Coherent manipulation of molecular qudits by broadband NMR

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Summary. — We review recent results showing the capability of broadband Nuclear Magnetic Resonance (NMR) to coherently manipulate the state of multi-level molecular qudits with radiofrequency pulses. Several qubit-qudit systems have been studied, paving the way for the realization of quantum-error correction protocols. Here we focus on the recent prototypical [VO(TPP)] complex, a very promising system with long coherence times and strong hyperfine interaction.

1. – Introduction

Molecular nanomagnets (MNMs) have been extensively studied as promising systems for quantum computation. Their intrinsic multi-level structure also allows one to go beyond the traditional two-level encoding, by exploiting them as molecular *qudits* (*i.e.*, quantum systems with d > 2 energy levels) with many accessible electronic and/or nuclear spin states [1]. The multi-level energy spectrum of a qudit provides additional resources for quantum information processing (QIP) [2]. For instance, qudits can be exploited to encode qubits with embedded quantum-error correction, the latest being an essential step to protect quantum information from its intrinsic fragility [3]. Single-ion MNMs embedding a nuclear spin strongly coupled to the electronic spin possess the suitable multi-level structure for QIP applications (see [VO(TPP)] energy level scheme in fig. 1(a)–(b)) [1, 2] together with additional advantages. Indeed, the weak coupling of the nuclear spin to the environment results in longer nuclear coherence [4]. Moreover, the strong hyperfine coupling between the nuclear and electronic spins largely reduce the nuclear manipulation time, which otherwise would be very slow due to the weak nuclear magnetic moment [5]. Here
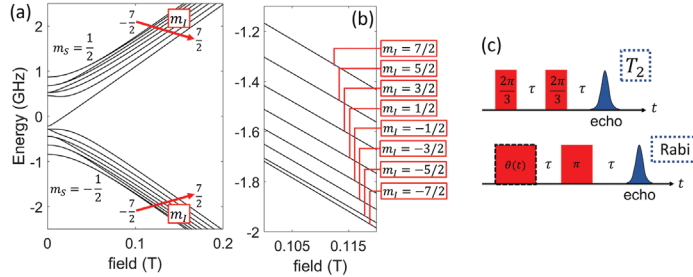
Fig. 1. – (a) Energy levels of [VO(TPP)] as a function of the field applied along the tetraphenyl-porphyrinate plane. (b) Close-up of the nuclear state levels. Reproduced from ref. [9] with permission from the Royal Society of Chemistry. (c) Sketch of the RF-pulse sequences exploited for the excitation and detection of nuclear spin echoes. For Rabi oscillations, the first pulse of variable length $\theta(t)$ induces a generic θ rotation of the spin system.

we show the particular capabilities of our custom broadband NMR hardware [6], optimized to investigate magnetic materials. We review NMR experiments on diluted (1–2% in their diamagnetic analogue) single crystals of prototypical qubit-qudit systems: [Yb-trensal] (trensal = 2,2′,2″-tris(salicylideneimino)triethylamine), [V(Cp)$_2$Cl$_2$] (Cp = cyclopentadienyl) and [VO(TPP)] (TPP = tetraphenylporphyrinate) [7-9]. In particular, we focus on the latter, which matches several requirements of a promising qudit: a large nuclear spin ($I = 7/2$), very long coherence times, and an effective quadrupolar coupling for individual addressing of nuclear transitions.

2. – Technique

The typical spin dynamics regime of a conventional magnetic material in its paramagnetic state is characterized by a hyperfine field fluctuating faster than the nuclear Larmor frequency. This results in ultra fast nuclear relaxation rates that hinders the detection of the resonance signal. However, dilute MNMs (as those described here) naturally display electronic spin-lattice relaxations at low temperatures much longer than the typical manipulation time of nuclear spins by radiofrequency pulses (RF). The latter, in turn, can be made very short thanks to the electron-nucleus hyperfine coupling, which enhances the nuclear resonance. As a consequence, the electronic environment probed by nuclei appears quasi-static on the timescale of a short-enough nuclear spin-echo pulse sequence, whose echo can be therefore detected by suitable NMR equipment. The required characteristics of the custom NMR apparatus include fast RF switching, broadband receiver stage, wide frequency span and fast signal averaging. Such specifications are met by our home-built NMR spectrometer specially designed for the investigation of hyperfine resonances in magnetic materials [6], featuring flat response over the 8–800 MHz frequency range, short dead time ($<2\,\mu$s), RF pulses with variable level and programmable duration in steps of 12 ns, and ± 3 MHz maximum receiver bandwidth. The effective signal bandwidth is slightly limited in our case to 1–2 MHz (depending on the operation frequency) by the finite passband of the LC resonator probehead. All these characteristics make the instrument suitable to excite and detect short-living spin echoes over the required frequency range. Spectra and phase memory times T_2 are collected by exciting spin echoes with Hahn-pulse sequence [10], optimized to achieve maximum resonance signals (see fig. 1(c)). Manipulation of nuclear state to generate arbitrary coherent superpositions is achieved by transient nutation experiments, inducing Rabi oscillation within specific nuclear transitions (see fig. 1(c)).
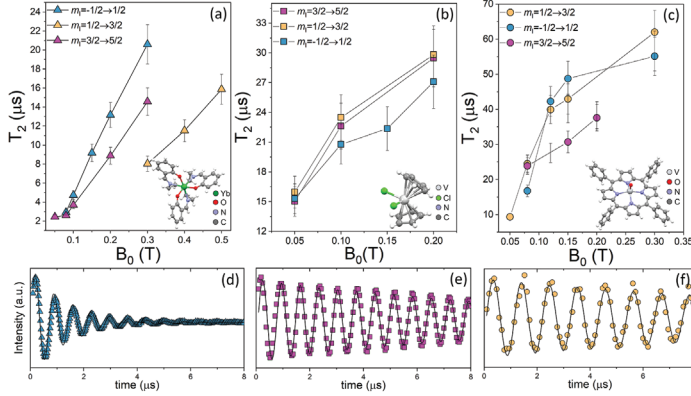
Fig. 2. – Field dependence of the Phase memory times T_2 for (a) [Yb(trensal)] ($T = 1.4\,\mathrm{K}$), (b) [V(Cp$_2$)Cl$_2$] ($T = 4\,\mathrm{K}$) and (c) [VO(TPP)] ($T = 1.4\,\mathrm{K}$) (molecule in inset). (d)–(f) Rabi manipulations of the system nuclear states for each system, respectively. Reproduced and adapted from refs. [7-9], with permission from the Royal Society of Chemistry (Copyright 2021) and the American Chemical Society (Copyright 2021 and 2018).

3. – Results

The first molecular qudit with an electronic spin 1/2 ancilla we investigated by broadband NMR was [Yb(trensal)] [7], in which the ^{173}Yb nuclear spin $I = 5/2$ provides a six-level qudit that can be rapidly manipulated with RF-pulses thanks to the strong hyperfine coupling with the electronic effective spin $S = 1/2$ and the significant electronic and nuclear phase memory times (fig. 2(a)). Indeed, we coherently controlled the nuclear states of [Yb(trensal)] inducing the Rabi oscillations shown in fig. 2(d), the basic steps for manipulating encoded states [7]. In order to further increase the qudit dimension and hence the QIP potential, vanadium(IV)-based complexes are among the most promising molecules. Indeed, the ^{51}V (natural abundance 99.75%) nuclear spin 7/2 of these complexes can encode an 8-level qudit with remarkably long electronic phase memory times [11]. Thus, we have characterized by broadband NMR the vanadium-based organometallic structure [V(Cp)$_2$Cl$_2$], showing results similar to those of [Yb(trensal)] in terms of phase memory times and manipulation of the nuclear state population (see fig. 2(b), (e)), as better detailed in [8]. Better performances were achieved with [VO(TPP)] [12], which can encode the same 8-level qudit (^{51}V $I = 7/2$, $S = 1/2$), with phase memory time of $T_2 \sim 60\,\mu\mathrm{s}$ in applied field $B_0 > 0.2\,\mathrm{T}$ (see fig. 2(c)) [9]. The parameters of the electro-nuclear spin Hamiltonian (fig. 3(i), (ii)) were determined by fitting the measured ^{51}V-NMR peak positions as a function of the applied field (see fig. 3). Because of the strong hyperfine interaction, the energy levels of the system (fig. 1) fulfil the fundamental requirements of a molecular qudit. Indeed, the splitting induced by the longitudinal part of the hyperfine interaction (with respect to the applied static field) enables the nuclear spin dynamics to be conditioned by the electronic spin state (see fig. 1(a)). Furthermore, the transverse hyperfine interaction modulates the nuclear energy gaps, acting as a second-order pseudo-quadrupolar contribution which enables the selective excitation of nuclear states. The remarkably long phase memory times enable many subsequent state manipulations before significant coherence losses (fig. 2(f)). We simulated the Lindblad evolution of the system density matrix ρ in a master equation approach, accounting for the coherent evolution of the system and the nuclear spin dephasing (see fig. 3(iii)). The simulated evolution confirms the possibility to selectively
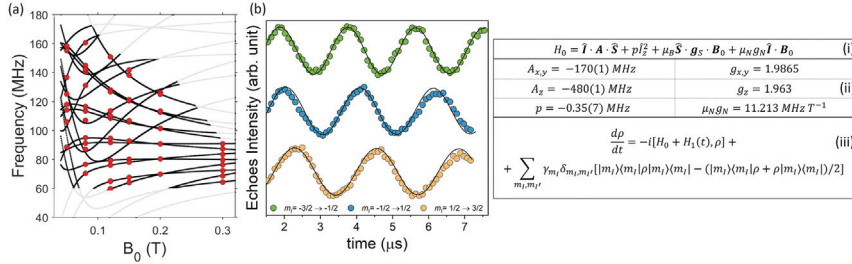
Fig. 3. – (a) Measured (dots) and calculated (lines) transition frequencies as a function of the applied field. Shaded areas are not explored. Reproduced from ref. [9] with permission from the Royal Society of Chemistry. (b) Nuclear Rabi oscillations (dots) induced on the specific nuclear transition shown, at $T = 1.4\,\mathrm{K}$. The black lines represent the simulation of Lindblad evolution under the same excitation pulse. (i),(ii) System spin-Hamiltonian and parameters: hyperfine and quadrupolar coupling, and the electronic and nuclear Zeeman interaction. (iii) Lindblad equation for the system density matrix, where $H_1(t)$ represents the exciting pulse.

manipulate the nuclear state population, *i.e.*, without affecting the surrounding states, using the NMR setup. Finally, monochromatic Rabi oscillation were induced on the nuclear spin system perturbed by specific RF pulses (see above). The nutation experiment is perfectly reproduced by the simulated evolution of the system (see fig. 3(b)). The manipulations do not display significant coherence losses, indeed the oscillation damping rate is remarkably longer than the time needed to implement a π rotation of the spin state, enabling the implementation of many successive operations. In conclusion, our broadband NMR setup allowed us to coherently manipulate the nuclear spin multi-level structures of MNMs. Thanks to the characteristics of the investigated systems, the resonant RF excitation pulses implemented in our experiments induce a selective variation of the nuclear state population, thus opening new perspectives for the development of qudit-based algorithms, such as QEC codes.

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