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Quantitative Structure-Based Prediction of Electron Spin Decoherence in Organic Radicals

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ABSTRACT The decoherence, or dephasing, of electron spins in paramagnetic molecules limits sensitivity and resolution in electron paramagnetic resonance (EPR) spectroscopy, and it represents a challenge for utilizing paramagnetic molecules as qubit units in quantum information devices. For organic radicals in dilute frozen aqueous solution at cryogenic temperatures, electron spin decoherence is driven by neighboring nuclear spins. Here, we show that this nuclear-spin-driven decoherence can be quantitatively predicted from molecular structure and solvation geometry of the radicals. We use a fully deterministic quantum model of the electron spin and up to 2000 neighboring protons with a static spin Hamiltonian that includes nucleus-nucleus couplings. We present experiments and simulations on two nitroxide radicals and one trityl radical, which have decoherence time scales of 4-5 μs below 60 K. We show that nuclei within 12 Å of the electron spin contribute to decoherence, with the strongest impact from protons 4-8 Å away.
KEYWORDS

nuclear spin diffusion, cluster correlation expansion, phase memory time, coherence, EPR, DNP
The spins of unpaired electrons in organic radicals and metal ions are extensively used in pulse electron paramagnetic resonance (EPR) spectroscopy to probe the structure and dynamics of the nano-environment around the electrons.\cite{1, 2, 3} Molecule-based unpaired electrons are also investigated as potential building blocks for devices useful to quantum information science (QIS).\cite{4, 5, 6} In this context, they are often referred to as “molecular spin qubits”. In both cases, a key limitation is the fact that excited electron spins lose coherence over time. This process, called decoherence, dephasing, or transverse relaxation, results in the loss of signal. In EPR, decoherence limits sensitivity and spectral resolution. In QIS applications, it impacts the efficient transfer of information between coupled qubits, and it limits the complexity of algorithms that can be executed. Extending coherence times is therefore an important development goal in both fields. For this, a detailed understanding of the physical origins of decoherence is crucial.

There are many processes that drive electron spin decoherence, including molecular motions and magnetic interactions.\cite{7} It is possible to eliminate the effect of motions (librations, thermal methyl rotations, etc.) on decoherence by operating at low temperatures. Magnetic interactions among electron spins, and between electron spins and nearby nuclear spins, also contribute to decoherence. Processes due to couplings between electron spins can be eliminated by dilution. At sufficiently low temperatures and low electron spin concentrations, decoherence is driven by nearby nuclear spins.\cite{8, 9} This mechanism, often called nuclear spin diffusion, has been described semi-classically as arising from stochastic energy-conserving flip-flops of pairs of nuclei, leading to spectral diffusion of the electron spin resonance frequency and consequently to decoherence.\cite{10, 11, 12} The problem with this stochastic model is that it is not predictive and does not provide insight into the physical origin of the assumed flip-flop rate.
Here, we experimentally determine the decoherence behavior of three prototypical organic radicals in frozen aqueous solutions, at temperatures and concentrations low enough to eliminate contributions of any motional or electron-electron processes to decoherence. We show that the nuclear-spin-driven decoherence of the radicals can be quantitatively predicted directly from their molecular geometry and solvation structure, using a combination of molecular dynamics (MD) and quantum spin dynamics, without the need for any adjustable free parameters.

Electron spin decoherence can be measured using various pulse EPR techniques. The most straightforward is the two-pulse echo decay (Figure 1). This technique uses the pulse sequence $\pi/2 - \tau - \pi - \tau -$ echo and records the decay of the echo amplitude resulting from increasing the inter-pulse delay $\tau$.

We investigated the decoherence characteristics of three different radicals: 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO), its perdeuterated isotopologue ($d_{18}$-TEMPO), and a perdeuterated trityl radical ($p_{1}$TAM) (Figure 2). TEMPO and $d_{18}$-TEMPO both are N/O-centered radicals with four neighboring methyl groups and differ only in that all $^1$H atoms in TEMPO are replaced with $^2$H atoms in $d_{18}$-TEMPO. The trityl radical, $p_{1}$TAM, is a C-centered radical and has 12 deuterated methyl groups. The concentrations of the radicals were kept low enough to minimize additional decoherence effects arising from instantaneous diffusion mediated by...
electron-electron couplings.\textsuperscript{14,15} Electron $T_1$ values are on the order of 0.1–1 s and do also not contribute to decoherence. All samples were prepared in a solution of 1:1 (w:w) H$_2$O:glycerol and were snap frozen in liquid nitrogen. The experiments were performed from 20-60 K at Q-band frequencies (ca. 33 GHz).

Figure 3 shows the experimental two-pulse echo decays at 20 K, presented in black. For all samples, the coherence decays on a similar timescale and is completely lost within 10 $\mu$s.

The decays are phenomenologically fitted well by stretched exponentials of the form $V(2\tau) = V_0 \cdot \exp(-(2\tau/T_M)^x)$, shown in gray. Here, $T_M$ is the phase memory time, and $x$ is a stretching exponent. This stretched-exponential form is predicted by the semiclassical model that uses stochastic nuclear flip-flops to describe the loss of electron spin coherence.\textsuperscript{10–12}

The experimental decay shape of $p_1$TAM (Figure 3, top) is the closest of the three molecules used in this study to a pure stretched exponential. $p_1$TAM does not have hydrons (protons or deuterons) neighboring the C-centered unpaired electron; the closest hydrons are about 4 Å away. The $d_{18}$-TEMPO decay (Figure 3, middle) shows oscillations at short times resulting from nuclear electron spin echo envelope modulations (ESEEM). This effect arises from the pseudo-secular parts of the hyperfine coupling to nearby nuclei, the deuterons on the radicals in this case.\textsuperscript{2,16} No ESEEM oscillations are visible in the TEMPO sample (Figure 3, bottom). Instead, the TEMPO decay shows a slight deviation from the shape of a stretched exponential at early times that may be
the result of thermal or tunneling methyl rotations.\textsuperscript{17,18} The p\textsubscript{1}TAM decay is slightly slower than those of TEMPO and d\textsubscript{18}-TEMPO, since the closest magnetic nuclei are farther from the electron spin in p\textsubscript{1}TAM.

To investigate the temperature dependence of the decoherence behavior at cryogenic temperatures, we performed experiments from 20-60 K; the decoherence behavior is unaffected by temperature in this range (Figures S2 and S3). This is consistent with previous experimental results.\textsuperscript{8}

To predictively model the experimental decoherence behavior, we performed explicit structure-based spin quantum dynamics simulations of the two-pulse echo decays. Structures of the solvated radicals were generated using molecular structures optimized by density functional theory (DFT) and solvation geometries obtained by molecular dynamics (MD). The system of spins used in the spin dynamics calculation comprises the unpaired electron, all magnetic nuclei on the radicals, and up to 2000 solvent protons within a radius of up to 20 Å from the electron. Full nucleus-nucleus coupling tensors as well as both secular and pseudo-secular parts of hyperfine coupling tensors between nuclei and the electron spins were included in the static spin Hamiltonian

\[
\tilde{H}_0 = \mu_B g_e B_0 S_z + \sum_{n=1}^{N} (-\mu_N g_n B_0 f_{z,n} + S_z (Z^T A_n) I_n + T_n^P P_n I_n) + \sum_{m=1}^{N-1} \sum_{n=m+1}^{N} \delta_{g_n,g_m} T_m^P b_{m,n} I_n.
\]

The individual terms in this Hamiltonian mostly follow standard notation and are described in the Supporting Information. Microwave pulses were modelled as ideal (i.e. infinitely short).
To handle the enormous spin Hilbert space, we employed the ensemble cluster correlation expansion (CCE) method\(^{19,20}\) that has been developed for predicting the decoherence behavior of spin centers in crystals.\(^{21-24}\) It is conceptually similar to the truncated Liouville space methods employed in nuclear magnetic resonance (NMR).\(^{25-29}\) The method simulates spin dynamics in Hilbert space using a truncated expansion approach that calculates the signal of the total spin system as a combination of the signals from many small clusters of spins (Figure 4). Algorithmic truncation parameters of the CCE method are the size of the total spin system, a neighbor cutoff that eliminates clusters with negligible internal couplings, the maximum cluster size used, and the number of orientations of the magnetic field to be averaged over. They are shown in Figure 4 and have been optimized to assure convergence of the result. Further details are given in the Supporting Information. It is important to note that the simulation is exclusively structure-based and does not contain any additional free physical parameters, neither static nor dynamic.

The simulated echo decays are shown in red in Figure 3. In all, the decoherence behaviors of all three radicals are quantitatively predicted both in shape and timescale. All three simulations result in a stretched exponential decay with oscillations from ESEEM at early times. Eliminating nucleus-nucleus couplings from the simulation completely eliminates the decays, showing that these couplings are key to the mechanism of nuclear-spin-driven electron spin decoherence. The slight timescale discrepancies between simulated and experimental decays may arise from errors

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure4.png}
\caption{Illustration of the truncation parameters, which are the system size \(r_{sys}\) (purple circle and arrow), the cluster sizes used (rust areas), and the clustering based on neighbor cutoff (green arrows).}
\end{figure}
in the MD prediction of the solvation geometries and solvent proton densities and from potential residual contributions of other decoherence mechanisms. The p1TAM simulation is in most agreement with experiment with or without the inclusion of ESEEM-generating terms in the Hamiltonian. The d18-TEMPO simulation required the inclusion of ESEEM-generating terms in the Hamiltonian to reproduce the oscillations at early times in the experimental decays. Inclusion of ESEEM in the TEMPO simulation did not reproduce the early time shape of the experimental decay. The simulations show increased ESEEM oscillation amplitudes that are likely due to incomplete averaging over solvation geometries. A measurement and simulation of d18-TEMPO at X-band (Fig. S4) demonstrate that the model works at different magnetic fields.

To gain more insight into the structural aspects that determine decoherence timescales, we devised a method to attribute decoherence effects to individual nuclei in the systems. To do so for a particular nucleus $i$, we simulated the echo decay of the system without nucleus $i$ (i.e. assuming it as non-magnetic). This results in a slightly prolonged echo decay compared to the full system. We capture this by the difference in phase memory times, $\Delta T_{M,i}$, between the full system and the reduced system (Figure S7); $\Delta T_{M,i}$ quantifies by how much the presence of nuclear spin $i$ shortens the phase memory time. It is important to note that individual $\Delta T_{M}$ values are not additive, as the decoherence mechanism is a cooperative effect driven by nucleus-nucleus couplings. Still, they
allow the assessment of the relative importance of individual nuclei to electron spin decoherence, within their context of neighboring nuclear spins.

The results of this analysis for TEMPO are depicted in Figure 5. Figure 5(a) shows a 3D cartoon of the solvated radical, with each proton colored according to $\Delta T_M, i$, where darker indicates larger values. No clear geometric patterns are discernible, although it is evident that some protons in the vicinity of the electron contribute much more than others. Figure 5(b) shows a scatter-plot of $\Delta T_M$ for all nuclei as a function of their distance from the electron spin.

The protons 4-8 Å from the electron have the largest effect upon electron spin decoherence. Their presence each shortens the predicted phase memory time by up to 28 ns. Protons that are less than about 4 Å from the electron, such as the methyl protons, contribute much less to decoherence. This volume of reduced decoherence contributions corresponds to the notion of the diffusion barrier observed in nuclear spin diffusion. The value obtained here (4 Å) is somewhat smaller than those reported for nuclear diffusion barriers (7-10 Å, $^{8,11}$ 4-6.6 Å$^{30}$, < 6 Å$^{31}$).$^{32,33}$ However, this direct

![Figure 5.](image.png)

**Figure 5.** (a) Map of decoherence effects $\Delta T_M$ of individual nuclei for TEMPO in H$_2$O demonstrating which nuclei contribute most to the dephasing of the electron spin. The color scale corresponds to that in (b), with darker blue indicating larger values of $\Delta T_M$. (b) Individual $\Delta T_M$ values as a function of distance (blue, left vertical scale) and calculated $T_M$ as a function of system size (red, right vertical scale).
comparison is not entirely valid, since we model loss of electron spin coherence, whereas the diffusion barrier relates to spatial transfer of polarization. Beyond 8 Å, the individual $\Delta T_M$ taper off rapidly with increasing distance. Figure 5(b) also plots the calculated overall $T_M$ as a function of system size and shows that in order to obtain a converged $T_M$, all nuclei up to at least 12 Å from the electron spin need to be included. The conclusions are similar for $d_{18}$-TEMPO and $p_1$TAM (Figure S8).

In combination with the experimentally validated simulations, the ability to examine decoherence effects due to individual nuclei greatly enhances insight into the structural origins of nuclear-spin-driven electron spin decoherence. As mentioned, this decoherence mechanism has traditionally been described semi-classically by a stochastic process of nuclear flip-flops involving pairs of surrounding nuclei, with an ad hoc flip rate constant. Within the quantum model presented herein, however, electron spin decoherence is the result of a coherent, deterministic evolution of a large closed system of nuclear spins coupled to each other and to the electron spin, without any external stochastic influence. Even after electron spin coherence has decayed, the coherent evolution of the spin system continues, even though it is not observable. Eventually, $T_1$ processes destroy the coherence, and the total spin system is brought back to equilibrium.

Extending the methodology to fully deuterated solvents is not straightforward. Deuterons lead to prolonged time scales of the echo decays, and the presence of nuclear quadrupole couplings results in deeper echo modulations. The longer time scales pose experimental challenges of isolating nuclear-spin-driven dephasing from other processes such as spectral diffusion and instantaneous diffusion. Both the longer time scales as well as the increased modulation depths create convergence challenges for the CCE method.34
In summary, we have shown that nuclear-spin-driven electron spin decoherence of radicals in sufficiently dilute frozen aqueous solutions at cryogenic temperatures can be quantitatively predicted directly from the solvation structure of the radicals using explicit spin quantum dynamics with a static spin Hamiltonian, without any free parameters. This methodology can be useful for designing molecules and platforms that maximize electron spin coherence lifetimes, both to increase sensitivity and resolution in EPR spectroscopy as well as to improve molecular spin qubits for potential QIS applications.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge. Detailed description of experimental parameters, MD simulations, summary of theory, temperature dependence experiments, X-band experiment and simulation of d18-TEMPO, decoherence effect maps and plots of TEMPO, d18-TEMPO, and p1TAM (PDF).

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Notes

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The authors declare no competing financial interests.

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