

Theory complements beta-NMR studies: correlation time of $^{23}\text{Na}^+$ in liquids

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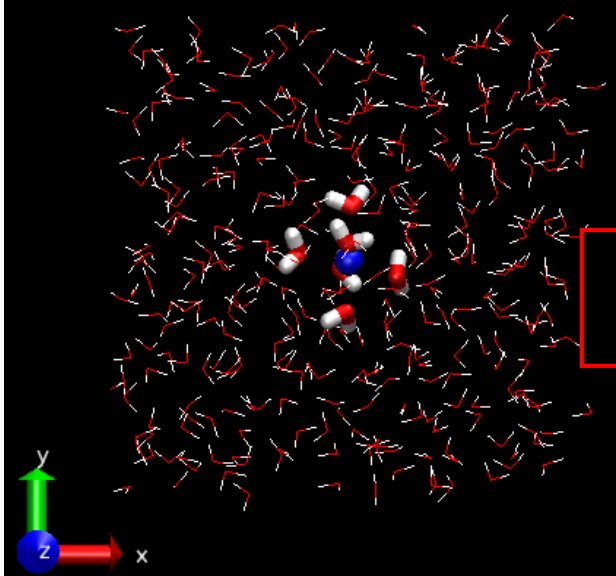
Introduction

- The molecular environment around different ions in liquids and solids can be determined experimentally using the technique of β -NMR, based for example on the relaxation time T_1 .
- To interpret T_1 correctly in liquids, one needs to take into account the underlying dynamics, which can be done by combining β -NMR results with calculations of the molecular correlation times.
- Several theoretical methods can be used, such as molecular dynamic (MD), density functional theory (DFT), or combination of quantum mechanics with molecular mechanics (QM/MM).
- In the present work, MD simulations have been applied to study the dynamics of water molecules around the Na^+ ion.

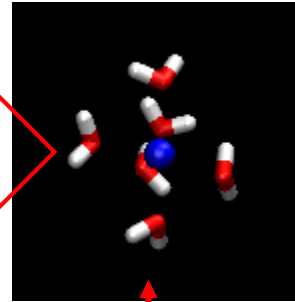
The preparation of MD trajectory

100 trajectories with different initial positions and velocities generate a good statistic ensemble for sampling and calculation of correlation time (τ).

Initial trajectory (20 ps)



Final trajectory (20 ps)



Second solvation shell

< 5.5 Å

Water molecules which placed in less than 5.5 Å compared to Na⁺ ion update in each frame

Average of 100 trajectories considered as a total C(t)

Curve fitting to obtain τ

The described process is repeated for 100 trajectories with different initial velocity and structure

Calculate correlation function
 $C(t) = \langle P_2(\vec{\mu}(0) \cdot \vec{\mu}(t)) \rangle$

Correlation function

- Reorientational correlation function is calculated by:

$$C(\tau) = \left\langle \frac{P_2(\cos\chi_{t,t+\tau})}{r^3(t)r^3(t+\tau)} \right\rangle$$

χ : angle between the interaction (inter-spin) vector at time t and $t + dt$

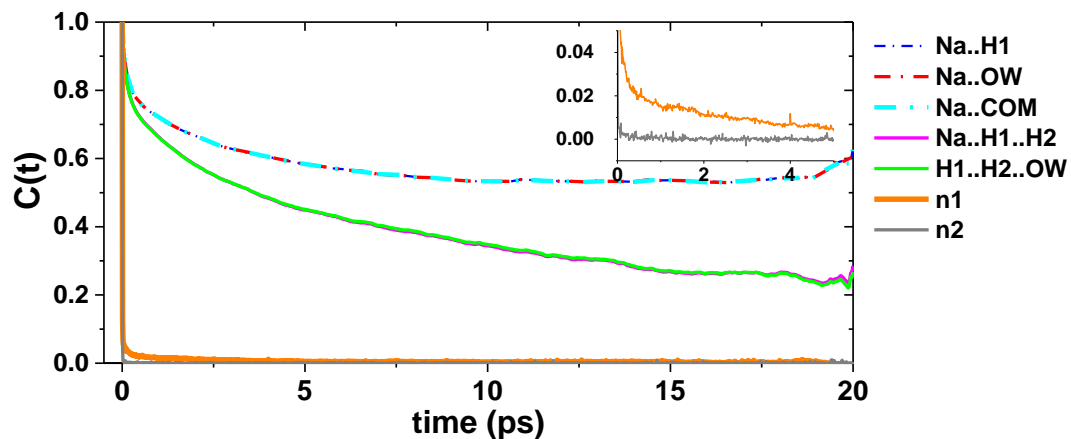
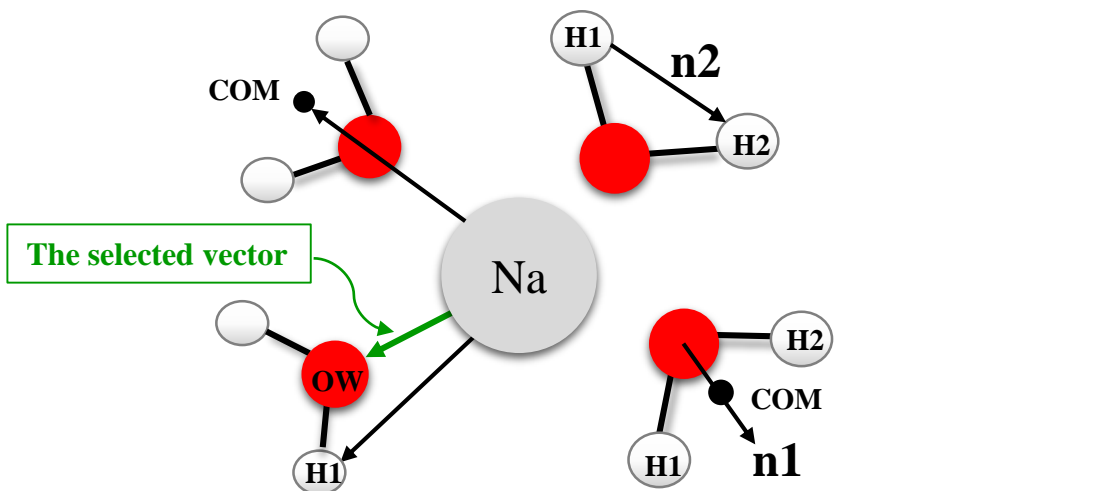
Weighted average

- The average C(t) is fitted to double exponential model.
- Fitting model has two time scales (fast & slow):

$$C_I(t) = S^2 + A_f e^{-t/\tau_f} + A_s e^{-t/\tau_s}$$
- The fast decay (τ_f) is the characteristic of small fluctuations in the local nuclear environment, while the slow decay (τ_s) describes the lower frequency and large scale motions [1].
- Our proposed method for averaging between τ_f & τ_s :

$$\frac{-\ln(A_f)}{\tau_f} + \frac{-\ln(A_s)}{\tau_s} = \frac{1}{\tau}$$

Inter-spin vectors



	Method	τ (fs)
Ours	MD based with weighted average	118
Carof 2016[3]	ff-md (ab initio MD)	285
Philips2017 [4]	ab initio MD based on average 10 trajectories	130
	ab initio MD based on one long 40 ps trajectory	420

Conclusion

- Engström and Carof et al. showed ion-water distance $C(t)$ bears strong resemblance to the EFG-ACF and relates to the rotation of the hydration shell around ion [2,3].
- Our obtained τ is in good agreement with other works [3,4].
- The obtained τ will be used for calculation of T_1 :

$$\frac{1}{T_1} = \frac{1}{T_2} = \frac{3}{8} \frac{2I + 3}{I^2(2I - 1)} \left(\frac{eQ}{h} \right)^2 \langle V_{zz}^2 \rangle \tau$$

Outlook

- This method can be now applied for other environments, like the ionic liquids (including BMIM and EMIM cations) and G4 DNA.
- It is also the basis for computations of the chemical shift and absolute shielding.

References

- [1] Bora, R. P. and R. Prabhakar (2009). J Chem Phys. 131(15): 10B610.
- [2] Engström, S., B. Jönsson and R. W. Impey (1984). J Chem Phys. 80(11): 5481.
- [3] Carof, A., et. al (2016). J Chem Phys. 145(12): 124508.
- [4] Philips, A., et.al (2017). J Chem Theory Comp 13(9): 4397.