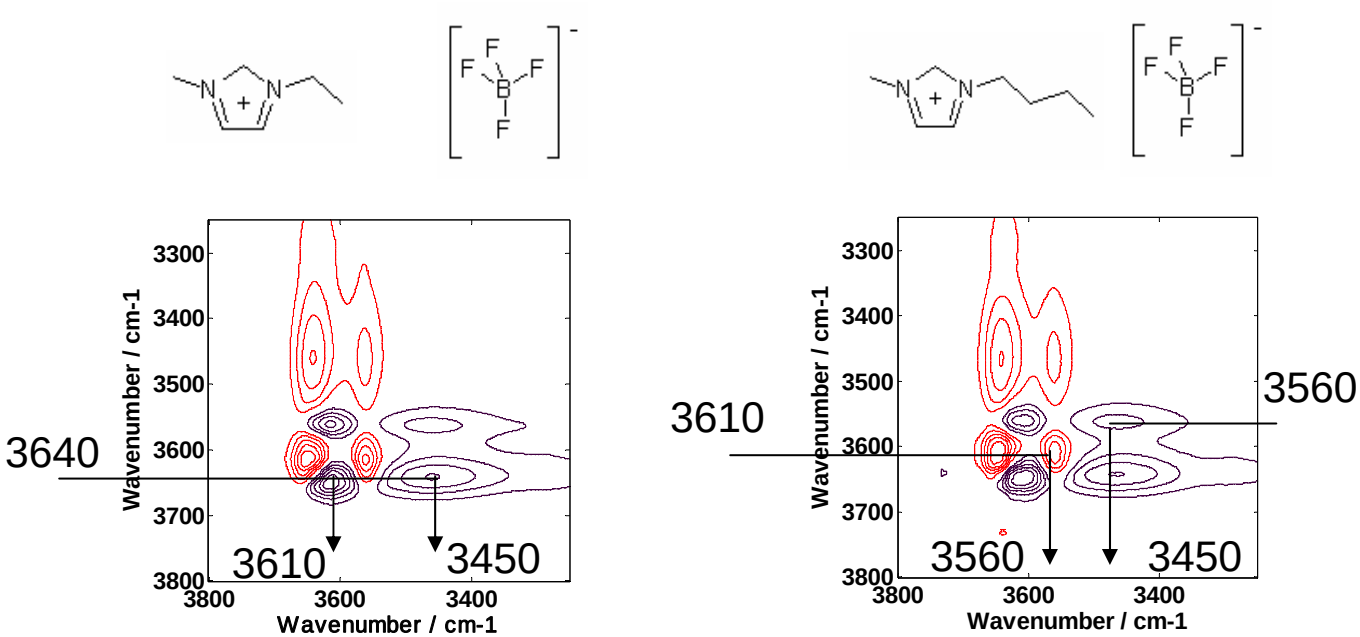


Spectral variable, ν_2

Spectral variable, ν_1

I. Noda Lecture 2DCoS-3, 2005

Asynchronous Correlation Map : H_2O in $emim^+[BF_4]^-$ and $bmim^+[BF_4]^-$



- Peaks in asynchronous correlation map:

3640 – 3610 cm^{-1}; 3640 - 3450 cm^{-1}; 3610 - 3560 cm^{-1} and 3560 - 3450 cm^{-1}

- No correlation between 3610 - 3450 cm^{-1} and 3640 - 3560 cm^{-1}

=> presence of 2 different species

1st Specie: Bands at 3640 - 3560 cm^{-1}

2nd Species: Bands at 3610 and 3450 cm^{-1}

Multivariate Curve Resolution (MCR-ALS)

Concept: Modeling of experimental data matrix *D*

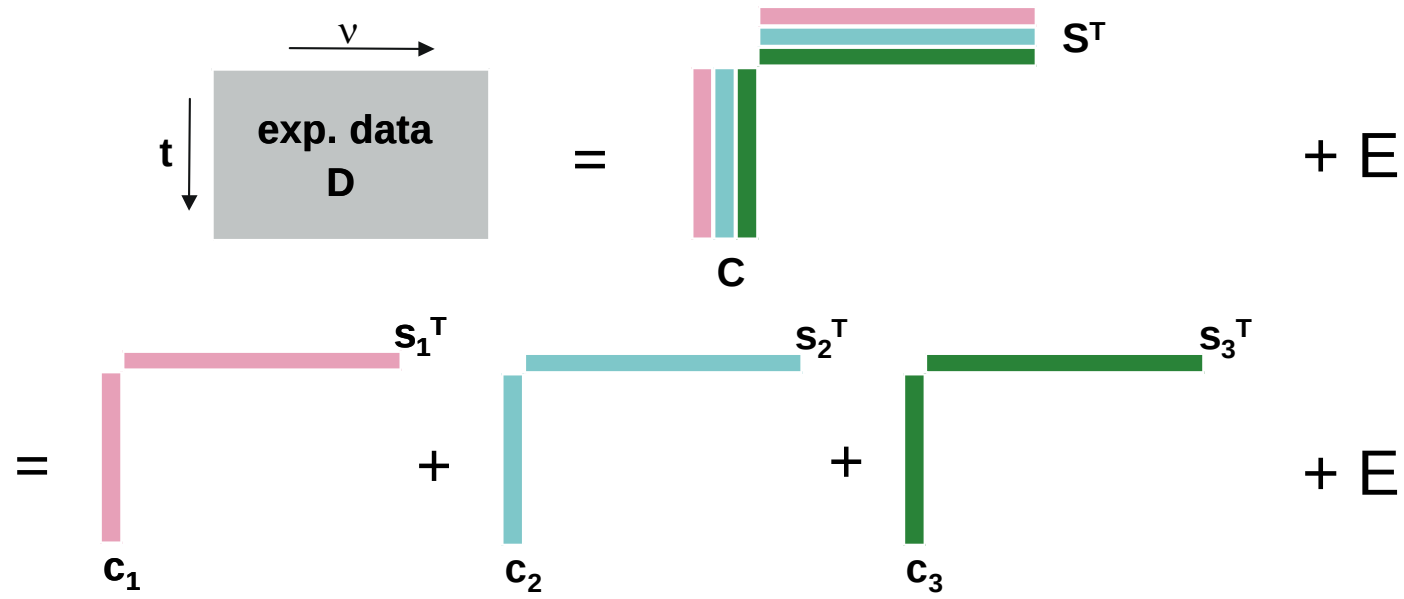
- Multi-component systems can be often be described with a simple model consisting of the composition-weighted sum of signals of their pure components
- Only condition: linear structure of data set

$$\boldsymbol{D} = C\boldsymbol{S}^{\mathrm{T}} + \boldsymbol{E}$$

D*(r × c)* is the original data matrix
C*(r × n)* and ***S***$^{\mathrm{T}}$*(n×c) contain pure response profiles related to the data variation in the* row *(r)* and column *(c) direction of* ***D****(r × c)*
E*(r × c)* is the error matrix

Multivariate Curve Resolution:

Graphical Representation



c_i...concentration profiles with time s_i...spectra of pure substances

2DCoS vs. MCR-ALS

Two complementary approaches which help to gain understanding of dynamic processes

2DCoS: Looking for correlation in the data set

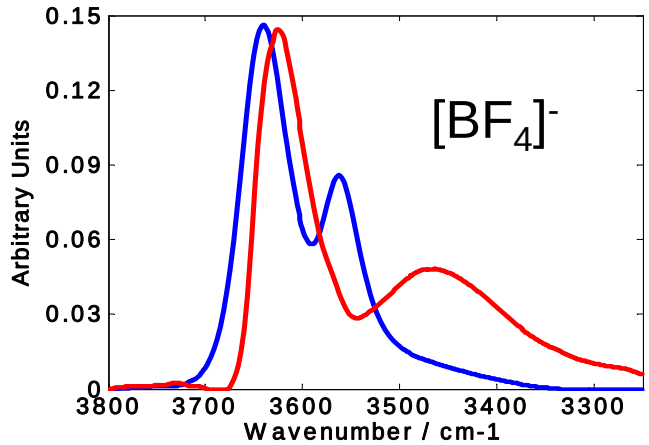
- **Output: synchronous and asynchronous correlation maps**
- **requires some art to read the maps**

MCR-ALS: Modeling of the data set

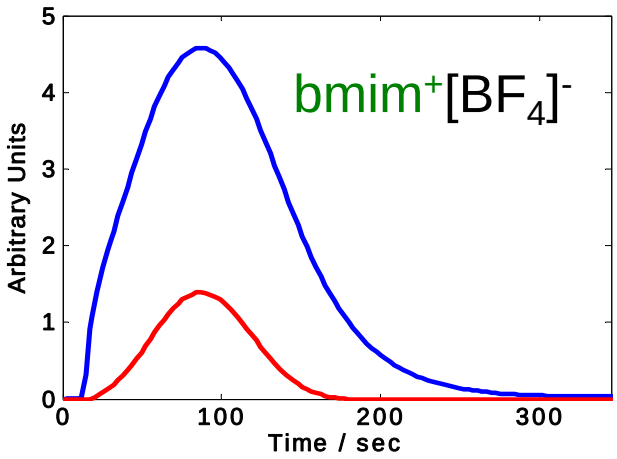
- **Output: spectra and concentration profiles of compounds**
- **requires definition of compounds**
- **rather objective criteria whether modeling was successful**

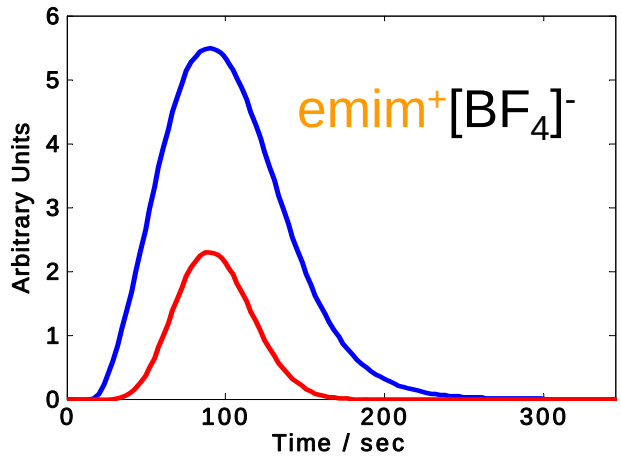
Results of MCR-ALS

Spectra of encountered compounds



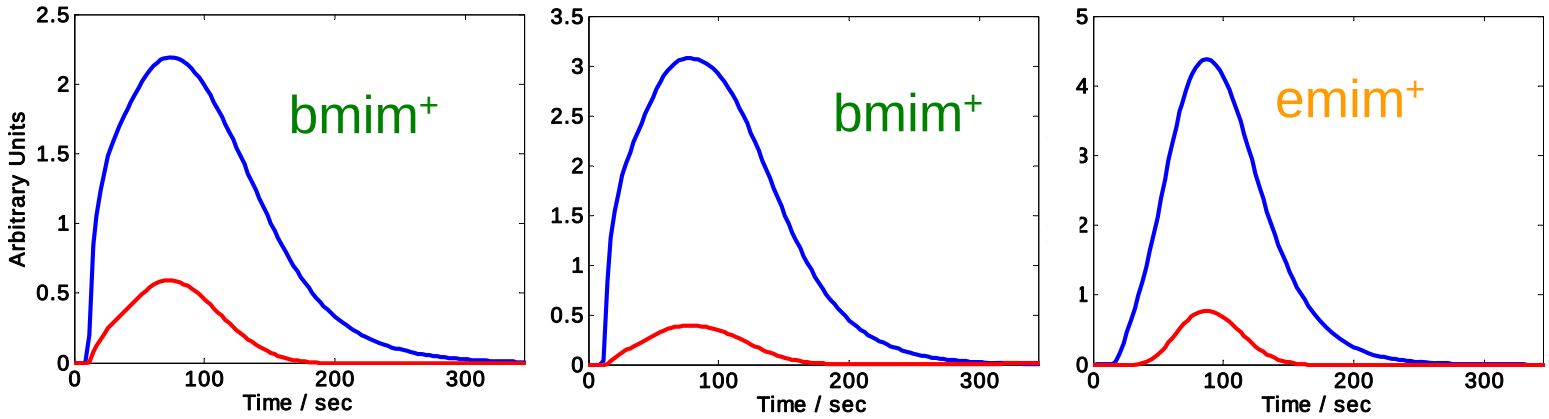
Concentration of encountered compounds





Influence of the Cation

- **Cation determines the dispersion profile of the FIA peaks**

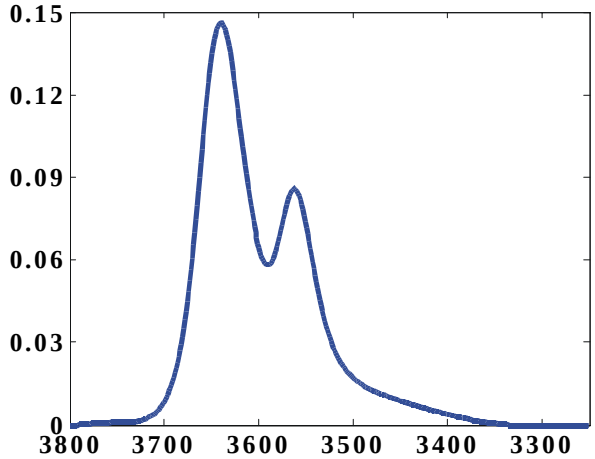


Theory of FIA explains the form of the FIA peaks as a result of convection (dominating) and diffusion
Upon increasing viscosity, radial diffusion is less pronounced
=> higher dispersion

First Water Species

Water species as resolved by MCR - ALS

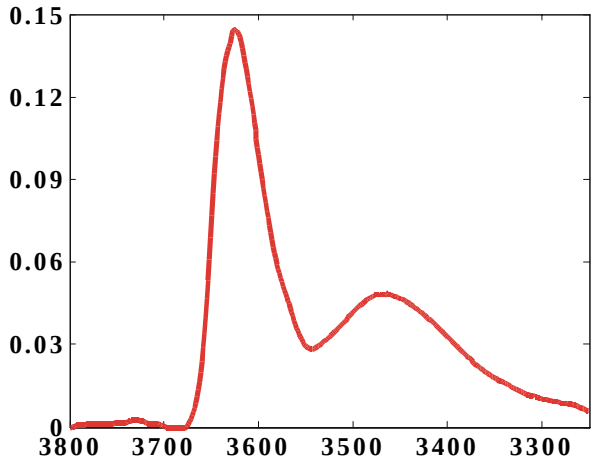
Only type present in PF_6^- based I.F. as well as first water species in BF_4^- containing I.L. is monomeric water:

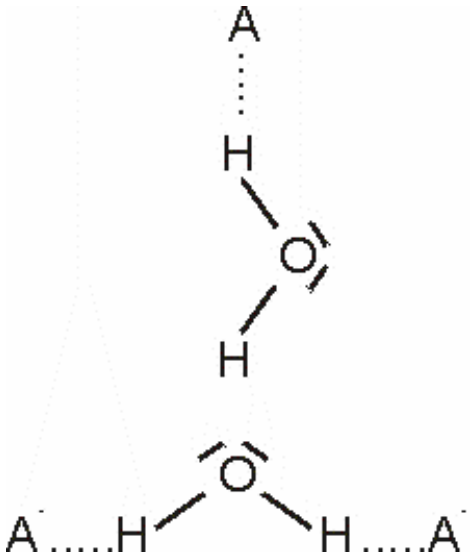


Pastor et al. *J Phys Chem. B* 110 (2006) 10896-10902

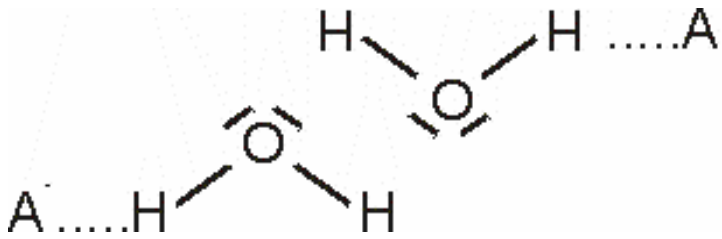
Second Water Spezie

- Bands at 3610 cm^{-1} and 3450 cm^{-1}
- Literatur: (Koeddermann et al. Absorptionen in CCl_4):
  Water dimer at 3553 cm^{-1}
  Cyclic water trimer at 3409 cm^{-1}



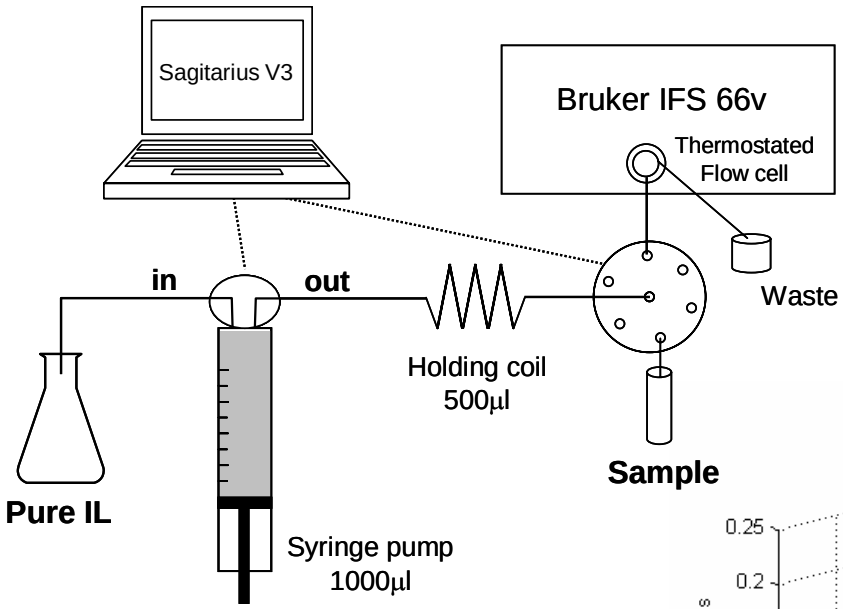


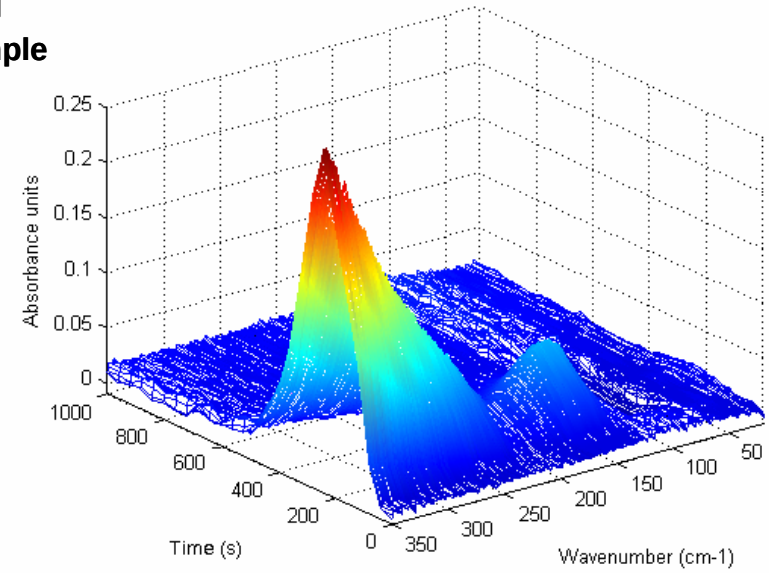
Our data suggest the following structure:



Pastor et al. *J Phys Chem. B* 110 (2006) 10896

Water - Ionic Liquid Interaction in the FIR

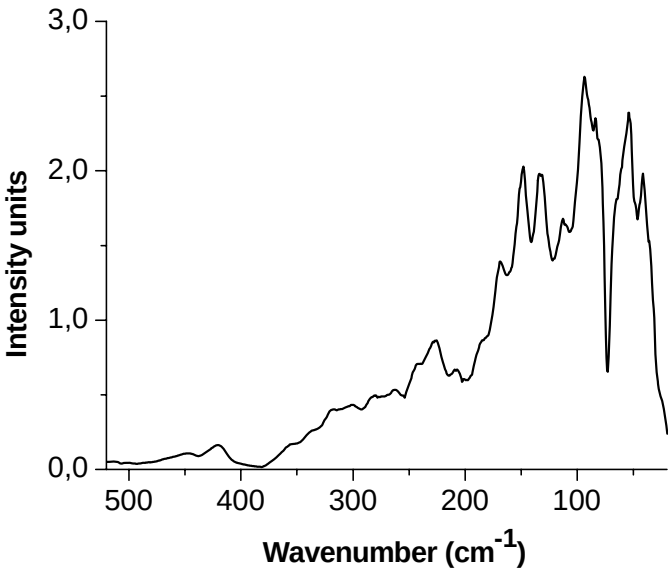


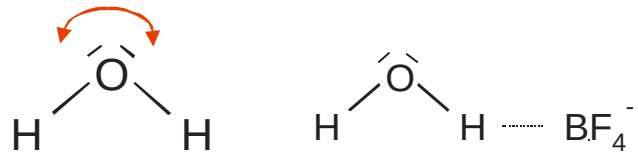


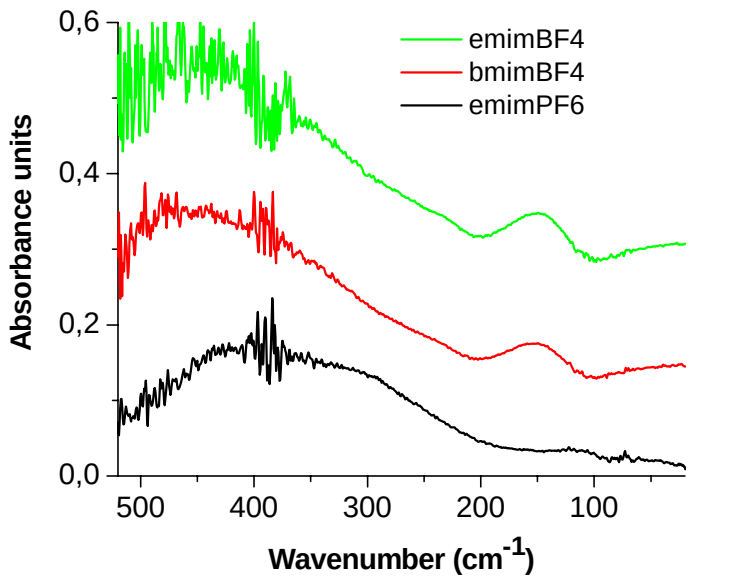
FIR (THz) Spectra Recorded at Bessy

- **FIR Spectra of 2% (w/w) of H2O in Ionic Liquids**

- Single Beam Spectrum



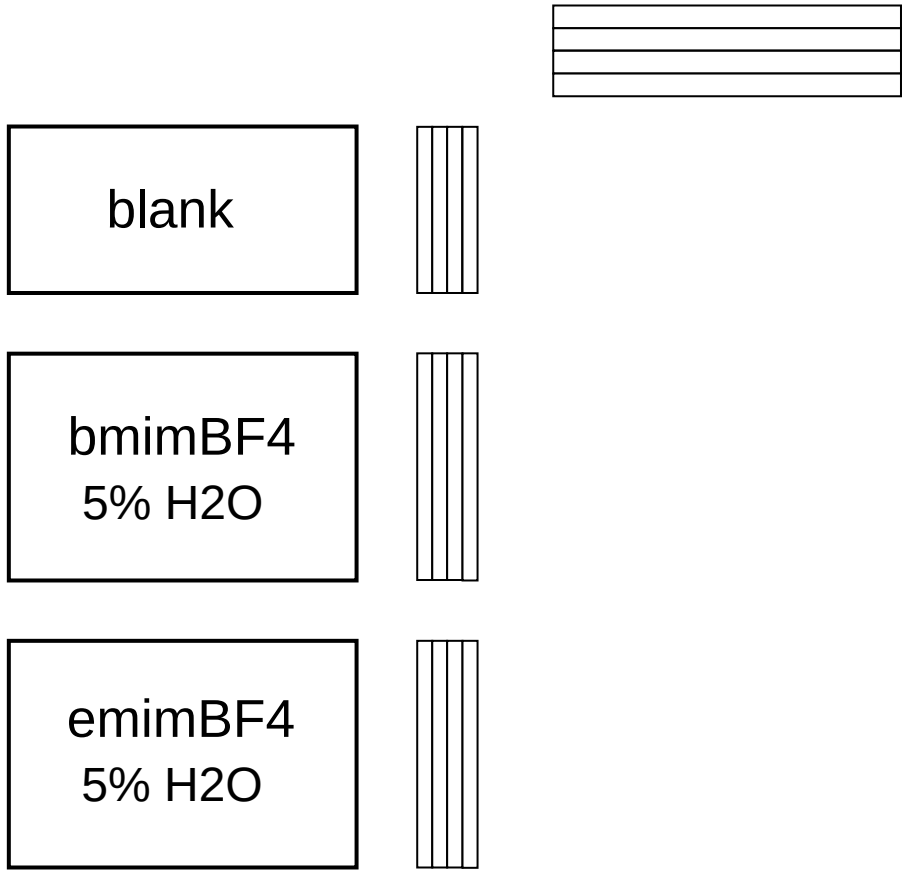




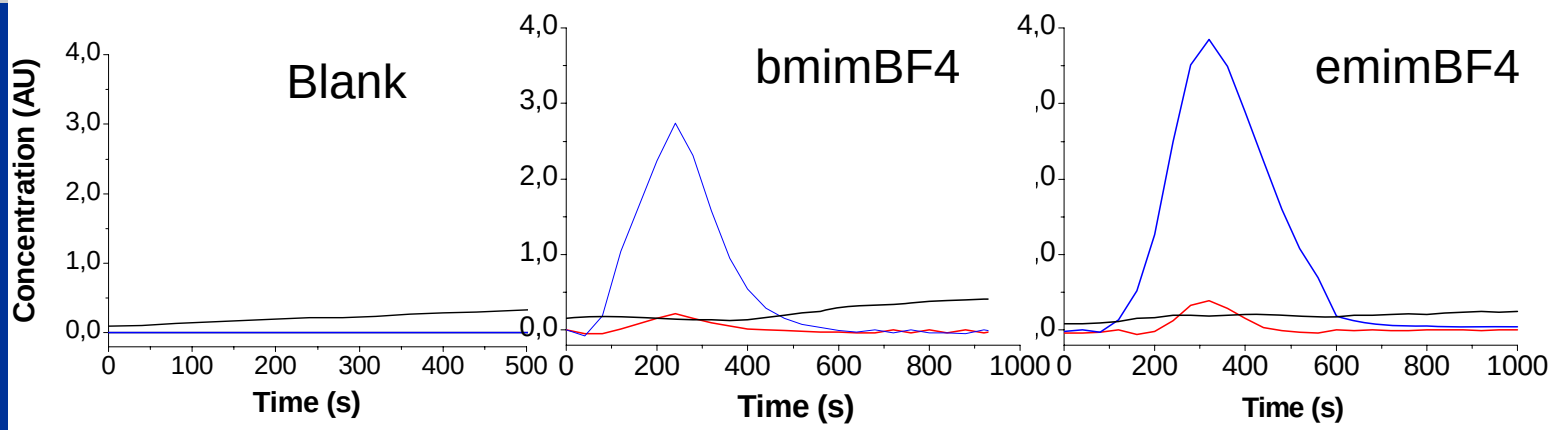
Dominguez et al. *J. Phys. Chem. B* 11 (2007) 4446-4452

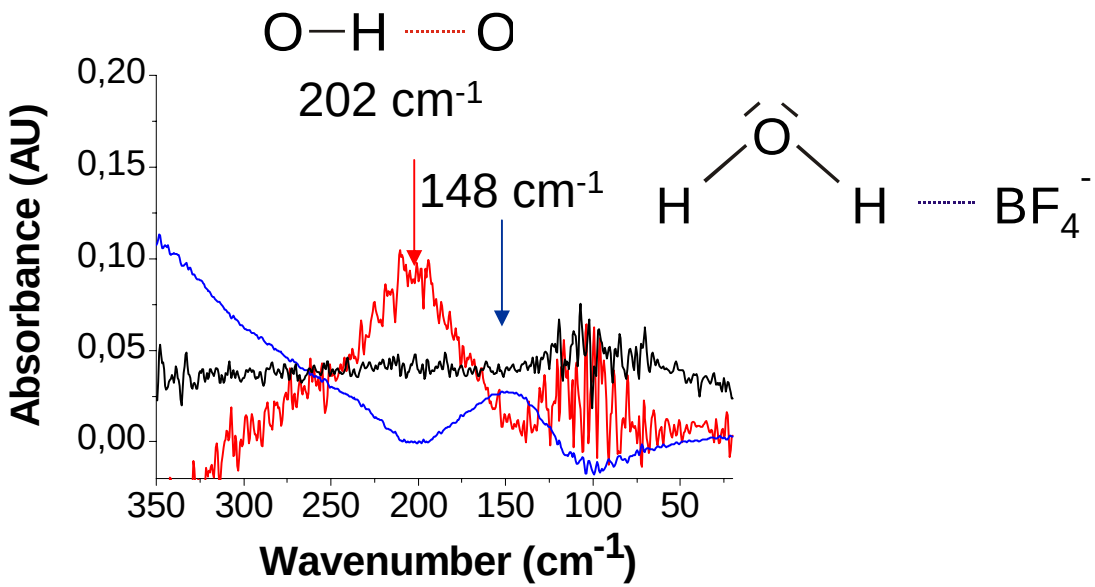
Matrix Augmentation in MCR Analysis

Simultaneous Analysis of Several Experiments



Results of Matrix Augmentation





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Conclusions

- **Spectra of Ionic Liquids from the MIR-FIR spectral region**
- **Flow Injection Analysis very suitable for generate of binary mixtures of ionic liquids and water**
- **In emimBF_4 water dimers can be found and a cyclic structure can be proposed**
- **In bmimPF6 only water monomers could be detected**
- **Successful use of 2DCoS and MCR-ALS as complementary techniques to resolve overlapping features and components**

Acknowledgements

Maria Jose Ayora Canada

Ana Dominguez Vidal

Mercedes Lopez Pastor

Nina Kaun - Ulli Schade