

Electronic Supplementary Information

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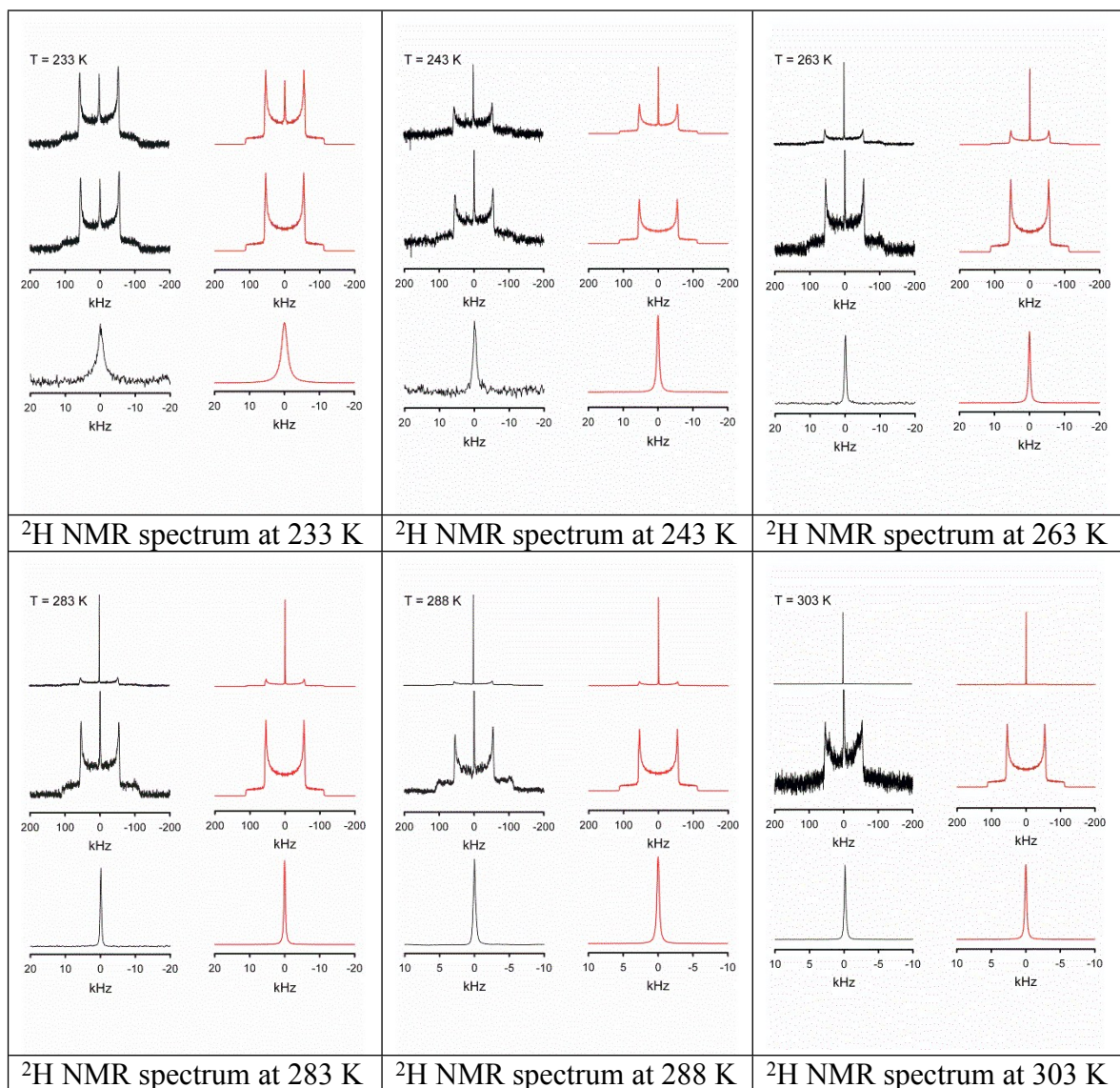
1. Experimental Section

In order to prepare the sample for the NMR experiments, the N–H-deuterated ionic liquid was loaded into a glass tube (5 mm o.d.; 20 mm long), connected to a high vacuum grade valve (HI-VAC). All manipulations were performed in argon atmosphere. The sample was then attached to a vacuum line and the argon was pumped off under vacuum to a final pressure above the sample of 10^{-2} Pa. To fully degas the material, the sample was slowly introduced into liquid nitrogen 2–3 times, while being connected to the vacuum line. After degassing, the neck of the tube was sealed off, while the material sample was maintained in liquid nitrogen in order to prevent its heating by the flame. The sealed sample was then transferred into an NMR probe for analysis with ^2H NMR spectroscopy.

^2H NMR experiments were performed at Larmor frequency $\omega_0/2\pi = 61.42$ MHz on a Bruker Avance-400 spectrometer, using a high power probe with 5 mm horizontal solenoid coil. All ^2H NMR spectra were obtained by Fourier transformation of quadrature-detected phase-cycled quadrupole echo arising in the pulse sequence ($90^\circ_x - \tau_1 - 90^\circ_y - \tau_2 - \text{acquisition} - t$), where $\tau_1 = 20$ μs , $\tau_2 = 21$ μs and t is a repetition time of the sequence during the accumulation of the NMR signal.[46,47] The duration of the $\pi/2$ pulse was 1.6–1.7 μs . Spectra were typically obtained with 50–20000 scans with repetition time ranging from 0.5 to 15 seconds. Inversion-recovery experiments to derive spin-lattice relaxation times (T_1) were carried out using the pulse sequence ($180^\circ_x - t_v - 90^\circ_x - \tau - 90^\circ_y - \tau - \text{acquisition } n$), where t_v was a variable delay between the 180° and 90° pulses.[48,49] The temperature of the samples was controlled with a flow of nitrogen gas by a variable-temperature unit BVT-3000 with a precision of about 1 K.

The software used for the data analysis was written by one of the authors (D. Kolokolov, daniil.kolokolov@gmail.com). The Fortran 90 source code is available on request.

2. ^2H NMR spectra of $[\text{TEA}][\text{OTf}]$



3. ^2H NMR T_1 , T_2 relaxation simulation

To understand the detailed mechanism of rotations and their kinetic parameters (the activation barriers and rate constants), a detailed fitting analysis of the ^2H NMR spin relaxation within experimentally studied temperature range is to be performed. Our homemade FORTRAN simulation routines are based on the general formalism proposed by Abragam⁵ and developed in details by Spiess⁶ and others⁷⁻¹⁰.

Spin relaxation times T_1 and T_2 are generally anisotropic and depend on the observation angles θ and φ in the powder pattern. They are given by the usual formula:⁶

$$\frac{1}{T_1} = \frac{3}{16} \left(\frac{e^2 q Q_{2H}}{h} \right)^2 (J_1(\omega_0) + 4J_2(2\omega_0)), \quad (1)$$

$$\frac{1}{T_2} = \frac{1}{32} \left(\frac{e^2 q Q_{2H}}{h} \right)^2 (9J_0(\omega_0) + 15J_1(\omega_0) + 6J_2(2\omega_0)) \quad (2)$$

Where $\frac{e^2 q Q_{2H}}{h} = Q_0$ is the quadrupolar coupling constant for the ^2H nuclei in Hz. The $J_q(0, \omega_0, \Omega^L)$ are the spectral densities of the fluctuations depending on the Larmor frequency $\omega_0 = \nu_0 2\pi$, ν in Hz, and the observation angles $\Omega^{\text{LAB}} = (0, \theta^{\text{LAB}}, \varphi^{\text{LAB}})$. The spectral densities represent the Fourier transform of the correlation function $g(t, \Omega^{\text{LAB}})$ characterizing the molecular reorientations in time. The orientational correlation function can be computed within a jump-exchange model, assuming usually that the jump exchange is a random Markovian process. In the absence of isotropic motions, the spectral densities can be computed as:

$$J_q(\omega) = 2 \sum_{a,b=-2}^2 D_{a,q}(\Omega_L)^* D_{b,q}(\Omega_L) \otimes G_{0,a|0,b}(\omega), \quad (3)$$

where

$$G_{c,a|d,b}(\omega) = \sum_{l,k,n=1}^N D_{c,a}^l(\Omega_l)^* D_{d,b}^k(\Omega_k) p_{\text{eq}}(l) V_{l,n} \left(\frac{-\lambda_n}{\lambda_n^2 + \omega^2} \right) V_{n,k}^{-1} \quad (4)$$

Here Ω_L are the observation angles θ and φ , which connect the molecular frame with the laboratory frame; Ω_k are the Euler angles which connect the molecular frame with the k -th distinct position of the O–D bond within the assumed geometry of the jump model; $V_{l,n}$ is a matrix composed by Eigen vectors of kinetic matrix K and λ_n are its Eigen values; N is the number of distinct jump-sites.

If one or multiple isotropic motions are present, the corresponding correlation function is no longer dependent on the polar angles and the resulting function is simply a tensor multiplication of correlation functions for distinct motional modes.

In the present case, for the anisotropic spectral component we have used a simple model for spectral function in the anisotropic case:

$$J_m(\omega) = 2 \sum_{a,b=-2}^2 D_{a,q}(\Omega_L)^* D_{b,q}(\Omega_L) \otimes G^1_{0,a|0,b}(\omega) \quad (5)$$

Here G^1 takes into account the fast anisotropic librations. In the function G^1 is computed using the Equation (4). The libration models are constructed by a free exchange with rate k_{lib}^i between n^i equally populated sites; each site represents one of the possible orientations (given by the axial rotation angle ϕ) of the linkers plane located within the limiting sector $\pm\Delta\phi^i$. For small angles (within $\pm 15^\circ$ degrees) a 2-site exchange model gives a satisfactory picture of the librations effect on the relaxation. The experimental relaxation was measured at the ($\theta=90^\circ$) position.

Since in the case of the simple isotropic rotation the correlation function is reduced to:

$$\langle D_{aq} [\mathcal{Q}_{\text{LAB}}(0)] D_{a'q} [\mathcal{Q}_{\text{LAB}}(t)] \rangle = G_{aa'}^{\text{iso}} = \frac{1}{5} \delta_{aa'} \exp[-6Dt], \quad (6)$$

where D is the rate defining the isotropic rotational diffusion, the analytical expression for the relaxation rates can be obtained and is well-known (see Ref. 5 for example).

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