

Ion-specific Translational and Rotational Motions in Isotopic Substituted ILs by Means of NMR Relaxometry

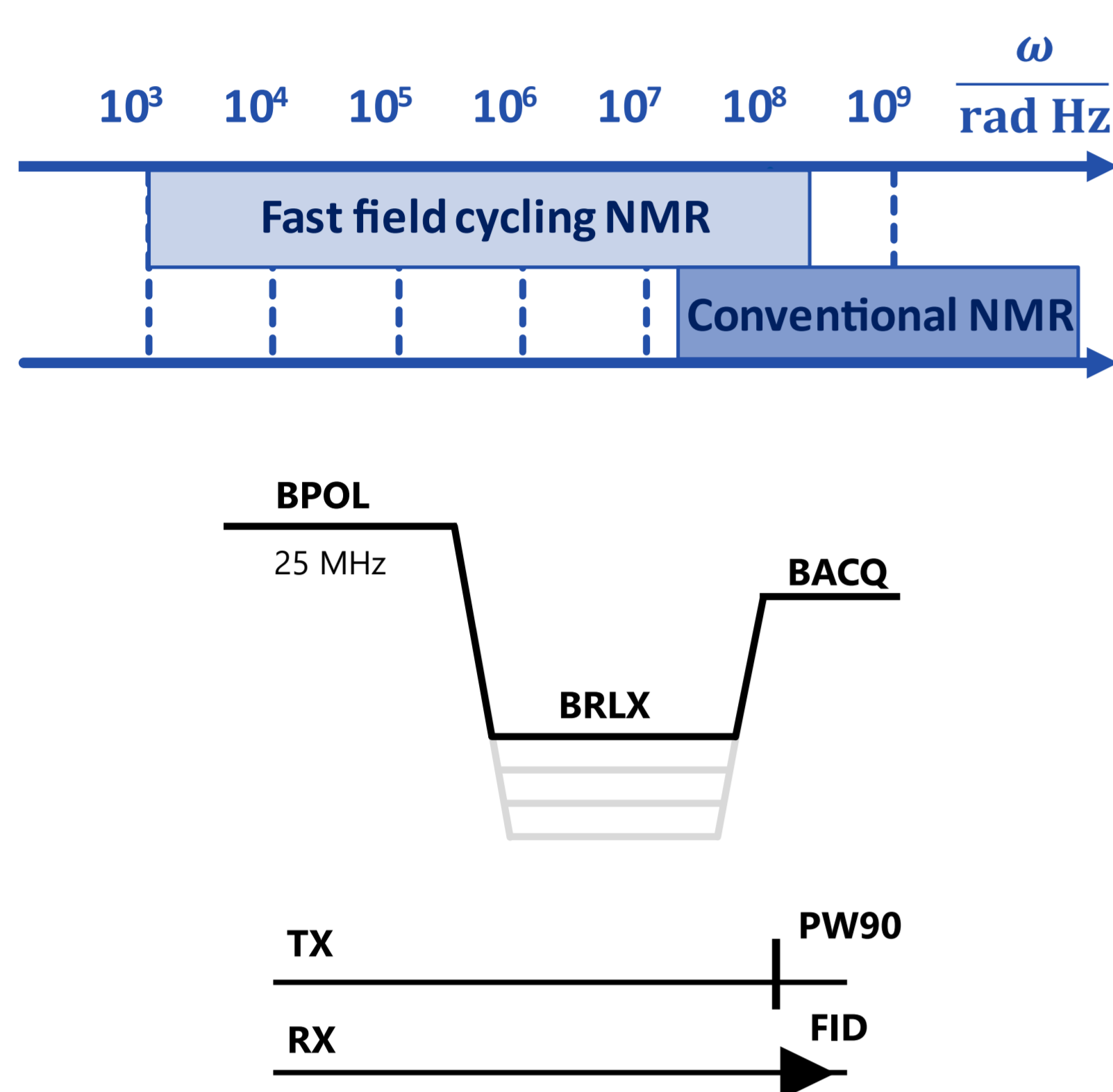


Overview

Fast field cycling (FFC) NMR relaxometry is a powerful method to probe the molecular dynamics of ILs, as it allows the determination of both rotational correlation times and self-diffusion coefficients from frequency-dependent spin-lattice relaxation data. However, the limited spectral resolution of FFC NMR relaxometry at low fields poses a real challenge. In many ILs, cation and anion dynamics can still be separated because only one ionic species contains protons, while the other often carries fluorine atoms. In such cases, ¹H and ¹⁹F relaxation measurements provide complementary information. However, this approach is no longer possible for fluorine-free ILs, such as [TEA][OMs],

where both, cation and anion, contain protons. Here, the measured spin-lattice relaxation rates provide an average of all the intra- and intermolecular contributions from protons, which makes it impossible to analyze ions separately. Still, this IL is particularly interesting because of its strong hydrogen bonding ability and high viscosity. We address this challenge by employing selective isotopic substitution through partial deuteration of either the cation or the anion. This strategy suppresses dipolar cation–anion contributions and enables the extraction of ion-specific relaxation dynamics. Finally, we are able to reconstruct the relaxation rate of the fully protonated [TEA][OMs].^[1]

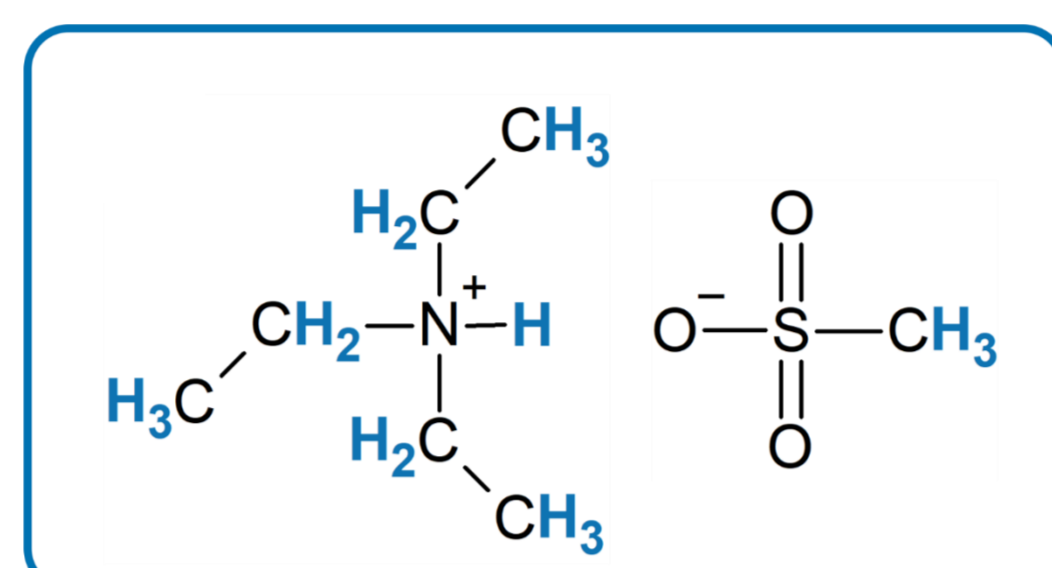
FFC NMR Relaxometry



- ◆ FFC NMR operates at comparatively **low magnetic fields**
- ◆ Variable magnetic fields (BRLX) enable **frequency-dependent measurements**

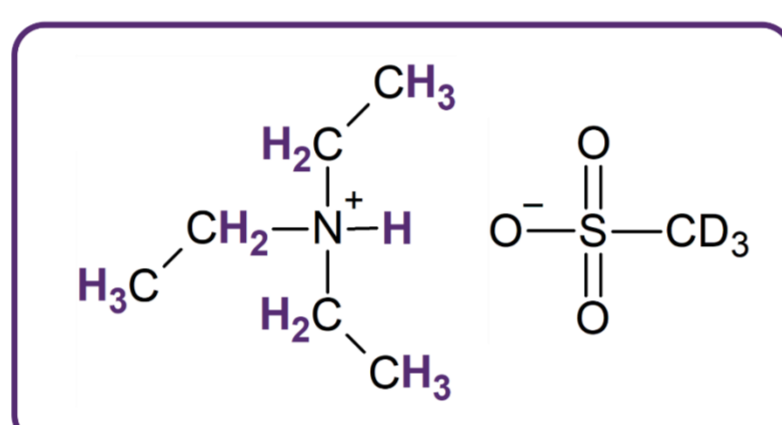
System & Challenges

Triethylammonium methylsulfonate
[TEA][OMs]



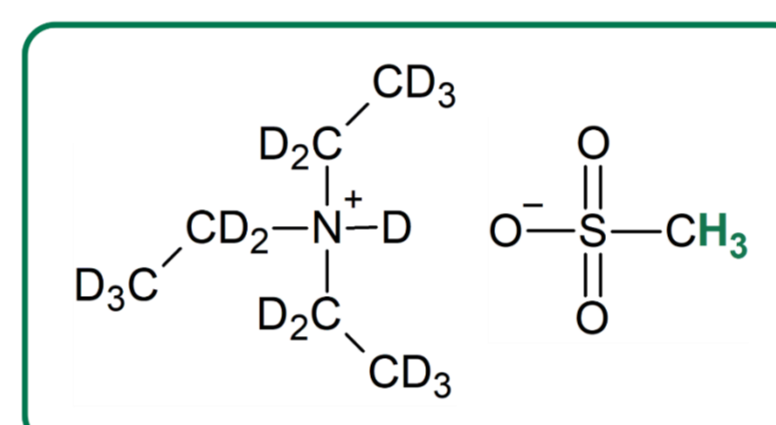
- ◆ **No resolution** between proton signals!
- ◆ Solution: **Deuteration** of anion or cation

[TEA][OMs]-d₃



cation dynamics

[TEA][OMs]-d₁₆



anion dynamics

Relaxation Theory

- ◆ FFC yields **NMR dispersion** (NMRD) profiles
- ◆ Measured relaxation rate (R_1) is **sum of inter- and intramolecular** relaxation processes

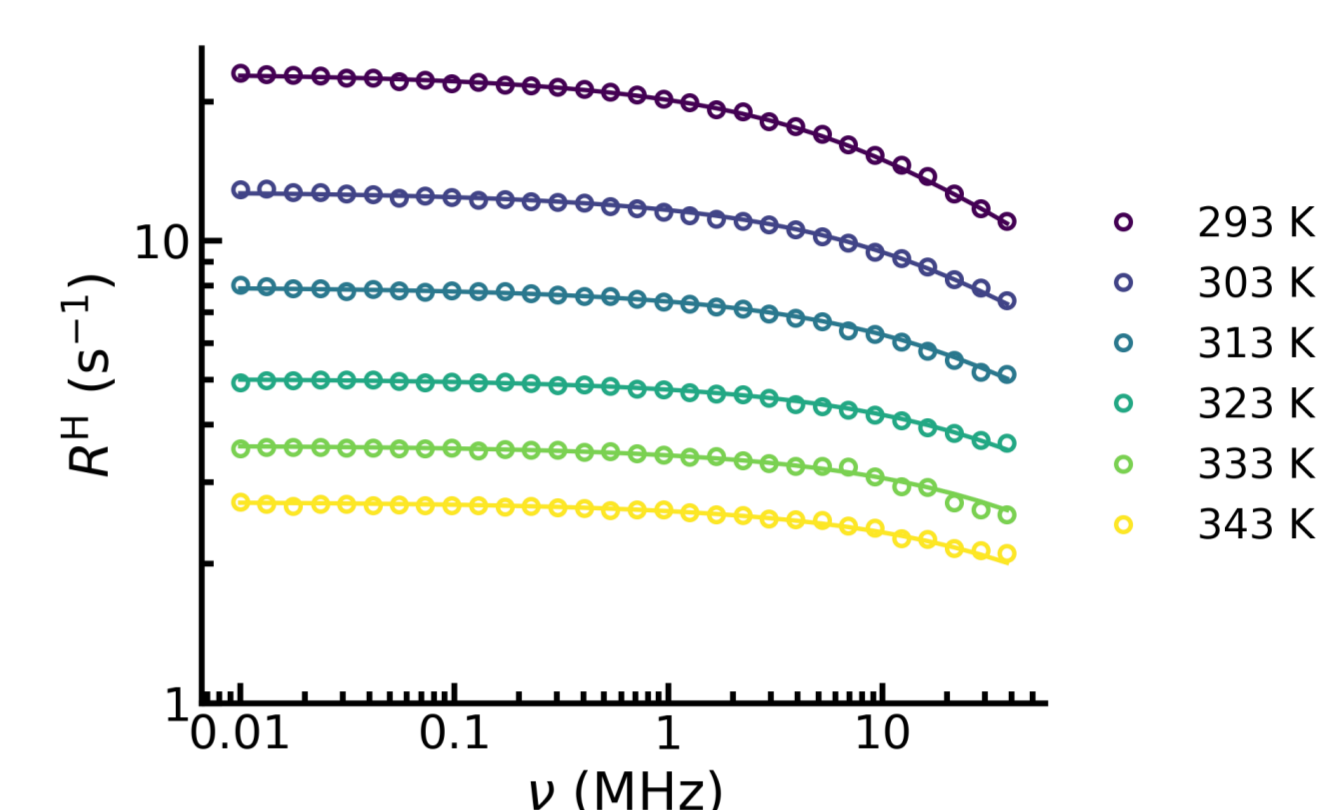


Fig. 1: Temperature-dependent NMRD profiles for [TEA][OMs]-d₃ plotted as circles. The solid lines correspond to the model fits.

$$R_1(\omega) = \frac{1}{T_1(\omega)} = R_1^{\text{inter}} + R_1^{\text{intra}}$$

$$R_1^{\text{inter/intra}} = C \cdot [J(\omega, \tau) + 4J(2\omega, \tau)]$$

Ion-specific Rotational and Translational Dynamics

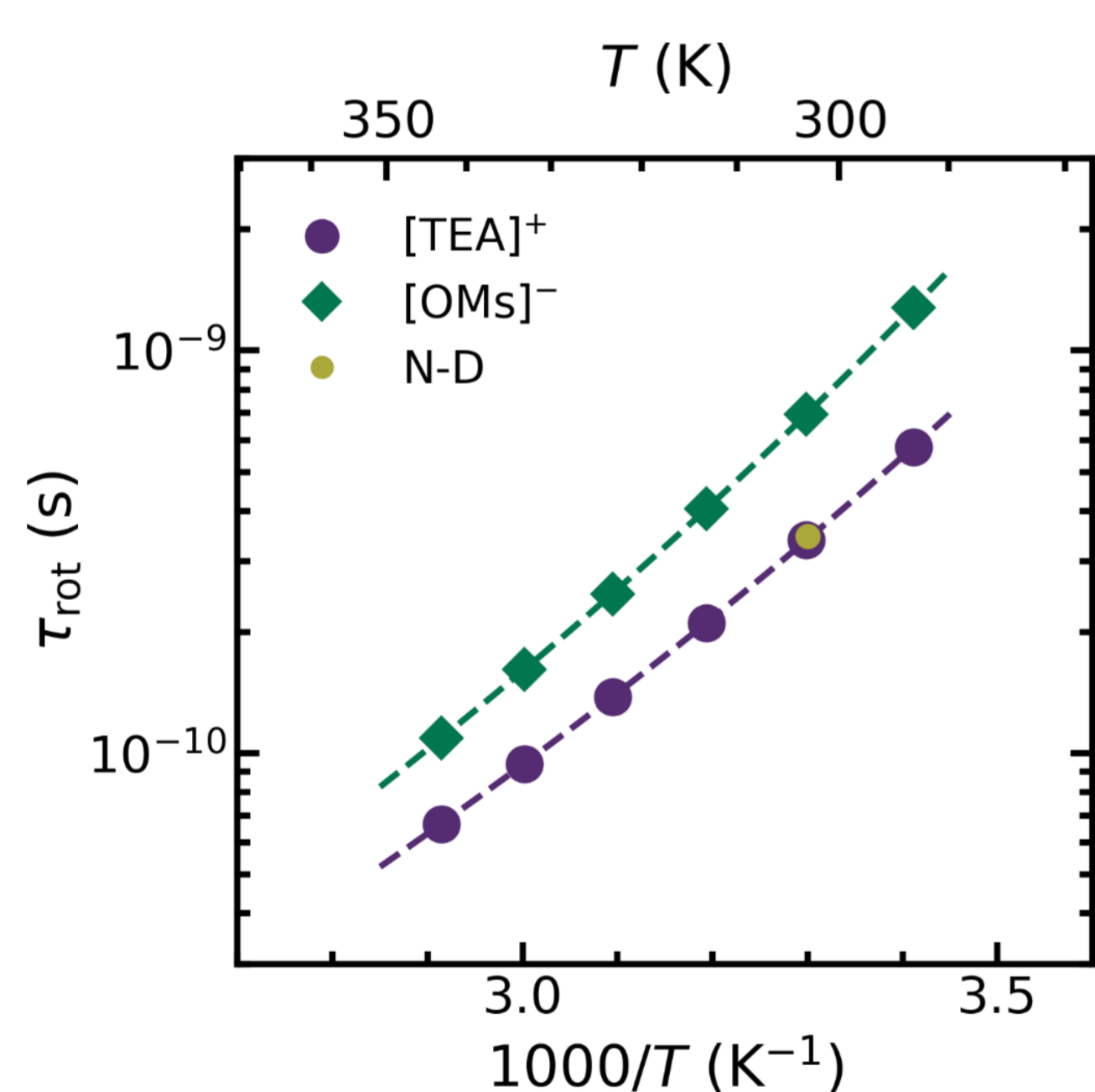


Fig. 2: Temperature-dependent rotational correlation times τ_{rot} for the [TEA]⁺ cation (purple) in [TEA][OMs]-d₃ and [OMs]⁻ anion (green) in [TEA][OMs]-d₁₆. Both data sets follow a Vogel-Fulcher-Tammann behavior (dashed). The data matches the reorientational correlation time obtained from deuterium quadrupole relaxation time measurements (yellow).^[2]

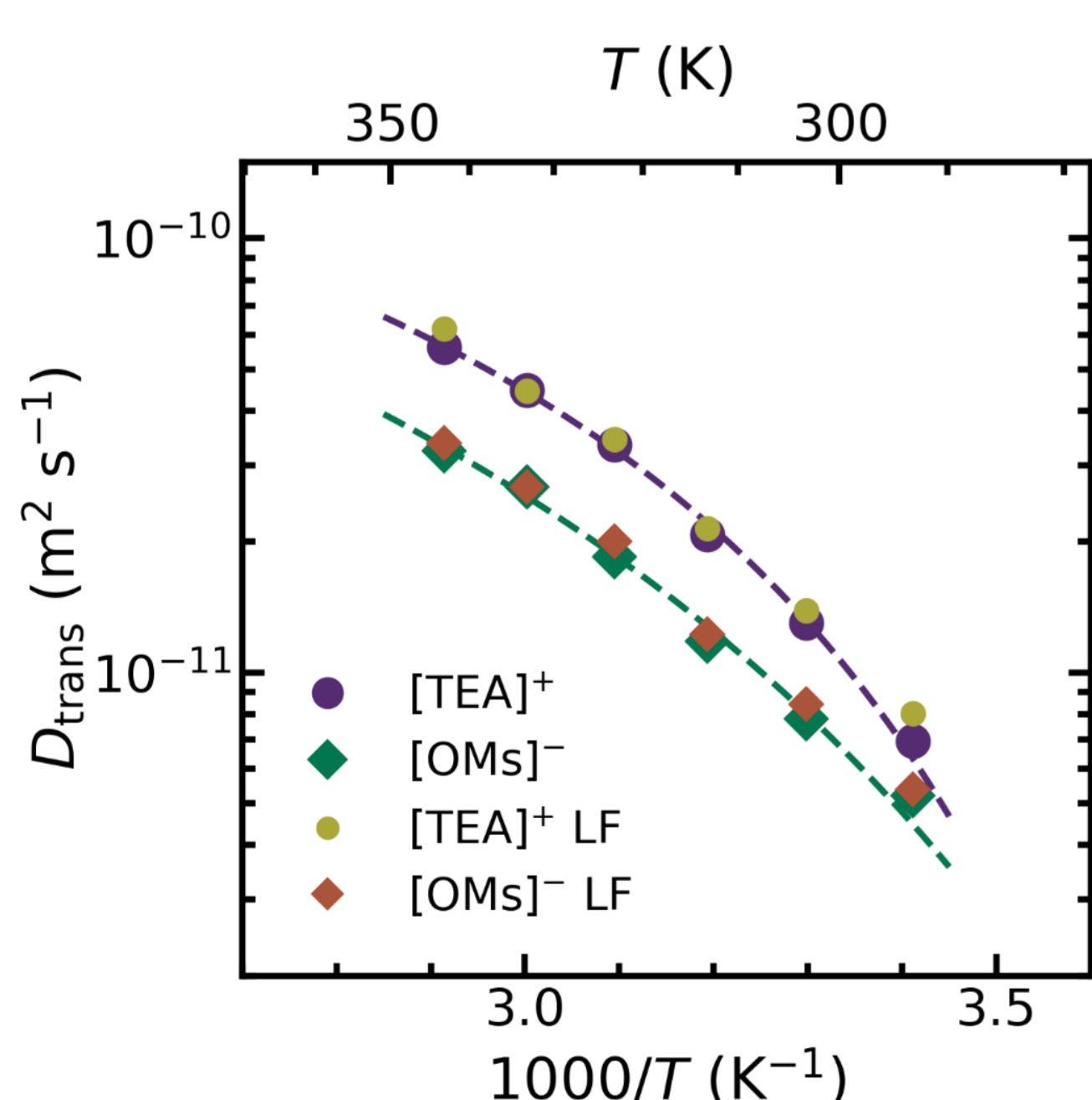


Fig. 3: Temperature-dependent self-diffusion coefficients D_H for the [TEA]⁺ cation (purple) and [OMs]⁻ anion (green). Self-diffusion coefficients are calculated from translational correlation times τ_{trans} and from the slope of the relaxation rates at low frequencies (LF) for both ions.^[3]

$$R_1(\omega) = R(0) - \frac{B}{D^{3/2}} \cdot \sqrt{\omega}$$

Reconstructing R_1 for [TEA][OMs]-d₀

- ◆ Inter **cation–anion interaction** need to be considered in fully protonated [TEA][OMs] → estimated from ion-specific dynamics
- ◆ Overall measured average relaxation rate is sum of **weighted** contributions **from cation and anion** with weighting factors W

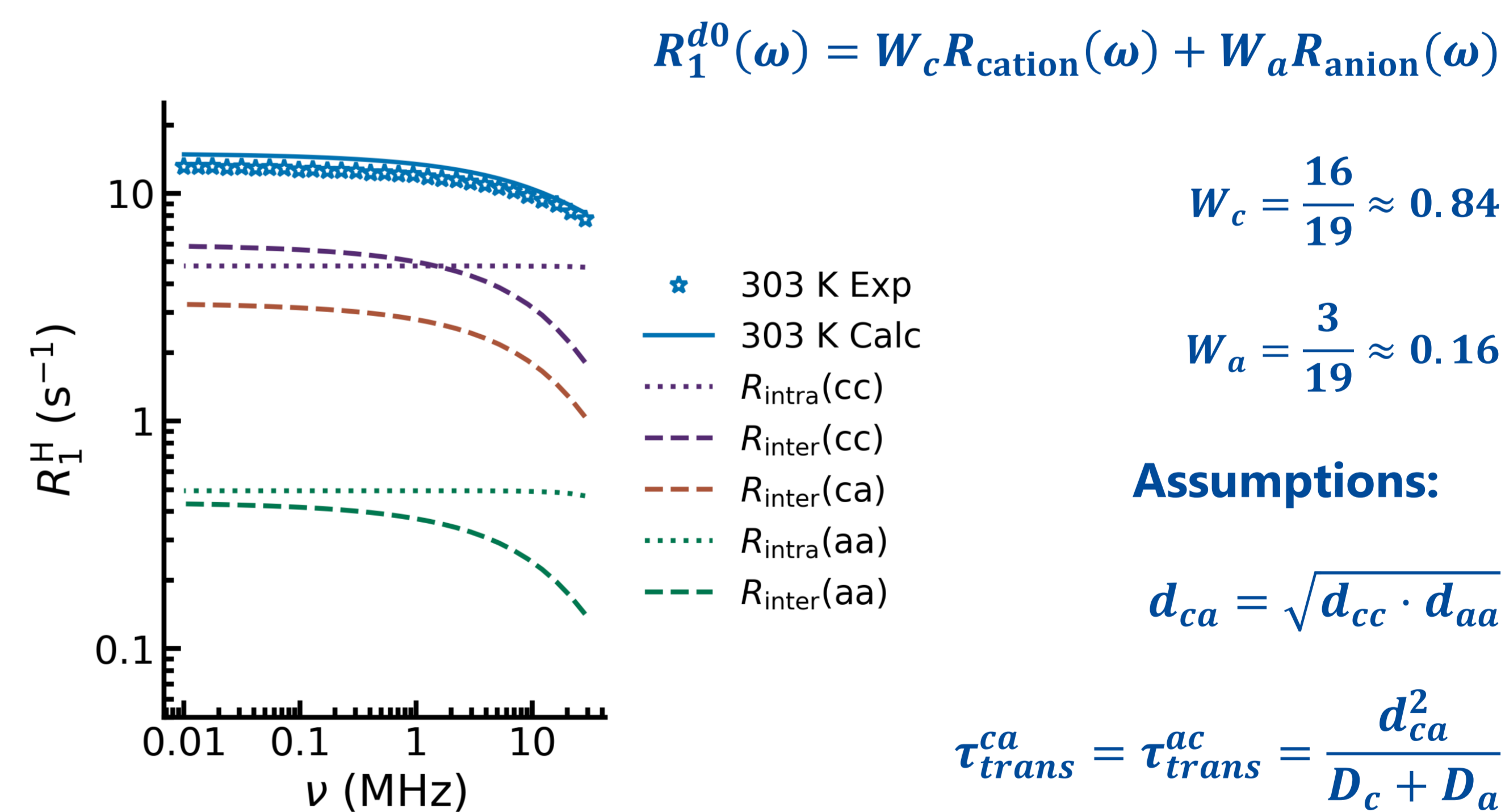


Fig. 4: Comparison of experimentally measured relaxation rates of fully protonated [TEA][OMs] (blue stars) and reconstructed relaxation rates (blue, solid line) calculated from the dynamics obtained for the partially deuterated ILs, including the weighted partial relaxation contributions stemming from cation (violet) and anion (green) considering the inter- (dashed) and intramolecular (dotted) interactions. The calculated interaction between cation and anion is shown in orange.^[1]

$$R_1^{d_0}(\omega) = W_c R_{\text{cation}}(\omega) + W_a R_{\text{anion}}(\omega)$$

$$W_c = \frac{16}{19} \approx 0.84$$

$$W_a = \frac{3}{19} \approx 0.16$$

Assumptions:

$$d_{ca} = \sqrt{d_{cc} \cdot d_{aa}}$$

$$\tau_{\text{trans}}^{ca} = \tau_{\text{trans}}^{ac} = \frac{d_{ca}^2}{D_c + D_a}$$

References

- [1] L. Kruse, A. M. C. Tony, A. Strate, D. Rauber, R. Ludwig, D. Paschek, A. Strate, *Magn. Reson. Chem.* **2025**, submitted
- [2] M. Strauch, A.-M. Bónsa, B. Golub, V. Overbeck, D. Michalik, D. Paschek, R. Ludwig, *Phys. Chem. Chem. Phys.* **2016**, 18, 17788.
- [3] D. Kruk, R. Meier, E. A. Rössler, *Phys. Rev. E* **2012**, 85, 020201.

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