Journal Club

M. Besnard and cowokers, "Interaction of Water Highly Diluted in 1-Alkyl-3-methyl Imidazolium Ionic Liquids with the PF_6^- and BF_4^- Anions ",
J. Phys. Chem. A **113**, 2873 (2009)

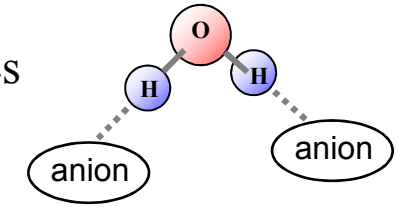
22th Aug. 2015 Yoonnam Jeon

We have investigated water highly diluted in 1-alkyl-3-methyl imidazolium ionic liquids (ILs) with hexafluorophosphate $\{PF_6^-\}$ and tetrafluoroborate $\{BF_4^-\}$ anions using vibrational spectroscopic measurements in the ν_{OH} spectral domain of water (3600−3800 cm^{-1}) and DFT calculations. The measured profiles exhibit two well-defined bands at coinciding vibrational transitions assigned with the ν_1 symmetric and ν_3 antisymmetric OH stretching modes of monodispersed water. The local organization and the vibrational spectra of water diluted in ILs have been assessed by DFT calculations (using the B3LYP functional and 6-31+G** basis set). We show that the predicted structures of water interacting (minimally) with two anions in nearly "symmetric" structures of type (A···H−O−H···A) lead to spectral features consistent with the previous spectroscopic observations as well as with those reported here. We emphasize the role of the non additive interaction forces (especially the 3-bodies electrostatic interactions) in the structural organization taking place between the cation−anion couples and for determining preferentially (A···H−O−H···A) associations of water with the anions as well as their consequences on the vibrational spectra of water. We show that the doubly hydrogen-bonded character of water in such associations leads to well-defined spectral features, which are the shifts of the ν_1 and ν_3 stretching modes of water, the separation $\Delta\nu_{13}$ between them (about 80 cm^{-1}), and the intensity ratio estimates $R = I\nu_3/I\nu_1$ (IR absorption and Raman). Finally, we evoke the fact that the H-bond interactions of water diluted in these ILs involve a more noticeable electrostatic character than for H-bond interactions of water in usual molecular solvents. In this context, we emphasize that the appearance of the Raman band of the ν_3 mode of water originates from a significant polarization of water due to the local electrostatic fields induced by surrounding ions.

Soft-Matter Optical Spectroscopy

Introduction

- Impurities : can drastically alter the IL's properties
  - density
  - viscosity
  - polarity
  - conductivity
- Presence of water : nanoscale structural organization of ILs

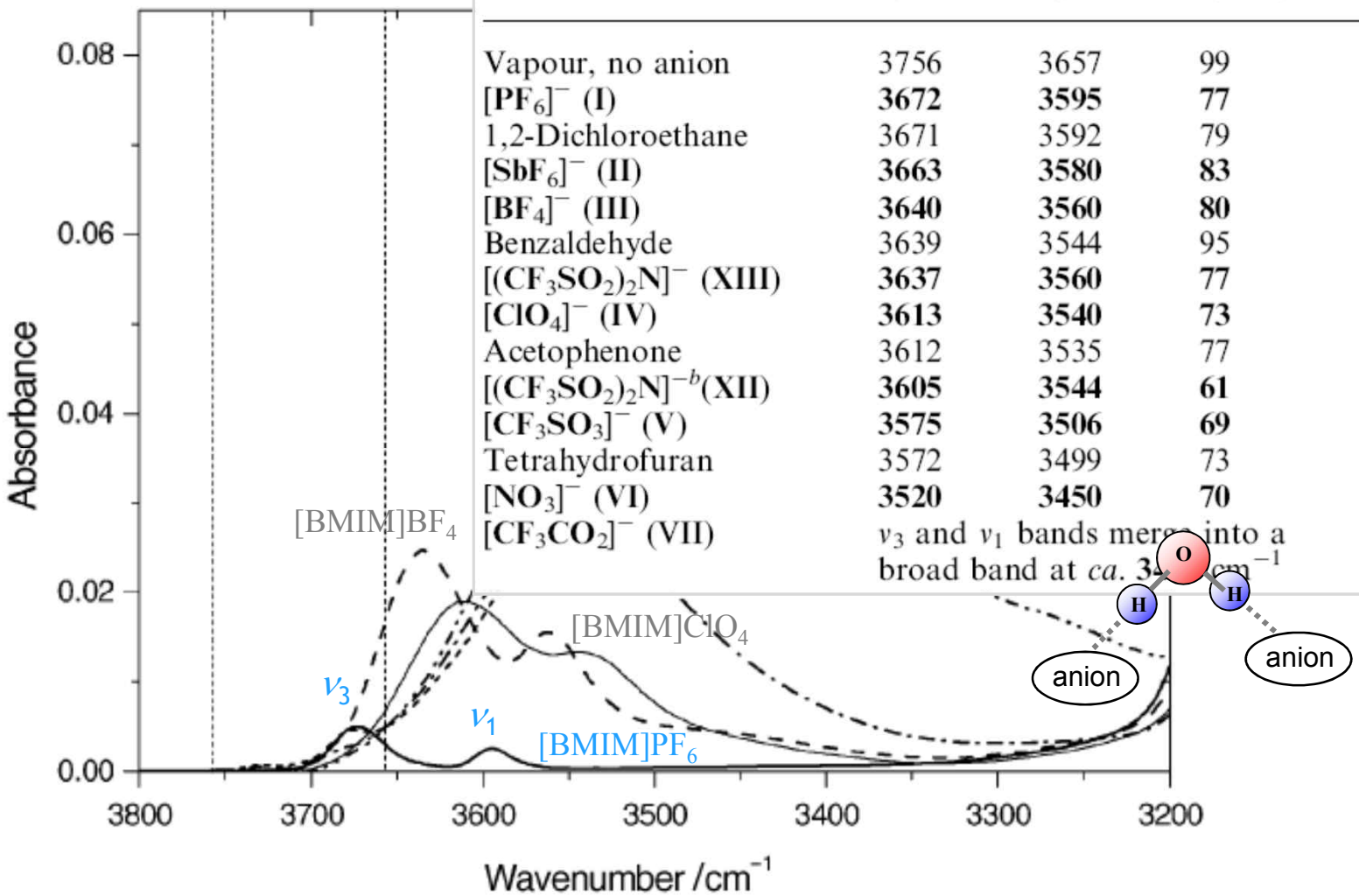


- Low concentration of water in ILs
  - monomeric form 1:2 H-bonded type complexes with two separate anions (Welton and coworkers, *Phys. Chem. Chem. Phys.* **3**, 5192, (2001))
- Solubility of water : related to the water-anion interaction strength

Aim Investigating the nature of interactions of water highly diluted in $[C_nMIM]X$ ($X=BF_4$ or PF_6)

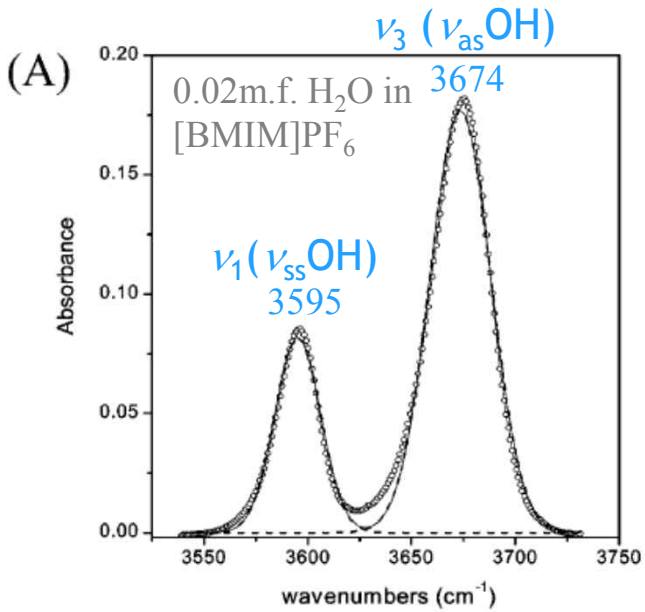
Introduction - Monomeric water peaks in IR spectra

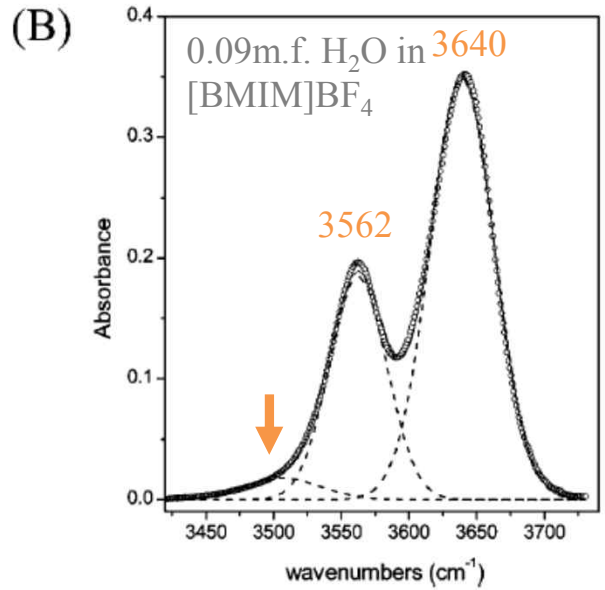
Anion	ν_3	ν_1	$\nu_3 - \nu_1$	ν_2
Vapour, no anion	3756	3657	99	1595
$[PF_6]^-$ (I)	**3672**	**3595**	**77**	**1610**
1,2-Dichloroethane	3671	3592	79	
$[SbF_6]^-$ (II)	**3663**	**3580**	**83**	
$[BF_4]^-$ (III)	**3640**	**3560**	**80**	**1625**
Benzaldehyde	3639	3544	95	
$[(CF_3SO_2)_2N]^-$ (XIII)	**3637**	**3560**	**77**	
$[ClO_4]^-$ (IV)	**3613**	**3540**	**73**	
Acetophenone	3612	3535	77	
$[(CF_3SO_2)_2N]^{-b}$(XII)	**3605**	**3544**	**61**	**1631**
$[CF_3SO_3]^-$ (V)	**3575**	**3506**	**69**	**1630**
Tetrahydrofuran	3572	3499	73	
$[NO_3]^-$ (VI)	**3520**	**3450**	**70**	**1640**
$[CF_3CO_2]^-$ (VII)	ν_3 and ν_1 bands merge into a broad band at *ca.* 3[illegible] cm^{-1}			



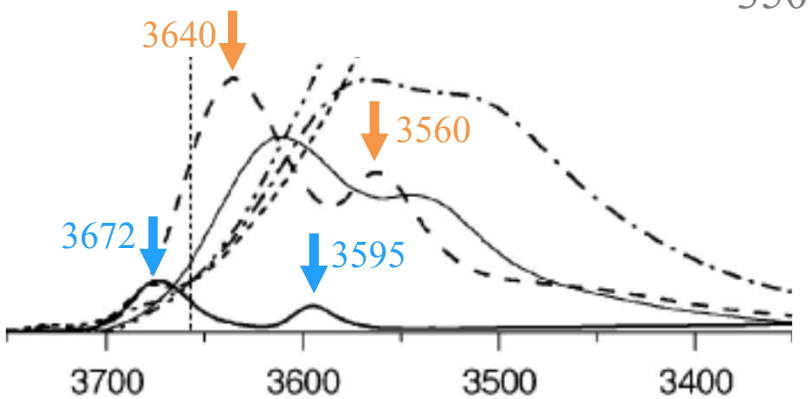
Welton and coworkers, *Phys. Chem. Chem. Phys.* **3**, 5192, (2001)

Results - IR absorption spectra





~3500 cm^{-1} : small water aggregate



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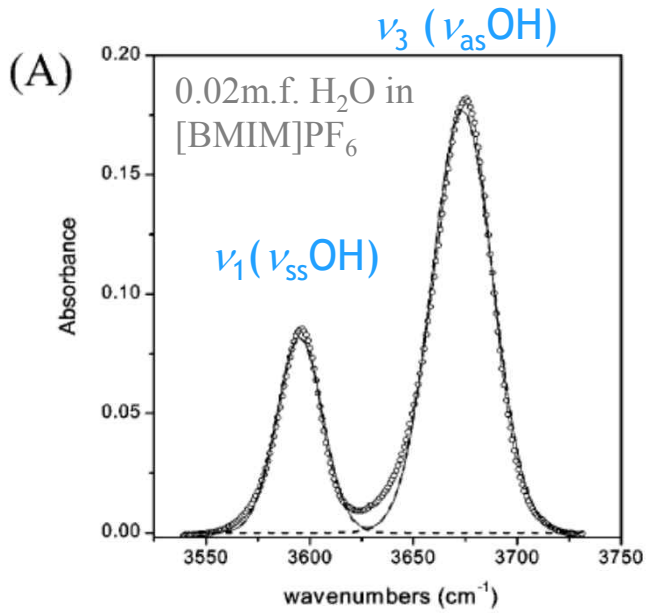
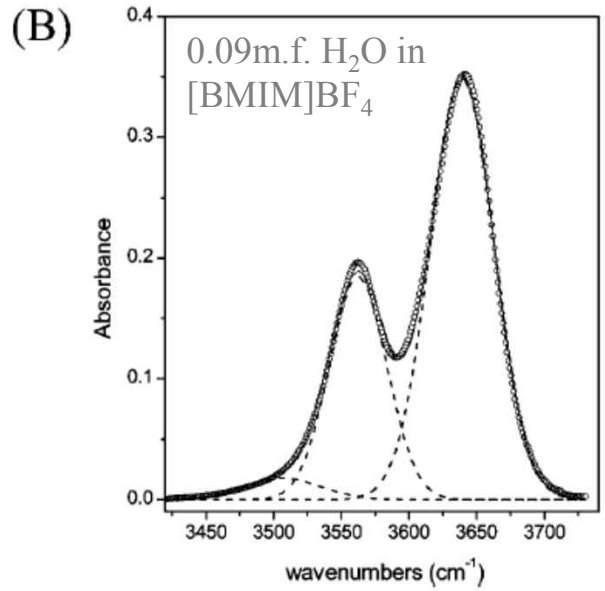
Results - IR absorption spectra



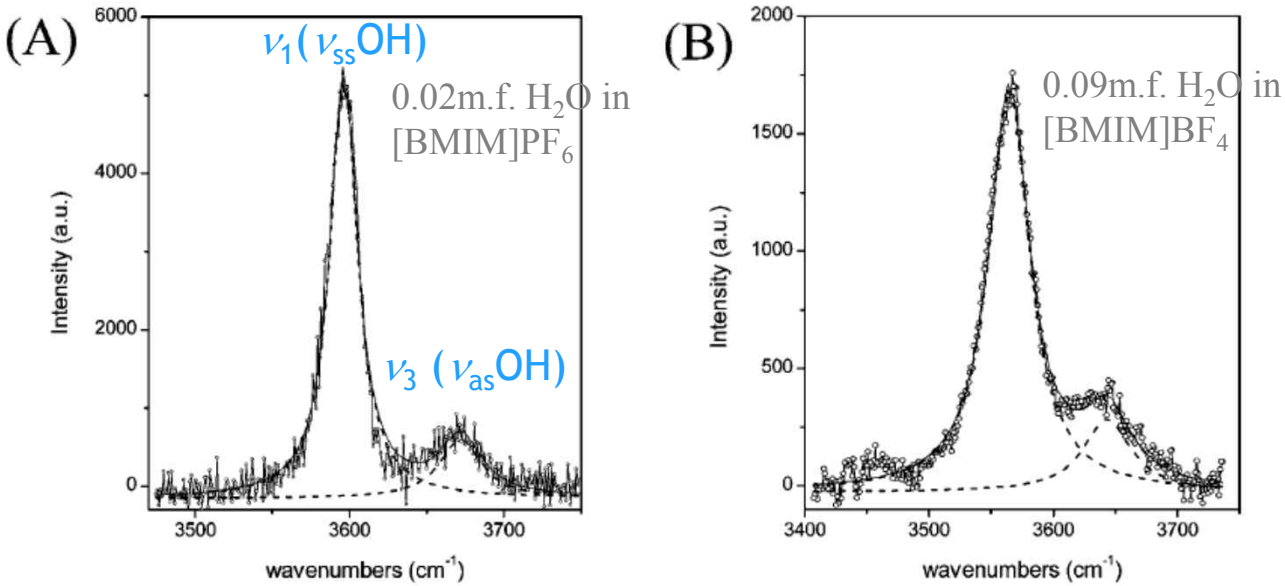


		ν_1 mode of water		ν_3 mode of water	
		IR	Raman	IR	Raman
$B_{Mim}-PF_6^-$	band center (cm^{-1})	3595	3600	3674	3677
	fwhh (cm^{-1})	19	20	28	30
	$R = I\nu3/I\nu1$	3.4	0.15		
$B_{Mim}-BF_4^-$	band center (cm^{-1})	3562	3565	3640	3643
	fwhh (cm^{-1})	47	39	46	41
	$R = I\nu3/I\nu1$	1.9	0.18		

fwhh (ν_3) > fwhh (ν_1) & fwhh (PF_6) × 2 ~ fwhh (BF_4)

R = I (ν_3) / I (ν_1) = 3.4 and 1.9

Results - Raman spectra



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fwhh (ν_3) > fwhh (ν_1) & fwhh (PF_6) × 2 ~ fwhh (BF_4)

R = I (ν_3) / I (ν_1) ~ 0.16

Discussion - IR and Raman spectra

IR & Raman profiles : depend on the H_2O…IL interaction

Nanoscaled structural heterogeneities : associated with the width of peaks

		ν_1 mode of water		ν_3 mode of water	
		IR	Raman	IR	Raman
$B_{Mim}-PF_6^-$	band center (cm^{-1})	3595	3600	3674	3677
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Discussion - IR and Raman spectra

Raman scattering activity : symmetric vibration > antisymmetric vibration
Infrared spectroscopy activity : symmetric vibration < antisymmetric vibration

R = I (ν_3) / I (ν_1) : strong **indicator of the nature**
& strength of the interaction of water with its surroundings

Solvent	Gaseous phase	Hexafluorobenzene	Benzene
R			3
			741, (2003)

Weak H-bonding of H_2O…IL

				le of water	
		IR	Raman	IR	Raman
$B_{Mim}-PF_6^-$	band center (cm^{-1})	3595	3600	3674	3677
	fwhh (cm^{-1})	19	20	28	30
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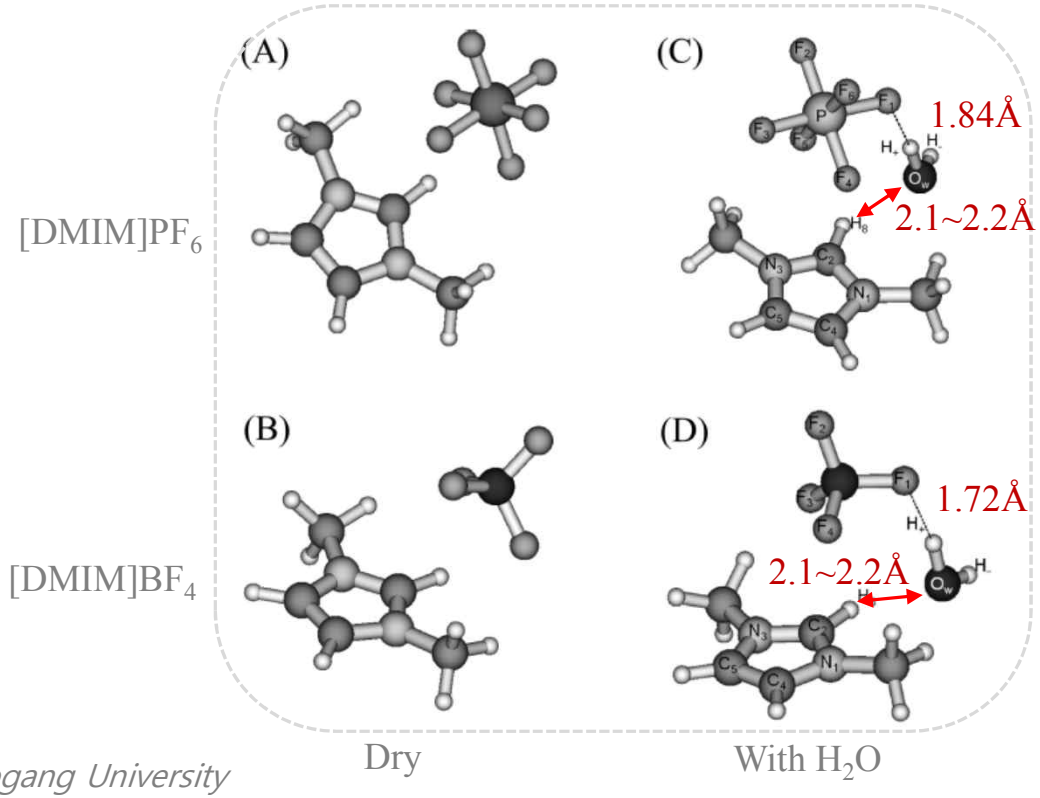
	$R = I\nu3/I\nu1$	1.9	0.18		

IR : R (water in ILs) ~ R (water in benzene)
Raman : R (water in ILs) << R (water in benzene)

Modeling - calculations

- DFT (quantum chemistry) calculations of water + IL (1:1 or 1:2)
  - Single water molecule interacting with one (or two) cation-anion pair(s)
  - Influence of the alkyl chain length on the local structural organization
  - Vibrational spectra (from methyl to octyl)

- Alkyl chain length : impact on the nanosegregated structure of ILs



Calculated energy minimum structure

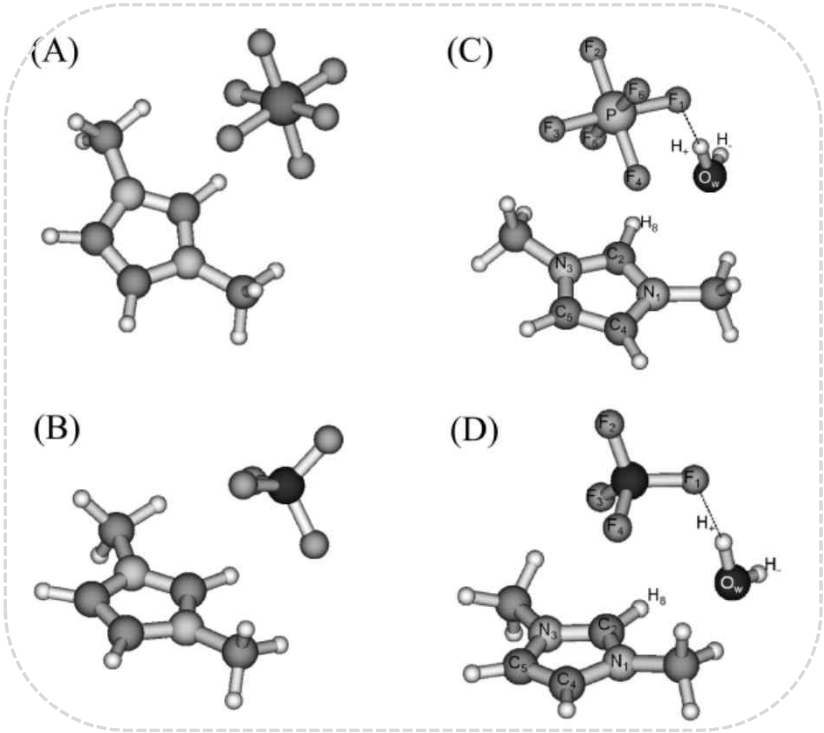
Modeling - Structure & Interaction energy for single pair

	ν_{calc} (cm^{-1})	I_{IR} (km/mol)	I_{IR}/I'_{IR}	I_{Ram} (Å^4/amu)	I_{Ram}/I'_{Ram}	ν_{calc} (cm^{-1})	I_{IR} (km/mol)	I_{IR}/I'_{IR}	I_{Ram} (Å^4/amu)	I_{Ram}/I'_{Ram}	assignment
	$\{PF_6^- \cdot D_{Mim}^+\} \cdot H_2O$					$\{BF_4^- \cdot D_{Mim}^+\} \cdot H_2O$					water modes
ν_3	3891.9 (−38.5)	97.2	0.6	88.4	2.3	3893.8 (−36.6)	78.0	0.5	102.7	2.7	ν_3 (OH) str.
ν_1	3637.5 (−170.6)	393.1	61.4	101.3	1.3	3512.9 (−295.2)	573.3	89.6	87.3	1.1	ν_1 (OH) str.
	1662.0 (+59.0)	74.0	0.8	0.8	0.3	1663.5 (+60.5)	74.7	0.8	1.2	0.4	ν_2 (HOH) bend.
	$\{PF_6^- \cdot C_{2Mim}^+\} \cdot H_2O$					$\{BF_4^- \cdot C_{2Mim}^+\} \cdot H_2O$					water modes
	3891.4 (−39.0)	95.8	1.7	87.3	2.3	3893.5 (−36.9)	80.4	1.4	95.8	2.5	ν_3 (OH) str.
	3644.2 (−163.9)	365.9	57.2	96.3	1.2	3558.7 (−249.4)	452.2	70.6	80.2	1.0	ν_1 (OH) str.
	1660.4 (+57.3)	77.6	0.85	0.9	0.3	1654.1 (+51.0)	75.8	0.8	1.2	0.3	ν_2 (HOH) bend.
	$\{PF_6^- \cdot C_{4Mim}^+\} \cdot H_2O$					$\{BF_4^- \cdot C_{4Mim}^+\} \cdot H_2O$					water modes
ν_3	3901.6 (−28.8)	109.3	1.9	99.3	2.6	3892.3 (−38.1)	79.5	1.4	96.6	2.6	ν_3 (OH) str.
ν_1	3668.6 (−139.5)	237.4	37.1	93.1	1.15	3572.9 (−235.2)	414.9	64.8	77.1	0.95	ν_1 (OH) str.
	1640.1 (+37.1)	93.3	1.0	1.8	0.55	1655.8 (+52.8)	81.8	0.9	1.1	0.3	ν_2 (HOH) bend.

4x 2x 7x 5x

[DMIM]PF_6

[DMIM]BF_4



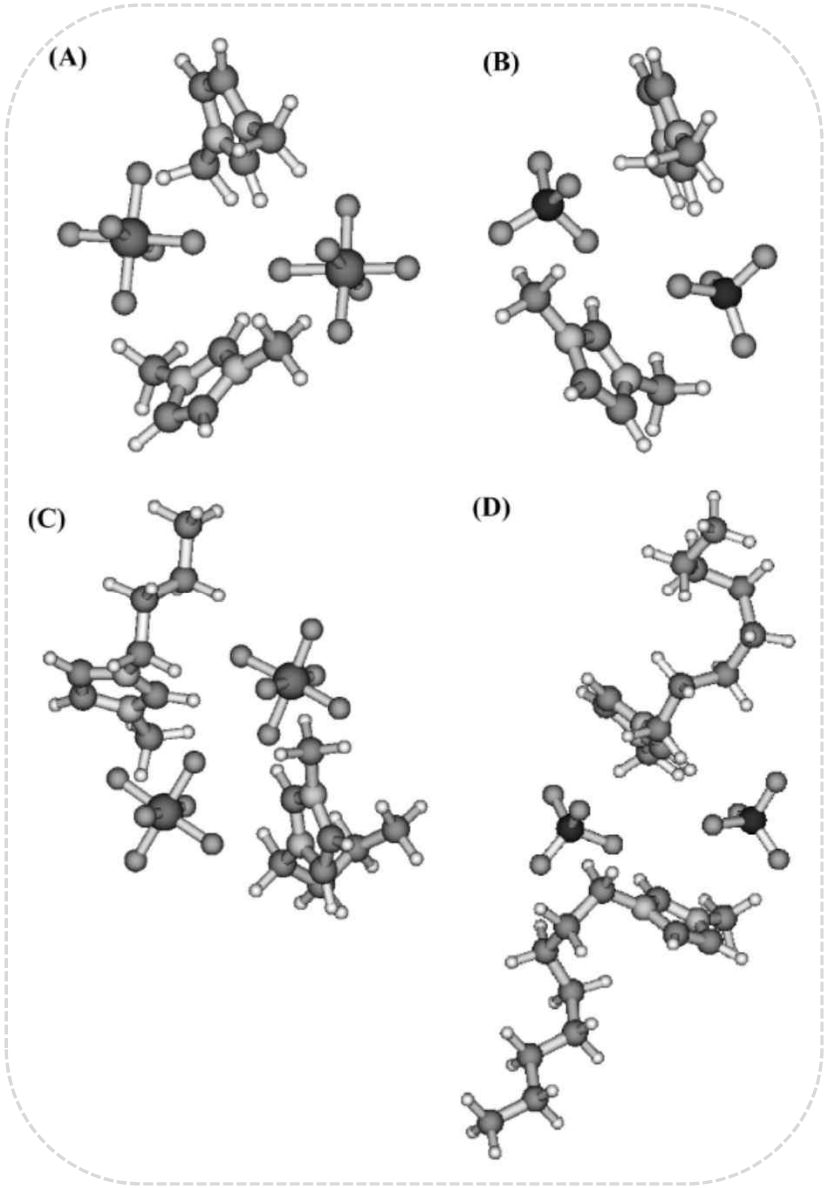
Dry

With H_2O

Water with doubly H-bonded with single anion

leads to **I** (ν_1)

Modeling - Ion pair dimers (without H_2O)



[DMIM]$^+$

[BMIM]$^+$

PF_6^- BF_4^-

Ion pair dimer

► organized to balance repulsive and attractive interactions

► **Total interaction energy : decreased less than 10%**

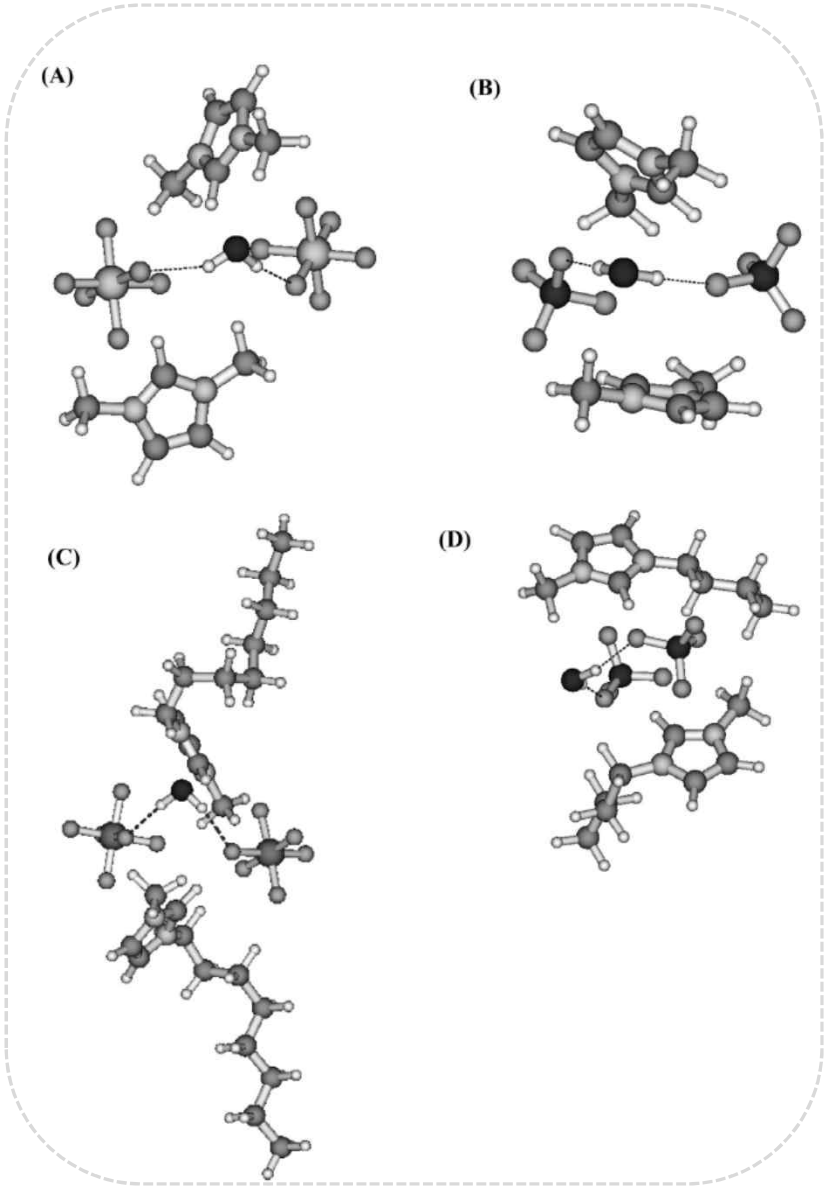
Increasing chain length

► d (cation-cation) : slightly increased

► **Weakening of anion-cation interaction** due to charge redistribution of imidazolium rings

► **Total interaction energy is increased** (less stable)

Modeling - Ion pair dimers (with H_2O)



$[DMIM]^+$

$[C_nMIM]^+$ (n=8,4)

PF_6^- BF_4^-

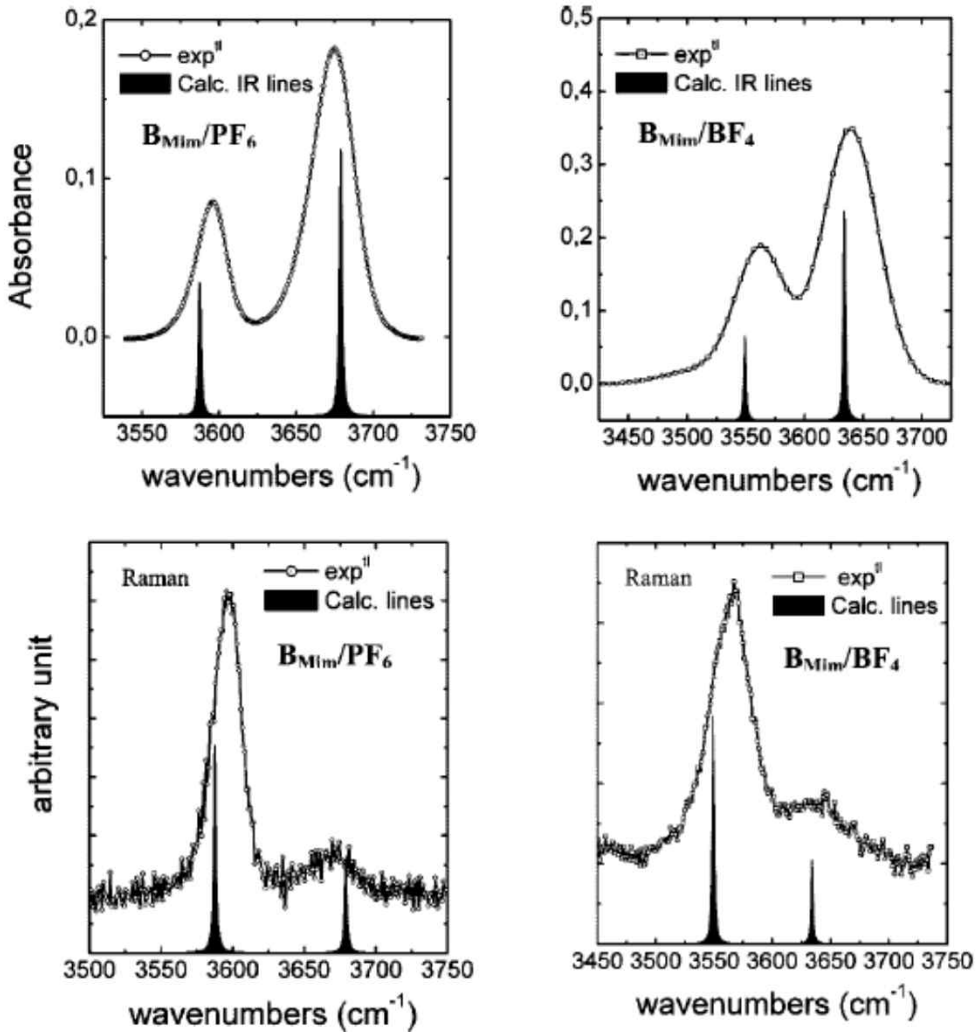
water

- ► **Role of proton double donor**
- ► d (H…F) : slightly greater than it for single ion pair system
- ► **Weakening of interaction energy** within the ion pair dimer
- ► **Weakening of anion-cation**

anions

- ► Favoring nearly **"symmetric" A…H-O-H…A structures**

Modeling - Spectra



Intensity calculation

► **Anharmonicity effects** using the scaling factor of 0.964

$R = I(\nu_3) / I(\nu_1)$

► **IR** : R = 2.0 (PF_6), 2.5 (BF_4)
(R_{exp} = 3.4 (PF_6), 1.9 (BF_4))

► **Raman** : R = 0.46 (PF_6), 0.37 (BF_4)
(R_{exp} = 0.15 (PF_6), 0.18 (BF_4))