Quadrupolar NMR relaxation for ions in aqueous solutions from classical molecular dynamics

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ABSTRACT

In nuclear magnetic resonance (NMR) experiments, the ions whose nuclei have spin $I > 1/2$ predominantly relax through the quadrupolar mechanism involving the interaction between the quadrupolar moment of the nucleus with the electric field gradient (EFG) at its position. While such experiments can potentially provide access to the structure, dynamics, and collective processes in ionic solvation shells, the amount of useful information that can be extracted in practice is often limited, as the quadrupolar coupling constant (QCC) that allows relating the measured NMR relaxation rate with a microscopic correlation time of EFG fluctuations are typically unknown. Both for aqueous ions at infinite dilution and in concentrated electrolytes, we show that a combination of classical molecular dynamics to sample long-time EFG fluctuations at the ion position with the consistently computed QCC at the ab initio level allows reaching a good agreement between the calculated and experimentally measured NMR rates [1, 2]. For ^{23}Na in aqueous NaCl, we find that the increase of the NMR rates with increasing the salt concentration or decreasing temperature is mainly due to the slowing down of EFG fluctuations, whereas the effect of the QCC change, related to the modification of the solvation shell structure, is rather small [2]. While the quadrupolar relaxation dynamics is often rationalized in terms of collective rotations of the ion's hydration shell, we show that the associated time scale (~10 ps) is at least an order of magnitude larger in comparison to typical correlation times of EFG fluctuations (~1 ps).

REFERENCES

[1]   I. Chubak, L. Scalfi, A. Carof, and B. Rotenberg. NMR relaxation rates of quadrupolar aqueous ions from classical molecular dynamics using force-field specific Sternheimer factors. *J. Chem. Theory Comput.* **17**, 6006-6017 (2021).

[2]   I. Chubak, L. Alon, E. V. Silletta, G. Madelin, A. Jerschow, and B. Rotenberg, *in preparation* (2022).