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Fast field cycling NMR relaxometry – Revealing molecular motion across different time scales

Molecular motion governs virtually every physicochemical process. For example, the diffusion of ions determines the performance of batteries and supercapacitors, while molecular reorientation controls dielectric and spectroscopic properties. Furthermore, the interplay between translational and rotational motion influences self-assembly and transport properties in complex liquids. Therefore, understanding these motions over a broad range of timescales is one of the central objectives of physical chemistry. However, experimental techniques typically only provide partial insights into molecular dynamics. For example, neutron scattering is sensitive to very fast motions, while pulsed-field-gradient NMR directly measures translational diffusion. Conventional high-field NMR relaxation experiments provide valuable information on molecular reorientation, but are restricted to a single Larmor frequency. Fast field cycling (FFC) NMR relaxometry overcomes this limitation by measuring spin-lattice relaxation rates $R_1(\omega) = 1/T_1(\omega)$ over a broad range of magnetic fields, typically corresponding to proton Larmor frequencies ranging from a few kilohertz to several tens of megahertz. Rather than providing a single relaxation time, the experiment yields an entire nuclear magnetic relaxation dispersion (NMRD) profile (Fig. 1). Here, high magnetic fields predominantly detect rapid local motions, such as molecular rotations, while lower fields increasingly detect slower processes, particularly translational diffusion. Consequently, one single experiment can be used to investigate rotational and translational dynamics simultaneously.

Over the last few decades, FFC NMR relaxometry has evolved into a versatile technique for investigating liquids and soft matter. Its applications range from polymers and porous media to food science, biological tissues, hydrogels and electrolytes [1, 2]. Among these diverse applications, ionic liquids (ILs) occupy a particularly interesting position. Their broad liquid temperature range, high viscosities and enormous structural diversity make them ideal model systems for studying molecular dynamics. Understanding their transport properties is also of considerable technological relevance, as ILs are being investigated as designer solvents, electrolytes, and functional materials for electrochemical energy storage [3].

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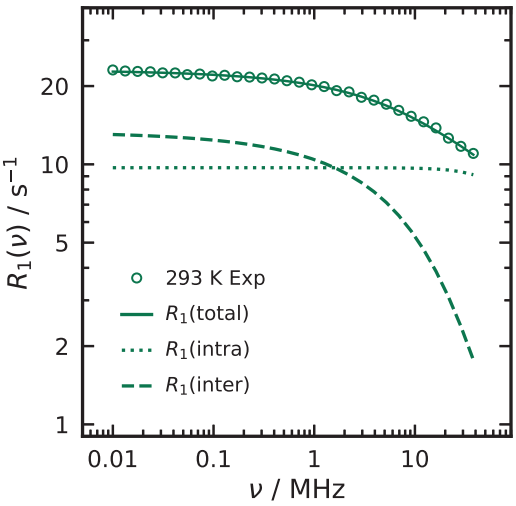

Fig. 1: Typical ^{1}H NMRD profile for the ionic liquid [TEA][OMs-d_3] illustrating the low-frequency region dominated by translational dynamics and high-frequency region dominated by rotational dynamics.

In recent years, our group has mainly focused on developing experimental strategies and analysis procedures that enable the reliable determination of rotational correlation times, translational diffusion coefficients and increasingly complex molecular motions. Using ionic liquids as model systems while complementing the analysis with molecular dynamics (MD) simulations, these developments establish a framework that can be transferred to many other classes of materials.

Although measuring NMRD profiles is experimentally straightforward, extracting quantitative molecular information is considerably more challenging. The measured frequency-dependent total relaxation rate represents the sum of several different relaxation pathways mostly originating from fluctuating dipole-dipole interactions between nuclear spins. These fluctuations are caused by different types of molecular motion occurring simultaneously. Rotational motion mainly contributes to the intramolecular relaxation, whereas translational diffusion dominates the intermolecular contribution, particularly at low frequencies. In real systems, however, these contributions are superimposed and cannot be observed separately. One of the greatest challenges in obtaining reliable dynamical information is therefore dissecting the total relaxation rates into their individual contributions in a reasonable way.

$$R_{1,\mathrm{total}}(\omega) = R_{1,\mathrm{intra}}(\omega) + R_{1,\mathrm{inter}}(\omega)$$

Reliable interpretation therefore requires physically meaningful relaxation models. For simple molecular liquids, classical models such as the Bloembergen-Purcell-Pound (BPP) approach often provide satisfactory descriptions [4]. ILs, however, are considerably more complex. Their ions exhibit different sizes and shapes, anisotropic molecular geometries as well as partially internal rotations. Consequently, extracting quantitative dynamic parameters from experimental relaxation curves requires models that go beyond this classical isotropic approximation. Systematically studying and validating more complex models with respect to ILs has become one of the central objectives of our recent research.

Extracting Dynamical Information from Measured NMRD Profiles for Ionic Liquids as Model Systems

One of the greatest advantages of ILs is that their molecular dynamics can be systematically tuned through chemical design. Varying the cation, anion and/or corresponding alkyl chain lengths significantly changes the ion shapes, viscosities and diffusion coefficients. This makes ILs ideal model systems for testing relaxation models. Our first studies focused on separating rotational and translational dynamics from experimental NMRD profiles. While rotational motions mainly determine the high-frequency part of the relaxation dispersion, translational diffusion becomes increasingly dominant at low frequencies. By exploiting this behaviour, reliable self-diffusion coefficients can be extracted directly from relaxation experiments by plotting the total relaxation rates versus the square root of the resonance frequency (Fig. 2), providing information that is complementary to pulsed-field-gradient NMR measurements.

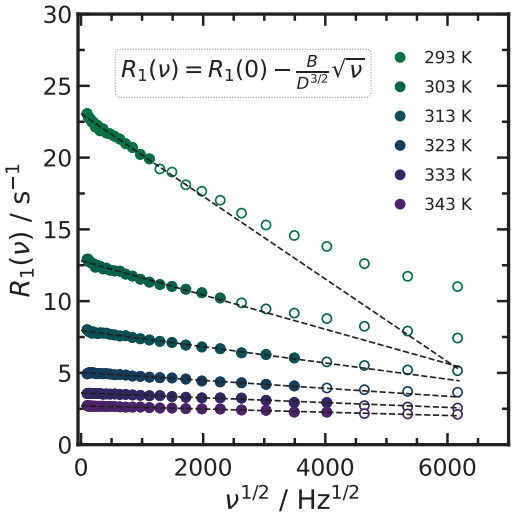

Fig. 2: Total ^{1}H relaxation rates for the ionic liquid [TEA][OMs-d$_3$] as a function of $\sqrt{\nu}$ for temperatures between 293 K and 343 K measured in 10 K steps. The slope of the linear parts based on the filled symbols at low frequencies yield the temperature-dependent self-diffusion coefficients.

As our work progressed, it became evident that some simplifying assumptions commonly employed in the literature are not universally valid. One important example concerns intermolecular heteronuclear dipolar interactions. ILs frequently contain different NMR-active nuclei on cations and anions, for example quite often ^{1}H on cations and ^{19}F on anions. In many previous analyses, the corresponding ^{1}H-^{19}F heteronuclear relaxation contributions had been neglected because they were assumed to be very small. Using selectively deuterated ILs together with complementary ^{1}H and ^{19}F FFC NMR relaxometry experiments, we demonstrated that these heteronuclear interactions can indeed substantially influence the experimentally observed relaxation rates. Neglecting them leads to systematic errors in the extracted cation or anion self-diffusion coefficients. These errors are even larger when analysing the ^{19}F relaxation rates due to the neglect of the corresponding ^{1}H at higher spin densities. Accounting explicitly for these heteronuclear interactions considerably improves the quantitative reliability of the analysis [5].

Selective isotope substitution proved particularly effective also in further studies, especially for ILs containing protons in both the cation and anion. By suppressing certain intermolecular dipolar relaxation pathways through selective deuteration of either the cation or the anion, the dynamics of both ions could be investigated separately from each other, even in systems where conventional FFC NMR relaxometry would only have yielded an averaged relaxation behaviour across all ions. Finally, it was even possible to recalculate the intermolecular contributions and therefore reconstruct the total relaxation rate for those systems. This approach opens up new avenues for investigating fluorine-free ILs and other multicomponent systems with overlapping relaxation pathways [6].

Another important outcome of our recent work concerns the description of molecular reorientation itself. Many relaxation models implicitly assume isotropic rotational diffusion, meaning that molecules rotate equally fast in all spatial directions. While this approximation is adequate for nearly spherical molecules

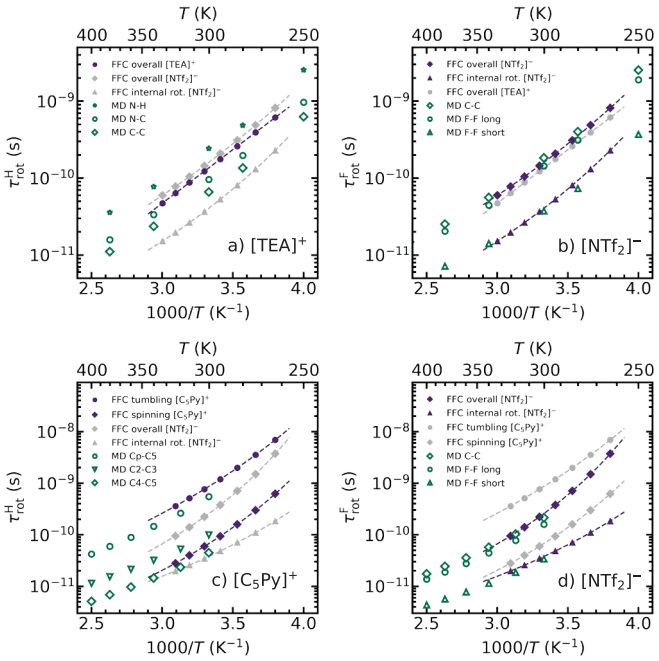

Fig. 3: Temperature-dependent rotational correlation times of ^{1}H carrying cations (a) and (c) and ^{19}F carrying anions (b) and (d) for the ionic liquids [TEA][NTf$_2$] (a) and (b) and [C$_5$Py][NTf$_2$] (c) and (d). Values from FFC NMR relaxometry are shown as purple filled symbols. Values from MD simulations are shown as green open symbols. Subfigures with cation data include anion data as gray symbols and vice versa. Reproduced from Ref. [7] with permission from the Royal Society of Chemistry.

and ions, it becomes increasingly inaccurate for elongated or structurally flexible identities. Here, using ILs containing either compact nearly spherical or elongated cations, we demonstrated that molecular shape strongly affects the observed relaxation behaviour. Whereas the former kind of ions can still be described reasonably well by classical isotropic models, the latter requires explicit consideration of anisotropic rotational diffusion (Fig. 3a and 3c). Moreover, many well-established anions exhibit rapid internal rotations of CF_3 groups in addition to the overall tumbling of the entire ion. These internal motions contribute measurably to the relaxation behaviour and therefore need to be incorporated into quantitative analyses (Fig. 3b and 3d) [7].

Combining FFC NMR Experiments and Molecular Dynamics Simulations

Although FFC NMR relaxometry is fundamentally an experimental technique, MD simulations have become an increasingly valuable companion. Rather than replacing experiments, simulations help to interpret them. They allow rotational correlation functions, intermolecular distances and diffusion processes to be analysed on the molecular level, thereby providing independent validation of experimentally derived models. One major challenge in directly computing spin-lattice relaxation rates from MD simulations concerns the intermolecular contribution, which is governed by translational diffusion over very long timescales. Recent methodological developments combining atomistic MD simulations with the analytical Hwang-Freed description of long-time diffusion have substantially improved the reliability of frequency-dependent relaxation calculations. Initial validation on liquid water provided the theoretical foundation [8, 9], while subsequent applications to the partially deuterated IL $[C_5Py\text{-}d_{16}][NTf_2]$ demonstrated that experimentally measured NMRD profiles can now be reproduced with remarkable accuracy [10]. The close agreement between experiment and simulation (Fig. 4) provides confidence that the extracted rotational correlation times and self-diffusion coefficients indeed reflect the underlying molecular dynamics.

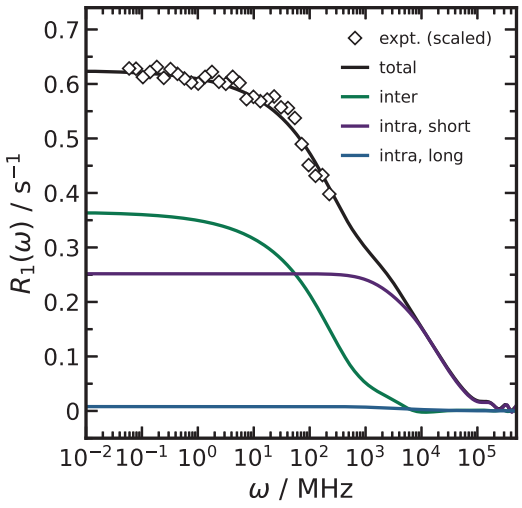

Fig. 4: Inter- and intramolecular contributions to the ^{19}F NMR relaxation rate $R_1(\omega)$ as well as their sum of fully deuterated $[C_5Py\text{-}d_{16}][NTf_2]$ at 323 K. The open diamonds represent experimental FFC NMR relaxation data. The shown experimental data were scaled by a factor of 0.445.

Next, we would like to calculate the relaxation rates for fully protonated ILs, taking into account all intermolecular heteronuclear relaxation contributions.

Outlook

Fast field cycling NMR relaxometry has developed from a specialized experimental technique into a versatile tool for investigating molecular dynamics across an exceptionally broad range of time scales. One of our future directions is the development of a more user-friendly version of our open-source software for quantitative analysis of NMRD data. Our group is currently preparing a comprehensive analysis package that will be made freely available via GitHub, facilitating different evaluation procedures and lowering the entry barrier for new users of FFC relaxometry. Another exciting perspective is the increasingly close integration of experiments and MD simulations. Rather than relying solely on empirical relaxation models, future analyses will benefit from simulation-assisted interpretations that connect experimentally observed relaxation directly to molecular structure and dynamics. Ionic liquids have proven to be ideal model systems for these developments, but the resulting concepts extend far beyond this fascinating class of materials. As instrumentation, theory and computational methods continue to converge, FFC NMR relaxometry is likely to become an increasingly important tool for understanding molecular dynamics in many different complex materials.

Finally, the growing international FFC community continues to drive innovation and interdisciplinary applications. In this context, we are particularly pleased that the University of Rostock will host the **15th International Conference on Fast Field Cycling NMR Relaxometry in 2028**. This will provide an opportunity to bring together researchers from physics, chemistry, materials science and life sciences to discuss future research questions, applications and potential connections to other disciplines.

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Anne Strate studied Chemistry at the University of Rostock. She received her PhD in 2017 for her work on cationic cluster formation in ionic liquids, which she mainly investigated using infrared spectroscopy. In 2017, she had a research stay at Yale University (USA) in Mark Johnson's group applying CIVP spectroscopy on IL clusters in the gas phase. Since 2019, Anne Strate has been a Research Associate at the University of Rostock, responsible for FFC NMR Relaxometry. Over the past three years, she has led an independent research project on the dynamics of ILs funded by the German Research Foundation (DFG).