

Slow Spin Relaxation in Mononuclear Spin-1/2 Complexes

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Abstract

Molecules with long relaxation times have various applications in fields from the high-density data storage to the modern quantum information processing. For the purpose of magnetic storage, the high-spin molecules with large uniaxial anisotropies have been developed, termed as single-molecule magnets (SMMs) and characterized by their long longitudinal relaxation times. On the other hand, in terms of the coherent manipulation of spins, the molecules (commonly $S = 1/2$) with long transverse relaxation times have been developed, termed as molecular spin qubits (MSQs). These two kinds of compounds have been studied independently due to the different requirements on the relaxation mechanism. However, recent studies have revealed that the longitudinal relaxation times restrict the transverse relaxation times. This result evokes great interest in the study of the spin-lattice relaxation in MSQ systems, and the AC magnetometry proves to be an efficient way for screening the potential MSQs.

In this thesis, we investigated the spin-lattice relaxation process in two families of spin-1/2 compounds by SQUID magnetometry and theoretical calculations. The solid-state measurements, rather than the ones taken in frozen solution in the recent EPR studies on MSQs, provide unique opportunity to study the impact of solid-state effect such as the elastic lattice interactions and hydrogen bonds, which proves to be important for the fabrication of MSQ based devices on the different substrates.

In **Chapter 1**, the fundamental concepts of molecular magnetism and the background of the single-molecule magnets and molecular spin qubits, and the theoretical description of the spin-lattice relaxation mechanism is reviewed. The scope of the thesis is introduced.

In **Chapter 2**, the detailed magnetic characterizations of two mononuclear Ru(III) complexes showing field-induced spin relaxation in the timescale of SQUID magnetometry were reported. Complex **2-1** ($\text{RuCl}_3(\text{PPh}_3)_2(\text{MeCN})$, PPh_3 = triphenylphosphine, MeCN = acetonitrile) was characterized to exhibit long relaxation time of tens of milliseconds in 200 mT external field. X-ray structural analysis reveals that three chloride ions and the nitrogen atom from MeCN molecules occupy the equatorial plane with average Ru-Cl bond distance of 2.340 Å, and Ru-N distance of 2.055 Å. PPh_3 ligands coordinate Ru(III) ion axially with bond lengths of 2.402-2.409 Å. The crystal packing of **2-1** is directed by the weak C-H--- π and C-H---Cl interactions, unfavorable to transmit the magnetic exchange effectively. The shortest inter-molecular separation is 9.713 Å, excluding the strong magnetic interactions between molecules.

Temperature-dependent direct current (DC) measurement shows that the $\chi_m T$ products remain almost constant in the measured temperature range, without showing the substantial decrease upon cooling, confirming that the ground doublet is well separated from other magnetic states. The small Weiss constant (-0.06 K) confirms the very weak magnetic interactions, as expected structurally. Theoretical *ab initio* calculation gives the highly anisotropic principal g values, as confirmed by the EPR spectrum. The ground state is separated from the first excited state by 5564 cm^{-1} , which is thermally unapproachable.

Alternating current (AC) magnetometry was conducted on the polycrystalline sample of **2-1**. Two distinct relaxation processes have been detected in field above 20 mT. The high-frequency (fast) relaxation gradually slows down and merges into the low-frequency (slow) relaxation upon increasing field, and the two processes become inseparable in field above 120 mT. The double relaxation nature was also confirmed in the finely ground powder and frozen solution.

The field-dependent relaxation times of the polycrystalline sample were extracted by fitting the Cole-Cole plots. The field dependent ratio of spins participating the slow spin-lattice relaxation was estimated from the adiabatic susceptibility ($r = 1 - \chi_s/\chi_T$). In the low-field region (below 70 mT), the relaxation times of both relaxation process decrease with the increasing field, while in higher field the relaxation times tend to slow down with increasing field. This feature is quite different from the field dependence of relaxation times for single-ion magnets or other spin qubits, in which the relaxation time slows down in low-field region due to the suppression of dipolar relaxation (or quantum tunneling) and becomes accelerated in high-field region due to the increase of the resonant phonon density. Temperature dependent AC measurements up to 10 K in 100 and 200 mT field were also conducted, and the relaxation time obeys the approximate inverse square law, which suggests the possibility of the presence of the phonon bottleneck effect in such systems.

Analyses of the relaxation times in the powder sample confirms the existence of significant size effect, which further corroborates the phonon bottlenecked direct process. To gain more insights into the phonon density of states, the field-dependent magneto-heat capacity was measured, giving Debye temperature of 54 K. The number of resonant phonons and the average wavelength of them were estimated to be $5.3 \times 10^{20} \text{ m}^{-3}$ (much lower than the density of spin centers, $1.2 \times 10^{27} \text{ m}^{-3}$) and $2.9 \times 10^{-7} \text{ m}$ (much larger than the shortest spin separations, $1.0 \times 10^{-9} \text{ m}$), further supporting that the spin relaxation process is subject to the low density of the resonant phonons, and this phonon bottleneck is furthermore enhanced by the resonant phonon trapping process.

Complex **2-2** ($\text{RuCl}_3(\text{AsPh}_3)_2(\text{MeCN})$, AsPh_3 = triphenylarsine) shows much faster spin relaxation rate. The molecular structure of it is very similar to that of complex **2-1**. However, the crystal packing is different, and the shortest inter-molecular separation is 7.942 Å. The larger inter-spin dipolar interactions could be confirmed by the larger Weiss constant (-0.87 K). Theoretical calculations gives the lowest electronic transition energy of 3208 cm^{-1} , confirming the well-separated ground doublet.

AC measurements have been conducted on the polycrystalline sample, and no clear maxima have been detected in various external fields below 200 mT, showing the faster spin dynamics in the crystalline sample of complex **2-2**. The field dependent ratio of spins participating the slow spin-lattice relaxation was estimated from the adiabatic susceptibility, suggesting the presence of the larger internal fluctuating field. The field-dependent relaxation times exhibit the typical “decrease after increase” behavior with increasing external field, and can be modelled by the Brons-Van Vleck equation with larger internal field term. All these features support the possibility that the relatively large dipolar fields, originating from either the inter-spin dipolar interactions or the hyperfine interactions, avail the much faster spin relaxation rate in **2-2**. The temperature dependence of relaxation times can be modelled by the presence of the one-phonon direct process and two-phonon Raman process without phonon bottleneck effect.

In conclusion, the magnetic relaxation of two complexes has been studied. Complex **2-1** exhibits the long spin relaxation time of tens of milliseconds due to the presence of phonon bottleneck effect, while complex **2-2** exhibits much faster spin relaxation rate due to the significant dipolar effect. The comparative study of these two complexes indicates that care should be taken when analyzing the slow spin relaxation in spin-1/2 molecules to distinguish the intrinsic phenomena from the bulk effects.

In **Chapter 3**, the detailed magnetic characterizations of a family of ferricyanide salts have been reported, showing that slow spin relaxation in the timescale of SQUID magnetometry could be observed in the weak external magnetic field (above 2 mT). The heptahydrate, **3-1h** ($(\text{PPh}_4)_3\text{Fe}(\text{CN})_6 \cdot 7\text{H}_2\text{O}$, PPh_4^+ = tetraphenylphosphonium), exhibits the maximal relaxation time in *ca.* 6 mT field. No significant size effect has been detected, suggesting the minor role of the phonon bottleneck. Similar results were also obtained on the diluted sample, **3-1h@Co** (showing longer relaxation times), and the deuterated sample, **3-1h@D** (showing shorter relaxation times). These results reveal the roles of dipolar interactions (accelerating relaxation) and the hydrogen bonds (reducing the vibrational and rotational energies when deuterated). Significant dehydration effect has been observed, and the relaxation times increase monotonically with increasing fields below 100 mT

in dehydrated sample. The reversibility of the water-tuned relaxation behavior was studied on the re-hydrated sample. Temperature-dependent relaxation times were analyzed by the model incorporating local vibration modes, and the vibration responsible for the relaxation process is further determined by THz domain Raman spectrum (*ca.* 40 cm^{-1}). Comparative study on the other ferricyanide salts were also studied. The study of this chapter show that the long spin-lattice relaxation times can be reached *via* fine control of the inter-spin separation and the elastic intermolecular interactions including hydrogen bonds.

In **Chapter 4**, conclusions about the spin relaxation in these two systems are made, and future developments based on the results are discussed.

The research in this thesis focuses on the spin relaxation in the spin-1/2 molecules in crystalline state, and reveals that the crucial roles of the elastic lattice interactions and the local vibration modes in the spin relaxation process in the spin-1/2 systems lacking the second-order anisotropy. The results of our study will help to clarify some debates about the relaxation mechanism in such systems, and also contribute to the fabrication of spin devices in future.