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Insights into the translational and rotational dynamics of cations and anions in Protic Ionic Liquids by means of NMR Fast-Field-Cycling Relaxometry

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-Supporting Information-

Table S1 Rotational correlation times τ_R and self-diffusion coefficients D_T of cations (H) and anions (F) for a) TEAOTf and b) TEANTf$_2$.

a) TEAOTf

T / K	τ_R^H / s	τ_R^F / s	D_T^H / (m²/s)	D_T^F / (m²/s)
273	6.97E-10	2.28E-10	1.18E-11	8.88E-12
283	4.64E-10	1.86E-10	1.88E-11	1.14E-11
293	3.18E-10	1.53E-10	3.09E-11	2.08E-11
303	2.23E-10	1.27E-10	4.98E-11	3.23E-11
313	1.60E-10	1.08E-10	8.19E-11	5.54E-11
323	1.18E-10	9.18E-11	1.12E-10	7.52E-11
333	8.78E-11	7.90E-11	1.14E-10	1.17E-10

b) TEANTf$_2$

T / K	τ_R^H / s	τ_R^F / s	D_T^H / (m²/s)	D_T^F / (m²/s)
263	1.11E-9	1.95E-9	5.80E-12	3.66E-12
273	6.77E-10	1.15E-9	1.45E-11	9.18E-12
283	4.27E-10	7.02E-10	2.58E-11	1.91E-11
293	2.78E-10	4.44E-10	4.82E-11	3.69E-11
303	1.86E-10	2.90E-10	7.10E-11	5.39E-11
313	1.28E-10	1.94E-10	9.36E-11	6.98E-11
323	8.98E-11	1.33E-10	1.07E-10	7.60E-11
333	6.45E-11	9.37E-11	1.26E-10	1.11E-10

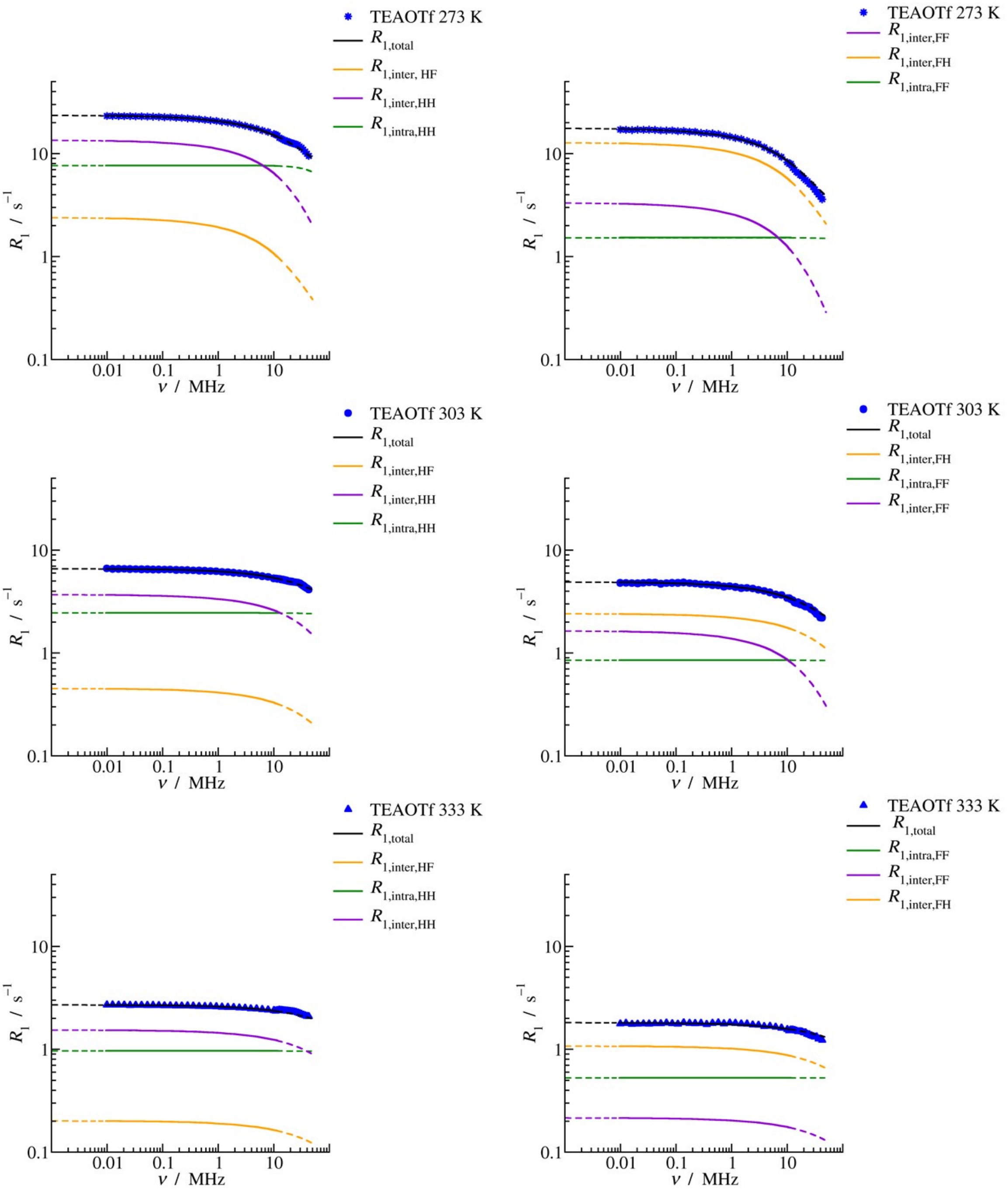

Fig. S1 Splitting of R_1^{H} (left) and R_1^{F} (right) into inter- and intramolecular contributions at 273 K (top), 303 K (middle) and 333 K (bottom) for TEAOTf.

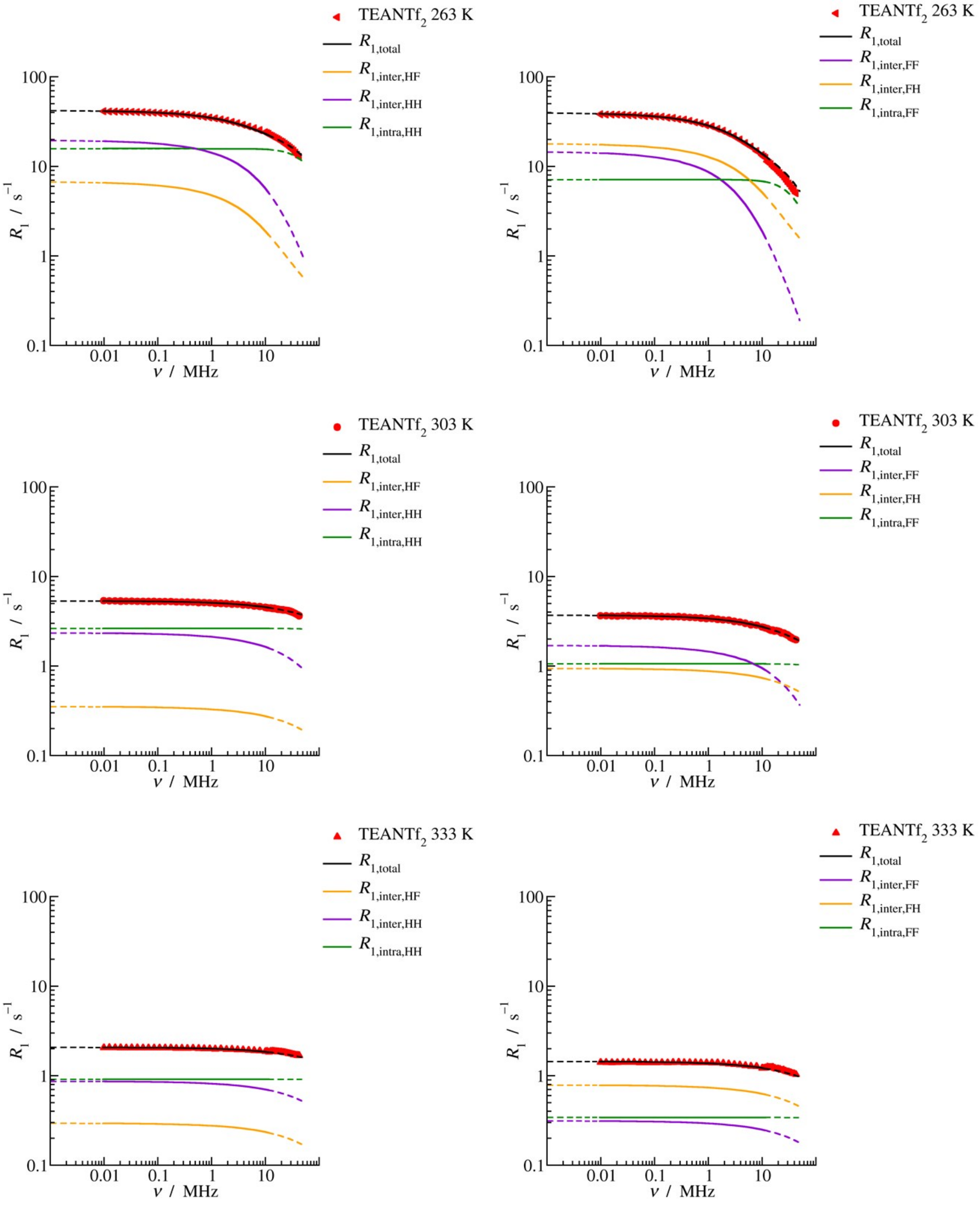

Fig. S2 Splitting of R_1^{H} (left) and R_1^{F} (right) into inter- and intramolecular contributions at 263 K (top), 303 K (middle) and 333 K (bottom) for TEANTf$_2$.

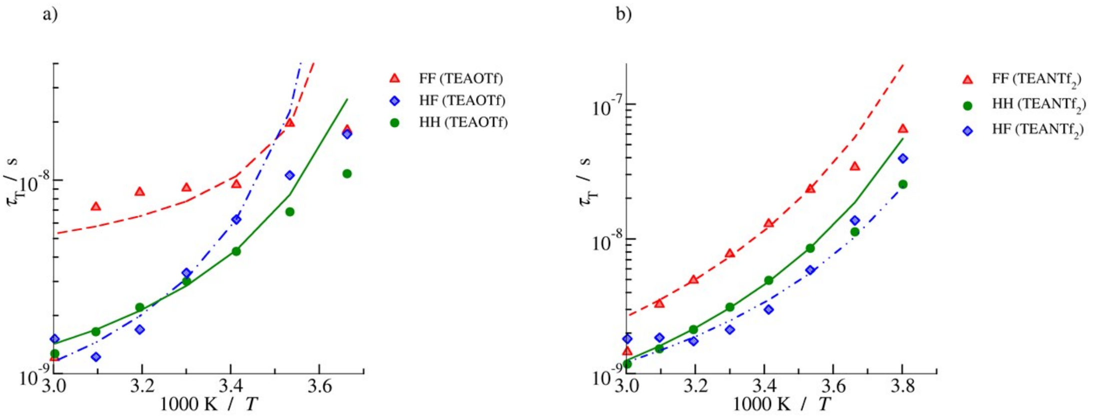

Fig. S3 Translational correlation times τ_{T} indicating the fluctuations of dipolar interactions between protons belonging to different cations $\tau_{\mathrm{T}}^{\mathrm{HH}}$ (circles), between fluorines of different anions $\tau_{\mathrm{T}}^{\mathrm{FF}}$ (triangles) and between protons and fluorines $\tau_{\mathrm{T}}^{\mathrm{HF}}$ = $\tau_{\mathrm{T}}^{\mathrm{FH}}$ (diamonds) for a) TEAOTf and b) TEANTf$_2$.

Table 2 Vogel-Fulcher-Tammann (VFT) fit parameters of self-diffusion coefficients D_T and translational correlation times τ_{T} are displayed. Note that regarding the fits of τ_{T} the two lowest temperatures (in the supercooled region) were not fitted and the T_0 values were fixed at the T_0 values of the corresponding D_T.

		$D_{T,0}$ / (m^{2}s^{-1})	$\tau_{T,0}$ / s	κ	T_0 / K
TEAOTf	D_T^H	4.96E-10		0.50	246.5
	D_T^F	3.83E-10		0.35	262.9
	τ_T^{HH}		3.85E-10	0.46	246.0
	τ_T^{FF}		3.16E-9	0.14	263.0
	τ_T^{HF}		2.68E-10	0.42	258.3
TEANTf$_2$	D_T^H	9.37E-10		1.13	212.9
	D_T^F	7.92E-10		1.15	214.4
	τ_T^{HH}		8.88E-11	1.47	214.0
	τ_T^{FF}		1.33E-10	1.67	214.0
	τ_T^{HF}		1.51E-10	1.16	214.0

$$D_T = D_{T,0}\exp\left(-\frac{\kappa T_0}{T - T_0}\right)$$

$$\tau_T = \tau_{T,0}\exp\left(\frac{\kappa T_0}{T - T_0}\right)$$

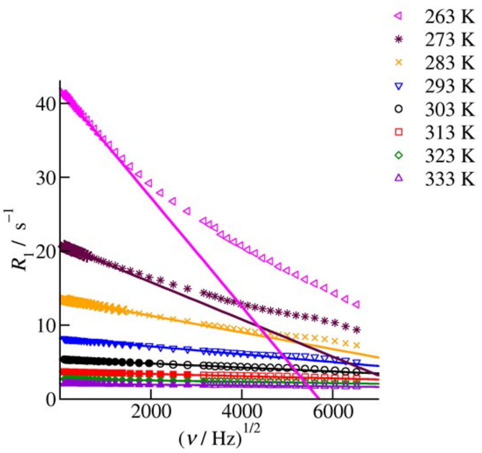

Fig. S4 Relaxation rates R_1^{H} as a function of resonance frequency $\nu^{1/2} = (\omega/2\pi)^{1/2}$ for TEANTf$_2$. At low frequencies, the slopes of the linear fits enable the determination of D_{T} directly from the relaxation dispersion curves according to a universal dispersion power law.

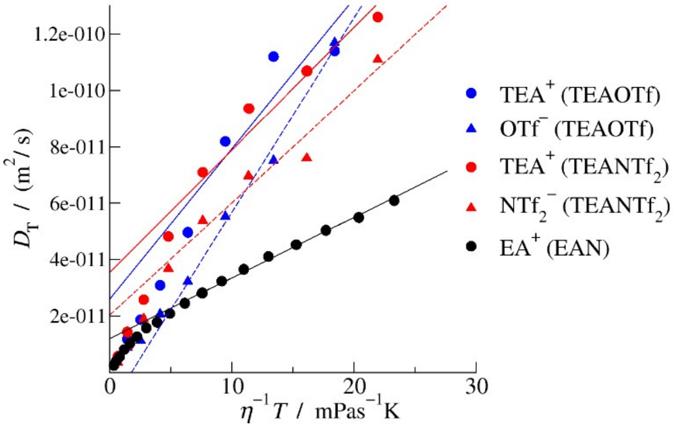

Fig. S5 According to the Stokes-Einstein (SE) relation, the translational diffusion coefficients D_{T} were plotted as a function of T/η. Solid lines indicate fits of cationic data, dashed lines of anionic data at high temperatures. The viscosities η were determined by a Vogel-Fulcher-Tammann fit of measured viscosities between 293 K and 343 K.