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Accurate Quadrupolar NMR Relaxation Rates of Aqueous Cations from Classical Molecular Dynamics

Antoine Carof,^{†,‡} Mathieu Salanne,^{†,‡} Thibault Charpentier,[¶] and Benjamin
Rotenberg^{*,†,‡}

*Sorbonne Universités, UPMC Univ. Paris 06, UMR 8234 PHENIX, 75005 Paris, France,
CNRS, UMR 8234 PHENIX, 75005 Paris, France, and CEA, IRAMIS, NIMBE, LSDRM,
UMR CEA-CNRS 3299, F-91191 Gif-sur-Yvette cedex, France*

E-mail: benjamin.rotenberg@upmc.fr

*To whom correspondence should be addressed

†UPMC

‡CNRS

¶CEA

Abstract

Nuclear Magnetic Resonance (NMR) Relaxation rates encode information about the collective and local dynamics around nuclei. Provided a suitable microscopic model is available, this allows investigating *e.g.* the solvation shell dynamics around aqueous ions. Previous attempts with Molecular Dynamics simulations faced the double challenge of calculating accurately the microscopic properties governing the relaxation process, such as the electric field gradient (EFG) at the nucleus, and of sampling the trajectories over sufficiently long times. Here we show how to compute the NMR relaxation rate from classical molecular dynamics simulations. We use a recently derived force field parametrized on ab initio calculations and show that the EFG predicted by this force field can be used to accurately estimate the one computed by DFT using the PAW method where the electronic structure is described explicitly. The predicted relaxation rates for aqueous alkaline and alkaline Earth cations are in good agreement with experimental data. Our approach opens the way to the quantitative interpretation of these rates with molecular simulation.

Keywords

NMR relaxometry, molecular simulation, PAW, electrolytes, aqueous cations

1 Introduction

Nuclear Magnetic Resonance (NMR) relaxation rates encode information on the microscopic dynamics around nuclei.¹ However the interpretation of experimental measurements usually relies on simple models, *e.g.* Brownian rotational diffusion, which may not apply down to the molecular scale.² Hence the amount of microscopic information that can be retrieved from such experiments remains rather limited in practice. For nuclei with spin $I \geq 1$, the main relaxation mechanism is the quadrupolar interaction involving the coupling of the nuclear quadrupole moment eQ with the Electric Field Gradient (EFG) $V_{\alpha\beta}$ at the nucleus. In the so-called extreme narrowing limit, the longitudinal and transverse magnetizations decay exponentially. The corresponding rates $1/T_1$ and $1/T_2$ reflect the fluctuations in time of the EFG and thus probe the environment of the nuclei. For an isotropic system, both rates are equal and usually written as:^{1,3}

$$\frac{1}{T_1} = \frac{3}{8} \frac{2I + 3}{I^2(2I - I)} \left(\frac{eQ}{\hbar} \right)^2 \langle V_{zz}^2 \rangle \tau_c, \quad (1)$$

with e the elementary charge, \hbar Planck's constant, I the nuclear spin and eQ the nuclear quadrupole moment of the nucleus under consideration, V_{zz} the zz cartesian component of the EFG in the laboratory frame and where the brackets denote an ensemble average. The correlation time τ_c of the EFG auto-correlation function (acf) is given by:

$$\tau_c = \frac{\int_0^\infty \langle V_{zz}(0)V_{zz}(t) \rangle dt}{\langle V_{zz}^2 \rangle}. \quad (2)$$

From the modelling point of view, the challenge is then to model the EFG acf in order to extract relevant information from the experimental relaxation rates. Here we show how classical Molecular Dynamics (MD) simulation calibrated on ab initio data can provide this quantity efficiently, by combining an accurate evaluation of the EFG for each configuration, a realistic description of the microscopic dynamics and a moderate computational cost allowing

for the sampling of trajectories over the required time scales.

Due to their ubiquity in chemistry or biology, the case of quadrupolar aqueous ions (${}^7\text{Li}^+$, ${}^{23}\text{Na}^+$, ${}^{25}\text{Mg}^{2+}$, ${}^{39}\text{K}^+$, ${}^{133}\text{Cs}^+$, ...) has attracted a lot of attention since the early days of NMR.⁴⁻⁷ Various NMR techniques can be used to probe their environment in complex materials such as zeolites,^{8,9} clays¹⁰⁻¹² and glasses^{13,14} or their binding to biological molecules such as DNA.¹⁵ Classical molecular simulations have demonstrated the shortcomings of theories based on continuous descriptions of the medium, such as a dielectric continuum or a viscous implicit solvent,¹⁶⁻¹⁸ or based on the dynamics of single water molecules^{4,5}, even in the simplest case of dilute electrolyte solutions. The local, molecular structure of the solvent around the ion cannot be neglected.¹⁹⁻²¹ Engström *et al.*²² as well as Roberts and Schnitker²³ underlined the role of the symmetry of the hydration shell on the resulting EFG at the nucleus site and showed that cross-correlations between water molecules around the ion cannot be neglected so that the collective dynamics of the shell should be taken into account. In addition, they found that the decay of the EFG acf displays two characteristic times, in contrast with the standard assumption of mono-exponential decay (Debye model). Until now, no clear physical interpretation was proposed for this two-step decay, even if this behaviour may be found for related properties (*e.g.* solvation energy, forces, etc.). In the case of ${}^7\text{Li}^+$, the relative contributions of dipole-dipole and quadrupolar relaxation mechanisms have also been examined using classical MD.^{24,25}

For such simulations to quantitatively reproduce the experimental results, thereby allowing the extraction of microscopic information from the data, it is essential that the model captures both the EFG on the nucleus for any given configuration and the microscopic dynamics of the system. In addition, the associated computational cost should not impede the proper sampling of trajectories required to compute the EFG acf. Since the fastest characteristic time of the EFG acf (typically tens of fs, see below) is larger than the MD timestep (typically 1 fs), it is not necessary to sample the EFG at every time step. A successful strategy generally adopted in most previous works thus consists in generating a trajectory

using a less expensive method than the one used to compute the EFG with a better accuracy on a limited number of configurations (or even a cluster extracted therefrom) along the trajectory. Configurations can be generated by DFT-based ab initio MD (AIMD) followed by EFG calculations at the Hartree-Fock level,^{26,27} DFT within the Zeroth Order Relativistic Approximation²⁸ or using an all-electron basis set instead of pseudo-potentials.²⁹ The computational cost of AIMD typically results in poor estimates of the correlation time τ_c . In addition, the small number of configurations and the fact that they are sampled from short trajectories limits the accuracy to which the ensemble average $\langle V_{zz}^2 \rangle$ can be estimated, even though the EFG is computed accurately for each configuration. The trajectory can also be obtained by classical MD and the EFG subsequently computed at the Hartree-Fock³⁰ or QM/MM level.³¹

Alternatively, the EFG at the site of the nucleus of interest can be determined for a given configuration using a simpler model parametrized on prior high-level calculations. Based on the observation of pair-additivity of the EFG on the deuterium nucleus for heavy water clusters,³² Müller *et al.* proposed an analytical function to determine the EFG from the position of the neighbouring atoms, parametrized on a water dimer. This model was then used to analyze classical MD trajectories of liquid water³³ and later extended to AIMD trajectories of water-DMSO mixtures.³⁴ Most classical MD studies rely instead on the so-called Sternheimer approximation.^{35,36} The latter assumes that the electronic cloud around the nucleus responds linearly to an external EFG V_{zz}^{ext} , arising from the surrounding charge distribution, resulting in an additional EFG at the nucleus site. The total EFG entering in 1 is thus written as:

$$V_{zz} = (1 + \gamma_\infty)V_{zz}^{ext}, \tag{3}$$

and similarly for all cartesian components $V_{\alpha\beta}$, with γ_∞ the Sternheimer anti-shielding factor. The contribution of the distorted electronic cloud may be much larger than the external one

$(\gamma_\infty \gg 1)$.^{35,36}

Several caveats are in order for the use of this expression with classical MD simulations. Roberts and Schnitker underlined that “because of the uncertainty in the constants Q and γ_∞ , not too much emphasis should be put on comparison of relaxation rates from experiments and simulation”.²³ In addition, the validity of the Sternheimer approximation in the condensed phase has been questioned and extensions have been proposed to include higher-order terms in the electronic response.³⁷⁻³⁹ Calandra *et al.* showed that short-range electronic effects, which result in reorganizations of the electronic density beyond the asymptotic (valid at large distance) linear response, are particularly important for anions in solids, but less dramatic for cations.⁴⁰ More recently, Aidas *et al.* suggested that the Sternheimer approximation may not hold for aqueous $^{23}\text{Na}^+$, due to polarization and short-range non-electrostatic interactions.³¹ Finally, even if such an approximation applies, it should be noted that the external EFG for a given configuration depends on the charge distribution associated with the force field (FF) used to model electrostatic interactions. Therefore, the linear relation between the true V_{zz} and that predicted by the classical force field V_{zz}^{ext} should be verified and the corresponding effective Sternheimer anti-shielding factor γ_{eff} determined accordingly.

Here we show that the EFG acf for aqueous cations can be obtained accurately in classical MD simulations using a Polarizable Ion Model (PIM) as a FF, parametrized on ab initio calculations. The PIM, initially developed for ionic liquids and solids, describes electronic polarization via induced point dipoles and accounts for short-range electronic effects via a modification of charge-dipole interactions⁴¹. The force field parameters are fitted so as to best reproduce the ab initio forces and atomic dipoles from DFT calculations in the condensed phase. We have recently parametrized such a PIM for aqueous ions and validated the force field on a number of structural, thermodynamical and dynamical properties.⁴² It combines the Dang-Chang water model⁴³ with ion-water and ion-ion interactions of the PIM form.⁴⁴ The paper is organized as follows. In 2 we describe the simulated system and the classical

MD and DFT calculation details. We then present in 3 the validation of the Sternheimer approximation and compare the computed NMR relaxation rates with the experimental ones.

2 Simulation details

For each of the 4 cations studied (Li^+ , Na^+ , K^+ and Mg^{2+}), we compute the ab initio EFG for 100 configurations from prior classical MD simulations of 1 ion and 63 water molecules in a cubic box of length 12.428 Å. Classical MD simulations over times sufficiently long (as discussed below) to correctly sample the EFG acf are performed on a larger system, consisting of ion and 215 water molecules in a cubic box of length 18.65 Å.

2.1 Classical simulations

For each cation, 5 independent trajectories of the smaller system, of 40 ps each, are obtained after annealing at 1000 K for 200 ps followed by 200 ps equilibration at 298 K. The EFG is computed for configurations sampled every 2 ps of each trajectory, totalling 100 configurations per cation. Similarly, for the larger system 5 independent trajectories of 500 ps each are obtained after at 1000 K for 150 ps followed by 50 ps equilibration at 298 K and the EFG is computed every 5 fs. The cut-off radii used to compute short-range interactions are 6.2 Å and 9.325 Å, for the smaller and larger system, respectively. A time step of 1 fs is used and the temperature is maintained at $T = 298$ K using a Nose-Hoover thermostat^{45,46} with a time constant of 1 ps.

Classical MD simulations are performed using the Polarizable Ion Model developed in Ref. 42. At each time step of the MD simulation, the dipoles are determined self-consistently by minimizing the polarization energy:

$$V_{\text{pol}} = \sum_I \frac{1}{2\alpha^I} \|\mu^{\mathbf{I}}\|^2 + \sum_{I,J} \left[(q^I \mu_\alpha^J - q^J \mu_\alpha^I) g^{IJ}(r_{IJ}) T_{IJ}^\alpha - \mu_\alpha^I \mu_\beta^J T_{IJ}^{\alpha\beta} \right] \quad (4)$$

with q_I the ion charge, α^I its isotropic polarizability and μ^I its induced dipole. The interaction tensors are $T_{IJ}^\alpha = \partial_\alpha(1/r_{IJ})$ and $T_{IJ}^{\alpha\beta} = \partial_\alpha\partial_\beta(1/r_{IJ})$ and the Einstein summation convention over directions α, β is assumed. A short-range correction to the multipolar expansion of the Tang-Toennies type is used:

$$g^{IJ}(r_{IJ}) = 1 - c^{IJ} e^{-b^{IJ} r_{IJ}} \sum_{k=0}^4 \frac{(b^{IJ} r_{IJ})^k}{k!} \quad (5)$$

Once the induced dipole are determined, including short-range electronic effects, they provide a simple description of the electronic density. In particular, we can compute the EFG generated by the set of point charges and induced dipoles (without short-range correction). Classical simulations are performed with the CP2K simulation package.⁴⁷ Electrostatic interactions and the EFG are computed using a dipolar Ewald sum,^{48,49} with a tolerance of 10^{-7} to obtain the self-consistent dipoles.

2.2 DFT calculation

In order to assess the ability of this model to capture the EFG on the ion, we compare its prediction to ab initio calculations. The projected augmented wave (PAW) method⁵⁰⁻⁵³ allows the DFT-based computation of all-electron EFG in the condensed phase, *i.e.* using periodic boundary conditions instead of clusters. Calculations are performed with the Quantum Espresso package,⁵⁴ using the PBE functional,⁵⁵ the norm-conserving pseudo-potentials provided with the QE-GIPAW Package⁵⁶ and a kinetic energy cut-off of 80 Ry.

3 Results and Discussion

3.1 Validation of Sternheimer approximation

1 compares the 6 cartesian components of the EFG tensor computed ab initio (AI) to the prediction of the classical PIM. The results confirm the linear relation between the external

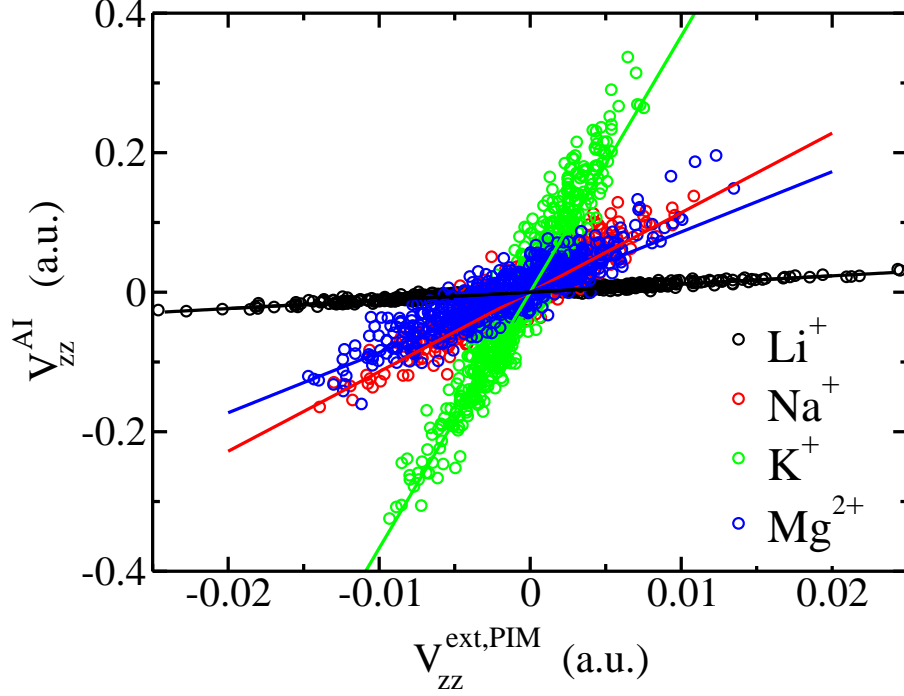


Figure 1: Electric Field Gradient: Ab initio vs Polarizable Ion Model (PIM). For each cation, the 6 cartesian components of the EFG tensor are reported for 100 configurations of 1 cation and 63 water molecules with periodic boundary conditions. The linear relation between the ab initio and classical results confirms the validity of the Sternheimer approximation and provides the corresponding effective anti-shielding factor γ_{eff} for each ion.

EFG computed by the PIM $V_{zz}^{ext,PIM}$ and the exact EFG V_{zz}^{AI} . The slope provides the effective Sternheimer anti-shielding factor γ_{eff} for each ion, which can then be used to determine the classical prediction of the total EFG:

$$V_{zz}^{PIM} = (1 + \gamma_{eff})V_{zz}^{ext,PIM}. \quad (6)$$

The values are summarized in 1, which also reports the error on the EFG predicted by the PIM (including the Sternheimer anti-shielding factor) compared to the AI result, defined

as:

$$\sigma(V_{zz}) = \sqrt{\frac{\langle(\delta V_{zz})^2\rangle}{\langle V_{zz}^2\rangle}} = \sqrt{\frac{\frac{1}{N} \sum_{i=1}^N |V_i^{AI} - V_i^{PIM}|^2}{\frac{1}{N} \sum_{i=1}^N |V_i^{AI}|^2}} \quad (7)$$

where the sums run over the 6 cartesian components of the 100 configurations. As expected from the broader electronic cloud around larger ions, γ_{eff} increases from Li^+ to Na^+ and K^+ and slightly decreases from Na^+ to Mg^{2+} . The slope $1 + \gamma_{eff}$ differs from $1 + \gamma_\infty$ (see Refs. ^{36,38,39}) by a factor of 1.5 to 1.9. Even though the EFG predicted by the PIM, 6, for any given configuration is not quantitative, the average error is reasonable. In addition, our sample is sufficient to determine the Sternheimer anti-shielding factor corresponding to the PIM with a good accuracy (uncertainties $< 3\%$). The external EFG of the PIM combined with the effective Sternheimer anti-shielding factor parametrized on ab initio calculation then provides an estimate of $\langle V_{zz}^2 \rangle$ in agreement with the AI one, as can be seen in 2. Even the most unfavorable case, namely Mg^{2+} , is still an improvement compared to the previous calculation of Ref. 23.

Table 1: Effective Sternheimer anti-shielding factor γ_{eff} for the Polarizable Ion Model and error $\sigma(V_{zz})$ between its prediction of the EFG, taking into account the corresponding effective Sternheimer anti-shielding factor, and the ab initio value.

	γ_{eff}	$\sigma(V_{zz})$
Li^+	0.17 ± 0.01	0.29
Na^+	10.4 ± 0.22	0.42
K^+	35.7 ± 0.51	0.32
Mg^{2+}	7.64 ± 0.21	0.50

3.2 Comparison with Experimental Data

Once the Sternheimer approximation is validated and the corresponding γ_{eff} determined, we can perform classical MD simulations of a larger system over times sufficiently long to

Table 2: Variance of the EFG $\langle V_{zz}^2 \rangle$ (in atomic units) obtained from ab initio (AI) calculations and with Polarizable Ion Model (PIM).

	$\langle V_{zz}^2 \rangle$ (a.u.)	
	AI	PIM
Li ⁺	$(8.94 \pm 2.47) 10^{-5}$	$(8.18 \pm 2.19) 10^{-5}$
Na ⁺	$(2.37 \pm 0.34) 10^{-3}$	$(1.95 \pm 0.26) 10^{-3}$
K ⁺	$(1.32 \pm 0.14) 10^{-2}$	$(1.19 \pm 0.14) 10^{-2}$
Mg ²⁺	$(2.25 \pm 0.41) 10^{-3}$	$(1.68 \pm 0.23) 10^{-3}$

correctly sample the EFG acf. The simulated system contains 1 ion and 215 water molecules in a cubic box of length 18.65 Å. A time step of 1 fs is used and the temperature is maintained at $T = 298$ K using a Nose-Hoover thermostat^{45,46} with a time constant of 1 ps. For each cation, the EFG acf is computed from 5 independent trajectories of 500 ps each. The EFG variances $\langle (V_{zz}^{ext})^2 \rangle$ and $\langle V_{zz}^2 \rangle$ are given in 3. Results for the latter are consistent with the one obtained for the smaller systems with a more limited number of configurations (see 2). This is due to the fact that the EFG on the ion depends mainly on the first solvation shell. The $\langle V_{zz}^2 \rangle$ for Li⁺ and Na⁺ are consistent with previous ab initio calculations.^{19,20,22,28} To the best of our knowledge, no such ab initio data is available for K⁺ and Mg²⁺.

Increasing the ion radius from Li⁺ to Na⁺ and from Na⁺ to K⁺ result in an increase in $\langle V_{zz}^2 \rangle$ by a factor of 20 and 10, respectively. Increasing the charge from Na⁺ to Mg²⁺, it decreases slightly (as does the ionic radius). These variations are essentially due to the variations of the anti-shielding factor γ_∞ . Indeed, the fluctuations of the external EFG $\langle (V_{zz}^{ext})^2 \rangle$ follow the opposite trends (see 3), in qualitative agreement with the results obtained by Roberts and Schnitker with a simpler force field.²³ Two effects results in a smaller EFG: Firstly, with larger ions each water molecules is further from the nucleus contributes less to the EFG; Secondly, the larger number of such molecules results in compensations between them.

The EFG acf are finally reported in 2. Results indicate averages over the 5 trajectories, together with the corresponding standard deviations. The moderate computational cost of

Table 3: Variance of the external and total EFG (atomic units) and EFG correlation time τ_c from 5×500 ps simulations of the large system using the PIM. The corresponding relaxation rate $1/T_1$ is compared to the experimental result.^{4,6,57}

	$\langle (V_{zz}^{ext})^2 \rangle$ (a.u.)	$\langle V_{zz}^2 \rangle$ (a.u.)	τ_c (fs)	$1/T_1^{\text{PIM}}$ (s ⁻¹)	$1/T_1^{\text{exp}}$ (s ⁻¹)
⁷ Li ⁺	$(7.44 \pm 0.16) 10^{-5}$	$(1.02 \pm 0.02) 10^{-4}$	180	$3.22 10^{-2}$	$2.70 10^{-2}$
²³ Na ⁺	$(1.56 \pm 0.02) 10^{-5}$	$(2.03 \pm 0.03) 10^{-3}$	285	7.07	16.2
³⁹ K ⁺	$(8.36 \pm 0.09) 10^{-6}$	$(1.13 \pm 0.01) 10^{-2}$	375	16.1	17.8
²⁵ Mg ²⁺	$(2.45 \pm 0.06) 10^{-5}$	$(1.83 \pm 0.04) 10^{-3}$	110	3.04	4.16

classical MD with the PIM, compared to AIMD, therefore allows a sufficient sampling of the acf to obtain the correlation time τ_c with a good accuracy 3. Note that the results are normalized by the initial value of the acf to facilitate the comparison between ions. The decay is not mono-exponential and the acf displays a fast initial decrease over ~ 100 fs followed by a slower decorrelation over a few ps, in agreement with previous findings.^{22,23} In the case of Li⁺, the acf oscillates with a period of ~ 85 fs. Such oscillations of the EFG acf have not been reported in previous works^{23,25} but are consistent (with the same period) with those observed for that of the velocity (VACF) and force (FACF)⁵⁸ and correspond to the rattling of the light Li⁺ inside its solvation shell. For Mg²⁺ one also observes an oscillation, with a negative part. The correlation time τ_c (3) increases from Li⁺ to Na⁺ and decreases from Na⁺ to Mg²⁺. The microscopic mechanisms leading to the observed behaviours will be discussed elsewhere.

The time-integral, used to compute the correlation time τ_c are illustrated in 3, which clearly shows that the EFG acf must be computed accurately over several picoseconds in order to reach the plateau corresponding to τ_c . This underlines the difficulty to determine the latter from AIMD only. Finally, 3 also compares the relaxation rates $1/T_1$ obtained by 1, using $\langle V_{zz}^2 \rangle$ and τ_c computed with the PIM and quadrupole moments from.⁵⁹ The results agree very well with the experimental values,^{4,57} to within a factor of 2.3 in the worse case (Na⁺) and only 10% for K⁺. The agreement for Mg²⁺ (within 25%) is remarkable, as the only previous estimate from MD simulations would differ by a factor of 20.²³ This confirms the

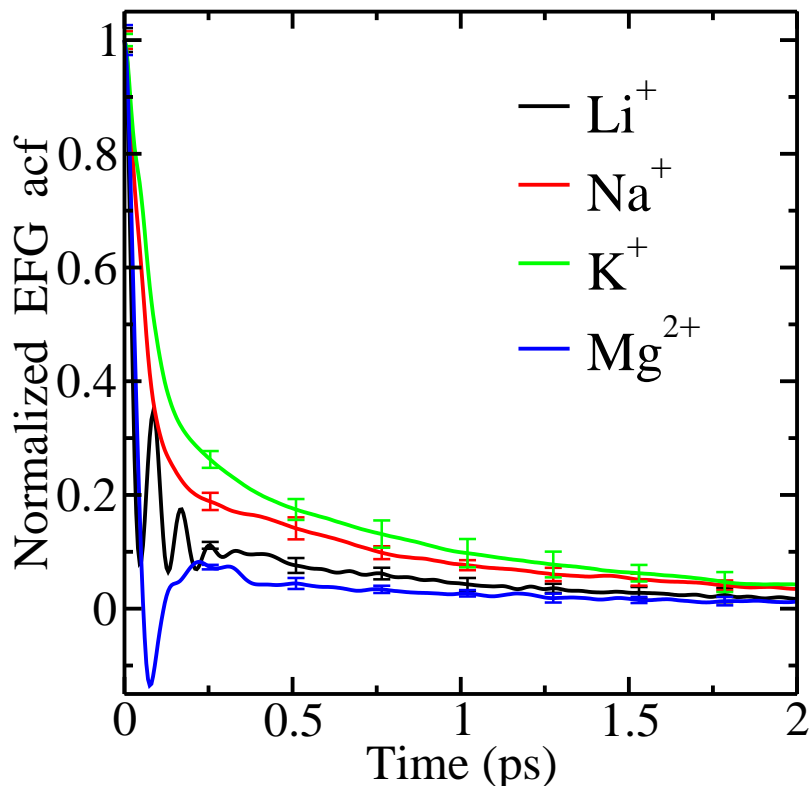


Figure 2: Electric Field Gradient auto-correlation function, normalized by their initial value $\langle V_{zz}^2 \rangle$, for Li^+ , Na^+ , K^+ and Mg^{2+} .

ability of the PIM force field of Ref. 42 to describe this multivalent ion and its solvation shell. Note that for ${}^7\text{Li}^+$ dipole-dipole relaxation may contribute to the measured relaxation rate: The larger MD value should therefore be an overestimate of the quadrupolar contribution considered here. The relative weight of the dipole-dipole mechanism could be investigated in a future work.²⁵

4 Conclusion

In conclusion, combining classical MD with an accurate force field parametrized on ab initio simulation with the prior determination of Sternheimer anti-shielding factors by comparing the classical and ab initio EFG, provides an efficient route to NMR quadrupolar relaxation

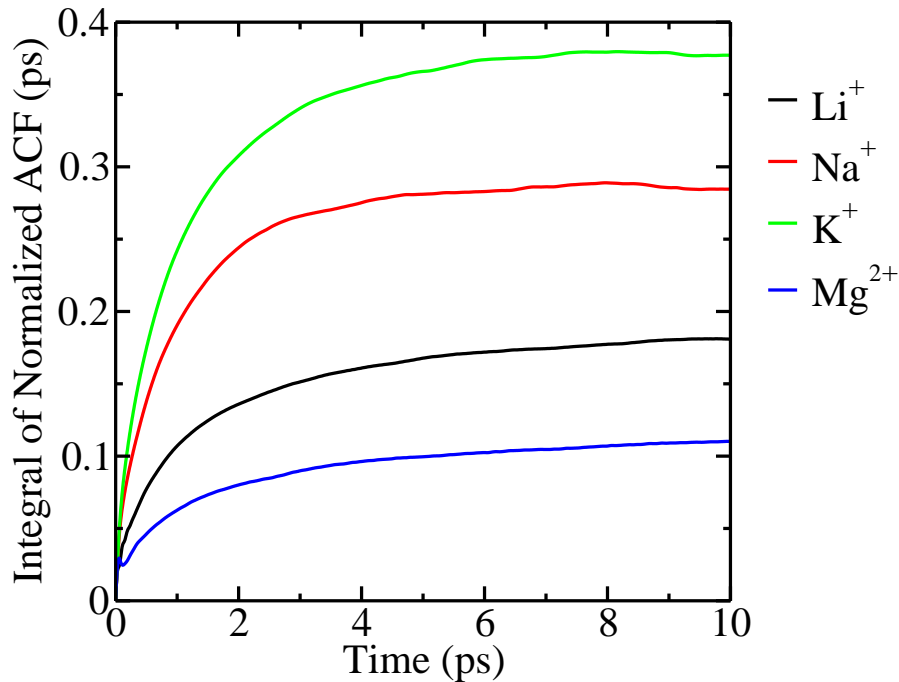


Figure 3: Integral of the normalized Electric Field Gradient auto-correlation function, normalized by their initial value $\langle V_{zz}^2 \rangle$. The plateau gives the correlation time τ_c .

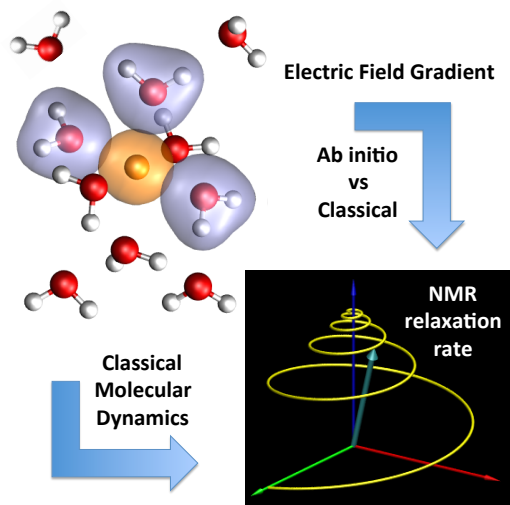
rates. This allows computing both $\langle V_{zz}^2 \rangle$ and τ_c , in contrast with more computationally demanding approaches based on AIMD, whose cost prevents the required sampling of trajectories. The advantage of present strategy would be even more evident for systems where the EFG evolves over longer time scales than the present case of aqueous ions at infinite dilution. We are currently applying it to the case of silicate glasses where a full AIMD determination is currently out of reach. Note that the contribution of dipole-dipole relaxation can also be determined from the classical trajectories.^{24,25}

Just as the accuracy of the PIM force field, the determination of the Sternheimer anti-shielding factor is limited by the quality of the AI calculations. More importantly, comparing the classical and AI EFG on the same configurations allows to assess the validity of the Sternheimer approximation. In case where it cannot be applied (it is expected to be less satisfactory for anions, for example⁴⁰), it would be possible to analyze the configurations of the classical MD including higher order terms,^{37–39} or even to parametrize a hypersurface

based on the local configuration around the nucleus.^{33,34} The accurate computation of the EFG acf on the molecular scale, or in the case of anisotropic environment of the nuclear quadrupole coupling constant, could then be coupled to coarse-grained simulations in the framework of a multiscale approach for complex materials.⁶⁰

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