



Optorelaxers: Achieving real-time control of NMR relaxation

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ABSTRACT

We present an approach to increase the detection sensitivity of NMR by shortening the spin-lattice relaxation time using transient paramagnetic species created by light irradiation of “optorelaxer” molecules. In the ultimate implementation of this concept, not yet realized here, these transient species are absent during the detection period, thereby avoiding the loss of spectral resolution caused by inhomogeneous broadening from paramagnetic species. Real-time control of NMR relaxation by visible light is demonstrated with Fe(II)(ptz)₆(BF₄)₂, (ptz = 1-propyltetrazole), abbreviated FePTZ. Illumination of FePTZ at 30 K results in a decrease of the ¹H NMR spin-lattice relaxation time T_1 due to formation of a high spin photoexcited state. The ¹H NMR of polystyrene containing a low concentration of FePTZ molecules shows a similar reduction in T_1 , establishing that FePTZ can act as an optorelaxer for the protons of a matrix. Numerical modeling of the spin-diffusion processes from the protons in a FePTZ core to those in a shell of polystyrene accounts for the observed T_1 effects under both dark and light conditions. Additionally, ¹H MAS (magic-angle spinning) NMR results for pure FePTZ provide information on the isotropic and anisotropic portions of the electron-nuclear hyperfine interactions.

1. Introduction

The interaction of unpaired electron spins with nuclear spins has played an important role in magnetic resonance spectroscopies since the earliest days of both NMR and EPR [1] [2]. The motivations for observing and interpreting such interactions vary widely. They range from obtaining atomistic information about electronic structure and delocalization of electrons (e.g. ENDOR hyperfine couplings [3] [4], NMR Knight shifts [5] [6], NMR contact and pseudocontact shifts in metal complexes [7] [8] [9]), to gaining chemical structure information from distances obtained from electron-nuclear anisotropic hyperfine couplings and their effects upon relaxation [10] [11], to improving the detection sensitivity of NMR by incorporating paramagnetic dopants. This last class of motivations includes two separate areas. First is the long-recognized ability of dopants such as transition metal ions to dramatically shorten the spin-lattice relaxation times of nuclei in solids via spin-diffusion [12] [13], permitting more rapid data acquisition. Paramagnetic Relaxation Enhancement (PRE) has been useful at ambient temperature in both solution NMR as well as solid-state NMR of proteins [14] [15] [16] [17]. The effects of electron spins in paramagnetic complexes as agents of rapid spin-lattice relaxation of the nuclear spins were analyzed in a highly-cited paper by Alexander Vega and Daniel Fiat [18]. This paper showed that in addition to the usual ‘S-mechanism’ an additional

‘ γ -mechanism’ arising from the thermal average of the electron spin polarization could significantly contribute to relaxation in tumbling paramagnetic molecules. The second area of application of paramagnetic agents relies upon the much higher Boltzmann polarization of electron spins compared to nuclear spins. It involves increasing the nuclear spin polarization with dynamic nuclear polarization (DNP) [19] by incorporating organic radicals and biradicals into samples and using microwave irradiation of the EPR transitions at temperatures of ca. 100 K or lower [20] [21] [22].

The interaction of light with matter affects nuclear spins only indirectly, via electronic excitations that directly alter the electron spin states. The indirect effects of light upon nuclear spins can have important consequences in such areas as Optically Pumped NMR (OPNMR) of semiconductors [23] [24] and NV-centers in diamond [25] and in photo-Chemically Induced DNP (photo-CIDNP) in photosynthetic reaction centers [26] [27] [28]. For specific organic molecular crystals doped with absorbers and at low temperature, photoexcited triplet states can be created and used during their short lifetime as a source for nuclear polarization via microwaves (Microwave-Induced Optical Nuclear Polarization, or MIONP) [29] [30] [31,32]. The aim of these NMR approaches involving irradiation with light is to achieve increased NMR sensitivity by greatly increasing the nuclear Zeeman spin level population differences beyond the Boltzmann level. Irradiation with light has also been

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observed to reduce nuclear T_1 values in specialized systems [30] [33] [34].

This paper presents an approach to increase the detection sensitivity of NMR. Light is used to create transient paramagnetic species from a compound introduced into the sample that we term an “optorelaxer”. The optorelaxer serves to decrease the spin-lattice relaxation time T_1 in a sample, either of nuclei that are being observed directly, or else of other abundant nuclei that are used to cross-polarize the nuclei of interest. Fig. 1 depicts schematically how the speeded-up acquisition of free-induction decays (FIDs) enabled by optorelaxers will improve the sensitivity compared to regular NMR.

Increasing NMR sensitivity by increasing nuclear spin-lattice relaxation rates has long been accomplished via the addition of paramagnetic species, as mentioned above. However, the concentration of paramagnetic species that can be successfully used is ultimately limited by the resultant paramagnetic broadening. The inhomogeneous spectral broadening effects result from electron-nuclear anisotropic hyperfine interactions. The advantageous aspect of the optorelaxer approach is the transient nature of the resultant photoparamagnetism (i.e. photomagnetism not involving ferromagnetism). The same advantage has also been noted for MIONP experiments [29] [31]. The photoparamagnetism may be absent during the acquisition period by natural decay of the excited state in the dark in some cases, or in others can be eliminated by thermal cycling or by illumination at a different wavelength. With conventional experiments involving addition of permanent paramagnetic reagents the sensitivity enhancements achievable are limited by the relatively low reagent concentrations used in order to avoid spectral broadening. Much higher concentrations of optorelaxers could be used in principle to further improve sensitivity.

The sensitivity gains from using optorelaxers will generally be greatest for samples having the longest T_1 values in the absence of optorelaxers. The sensitivity gain from using optorelaxers at a given sample temperature is shown to be $\sqrt{T_1/T_{1(opt)}}$. Optorelaxers thus also have great potential value at cryogenic temperatures, where T_1 values are usually very long. The Boltzmann population differences between Zeeman levels, and thus the NMR signal strength at equilibrium, are also larger at cryogenic temperatures, scaling as $1/T$.

Effective optorelaxers must satisfy some general requirements. They must be capable of being incorporated into the sample of interest as isolated molecules, or possibly as nanocrystallites. Photoexcitation should transform a large fraction of optorelaxers from their diamagnetic ground state to the paramagnetic excited state, which should have electron spin lifetimes that result in efficient nuclear spin relaxation. The decay from the excited state to the ground state should be controlled by the illumination conditions or other means, with decay times suitably

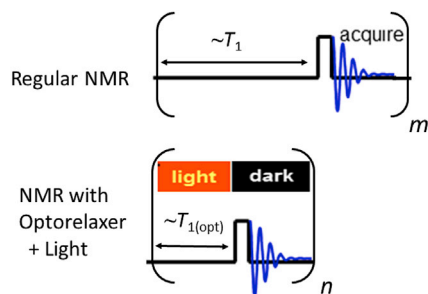


Fig. 1. Schematic illustration of optorelaxer concept, showing how transient photoparamagnetism created by light results in more rapid recovery of magnetization and decreases the waiting time from ca. T_1 to the shorter $T_{1(opt)}$. The absence of photoparamagnetism during the typically much shorter acquisition period avoids inhomogeneous spectral broadening from paramagnetic species that degrades both resolution and sensitivity. For a given total experiment time, using optorelaxers results in $n \gg m$ and a sensitivity gain of $\sqrt{T_1/T_{1(opt)}}$. A single-pulse NMR experiment is illustrated, but the method is applicable to more complicated pulse sequences as well.

short for any given NMR experiment. Optorelaxers should also be photostable. Our strategy to experimentally demonstrate the optorelaxer concept makes use of the transient photoparamagnetism of the high spin ($S = 2$) form of a complex of Fe(II) whose ground state is low spin ($S = 0$) at cryogenic temperatures (see Fig. 2a). The specific complex chosen is Fe(II)(ptz)₆(BF₄)₂, where ptz = 1-propyltetrazole, and which is abbreviated to FePTZ. It belongs to a class of compounds known as spin-crossover complexes [35]. The ability of irradiation with visible light to induce a transition from the low spin to the high spin form of a spin-crossover complex, with the high spin form persisting for a long time at low temperatures, is known as the LIESST (Light Induced Excited State Spin Trapping) effect [36] [37] [38] (Fig. 2b). The lifetimes of the photoexcited high spin form vary enormously, depending upon the complex, the matrix, the temperature and, in the case of the reverse-LIESST effect, irradiation at longer wavelengths [39]. The quantum efficiency of LIESST in FePTZ at 10 K is very high, 0.8 [39]. Thus the photon flux is used efficiently, a desired feature for optorelaxers. The molecule is photostable as well. Reference [40] provides a good summary of the photophysical properties of FePTZ relevant to the present study.

In this study, the ¹H MAS (magic-angle spinning) NMR spectrum of FePTZ is used to obtain information about the electron-nucleus anisotropic hyperfine dipolar and the isotropic contact interactions. The static ¹H NMR T_1 values at 30 K in the presence and absence of light for both the pure FePTZ complex as well as FePTZ in a polystyrene (PS) matrix are reported as indicators of optorelaxer behavior. The results are incorporated into a numerical model of the spin-diffusion processes taking place in the matrix sample.

2. Materials and methods

2.1. Sample preparation

The synthesis of FePTZ was carried out using a preparation altered from a previously-published method [40] (see [Supplemental Information](#)

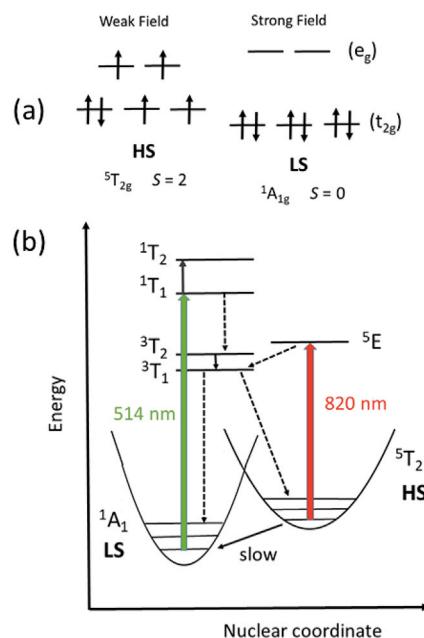


Fig. 2. (a) High spin (HS) and (low temperature) low spin (LS) configurations of d^6 Fe(II); (b) Jablonski diagram for FePTZ showing LIESST (green) and reverse LIESST (red) optical transitions. For simplicity, vibrational levels are depicted only for the two lowest states. Fast intersystem crossing processes are indicated by dashed arrows. The diagram was adapted from Ref. [41] and shows the most recent ordering of the 3T_2 state with respect to the 5E state. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

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