Magnetic Relaxation Dispersion of ^{7}Li: Interaction with Mn(II) in the Aqueous Solvent Cage

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Abstract: Measurements of ^{7}Li nuclear spin−lattice relaxation times are made at applied magnetic field strengths from 0.25 mT to 7.05 T, in order to determine directly the form of the frequency dependent spectral densities that modulate relaxation. This Magnetic Relaxation Dispersion (MRD) technique provides detailed information regarding molecular dynamics down to the picosecond time scale. ^{7}Li MRD measurements on aqueous lithium ion relaxed by the paramagnetic Mn(II) ($S = 5/2$) ion reveal the formation of a cation−cation complex that has a lifetime at least as long as the rotational correlation time of approximately 100 ps. Translational electron-nuclear dipole−dipole contributions are resolvable, and there is a significant change in the nuclear electric quadrupole contribution to the ^{7}Li relaxation. The results obtained from solutions of LiCl and $LiNO_3$ are compared and found to be similar.

1. Introduction

Ion−ion interactions participate in a great variety of chemical, biochemical, and physical processes. Ion pairing effects between cations and anions are well and widely known, but intimate interactions between ions of like charge are less often a theme of chemical reasoning because of the qualitative arguments concerning the repulsive forces presumed to separate ions of like charge. Nevertheless, pioneering work by Friedman and co-workers[1−3] has laid a clear foundation for understanding that close encounters between ions of like charge may not only be common but also a central mechanism of some crucial chemistry such as electron transfer processes between cations.[4−6] Direct experimental characterization of ion−ion interactions has been difficult because time scales of some of the interactions are short and instantaneous populations of intimate complexes may be small. Nuclear magnetic relaxation has provided one fruitful approach, in that while signal integration is performed over a long time period because of the long relaxation times, the spin relaxation itself is driven by fluctuations at the nuclear or electron Larmor frequencies, which may correspond to time scales from picoseconds to hundreds of microseconds, depending on the magetic field strength. For those few ions that are in close proximity to a paramagnetic relaxation sink, these local fluctuations caused by changes in the orientation of the internuclear vector result in very large spin−lattice relaxation rates on the order of 10^4 s^{-1}. Thus, the weighted contribution of very small concentrations of ion pairs results in an experimentally resolvable component of the observed relaxation rate.

Friedman and co-workers studied lithium nuclear spin relaxation induced by Ni(II) ion,[4] which has a short electron spin relaxation time that dominates the time dependence of the electron-nuclear dipole−dipole coupling. Because the electron relaxation time is very short, the nuclear relaxation rate is insensitive to the details of the relative translational diffusion of the spin bearing molecules, and they were able to deduce a distance of closest approach between the lithium and Ni(II) ion of about 5.5 Å for the hard-sphere-pair-correlation function, demonstrating an intimate collision. Tembe *et al.*[5] showed that for electron transfer in +2/+3 systems, almost all of the calculated exchange derives from configurations in which the metal−metal distance is < 7 Å.

Electron spin relaxation of $S \geq 1$ ions derives primarily from thermal modulation of the zero field splitting (ZFS) tensor. Transient ZFS are correlated on the time scale of intramolecular motions ($\tau_v = 2-10$ ps) associated with collisionally induced vibrational motions of the ligand field. Short electron relaxation times indicate a static ZFS, which is an average over all configurations of the coordinate shell, correlated on the time scale of Brownian motion of the entire molecule. The spherical distribution of valence electrons in Mn(II), in a symmetrical hexa-aquo environment results in long electron spin relaxation times of several nanoseconds. On this time scale, the details of electron spin relaxation mechanisms are unimportant, and the nuclear relaxation is not explicitly determined by the lattice dynamics.

Lithium ion is convenient for study because it has a small nuclear electric quadrupole moment that is inefficient in causing nuclear spin relaxation which permits easy resolution of the effects induced by the paramagnetic ion. We have constructed an instrument that will measure the dependence of solute particle spin−lattice relaxation rates on the magnetic field strength between 7.05 T and the earth's field, thus permitting extension of the dynamical characterization of the cation−cation interaction. We find striking evidence supporting the formation of a complex between the hydrated cations, which has a lifetime sufficiently long to rotationally reorient in water, *i.e.*, the cation−cation complex has a lifetime of at least 100 ps.

At currently achievable magnetic fields, nuclear spin relaxation is not a spontaneous process and must be stimulated by

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fields fluctuating at the resonant frequency. Generally, the fields to which spin systems couple fluctuate with the random rotational and translational motion of surrounding spin-bearing molecules. The spin−lattice relaxation rate is then proportional to the real-valued spectral density at the Larmor frequency and its first harmonic, even though the observed relaxation time may be on the order of a second. The magnetic relaxation dispersion (MRD) is a graph of the spin−lattice relaxation rate versus the Larmor frequency, that is directly proportional to the applied magnetic field strength, thus directly mapping the spectral density functions, which are the Fourier transforms of the time correlation functions that characterize the spatial flucuations. Therefore, the MRD provides direct insight into *inter*- and *intra*molecular dynamics over a very wide time scale range that is approximately given by the reciprocal of the Larmor frequencies studied. Should these relaxation interactions involve paramagnetic compounds, molecular dynamics on the picosecond scale may be probed because the relaxation equations then contain terms in the electron Larmor frequency which is usually three orders of magnitude larger than its nuclear counterpart.

2. Theory

In aqueous solution, the Li$^+$ ion is symmetrically coordinated by solvent molecules that are reported to be very labile, with exchange lifetimes on the order of 20 ps.[4,7] Since the electric quadrupole moment (eQ) of the ^{7}Li nucleus ($I = 3/2$) is also small,[8] dipole−dipole coupling with surrounding water protons is a significant relaxation mechanism. Designated $R_{1_D} = T_{1_D}^{-1}$, the diamagnetic contribution to the total relaxation of ^{7}Li$^+$ in solution is thus due to interactions with field gradients at the nucleus and dipolar coupling with both ligated water protons (*is*) and those inhabiting the outer sphere (*os*).

$$T_{1_D}^{-1} = T_{1_{H,is}}^{-1} + T_{1_{H,os}}^{-1} + T_{1_Q}^{-1} \tag{1}$$

This relaxation is concentration dependent[9] and amounts to a baseline shift of the dispersion data.

Addition of even a small amount of a paramagnetic species changes the situation dramatically, because the nucleus interacts with the much larger magnetic induction fields generated by the magnetic moments of unpaired electrons. Since $\gamma_e = 658\gamma_{^1\mathrm{H}} = 1693\gamma_{^7\mathrm{Li}}$, the dipolar fields produced by the presence of unpaired electron spin density provide much more efficient relaxation mechanisms, particularly for those nuclei in close proximity to the paramagnetic center. For nuclei that participate in some binding process with the paramagnetic electron spin bearing molecule, the total observed relaxation rate is[10,11]

$$T_{1_{obs}}^{-1} = P_{free}(T_{1_D}^{-1} + T_{1_{trans}}^{-1}) + P_{bound}(\tau_{ex} + T_{1_M})^{-1} \tag{2}$$

where $T_{1_M}^{-1} = T_{1_P}^{-1} + T_{1_Q}^{-1}$, and where the mole fraction of bound ^{7}Li is denoted $P_{bound} = 1 - P_{free}$. Here, the definition of a bound complex is taken to mean one in which the intermoment vector is rotationally correlated, as opposed to a translational pair. Because the total lithium ion concentration $[\mathrm{Li(I)}]_{\mathrm{TOT}}$ is very large compared with that of the Mn(II) ion $[\mathrm{Mn(II)}]_{\mathrm{TOT}}$, we may write

$$P_{bound} = \frac{[\mathrm{Mn(II)}]_{\mathrm{TOT}}}{[\mathrm{Li(I)}]_{\mathrm{TOT}} + K^{-1}} \tag{3}$$

where K is the ion pair association constant. We denote the mean lifetime of the complex as τ_{ex}, and the relaxation attributable to the intramolecular mechanisms associated with the presence of the paramagnetic spin density in the first coordination sphere by T_{1P}. The intramolecular electron-nuclear dipolar and Fermi contact contributions to the relaxation have been descibed in a series of papers by Solomon,[12] Bloembergen,[13,14] and Morgan[14] and have been reviewed extensively elsewhere.[15] For relaxation in the weak coupling approximation, the result for isotropic rotational diffusion is

$$\frac{1}{T_{1_P}} = \frac{2}{15}\left(\frac{\mu_0}{4\pi}\right)^2 \gamma_I^2\,\gamma_S^2\hbar^2\frac{S(S+1)}{r_{IS}^6} \times \left[3\frac{\tau_c}{1+(\omega_I\tau_c)^2} + 7\frac{\tau_c}{1+(\omega_S\tau_c)^2}\right] + \frac{2}{3}S(S+1)\left(\frac{a}{\hbar}\right)^2\left(\frac{\tau_e}{1+(\omega_S\tau_e)^2}\right) \tag{4}$$

given that $\gamma_S \gg \gamma_I$. The γ_i are the magnetogyric ratios with corresponding angular frequencies

$$\omega_i = \gamma_i B_L \tag{5}$$

$\mu_0 = 4\pi \times 10^{-7}$ TmA^{-1} is the free space permeability, r_{IS} is the radial separation between the nucleus and the center of paramagnetic spin density, a is the hyperfine coupling constant, and S is the electron spin quantum number of the paramagnetic species ($S = 5/2$ for Mn(II)). The relevant correlation times are given by

$$\tau_c^{-1} = \tau_{rot}^{-1} + \tau_{ex}^{-1} + T_{1_e}^{-1} \tag{6}$$

$$\tau_e^{-1} = \tau_{ex}^{-1} + T_{1_e}^{-1} \tag{7}$$

The electron relaxation times $T_{1_e} \approx T_{2_e}$ are expected to be on the order of 2 ns[16] and so should not be significant relative to the fast rotational correlation time τ_{rot}. Furthermore, the long electron relaxation times permit decoupling of the electron spin and spatial variables, a required condition for the validity of eq 4.[17,18] Complexation with $[\mathrm{Mn(H_2O)_6}]^{2+}$ brings about a change in the symmetry of the electronic environment at the ^{7}Li nucleus from that in $[\mathrm{Li(H_2O)}_n]^+$. Interaction of the ^{7}Li electric quadrupole moment, eQ, with the electric field gradient at the nucleus along the Li···Mn axis, eq, is given by

$$T_{1_Q}^{-1} = \frac{3}{40}\,\frac{2I+3}{I^2(2I-1)}\left(\frac{eQ}{\hbar}eq\right)^2\tau_c' \tag{8}$$

where the extreme narrowing limit ($\omega\tau_c' \ll 1$) is assumed and the asymmetry parameter has been neglected. Beyond the

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extreme narrowing limit, *e.g.*, for slowly rotating macromolecules, relaxation under the quadrupolar Hamiltonian can no longer be described by a single exponential, and a manifold of coupled differential equations must be considered.[19] No attempt is made to seek resolution on the time scale of internal motion; hence, lattice dynamics determining the explicit time evolution of the geometric coupling terms r_{IS}, a, and eq are neglected. Disregarding the high frequency internal motions yields a rigid molecule model. At this level of approximation, $\tau_c' = \tau_{rot}$, but this is a tentative assertion since the dispersion of the quadrupolar relaxation is not observed over the accessible time scales of these experiments, and the localized motions determining the time correlation of the quadrupole coupling may be complex indeed.[7]

Regardless of whether or not a rotationally correlated complex is formed, the ubiquitous intermolecular relaxation mechanisms must be considered. Liquid phase intermolecular correlation functions are appropriately treated in the classical limit, and for the dipolar interaction between spins I and S are written[20]

$$G_m^{IS}(t) = \int \mathrm{d}^3\mathbf{r} \int \mathrm{d}^3\mathbf{r}_0 D_{0m}^{(2)\dagger}(\Omega_r) D_{0m}^{(2)}(\Omega_{r_0}) P(\mathbf{r}_0, t|\mathbf{r}) \frac{g(r_0)}{r^3 r_0^3} \quad (9)$$

The pair correlation functions $g(r_0)$ describe the initial equilibrium pair distribution and are related to the intermolecular electrostatic potential $U(r)$ of averaged forces between the spin bearing molecules[21] and to the number density of S spins $\aleph$ in an infinitesimal volume contained by $\mathbf{r}$ centered about the spin I.

$$g(r_0) = \frac{5}{4\pi} \aleph f_0(r) \quad (10)$$

Radial probability distributions $P(\mathbf{r}_0, \mathbf{t}|\mathbf{r})$ determine the likelihood that an initial intermoment vector $\mathbf{r}_0$ will evolve into $\mathbf{r}$ after some time t, and as solutions to a stochastic differential equation, determine the time evolution of Brownian motion. The seminal work of Torrey,[22] describing the molecular motion as a sequence of random jumps between nodes of a discrete lattice, was later modified by Hwang and Freed[21,23] to exclude from the diffusive path the spherical volume occupied by the colliding molecules. Moreover, the potential of averaged forces between diffusing molecules was formally included in this development via the Smoluchowski equation. This potential is assumed to have only a radial dependence and does not account for any molecular orientations that might be preferred at close range. Hydrodynamic effects, which would lead to a space-dependent diffusion equation are also ignored. Using Debye−Hückel theory to examine the effect of ionic interactions on dipolar relaxation in liquids, Hwang and Freed confirmed the intuitive expectation that repulsive potentials reduce the magnitude of the spectral density functions governing the relaxation while attractive potentials enhance relaxation. Taking the limits of continuous diffusion and $T_{k_e}\omega \gg 1$ one obtains for the force free model[24]

$$J(\omega) = \left(\frac{1 + \frac{5z}{8} + \frac{z^2}{8}}{1 + z + \frac{z^2}{2} + \frac{z^3}{6} + \frac{4z^4}{81} + \frac{z^5}{81} + \frac{z^6}{648}} \right) \quad (11)$$

with

$$z = \left(2\omega \frac{d^2}{6D} \right)^{1/2} \quad (12)$$

where $D = D_I + D_S$ is the relative diffusion constant between the two spin-bearing molecules, and d is the distance of closest translational approach. The resulting contribution to spin−lattice relaxation resembles the dipolar part of eq 4.

$$\frac{1}{T_{1_{trans}}} = \frac{32\pi}{405} \left(\frac{\mu_0}{4\pi} \right)^2 \gamma_I^2 \gamma_S^2 \hbar^2 S(S+1) \frac{\aleph}{dD} \times f_0(r)[J(\omega_S - \omega_I) + 3J(\omega_I) + 6J(\omega_S + \omega_I)] \quad (13)$$

The translational correlation time, τ_{trans}, of random Brownian motion is

$$\tau_{trans} = \frac{\overline{\lambda^2}}{6D} = \frac{d^2}{6D} \quad (14)$$

in terms of the mean squared displacement λ, which we approximate by d. Repulsive electrostatic potentials $U(r)$ tend to reduce the effective spectral densities determined from the force free result.[21] The relative contribution of translational diffusion to the relaxation is thereby scaled by the factor $f_0(r)$, which will be some function of $U(r)$ and will be taken to be invariant with frequency. To the extent that fully hydrated cations in aqueous solution may be characterized as spheres, their diffusive behavior should be well accounted for by Freed's formalism. While it would be more satisfying to include both a formal ionic potential in the pair-correlation function used to analyze the translational contribution to ^{7}Li relaxation and the appropriate propagators in the diffusion equation, we elected to make use of Freed's observation and regard the pair-correlation function as a scaling factor that reflects the reduced number of effective encounters between molecules of like charge. Even in the absence of a detailed functional form of the interionic potential, and though at 2 M ionic strength it is likely that the diffusive characteristics will be spatially dependent, we believe this to be an adequate treatment of the problem. If a more realistic form of the potential is used in an improved version of the diffusion equation, these would manifest as relatively minor corrections to the theory used here, and would necessitate the introduction of several additional parameters, which would be difficult to verify independently. This simplified model is assumed to be sufficient given the resolution of the data to be discussed.

These equations assume that the paramagnetic electron spin density may be treated as a point dipole centered at the Mn(II) ion. Kowalewski and co-workers have tested this approximation for aquo-complexes, and find only small effects for ^{1}H relaxation of coordinated water molecules.[25] The approximation is, thus, easily justified for the present case where interactions are at longer distances and direct interactions moderated by strong bonding are absent.

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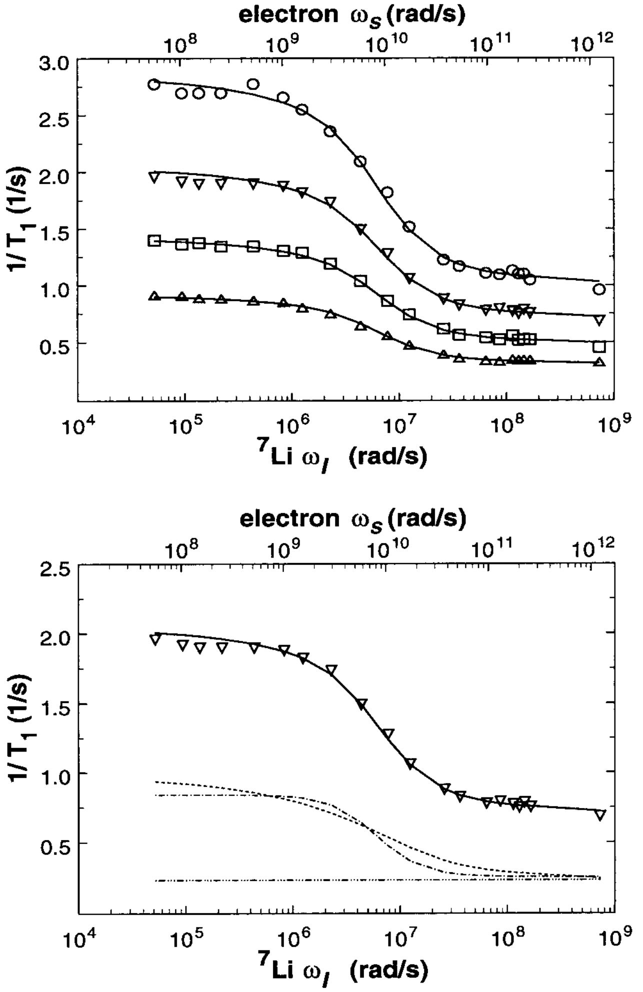

Figure 1. MRD data for 1.0 M ^{7}LiNO$_3$ by Mn(II) (a) (top) [MnSO$_4$] = 2.25 mM (△), 3.48 mM (□), 4.91 mM (▽), 6.74 mM (○). (b) (bottom) Relative contributions from translationally correlated dipolar (dash), rotationally correlated dipolar (dash-dot) and quadrupolar (dash-dot-dot) relaxation mechanisms. All lines are least-squares fits to the data as discussed in the text.

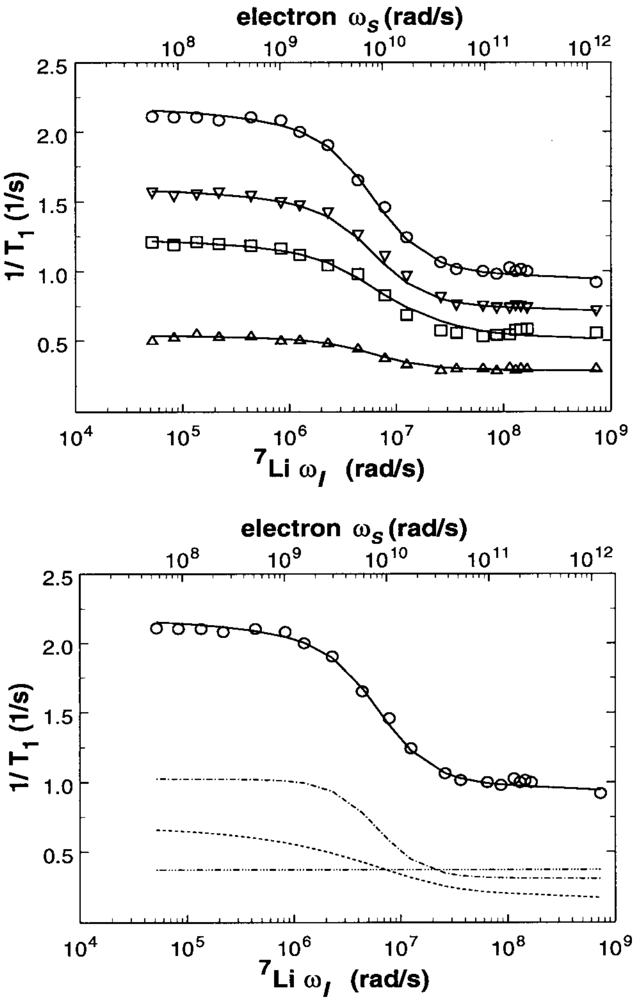

Figure 2. MRD data for 2.0 M ^{7}LiCl by Mn(II) (a) (top) [MnSO$_4$] = 1.02 mM (△), 2.50 mM (□), 3.48 mM (▽), 4.90 mM (○). (b) (bottom) Relative contributions from translationally correlated dipolar (dash), rotationally correlated dipolar (dash-dot) and quadrupolar (dash-dot-dot) relaxation mechanisms. All lines are least-squares fits to the data as discussed in the text.

3. Experimental Section

Relaxation time measurements were made as a function of magnetic field strength on an instrument to be described elsewhere that was assembled in this laboratory and utilizes a 7.05 T superconducting Magnex solenoid in close proximity to a GMW 4-in. electromagnet which is isolated magnetically from the higher field by an iron shield. The sample is stored in the high field, moved pneumatically to the variable lower field for various relaxation delay periods, and then returned pneumatically to the high field where the remaining magnetization is measured with a 90° pulse or other sequence. The liquid sample is degassed with an Ar stream and sealed in a threaded delrin cylinder. The sample movement is controlled by a Tecmag Libra system controlled by a MacIntosh Quadra 800 computer, which activates dual dc solenoid valves to control the air/vacuum pressure that drives the sample through the field cycle. The magnetic resonance probes were constructed in this laboratory employing commonly used LRC single resonance circuits. All experiments were performed at ambient temperature which was maintained near 294 K.

LiCl (99.99%) and LiNO$_3$ (99.99%) was used as received from Aldrich. The manganese sulfate monohydrate obtained from Mallinckrodt contains less than 0.01% (wt/wt) total metallic impurities.

4. Results and Discussion

Figures 1 and 2 show the least squares fits of eq 2 to the data collected from 1.0 M LiNO$_3$ and 2.0 M LiCl solutions containing varying amounts of MnSO$_4$. The total observed relaxation rate consists of distinct contributions: the diagmagnetic relaxation of unbound lithium ion ($T_{1_D}^{-1}$), the intermolecular electron-nuclear dipolar interaction ($T_{1_{trans}}^{-1}$), and the intramolecular mechanisms ($T_{1_M}^{-1}$). $T_{1_D}^{-1}$ is concentration dependent and frequency independent,[24] so measurement of ^{7}Li $T_{1_{obs}}$ in the absence of any paramagnetic agent gives the baseline correction applied both to individual samples and eq 2, *i.e.*, $T_{1_D}^{-1} = 0$. Experiments were performed in which the lithium concentration was varied between 0.5 and 4.0 M, and it was found that apart from the expected baseline shift, there was no significant departure from the mass law established by varying the concentration of manganese. At the concentrations used, it is not unreasonable to expect the formation of Mn-X type complexes. Such a reduction in point symmetry at the Mn(II) center would have a dramatic effect on the electron T_{1_e}. However, measurement of ^{1}H T_2 in solutions of MnSO$_4$ reveal only small perturbations of the proton hyperfine coupling over a wide range of anion concentrations. There was no difference in the data obtained from solutions buffered at pH 4.0 and 7.0, although no general effort was made to control pH in the reported experiments in order to avoid complexation between the buffer ions and Mn(II), and formation of [Mn(H$_2$O)$_5$OH]$^+$ in basic conditions.

Table 1. Molecular Parameters Determined from Theoretical Analysis of ^{7}Li/Mn(II) MRD Data

	LiCl/MnSO$_4$	LiNO$_3$/MnSO$_4$
d (m)	6.0×10^{-10}	5.85×10^{-10}
D (m^2 s^{-1})	2.2×10^{-9}	2.2×10^{-9}
f_0	0.40	0.54
r_{IS} (m)	5.6×10^{-10}	5.5×10^{-10}
τ_c (s)	1.00×10^{-10}	0.97×10^{-10}
K (M^{-1})	0.221	0.126
$\frac{eQ}{h}\frac{\partial^2 V}{\partial z^2}$ (MHz)	1.20 ± 0.06	1.00 ± 0.05

Theoretical results for both sets of experiments presented in Table 1 reveal nearly identical molecular parameters. Here, attention is restricted to the results for the LiNO$_3$/MnSO$_4$ system. The dashed line in Figure 1b represents the translational term of the total relaxation and is modeled after eq 13. The values that minimize the sum of the squares of the deviation are d = 5.85 Å and $D = 2.25 \times 10^{-9}$ m^2 s^{-1}, which imply that through eq 14 τ_{trans} = 25 ps. Both τ_{trans} and the relative diffusion constant are reasonable for strong electrolytes in solution.[4] More significantly, the distance of closest approach is consistent with the sum of two hydrated radii, indicating that while the hydration shell water molecules may be labile, on the level of resolution afforded by macroscopic relaxation, the integrity of the first hydration shell of the Li(H$_2$O)$_n^+$ complex is intact during a translational encounter with Mn$^{2+}_{(aq)}$. The relative weight given to this translational contribution was set at $f_0(r) = 0.54$ for the best overall fit to the data. Without explicit knowledge of the intermolecular potentials (likely complicated, particularly at short range), it is difficult to judge the accuracy of this parameter, beyond suggesting that it is consistent with the expected order of magnitude reduction in the number of effective encounters between like-charged species, especially given that short-range interactions are most efficient at inducing relaxation.

Regardless of the detailed analysis of translational diffusion, the form of the MRD profile itself clearly demonstrates the presence of a rotationally correlated Lorentzian contribution to the relaxation. The substantial change in the relaxation rate over a small frequency range cannot be completely accounted for by a model of liquid phase translational diffusion with physically reasonable parameters. The integral in eq 9 is taken over the entire sample volume and includes both short- and long-range interactions corresponding to variations over a large frequency range. Intramolecular electron-nuclear dipole coupling, eq 4, is shown by the dash-dot line for a displacement between the molecular centers of r_{IS} = 5.50 Å and an intramolecular dipolar correlation time of τ_c = 97 ps. With this large separation, it is not reasonable to expect significant overlap of paramagnetic spin density at the lithium nucleus, thus we ignore the Fermi contact interaction. Without direct scalar coupling and significant perturbation of the first coordination sphere symmetry, the Mn(II) electron T_{1_e} should not be significantly changed by transient interaction with the lithium nucleus. As mentioned, we expect the electron T_{1_e} to be one order of magnitude larger than the observed τ_c, but we cannot resolve the relative sizes of τ_{rot} and τ_{ex} without an observable dispersion caused by a finite Fermi interaction (eqs 6 and 7). However, the value of τ_c obtained from this analysis is consistent with the correlation time expected for rotation of a bimolecular complex in water.[20] Upon the formation of a rotationally correlated, cation−cation outer sphere complex, transient field gradients arising from a reduced electronic field symmetry induce greater quadrupole relaxation of ^{7}Li via eq 8. The dash-dot-dot line was computed with $\tau_c = \tau_{rot}$ = 97 ps and an average quadrupole coupling constant $e^2qQ/h = 1.00 \pm 0.05$ MHz.

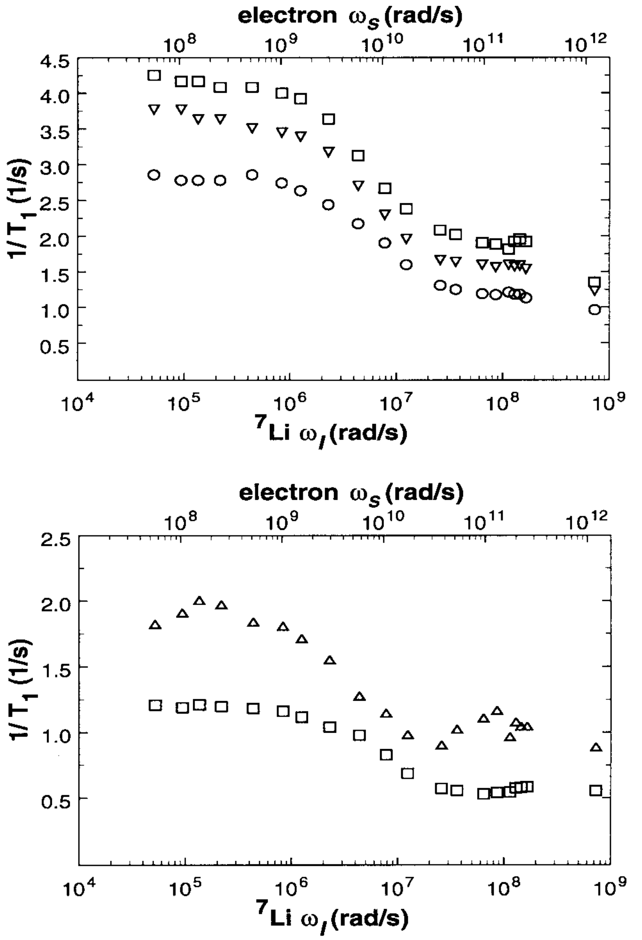

Figure 3. MRD data for 2.0 M ^{7}LiCl by Mn(II) (a) (top) [MnSO$_4$] = 6.74 mM: acetone = 0 % w/w (○), acetone = 15 % w/w (▽), acetone = 25 % w/w (□). (b) [MnSO$_4$] = 2.50 mM: acetone = 0 % w/w (□), acetone = 50 % w/w (△).

A good measure of the efficacy of this model can be read from Figure 1a, where the data from four different samples, each containing different concentrations of Mn(II), is shown. The equilibrium fraction of lithium bound in a complex with manganese will vary as eq 3 and directly affects the observed relaxation through eq 2. Using exactly the parameters determined from the fit in Figure 1b, eq 2 simultaneously converges to all four sets of data for K = 0.125 M^{-1}. Only the quadrupole coupling term was allowed to vary, and this only over a 10% range. To our knowledge, this is the first equilibrium constant determined from direct spectroscopic evidence reported for such an ion pair. Qualitatively, the free energy of complex formation is consistent with hydrogen bond enthalpies and a small (negative) entropic contribution. From Coulomb's law, a simple calculation of the magnitude of the electrostatic force between a +/2+ ion pair in aqueous solution with a dielectric constant near 80 shows that the energy required to bring these two ions within 6 Å of each other is less than 6 kJ mol^{-1}. This repulsive energy can, in principle, be overcome by the formation of one or more H-bonds, as suggested by earlier theoretical studies. Furthermore, it is reasonable to expect that the cation−cation complex may be stabilized by counterions.

From the distance constraints obtained, a bonding event would be mediated by the formation of hydrogen bonds between bridging water molecules and those from the first coordination spheres. Table 1 shows that the Li···Mn vector contracts by about 0.4 Å from the sum of hard-sphere radii. Notably, the value of $K = 0.224$ M^{-1} obtained from the LiCl data, hints at the possible role played by the counterion in stabilizing the cation−cation complex by reducing the effective charge. From steric considerations, chloride might be more effective than nitrate in this regard. Yet, comparing the effective translational collision factors $f_0(r)$ for the two anions reveals that chloride reduces the relative efficiency of collisionally induced relaxation. Clearly, however, formation of cation−cation outer sphere complexes intimately depends on factors that influence diffusive mobility and charge dispersion.

To verify the existence of a bimolecular complex, attempts were made to repeat these experiments in solvents with both lower dielectric constants and reduced capacities to form hydrogen bonds. Both the lithium and manganese salts were soluble in a water−acetone mixture. As Figure 3 shows, the MRD profiles from these experiments reveal a trend toward a more slowly varying translational modulation as the acetone content is increased, indicating a destabilization of the cation−cation complex. At higher fractions of acetone, the rotationally correlated component is further diminished, but under these conditions the results are complicated by complex formation between acetone and the metal ions. Substitution of acetone for water in the ion solvation sphere reduces the octahedral point symmetry at the lithium nucleus and induces relaxation through the nuclear electric quadrupole interaction that causes a baseline shift toward higher observed relaxation rates. Presence of solvent substituition in the manganese coordinate sphere induces the formation of a ZFS in the electron spin manifold that increases the electron relaxation rate dramatically. The relative maximum apparent in the high frequency portion of the MRD curve in Figure 3b is characteristic of a field dependence in the electron relaxation time which contributes significantly to the correlation time for the electron-nuclear coupling in this aceteone rich solution. While a discussion of the lattice modulation can be presented in terms of the correlation times for electron spin relaxation, the situation is further complicated by the fact that several chemical species are likely to coexist in this system. Although detailed modeling of these data is difficult, qualitatively, the increased width of the relaxation dispersion and loss of the Lorentzian component are consistent with loss of cation−cation pairs in the mixed solvent.

5. Conclusion

In concert with the theory of magnetic relaxation, these MRD data have provided experimental evidence for the formation of cation−cation outer sphere complexes, revealing a clear physical model of the encounter between like-charged species in aqueous solution. As expected, translational dynamics within the solvent cage are a significant source nuclear relaxation, regardless of repulsive electrostatic potentials. The distance of closest translational approach between the cations is consistent with an encounter between two solvated species, although little detail can be given regarding the hydration shell dynamics. Counterintuitively, most of the nuclear relaxation is derived from the formation of a rotationally correlated outer sphere complex. The calculated intermoment vector is consistent with the formation of hydrogen bonds between bridging water molecules and those in the first coordination sphere of each metal ion. Furthermore, the intramolecular correlation time is consistent with the Brownian rotation of a complex with the dimensions expected of the cation−cation pair. Apart from these geometrical constraints, which are consistent with those derived from previous independent studies,[4−6] several properties particular to the Li^+/Mn^{2+} system have also been determined. While the electron ZFS at the Mn(II) center remains unperturbed in the presence of the anions studied, the relative effects on diffusional characteristics and complex stability were resolved. There is no direct coordination of the lithium and manganese ions, as this would imply a strong relaxation due to Fermi coupling, and this was not observed. However, formation of this outer sphere complex causes formation of an electric field gradient at the ^{7}Li nucleus inducing an observable contribution to the relaxation.

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