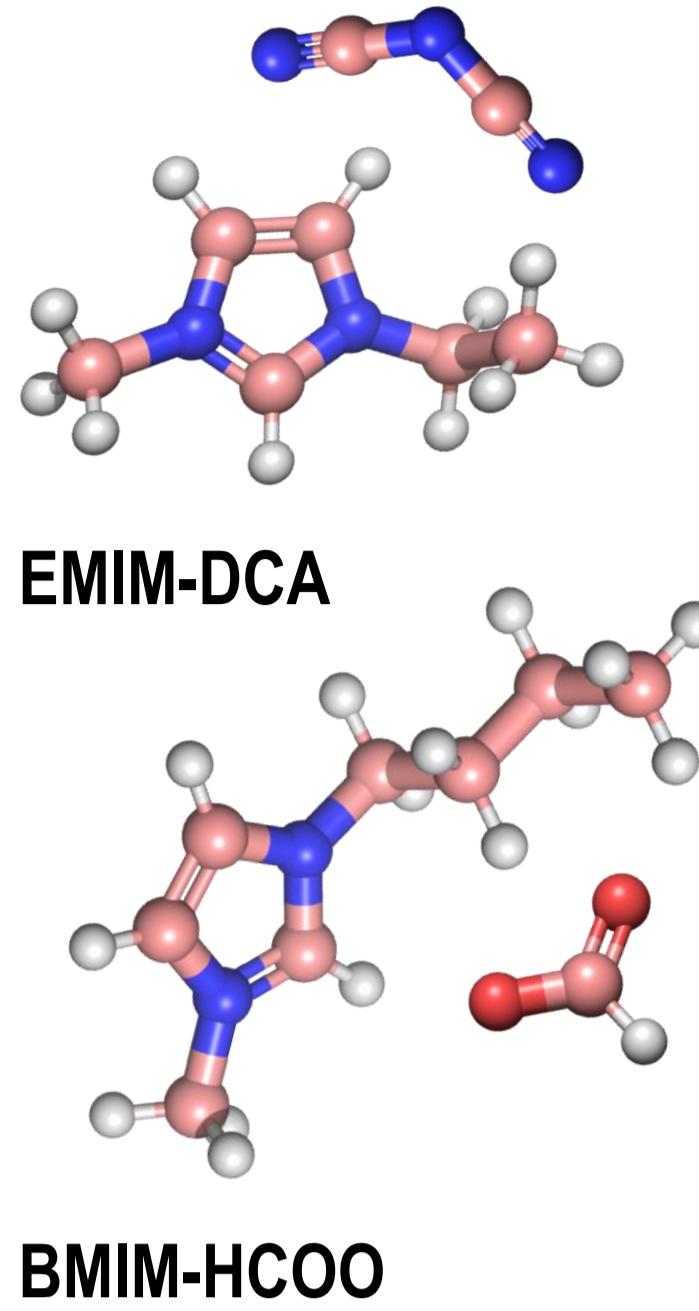
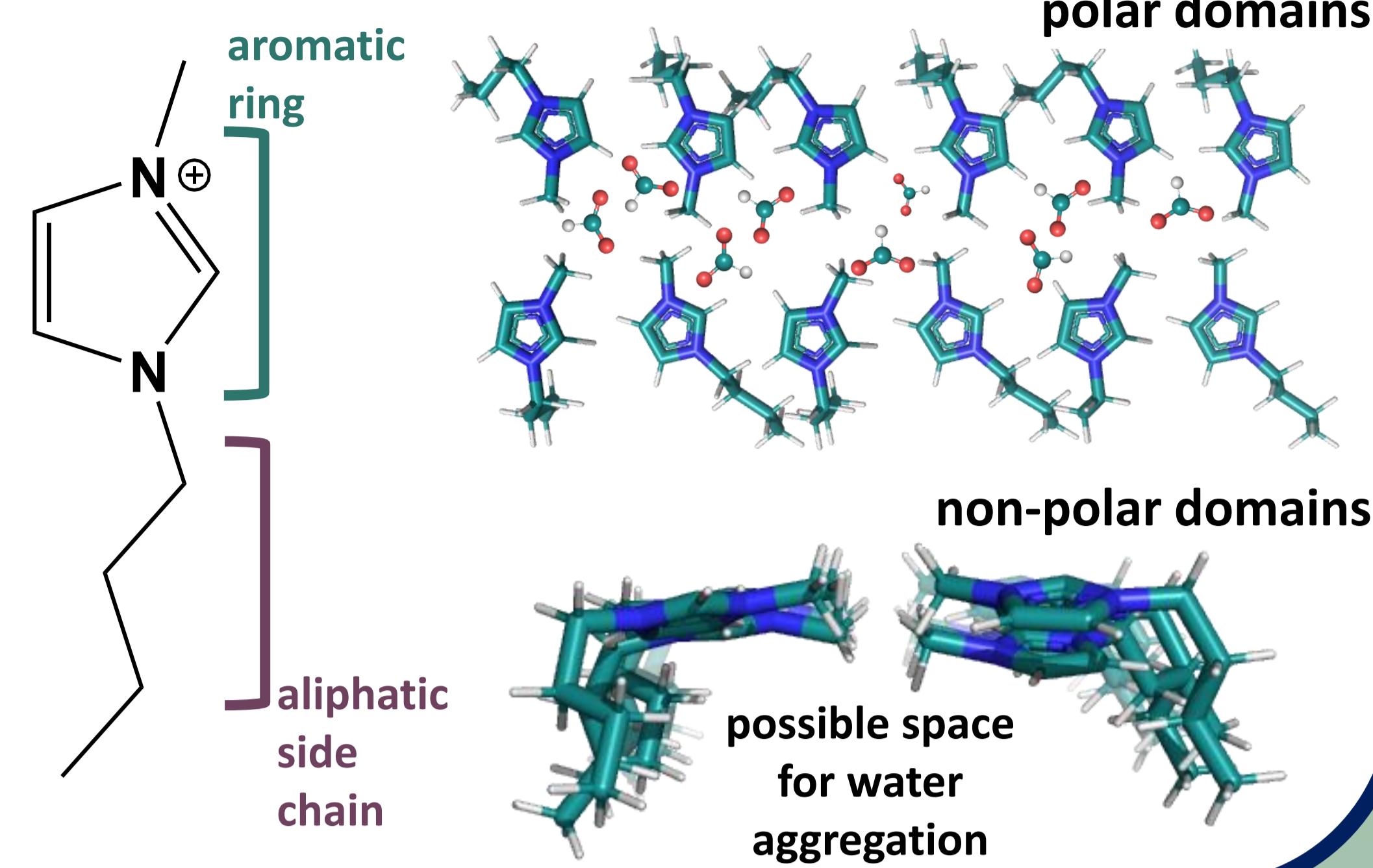


## Room Temperature Ionic Liquids (RTILs)

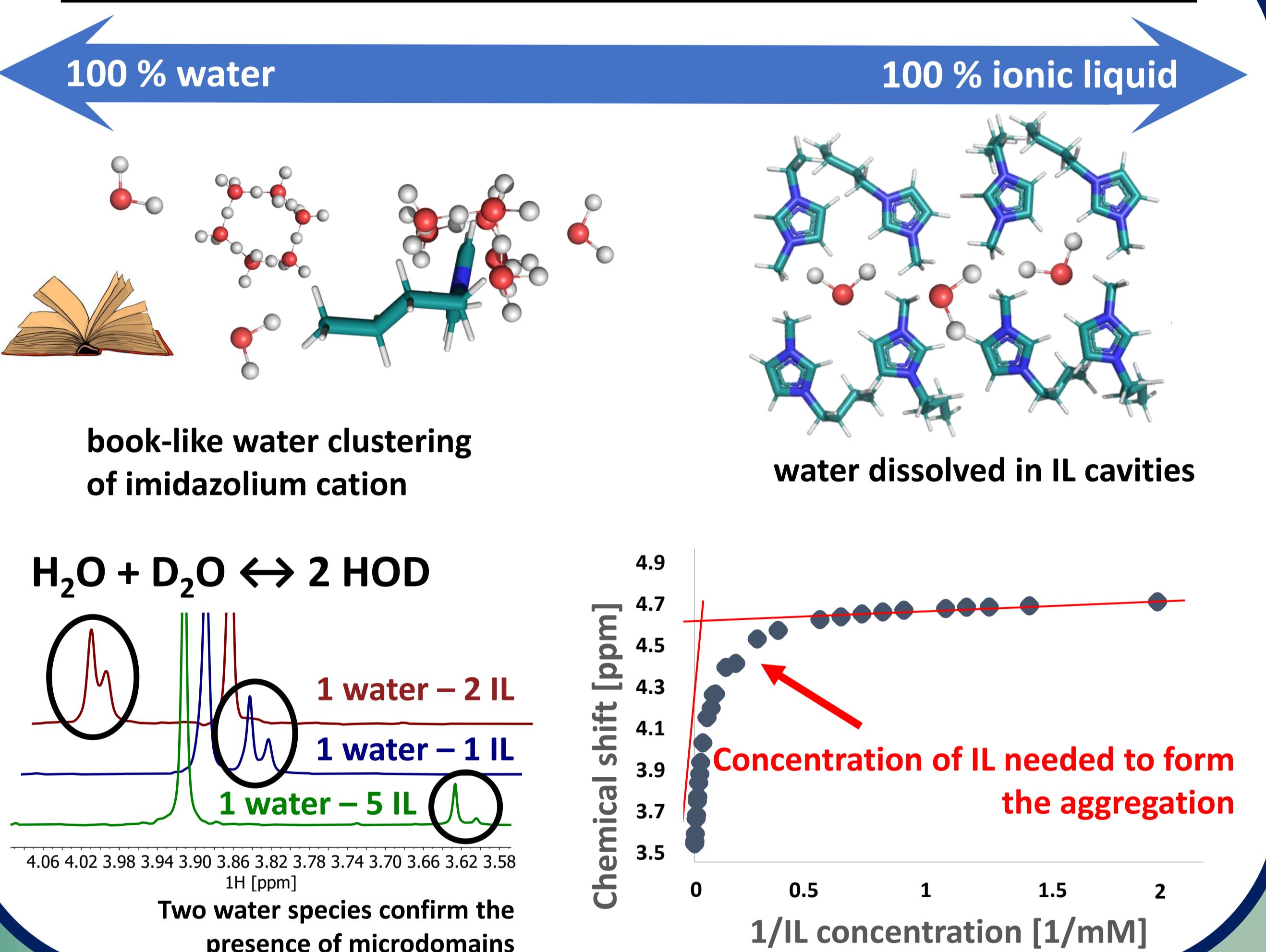


...not only high vacuum solvents

- built from bulky, asymmetric organic cations and weak basic anions
- extremely low melting point and liquid state at low pressures
- negligible vapor pressure, high thermal and electrochemical stability (low risk of degradation)
- more viscous than organic solvents and water
- green solvents – biodegradable and non-toxic



## Water – Ionic Liquid binary solvents



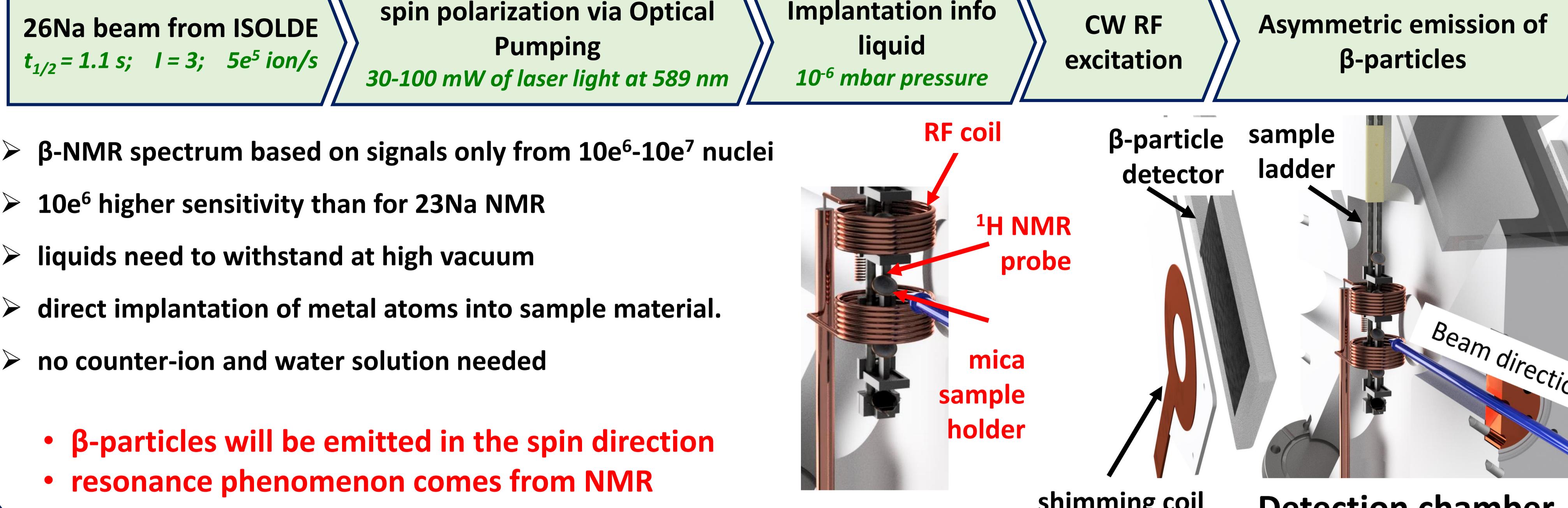
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# β-NMR analysis of Ionic Liquids

K. Dziubińska-Kühn, B. Karg, A. Antusek, N. Azaryan, M. Baranowski, M. Bissell, L. Cerato, J. Croese, R. Harding, R. Jolivet, T. Kanellakopoulos, M. Kozak, K. Kulesz, M. Madurga Flores, J. Matysik, S. Mohr, G. Neyens, S. Pallada, M. Pupier, A. Skrzypczak, J. Viger-Gravel, S. Warren, J. Wolak, D. Zakoucky, M. Kowalska

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## β-NMR on $^{26}\text{Na}$



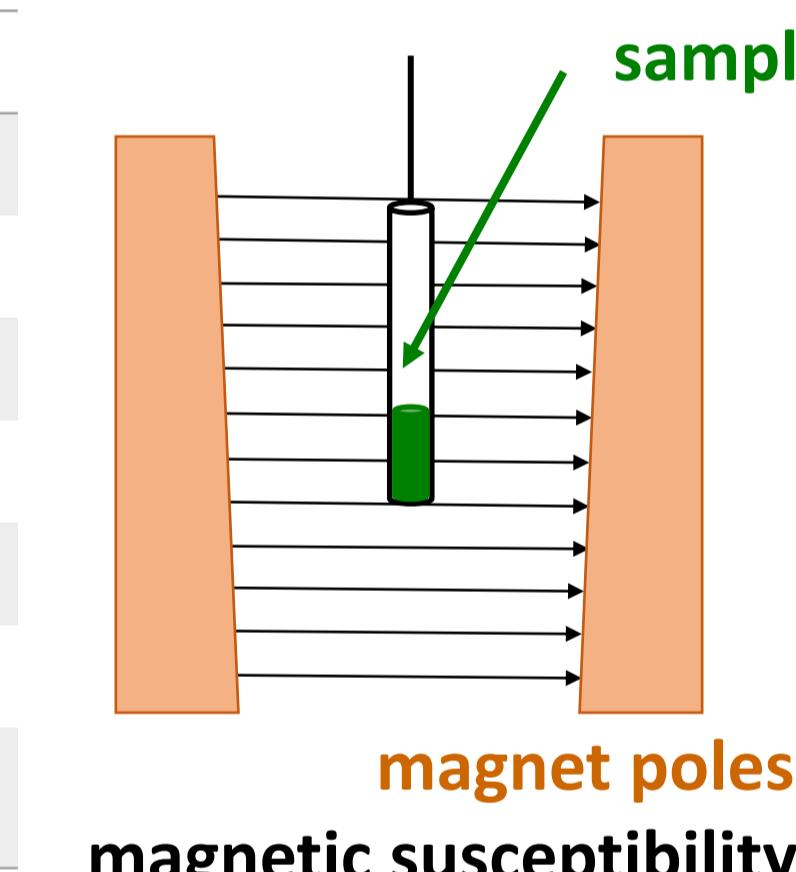
## Absolute shielding of $^{26}\text{Na}$

$$\sigma_{26\text{Na}} = 1 - \frac{v_{26\text{Na}}}{v_{1\text{H}}} \frac{|\mu_{1\text{H}}|}{|\mu_{26\text{Na}}|} \frac{I_{26\text{Na}}}{I_{1\text{H}}} \frac{1 + \left(\frac{1}{3} - \alpha_{1\text{H}}\right) \kappa_{1\text{H}}}{1 + \left(\frac{1}{3} - \alpha_{26\text{Na}}\right) \kappa_{26\text{Na}}} (1 - \sigma_{1\text{H}})$$

Required:

- accurate (ppm level) magnetic moment of β-NMR nucleus ( $\mu$ )
- in-situ  $^1\text{H}$  NMR measurement in a known host ( $\sigma$ ) next to β-NMR sample ( $v$ )
- magnetic susceptibility ( $\kappa$ ) and geometrical factor ( $\alpha$ ) for β-NMR and  $^1\text{H}$  hosts

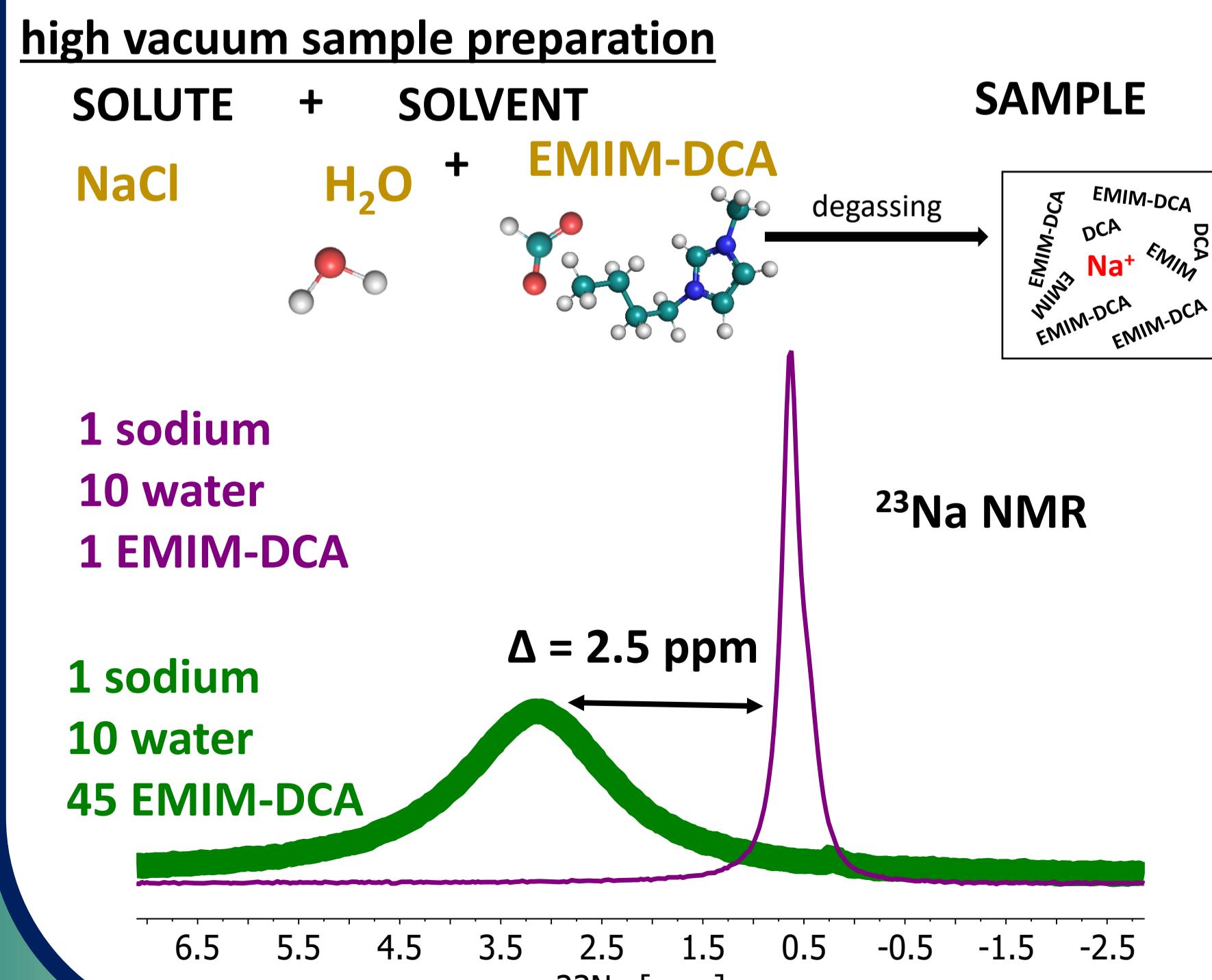
Isotope	I	$t_{1/2}/(\text{ms})$	$Q(\text{mb})$	old $\mu(\mu_N)$	new $\mu(\mu_N)$
$^{23}\text{Na}$	3/2	stable	+106(1)	2.217500(7)	
$^{26}\text{Na}$	3	1071	-5.3(3)	2.851(2)	2.849390(20)
$^{27}\text{Na}$	5/2	301	-7.2(3)	3.894(3)	3.89212(24)
$^{28}\text{Na}$	1	31	+39(1)	2.420(2)	2.41844(19)
$^{29}\text{Na}$	3/2	44	+86(3)	2.457(2)	2.45535(17)
$^{30}\text{Na}$	2	48		2.069(2)	2.0681(11)
$^{31}\text{Na}$	3/2	17		2.298(2)	2.29670(17)



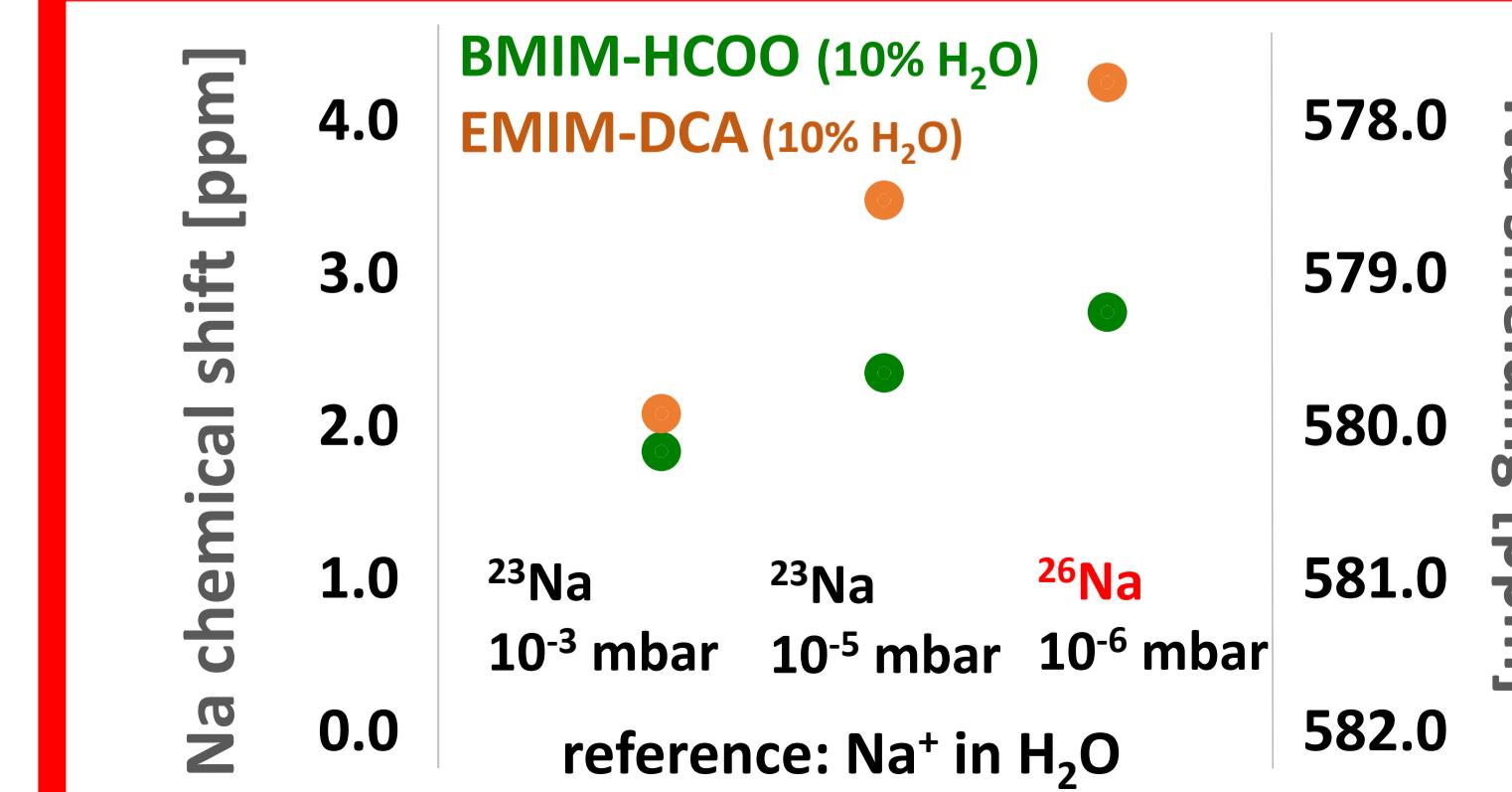
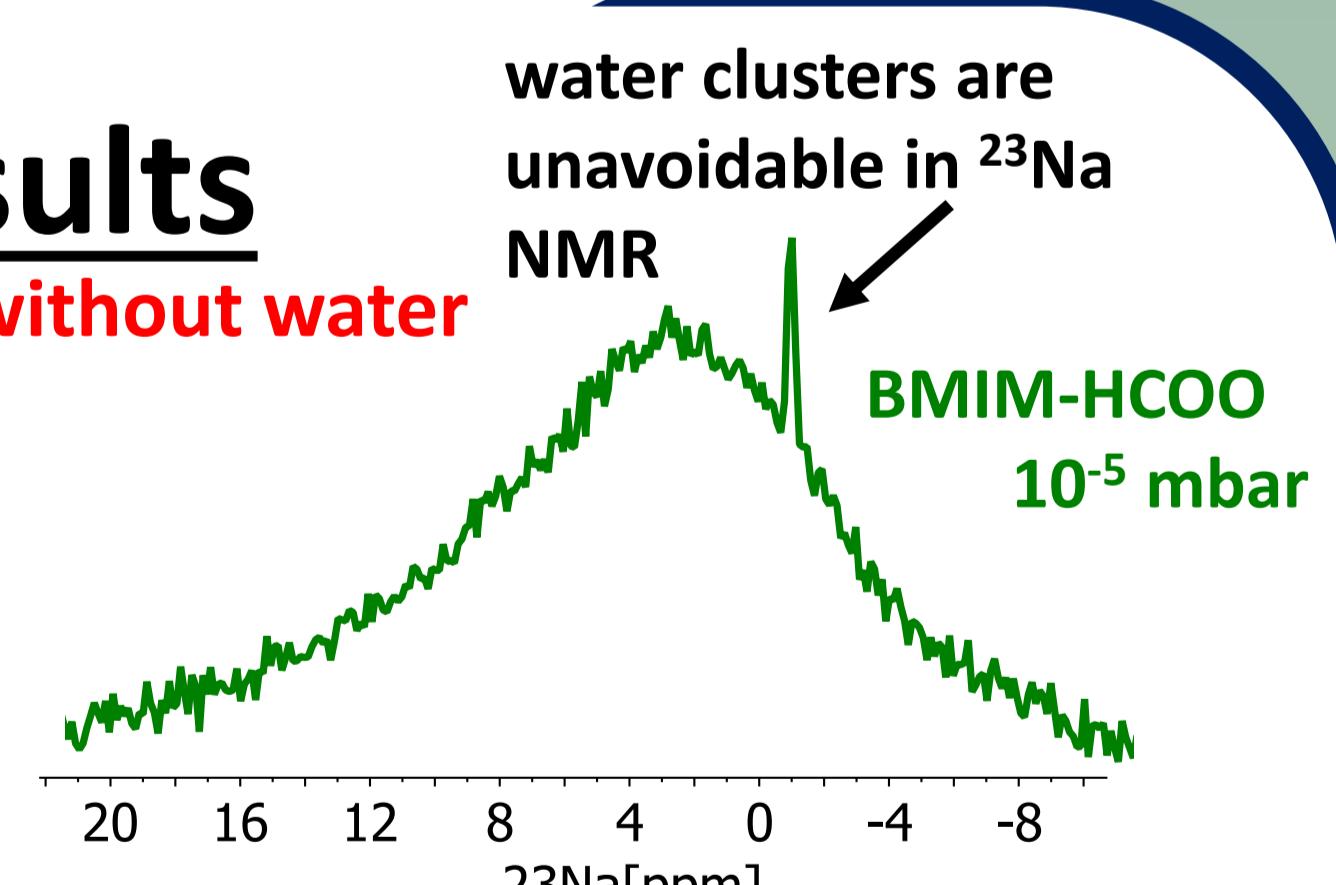
Ref. R. D. Harding, S. Pallada, J. Croese, et al. accepted by PRX, 2020

## $^{23}\text{Na}$ high vacuum NMR results

It is not possible to prepare ionic liquid –  $\text{Na}^+$  solution without water



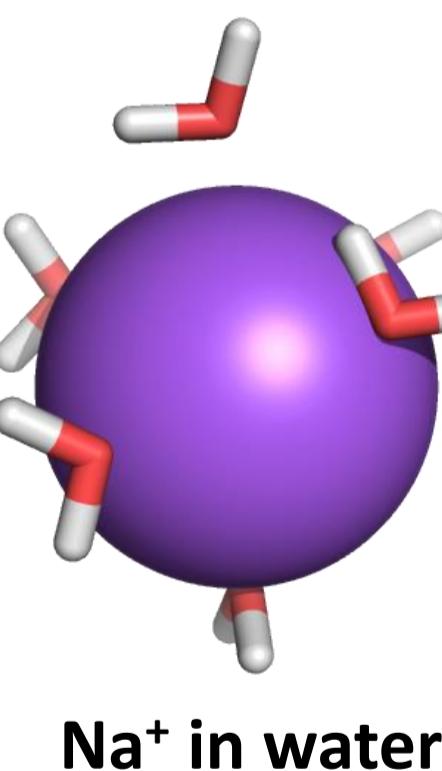
- $^{23}\text{Na}$  NMR standard: 0.1 M NaCl in  $\text{H}_2\text{O}$
- sodium environment depends strongly on the sample preparation
- samples with changed water : ionic liquid ratio represents different chemical environment of sodium, as revealed by:
  - chemical shifts
  - resonances' full width half maximum
  - signal-to-noise ratio



Shielding and chemical shift reference:

$$\sigma_{[\text{Na}(\text{H}_2\text{O})_6]} = 582 \text{ ppm}$$

Ref. A. Antusek, Bratislava, in Harding et al. accepted by PRX, 2020



## Advantages of β-NMR

- no need for β-NMR reference measurements
- acquisition of the signal coming from the selected volume of the sample
- precise quantification of metal atoms implanted into the host
- ONLINE studies of the chemical reactions catalysed by the metal atoms

## $^{26}\text{Na}$ high vacuum β-NMR results

