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Slow Molecular Motions in Ionic Liquids Probed by Cross-Relaxation of Nuclear Spins During Overhauser Dynamic Nuclear Polarization

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Abstract: *Solution-state Overhauser dynamic nuclear polarization (ODNP) at moderate fields, performed by saturating the electron spin resonance (ESR) of a free radical added to the sample of interest, is well known to lead to significant NMR signal enhancements in the steady state, owing to electron–nuclear cross-relaxation. Here it is shown that under conditions which limit radical access to the molecules of interest, the time course of establishment of ODNP can provide a unique window into internuclear cross-relaxation, and reflects relatively slow molecular motions. This behavior, modeled mathematically by a three-spin version of the Solomon equations (one unpaired electron and two nuclear spins), is demonstrated experimentally on the* $^{19}F/^{1}H$ *system in ionic liquids. Bulky radicals in these viscous environments turn out to be just the right setting to exploit these effects. Compared to standard nuclear Overhauser effect (NOE) work, the present experiment offers significant improvement in dynamic range and sensitivity, retains usable chemical shift information, and reports on molecular motions in the sub-megahertz (MHz) to tens of MHz range—motions which are not accessed at high fields.*

Magnetic resonance (MR) is a versatile probe of molecular structure, dynamics, and distribution. Spin relaxation, which is the process that returns spin ensembles non-radiatively to thermal equilibrium following a perturbation, is a phenomenon that offers insights in all these respects. Relaxation of longitudinal spin magnetization components (i.e., components parallel to the Zeeman magnetic field direction z), which invokes fluctuating interactions involving spin-pairs, is of special interest as it sheds light on inter- and intramolecular interactions by probing molecular motions occurring not only at the Larmor magnetic resonance frequencies of the individual spins in the pair, but also at the corresponding sum and difference frequencies. Other longitudinal single-spin relaxation processes do not reflect pair interactions, and report only on molecular motions at the individual Larmor frequency of the spin in question. Spin pair relaxation has been extensively employed in studies of molecular structure and dynamics, especially in NMR spectroscopy, and is termed the nuclear Overhauser effect (NOE),[1] with either homo- or heteronuclear spin pairs being involved. In the present work, we introduce a novel experiment that permits indirect measurement of the NOE with high dynamic range and sensitivity at low frequencies by measuring the build-up rate of the electron–nuclear Overhauser effect [OE, or Overhauser dynamic nuclear polarization (ODNP)] under conditions which exploit interactions among three spins (i.e., the unpaired electron and two different nuclear spins).

It may be recalled that for a pair of spins with the same sign of the magnetogyric ratio γ, the "double quantum" relaxation transition involves the simultaneous correlated spin flip of both the partner spins in the same sense, that is, $|\alpha\alpha\rangle \leftrightarrow |\beta\beta\rangle$, with its rate ($W_2$) being governed by molecular motions at the sum of the two Larmor frequencies. The "zero quantum" relaxation transition, in contrast, involves the simultaneous correlated spin flip of the two partner spins in the opposite sense, that is, $|\alpha\beta\rangle \leftrightarrow |\beta\alpha\rangle$, and its rate ($W_0$) is governed by molecular motions at the difference of the two Larmor frequencies. The difference between the rates of double and zero quantum relaxation transitions (i.e., $W_2 - W_0$, usually denoted as σ) is termed the cross-relaxation rate. This rate is a frequency- and distance-dependent quantity which has been extensively employed in NOE-based studies of molecular structure and dynamics, with both the spins in the pair being nuclear spins, whether they are homo- or heteronuclear.

The NOE experiment is typically performed in the one-dimensional (1D) transient mode, or in the popular two-dimensional (2D) mode, termed NOESY[2a,b] (or HOESY[2c] for heteronuclear work). Since NMR sensitivity increases as the three-halves power of the magnetic field, and improved spectral dispersal is anticipated in direct proportion to the field strength—although often marred by larger linewidths at higher fields—the general trend has been to measure NMR spectra at ever higher frequencies. This procedure has the unfortunate consequence that slow molecular motions would not be probed adequately when heteronuclear spin pairs are involved.[*] As an example, a $^{1}H/^{19}F$ NOE experiment performed on a 600 MHz spectrometer measures internuclear cross-relaxation mediated by molecular motions at frequencies as high as about 35.44 MHz and 1164.82 MHz.

The electron-nuclear Overhauser effect (OE, or ODNP), is however, probably the earliest known experiment[3] that

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[*] Spin-lock experiments, field cycling experiments, or Carr–Purcell-type experiments may be employed[4] to shed light on ultraslow molecular motions. High-field NOE experiments involving two distinguishable homonuclear spins probe motions essentially at zero frequency and at double the Larmor frequency of the nuclear spins in question, thus missing once again low frequency motions in the sub-MHz to tens of MHz range.

relies on spin relaxation involving a spin pair, specifically, an electron-nuclear spin pair, and has been employed to polarize nuclear spins. ODNP may be generated by irradiating the ESR transition of a free radical which is added to the sample in solution state. The steady-state nuclear spin polarization generated as a result, typically under continuous ESR irradiation, is a function of the cross-relaxation rate involving the radical unpaired electron and the nuclear spin in the substrate molecule in question. It is known that significant NMR signal enhancements may be obtained by employing ODNP at moderate fields, while the resulting NMR spectrum of the substrate molecule generally retains usable chemical shift information as well, despite some line broadening caused by fluctuating interactions of the substrate molecule with the unpaired electron of the free radical. Hydration dynamics in biomolecules have also been studied with this approach.[5]

In standard ODNP experiments, electron spins (S) cross-relax nuclear spins (I_1), with the fluctuating electron–nuclear interaction being the dominant nuclear spin relaxation mechanism. Steady-state ^{1}H ODNP enhancements are typically negative owing to dipolar cross-relaxation. Dipolar enhancements decrease in magnitude monotonically with either increasing field or frequency. Steady-state ^{19}F ODNP enhancements, in contrast, can be either negative or positive, the latter owing to scalar cross-relaxation. Scalar enhancements are inherently field independent, except for leakage effects. Indeed, ^{19}F ODNP exhibits a complex dependence on the field and radical.[6]

Here we show for the first time that by involving an unpaired electron spin, but limiting the radical access to the substrate molecules, ODNP at moderately low fields may be made to reflect internuclear cross-relaxation, that is, the NOE. Slow molecular motions (at 863.5 kHz and 28.34 MHz in the present case) may thus be probed with high dynamic range and sensitivity, as well as acceptable NMR spectral resolution. This approach offers a unique window into relatively slow molecular motions in viscous media, and is showcased with our results on ionic liquids involving the ^{19}F-^{1}H spin pair. Such indirect detection of heteronuclear cross-relaxation exploiting this ménage-à-trois of spins (one electron spin and two nuclear spins) is accomplished by measuring the build-up rate of ODNP of either one or both of the relevant heteronuclei in turn. The experiment starts with both nuclei in their thermal equilibrium states, but with the electron spin in a steady state of either partial or complete saturation, typically under continuous microwave (MW) irradiation. For the experiment on either nucleus, a single NMR channel suffices on the probehead and the spectrometer. In contrast, direct measurements of heteronuclear NOEs involving ^{1}H and ^{19}F require special hardware including probeheads and transmitters which permit RF pulsing on both nuclear channels during the same scan, as well as the capability to observe either spin.

The Solomon equations may be employed to model ODNP polarization build-up mathematically. These equations describe the time course of relaxation of longitudinal magnetization of a pair of spins which have fluctuating interactions with each other.[7] They describe for each spin the time course of its return to equilibrium after one (or both) of the partner spins has (or have) been disturbed from thermal equilibrium. In particular, in the Solomon framework the rate of return to equilibrium of each spin is governed by its own deviation from equilibrium and also by the deviation from equilibrium of its relaxation partner. The relevant coupled first-order differential equations may be solved by standard techniques, thus yielding insights into the steady-state Overhauser effect, transient Overhauser effect, as well as the time course of build-up of polarization of one spin, with the other one being maintained in a steady state of saturation that has been rapidly attained. The latter case is of particular relevance in the context of ODNP build-up rate studies, because unpaired electron spins in free radicals reach their steady state of either partial or complete saturation very rapidly at room temperature in solution state, while nuclear spins, which have much longer relaxation times, equilibrate or reach their steady state at a far more leisurely pace.

It is readily seen (see the Supporting Information) by solving the standard two-spin Solomon equation that the time course of build-up of the nuclear polarization to its steady state (i.e., the ODNP build-up rate), following rapid establishment of a steady state of either partial or complete electron spin saturation, is monotonic in time (as depicted schematically in Figure 1a), and is described by a simple exponential function, with a rate constant (ρ_1) which reflects the overall relaxation rate of the nuclear spin I_1.[8] ρ_1 is very often primarily a function of fluctuating electron–nuclear

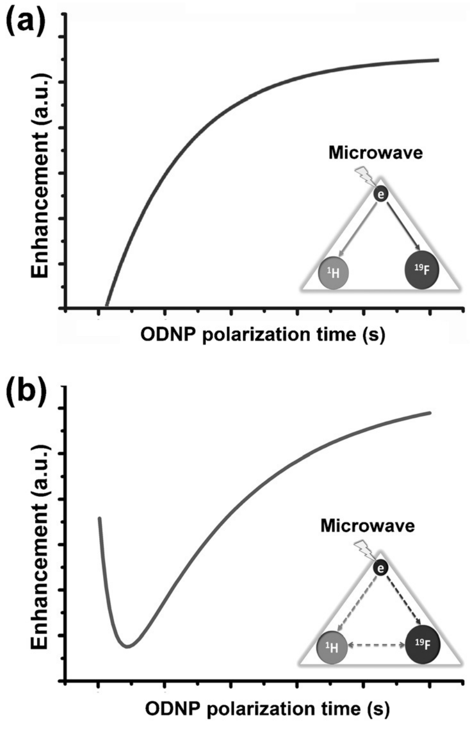

Figure 1. Schematic polarization build-up curves derived from the analytical solution of the Solomon equations in the case of: a) either one of two non-interacting two-spin systems (each comprising a different nuclear spin but a common electron spin); and b) a three-spin system (two interacting nuclear spins and an electron spin that interacts with both).

interactions. It is to be noted that the rate constant of the exponential build-up curve does not reflect the electron–nuclear cross-relaxation rate constant σ_1, although the initial rate of ODNP build-up does.

Here, however, we deal with a situation where nuclear spin relaxation processes are not dominated by interaction with the electron spin. These conditions may be created by limiting radical access to the substrate molecule of interest, for example, by using bulky radicals in viscous media, and/or at low radical concentrations. This approach results in a low "leakage factor", which is defined as the ratio of the nuclear spin relaxation rates in the absence and in the presence of the radical, subtracted from 1. We show that under these conditions the ODNP build-up rate constants of either nuclear spin in a three-spin system reflect in fact the overall average relaxation rate of the two nuclear spins in question (ρ_1 and ρ_2) and their difference, as well as their cross-relaxation rate (σ). This feature offers a unique window into slow motions in viscous media when carried out at moderately low magnetic fields. At such fields, ODNP enhancements of NMR signals are generally usefully large in magnitude, thus leading to good NMR sensitivity, while NMR chemical shift resolution is normally more than adequate for ^{19}F and tolerably usable for even ^{1}H, although ^{1}H NMR spectra have among the lowest frequency dispersals.

Such relaxation behavior may be modeled by extending the Solomon treatment in a straightforward manner to the group of three spins,[3d][*] which are relevant for the present discussion: two different nuclear spins and one electron spin. Of these, both the nuclear spins are at equilibrium to begin with, while the electron spin starts in a steady state of either partial or complete saturation, which it has rapidly attained, typically under strong continuous irradiation near its resonance frequency.

A general treatment that includes two unequal overall nuclear spin relaxation rates, ρ_1 and ρ_2, their mutual cross-relaxation rate, σ, and the ESR saturation parameter s yields the expressions given in Equation (1). These expressions

$$\begin{aligned}
&\frac{\langle I_{1z}(t)\rangle - \langle I_{10}\rangle}{\langle I_{10}\rangle} = s\,\frac{\gamma_s}{\gamma_{I_1}}\left(C_1 e^{r_- t} + C_2 e^{r_+ t} + A_0\right);\\
&\frac{\langle I_{2z}(t)\rangle - \langle I_{20}\rangle}{\langle I_{20}\rangle} = s\,\frac{\gamma_s}{\gamma_{I_2}}\left(C_1^{'} e^{r_- t} + C_2^{'} e^{r_+ t} + A_0^{'}\right);\\
&r_\pm = -\frac{(\rho_1+\rho_2)}{2} \pm \frac{1}{2}\left[(\rho_1-\rho_2)^2 + 4\sigma^2\right]^{\frac{1}{2}}
\end{aligned} \qquad (1)$$

attest to the occurrence of ODNP build-up curves which exhibit maxima or minima with respect to the ODNP polarization time t (i.e., the MW irradiation time t) as depicted schematically in Figure 1b, instead of the monotonic exponential behavior which is encountered normally. The expressions for the coefficients C_i, A_0, etc., are all given in the Supporting Information.

It may be noted from Equation (1) that such ODNP build-up rates reflect in their exponents the average of the overall relaxation rate constants of the two nuclear spins, their difference, as well as their mutual cross-relaxation rate constant. It is this feature that allows dynamic and structural information to be gleaned about the substrate molecule under investigation. At the same time, it may also be noted that there is significant improvement in the dynamic range of internuclear cross-relaxation curves obtained under ODNP conditions, as compared to standard internuclear cross-relaxation experiments (see below). It is important to note that there is no separate mixing time in our experiments earmarked for cross-relaxation of the nuclear spins to take effect: all relevant nuclear relaxation processes involving the unpaired electron as well as the two nuclear spins are simultaneously active during the MW irradiation time. Thus, such measurements constitute an indirect detection of internuclear cross-relaxation without the requirement of preparing either nuclear spin initially in a non-equilibrium state, and without even requiring a two-channel NMR system. Note once again that these rate constants of the ODNP build-up curve are independent of the electron nuclear cross-relaxation rate constant (σ_1 or σ_2 for the two nuclei I_1 or I_2 respectively), although the initial rate of ODNP build-up does depend on it (see the Supporting Information).

We have found considerable experimental evidence for the non-monotonic nature of ODNP build-up curves from measurements on a number of room-temperature ionic liquids (RTILs). RTILs have gained much prominence in recent years in the context of their potential in green chemistry, as well as in electrochemistry.[11,12] However, much still needs to be understood about their structure and dynamics in relation to their function. They have relatively high viscosity, and it is known that despite the cation and anion being comparatively small species, their motional characteristics at frequencies typical of modern NMR spectrometers (500 MHz or higher) may fail to satisfy the behavior that is generally classified as extreme narrowing. It may be recalled that extreme narrowing signifies that spectral densities of molecular motion are essentially constant over the range of frequencies relevant to spin relaxation, thus leading in turn to sharp NMR spectral lines. This motional regime is characterized by $\omega\tau \ll 1$ for simple motional models, such as rotation, with ω being the relevant transition frequency and τ as the motional (rotational) correlation time.[10,11] Under these conditions, relaxation rates have an inverse sixth power dependence on the relevant interspin distance. However, it has been recognized again[13,14] that such a simple short-range rotational model is not valid for intermolecular NOEs involving translational motion, which could be encountered in ionic liquids. In such a case the relaxation rate is governed instead by a suitable longer range ro-translational relaxation model which leads in the limit of pure translational motion to a simple inverse dependence on distance. Interpretation of high-field NOEs in ionic liquids has therefore been a matter for discussion and debate, especially given that the amplitude and distance dependence

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[*] The present situation is to be clearly distinguished from experiments where nuclear spin cross-relaxation is measured in the standard manner after hyperpolarization of one or both nuclear spins, e.g., CIDNP or dissolution DNP.[9a,b] It is also to be distinguished from three-spin effects which involve, other than the unpaired electron, a nucleus such as ^{13}C in the molecular interior (that polarizes very slowly), and a spin such as ^{1}H or ^{19}F at the molecular periphery (that polarizes relatively rapidly).[10]

sampled by the spectral densities corresponding to zero and double quantum internuclear relaxation transitions could be significantly different at high fields, owing to their very large frequency difference. Some of these complications would be minimized at first with low-frequency ODNP measurements, where the amplitude and distance dependence of spectral densities would be very similar for both these kinds of internuclear relaxation transitions, which are spaced much closely in frequency.

Our ODNP experiments (whose pulse sequence diagram is depicted in Figure 2a) have been carried out on ionic liquids at room temperature (ca. 27 °C) at X-band (ca. 9.6 GHz), thus employing a coil-in-cavity system which is simultaneously resonant to MW for ESR, as well as to the desired RF frequencies for NMR spectroscopy. More details of the sample preparation are given in the experimental section, while details of the ODNP experiments are given in the Supporting Information.

The ^{1}H resonance frequency in our experimental studies is about 14.6 MHz, while the corresponding ^{19}F resonance frequency is about 13.74 MHz. These frequencies imply that our internuclear cross-relaxation rates reflect molecular motions at 863.5 kHz (the zero quantum relaxation transition), as well as motions at 28.34 MHz (the double quantum relaxation transition; this range is to be contrasted with standard ^{19}F/^{1}H NOE experiments at 600 MHz, which depend on molecular motions at about 35 MHz and 1165 MHz as noted earlier). Our overall nuclear spin relaxation rates under ODNP conditions report, in addition, on molecular motions at 14.6 MHz and 13.74 MHz, as well as on motions near the electron Larmor frequency (ca. 9.6 GHz), with the latter corresponding to fluctuating electron-nuclear interactions.

As one experimental example of an ODNP build-up study which demonstrates non-monotonic behavior, the data for 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)-imide, BMIM-NTf2, in the presence of 15 mM galvinoxyl radical is shown in Figures 2b and c. This Figure depicts the integral of the NMR signal relative to the signal under Boltzmann conditions, [i.e., $(\langle I_{1z}\rangle-\langle I_{10}\rangle)/\langle I_{10}\rangle$] plotted as a function of the MW irradiation time (i.e., the ODNP polarization time). The plots in this figure clearly demonstrate that the ODNP goes through a minimum, with respect to polarization time, in this experimental sample. Both ^{19}F and ^{1}H ODNP are seen to exhibit a common mean relaxation rate. This common rate establishes the cross-relaxation between the ^{19}F of the anion and ^{1}H of the cation. These curves also exhibit a dynamic range corresponding to about five units or more of variation in ODNP enhancement, whereas standard ^{19}F/^{1}H cross-relaxation curves would, at best, involve at this field only 0.41 units of variation in nuclear Overhauser enhancement. This data clearly establishes an order of magnitude improvement in the dynamic range in our experiments.

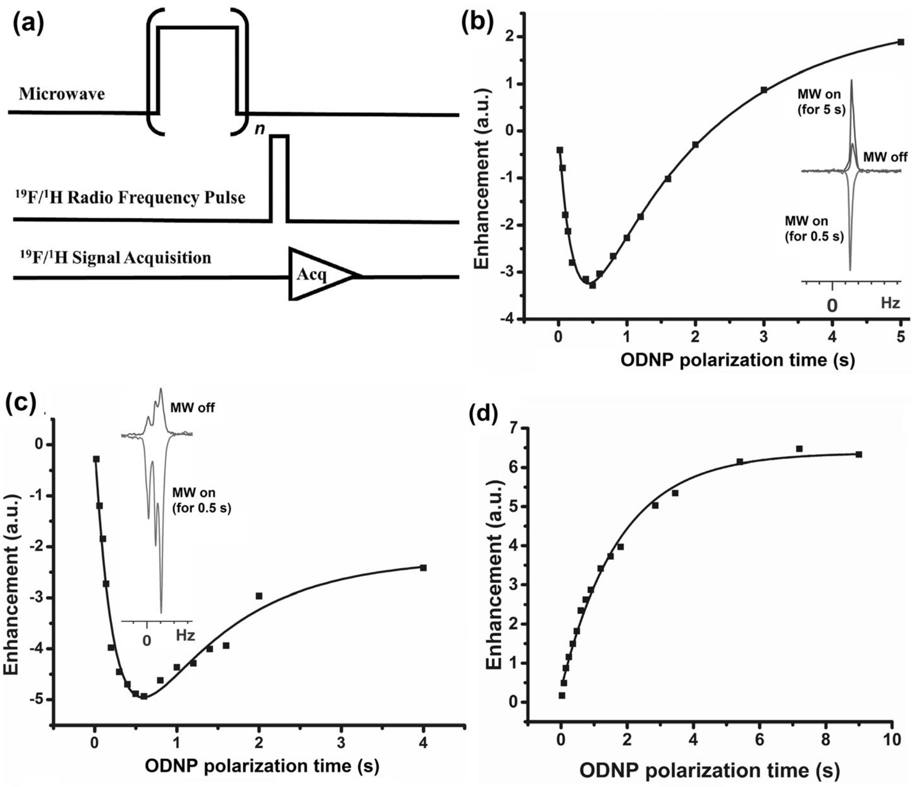

Figure 2. a) Pulse sequence diagram for the ODNP-detected NOE experiment: the loop index *n* permits variation of the MW irradiation time before the NMR signal is interrogated. Polarization build-up curves of BMIM-NTf2 with 15 mM galvinoxyl free radical for ^{19}F (b), ^{1}H (low field signal, after deconvolution; c), and ^{19}F of a 1:1 v/v mixture of BMIM-NTf2 and benzene (d). (b) and (c) are fitted as per Equation (1). Fit parameter: b) $r_{-}+r_{+}=-\rho_1-\rho_2=-5.16\ \mathrm{s}^{-1}$; c) $r_{-}+r_{+}=-\rho_1-\rho_2=-4.99\ \mathrm{s}^{-1}$. The inset in (b) displays ^{19}F spectra under Boltzmann conditions ("MW off") and under ODNP enhanced conditions ("MW on" for 0.5 s and 5 s polarization time, respectively). The inset in (c) displays the ^{1}H spectrum under Boltzmann conditions ("MW off") and under ODNP enhanced conditions ("MW on" for 0.5 s polarization time). d) Displays the monotonic exponential build-up of ^{19}F polarization and is fitted with Equation (1B) of the Supporting Information.

When the ionic liquid was diluted to either 1:1 v/v or 1:2 v/v in cyclohexanol (which is almost isoviscous with the ionic liquid in question) the minimum in ODNP occurred once again. In contrast, experiments where the ionic liquid was diluted 1:1 v/v in benzene[15] (Figure 2d) or 1:3 v/v in cyclohexanol resulted in normal monotonic exponential build-up curves. We believe these observations establish a significant role of viscosity in determining access of the free radical to the ionic liquid moieties. Further, the behavior of ODNP build-up under isoviscous dilution suggests that clusters of oppositely charged ions exist in the ionic liquid at either low or no dilution, and are disrupted at higher dilutions. This dynamic picture emerges over a time scale of the order of 0.1 to

10 ns (the range of typical rotational or translational dynamics in such species[14]), and a distance scale of the order of nanometers. If such clusters persist over time scales of the order of milliseconds and distance scales of the order of microns, their sizes may then be estimated, for example, by ODNP-enhanced ^{19}F self-diffusion experiments. It may be recalled however that such diffusion experiments employing either pulsed field gradients (PFG) or constant field gradients are in themselves not sensitive to the time and distance scales probed by cross-relaxation.

Notwithstanding the possible complexities of the relevant motional model, the low frequencies of operation in our ODNP experiment imply that internuclear cross-relaxation carries a more significant contribution from the internuclear double quantum relaxation transition, as compared to the zero quantum relaxation transition, since the relatively flat, high amplitude portion of the spectral density function is sampled under these conditions. This scenario leads to a positive internuclear cross-relaxation rate constant. Analysis of our experimental ODNP build-up curves enables inference of the cross-relaxation rate constant as well as the sum (or average) of the overall nuclear relaxation rate constants, by extrapolating the radical concentration dependence[16] of the fit parameters of the polarization build-up curves to zero radical concentration (see the Supporting Information). We employ a linear fitting of the experimental build-up curve fit parameters versus radical concentration, thus dropping the quadratic term in radical concentration since our radical concentrations are low.

Cross-relaxation rates are a function of the motional correlation time and the relevant interspin distance, which may then be inferred from the experimental results using suitable motional models.

Despite the fact that the present experimental sample is, in reality, one that involves many proton and fluorine spins which interact with the unpaired radical electron, the specific deconvoluted proton signal that exhibits the same average overall nuclear spin relaxation rate constant $[(\rho_1+\rho_2)/2]$ as the ^{19}F signal is in accord with the known specificity of the heteronuclear spin interaction[13,14c,17] in this ionic liquid system. The upper bound for the value of the cross-relaxation rate constant based on our simple three-spin model, inferred by extrapolating the radical concentration dependence of the fit parameters as noted above, turns out to be $0.42\,\mathrm{s}^{-1}$ for the BMIM-NTf2 system, and results from dynamics in the 0.1 to 10 ns range. This value is subject to further refinement with a more detailed, but complex model. This estimate is to be compared with the average overall nuclear spin relaxation rate constant inferred from our experiments for this system, which is $1.48\,\mathrm{s}^{-1}$. Preliminary information gleaned by some other ionic liquid systems we have investigated is summarized in the Supporting Information.

A detailed analysis of our experimental results in terms of dynamics is beyond the scope of the present report, and will be actively pursued subsequently in our laboratory. However, at present the following visualization appears suggestive. Based on our dilution studies, which result in a switch from an ODNP build-up curve that exhibits a minimum (for the "pure" ionic liquid in the presence of radical) to a normal monotonic exponential ODNP build-up curve on dilution, it seems reasonable to consider a model of a short-lived cluster of ions which would then be subject to rotational dipolar relaxation[14c] of the counterions. Indeed, it appears to us that the sticking model,[3d,18] which is well established in Overhauser DNP as a model for radical-substrate interaction, may well be invoked in the present context too, to describe the relaxation interaction between the ions. In general, the rotational correlation time is proportional to the cube of the radius of a spherical model of the molecular species in question[19] (at its simplest, a species comprising a cation and an anion in the present case), while the relaxation rate has an inverse sixth power dependence on the interspin distance. However, in the present case these two parameters are not geometrically independent of each other, and could lead to an unusual power law dependence on the inverse interspin distance. We hope to investigate these issues more fully in the future, and also propose, if required, more complex models, especially one including reorientation mediated by translational displacements (RMTD),[4] and other ro-translational models.[14a]

In conclusion, we have established that measurement of ODNP build-up rates at moderately low fields under conditions in which electron spins do not dominate nuclear spin relaxation permits the indirect characterization of internuclear cross-relaxation rates with high dynamic range and sensitivity, thus reflecting slow molecular dynamics. In particular, our experimental studies on the ^{19}F-^{1}H nuclear spin pair in ionic liquids uniquely allow the registration of positive internuclear cross-relaxation rate constants as a consequence of conditions in which the rate of internuclear double quantum relaxation transitions is higher than that of zero quantum relaxation transitions. The switch from an ODNP build-up curve which exhibits a minimum to a normal monotonic exponential ODNP build-up curve, which occurs in the presence of the radical when going from the "pure" ionic liquid (or ionic liquid diluted 1:1 v/v or 1:2 v/v in equiviscous cyclohexanol) to the ionic liquid diluted 1:3 v/v in cyclohexanol, clearly suggests that structured clusters of oppositely charged ions exist in the ionic liquid at either no or low dilution, but are broken up under conditions of significant dilution. Finally, while the present work reports the application of our approach of ODNP-detected NOE measurements to ionic liquids at a moderately low field, we anticipate applications to other systems, and this is being explored in our laboratory.

Experimental Section

Room-temperature ionic liquids (RTILs) (e.g., BMIM-NTf2, BMIM-PF6, BMPIP-NTf2, and C1PPYR-NTf2), as well as the cyclohexanol and benzene used for dilution studies were all purchased from TCI Chemicals or Sigma Aldrich. RTILs were stored in a glove bag filled with dry nitrogen gas, and used without further purification. Samples were prepared with different concentrations of the galvinoxyl free radical (3–15 mM), and were then sonicated and degassed by bubbling pure, dry nitrogen through them. The experiments were performed at room temperature (ca. 27 °C) in 2 mm o.d. sample tubes at X-band, dry nitrogen being continuously passed through the cavity. BMPIP = 1-butyl-3-methylpiperidinium; PF6 = Hexafluorophosphate, C1PPYR = 1-methyl-1-propylpyrrolidinium.

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