

Origins of Slow Magnetic Relaxation in Single-Molecule Magnets

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Exponential and power law temperature dependences are widely used to fit experimental data of magnetic relaxation time in single molecular magnets. We derived a theory to show how these rules arise from the underlying relaxation mechanisms and to clarify the conditions for their occurrence. The theory solves the puzzle of lower-than-expected Orbach barriers found in recent experiments, and elucidates it as a result of the Raman process in disguise. Our results highlight the importance of reducing the rate of direct tunneling between the ground state doublet so as to achieve longtime coherence in magnetic molecules. To this end, large spin and small transverse magnetic anisotropy can reduce magnitude of the transition operator, and rigid ligands may weaken the spin-phonon coupling in that they raise the energy of vibrational modes and better screen the acoustic phonons.

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Advances in quantum computing and quantum sensing technologies rely on the synthesis of innovative materials with predesigned properties and thorough fundamental understandings of their behavior. The electron spins in quantum dots were first suggested as qubits by DiVincenzo [1], as their quantized spin states can be controlled and measured with electromagnetic stimuli. To extend the decoherence time for quantum operation, a robust qubit should be well isolated from its environment, yet effective communication is still needed for information exchange with others. To this end, single-molecule magnets (SMMs) are regaining exceptional research interest for developing platforms of quantum computation and information storage [2,3], as their spin is mostly protected by organic ligands and the exchange interaction across them can be easily controlled by varying the distance, substrate, or charge state. Nevertheless, SMMs have numerous vibrational modes that may couple to spin excitation and hence how to extend the relaxation time of spin states is a central issue for the practical applications. It is perceived that molecules with large zero field splitting (e.g., large magnetic anisotropy energy), or, equivalently, with wide magnetic hysteresis [4–9] may have slow magnetic relaxation [10–19]. However, the general guiding rule for the search of molecular qubits has not been established.

Typical SMMs are complexes that involve a magnetic center and organic backbones. Together with solvent molecules, they may form molecular crystals. Because of strong coupling between the spin and organic backbones, the local vibrational modes play important roles in the quantum behaviors of SMMs. The Jahn-Teller effect [20] may arise from coupling between local modes and excitation doublets [21]. The interaction between the local modes and acoustic modes may essentially change the energy spectra [22] and cause cooperative spin crossover [23].

For the spin-lattice relaxation, the development of *ab initio* spin dynamics simulation [24,25] allows quantitative investigations of spin-local mode coupling and recovers experimental relaxation rates. While the Orbach regime can be well accounted by *ab initio* calculations, the establishment of power laws requires other factors [7]. It is well known that coupling to acoustic modes can render power laws [26]. In molecule crystals, however, energies of the acoustic modes are low due to weak intermolecular interactions, so that they are likely incapable of exciting spin states. The condition for the power laws is a fundamental problem that has not been clarified.

Although existing theories of nuclear spin assisted tunneling [17,27–29], dipolar interaction [13,30], and spin-lattice interaction [25,26,31–34] can explain some phenomena in magnetic relaxation of SMMs, there are decades long puzzles in this realm. One of them is the presence of two Orbach barriers in some observations [13,35]. Another one that is more prevalent [13,14,36–42] and still receives increasing attention [19,43,44] is the underbarrier relaxation, where the observed barrier is significantly lower than that set by the magnetic anisotropy.

Here, we propose a theory of spin-lattice relaxation in SMMs by combining the Redfield equation [45] and the nonequilibrium Green's function (NEGF) method [46,47]. The Redfield equation is a microscopic master equation describing evolution of an open quantum system. Given a microscopic Hamiltonian, NEGF derivations are deductive and automatically include various relaxation processes in a unified manner. Using models with large zero field splittings and local vibrational modes, we show that the low barriers have nothing to do with the Orbach process, but arise from direct tunneling between the (pseudo) ground state doublet. In addition, it shows that power laws can only arise from direct tunneling, and involvement of spin excited

states compromises these laws. These results highlight the importance of reducing the tunneling rate for the design of practical SMMs devices.

Casting the correlation functions in the Redfield equation [45] into NEGF, phonon induced relaxation is governed by

$$\frac{d}{dt}\rho_S(t) = \sum_{\omega,q} iG_q^<(\omega) \times \left[A_q(\omega)\rho_S A_q^\dagger(\omega) - \frac{1}{2} \{A_q^\dagger(\omega)A_q(\omega), \rho_S\} \right], \quad (1)$$

where $\rho_S(t)$ is the density matrix of the open system, $G_q^<(\omega)$ is the lesser Green's function for phonons, the curly brackets denote the anticommutation, and $A_q(\omega)$ is the transition operator for spin eigenstates. For the transition from state n to m , the operator elements are $A_q^{ij} = a_q \delta_{im} \delta_{jn}$, and the energy in Eq. (1) is defined as $\omega = \omega_m - \omega_n$. $A_q^\dagger(\omega) = A_q(-\omega)$ represents the reverse transition. Subscript q means that the transition is caused by coupling with the q th phononic degree of freedom, a single phonon for the first-order spin-phonon coupling and a pair of phonons for the second order coupling.

To the quadratic order, the spin Hamiltonian of a SMM takes the form as $H_{\text{spin}} = -DS_z^2 - E(S_x^2 - S_y^2)$. Most of SMMs designed for slow magnetic relaxation are easy axial ones, and a strong easy axial magnetic anisotropy ($D \gg E$) results in an ideal parabolic Orbach barrier. As E is nonzero, direct tunneling between the ground state doublet is possible and an energy splitting renders the doublet a pseudo one (explained later). Assuming dominance of the direct tunneling, relaxation pathways via the excited states can be neglected. Magnetic relaxation of the ground state is described by

$$\begin{cases} \frac{d}{dt}M = -2p_u M, \\ p_u = \sum_q i|a_q|^2 G_q^<(\omega), \end{cases} \quad (2)$$

where p_u denotes rate of the upward transition from the ground state to the state slightly lifted.

Because of the strong axial magnetic anisotropy ($D \gg E$), the energy splitting (denoted by ω_Δ hereafter) between the ground state doublet is very small. Lack of energy match implies that the direct process through energy exchange with a vibrational mode is unviable, and the second order processes are needed. They arise from the coupling $H_2 = \sum_{qq'} (\partial^2 H_{\text{spin}} / \partial V_q \partial V_{q'}) V_q V_{q'}$, where V_q denotes the momentum space displacement. Here, the pair (q, q') should be taken as a single phononic degree of freedom, and its Green's function can be calculated using $G_{qq'}^<(\omega) = (i\hbar/2\pi) \int d\omega' G_q^<(\omega) G_{q'}^<(\omega - \omega')$, where $G_q^<(\omega)$ is the single phonon lesser Green's function. Accordingly, the upward transition rate can be derived as

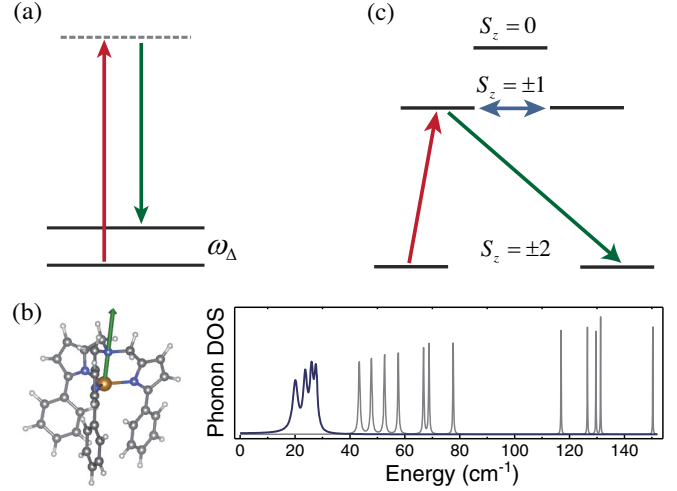


FIG. 1. (a) Coupling between the spin and the vibrational modes causes direct tunneling via the Raman process. (b) The $[\text{tpa}^{\text{Ph}}\text{Fe}]^{-1}$ is a $S = 2$ molecule and possesses an easy axial magnetic anisotropy of 26 cm^{-1} , and the four lowest vibrational mode energies range from $20.1\text{--}27.6 \text{ cm}^{-1}$. (c) Quadratic anisotropy can only yield $\Delta S_z = \pm 1, \pm 2$ transitions. Because of the divergent transition rate between degenerated states (here $S_z = \pm 1$), we can effectively take $|\pm 1\rangle$ as a single state and the magnetic relaxation involves the upward and downward transitions.

$$p_u \propto N(\omega) \iint \frac{d\omega_q d\omega_{q'}}{\omega_q \omega_{q'}} \sigma(\omega_q) \sigma(\omega_{q'}) \times \{ [N(\omega_q) + N(\omega_{q'}) + 1] \delta(\omega - \omega_q - \omega_{q'}) + [N(\omega_q) - N(\omega_{q'})] \delta(\omega + \omega_q - \omega_{q'}) \}, \quad (3)$$

with $\omega = \omega_\Delta$ specifying the energy gain and $\sigma(\omega_q)$ denoting the phonon DOS. Because of the inter-molecular interactions, the phonon DOS is not summation of delta functions, but has Lorentzian peaks around the mode energies ω_α [e.g., see Fig. 1(b)]. By energy conservation, we can identify the first term as the double phonon process whereby two phonons are absorbed, and the second terms as the Raman process whereby a phonon is absorbed ($\omega_{q'}$) and a phonon of lower energy is emitted (ω_q).

In the double phonon processes, energy summation of two phonons should match the transition energy, so they are also unviable due to the energy conservation. What matters are the Raman processes [Fig. 1(a)], which are represented by the second term in Eq. (3). Since $\omega = \omega_\Delta \ll 1 \text{ cm}^{-1}$, $\omega_q - \omega_{q'} = \omega_\Delta$ implies that $\omega_q, \omega_{q'}$ are close. Namely, the absorbed and emitted phonons should be around the same Lorentzian DOS peak. Carrying out the integral with respect to the Lorentzian peak at ω_α , we obtain

$$\tau^{-1} = 2p_u \simeq \frac{4\omega_\alpha \Gamma_\alpha |a_\alpha|^2}{(\omega_\alpha^2 \omega_\Delta)^2 + (2\omega_\alpha \Gamma_\alpha)^2} e^{-\omega_\alpha/k_B T}, \quad (4)$$

where Γ_α is the broadening width, and a_α an overall alias of $a_{qq'}$ for $\omega_q, \omega_{q'} \approx \omega_\alpha$.

Equation (4) indicates a vibronic barrier equal to the mode energy and explains the underbarrier relaxation. Because of the exponential form, it is likely that one or several of the lowest vibrational modes strongly coupling to the spin dominate the process. As a concrete test of the result, we calculated the vibration spectrum of $[\text{tpa}^{\text{Ph}}\text{Fe}]^{-1}$ [Fig. 1(b)], a typical SMMs with slow magnetic relaxation [13]. Its four lowest vibrations fall in the range $20.1 \sim 27.6 \text{ cm}^{-1}$, followed by a much higher one at 43.4 cm^{-1} . The transition rate p_u in Eq. (4) is summation over these vibrational modes, and leads to an effective barrier $20.1 < U_{\text{eff}} < 27.6 \text{ cm}^{-1}$. This value is in accordance with the observed barrier of $26(2) \text{ cm}^{-1}$ [13], while the magnetic barrier of $3D = 78 \text{ cm}^{-1}$ is too high.

Based on Eq. (4), the puzzle of barrier lowering can also be explained. The ratio of transition rates for two DOS peaks reads $p_u(\omega_\alpha)/p_u(\omega_\beta) \propto e^{(\omega_\beta - \omega_\alpha)/k_B T} |a_\alpha|^2 / |a_\beta|^2$. A lower vibrational mode with weaker spin-phonon coupling (say, $\omega_\alpha < \omega_\beta$ and $|a_\alpha| < |a_\beta|$) might have an advantage when the temperature is low. As a result, a lower barrier characterizes the relaxation. For this lowering to be actually observed, however, a sizable energy difference between the two modes is required. Otherwise, what shows up would be an averaged barrier. Moreover, the lower mode should have much weaker spin-vibration coupling, so that it is dominant only at low temperature rather than for all temperatures. These requirements explain why this barrier lowering is much less prevalent than observation of the underbarrier relaxation.

Applying Eq. (3) to the Orbach process, we can see why the spin dynamics simulation in Ref. [7] cannot yield power laws. Without compromising the physical essence, we take $S = 2$ as an example. The Orbach process for $S = 2$ spins with easy axial magnetic anisotropy follows the pathway in Fig. 1(c). The magnetic relaxation rate also takes the form in Eq. (3) [48], with ω_Δ changing to the magnetic barrier $3D$. The second order processes does not give rise to power laws, since the factor $N(3D)$ sets the dominant time scale $\tau = \tau_0 e^{3D/k_B T}$, and the integration part only modifies the factor τ_0 . Carrying out the integral in Eq. (3) with respect to certain dominant DOS peaks, we have $\tau_0 \propto T^0$ (temperature independent), an imperceptible modification. When the acoustic phonons are considered, one may have $\tau_0 \propto T^{-1}$, which is still an insignificant modification compared to the exponential form itself. Clearly, we cannot obtain power laws for large zero field splitting, even if the second order processes and acoustic phonons are considered.

Going back to the direct tunneling by changing $3D$ to ω_Δ , and considering the coupling between spin and acoustic phonons, the standard derivations for the power laws are applicable, as the small transition energy ω_Δ makes expansion with respect to $\omega_\Delta/k_B T$ and the Debye

integral legitimate. While these standard results for small energy splittings are well known, the unviability to generate power laws for large zero field splittings appears to be not well aware of, and the community is puzzled on the origins of these relations [7,25]. This unviability indicates a correspondence between emergence of power laws and dominance of the direct tunneling. That is, upon observing the power laws, one can safely infer the dominance of the direct tunneling.

This correspondence has direct implication for the practical design of SMM devices. In the regime of exponential dependence, the relaxation time can be dramatically lengthened with small temperature reduction. The transition point from the exponential law to the power laws is the sweet point of long relaxation time at high temperature. For this reason, magnetic hysteresis usually co-occurs with the dominance of power law dynamics [7–9], and this regime is the most suitable one for practical applications of SMMs. While the large Orbach barriers and wide molecular magnetic hysteresis in recent dysprosocenium SMMs [7–9] are appealing and receive lasting attentions, occurring in the power law regime, the broad magnetic hysteresis is due to the small direct tunneling rate, instead of the Orbach barrier. This calls for attention to reduce the tunneling rate besides the obsession on super large Orbach barriers.

Before systematic remarks on how to reduce the rate of direct tunneling, we need to address the question why the vibronic barrier can be raised, provided the optical phonons (vibrational modes) have much higher energies than the acoustic ones. In other words, why the acoustic phonons cannot always dominate, albeit they are energetically more accessible. To illustrate the reason, we calculated phonon modes of a 3D harmonic oscillator where the intermolecular interaction is assumed to be 1 order smaller than the intramolecular interaction, i.e., $k_{\text{intra}} = 10k_{\text{inter}}$. Figure 2(b) shows atomic motions for an acoustic phonon (left) and optical phonon (right) with a momentum $((\pi/2a), (\pi/2a), 0)$. As spin-phonon coupling essentially represents the variation of electronic states due to atomic displacements, small relative motions in acoustic modes imply weak phonon-spin coupling. Moreover, it can also be seen that the DOS of the acoustic phonons is small too. Because of the weak coupling and small DOS compared to the optical phonons, the acoustic phonons can only be dominant at low temperature, when the high energy optical phonons are quite hard to access.

With all these understandings, we can relate our theory to the measured curves. With estimation on typical parameters, we produced the curves in Fig. 3. The color code marks the correspondence among the relaxation processes, the phonons in charge, and the resultant relaxation time curves. Figure 3(a) gives the generic curve in most experimental observations, and Fig. 3(b) is the case when two barrier are observed [13,35]. Here, in the low

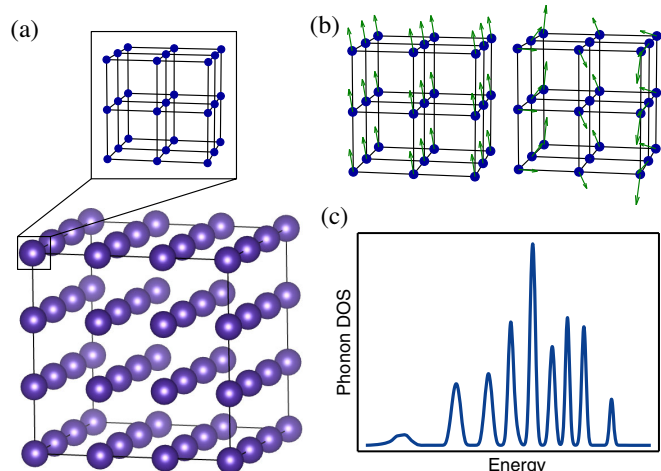


FIG. 2. (a) A 3D harmonic oscillator, where each cell is a $3 \times 3 \times 3$ cubic molecule. The intermolecular force constant is 1 order smaller than that of intramolecular interaction. (b) Relative atomic motion within a molecule is small for acoustic phonons (left) and significant for optical phonons (right). (c) The phonon spectrum consists of low energy Debye phonons and optical phonons resulting from broadening of local vibrational modes.

temperature range, we assume dominance of direct process ($\tau \propto T^{-1}$) for the acoustic phonons. Depending on the first and second order spin-phonon coupling strength, the Raman or double phonon processes may be dominant and raise other power laws.

To this point, the reasons for the slow magnetic relaxation are clear. At very high temperatures, the spin excited states are well accessible, and the Orbach process dominates. In this regime, the high Orbach barrier is responsible for the slowness, which is our conventional

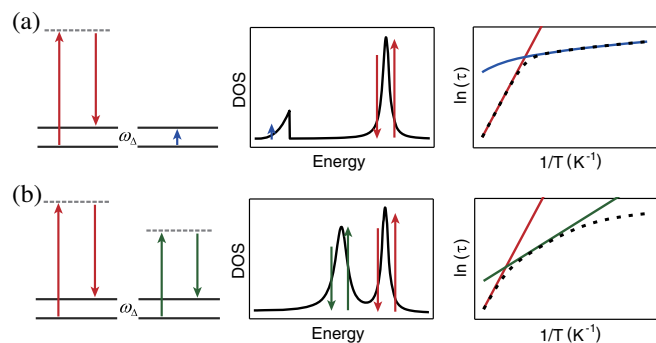


FIG. 3. Left, schematics of the relaxation processes; middle, phonons responsible for the processes; right, the corresponding relaxation-time-temperature dependences. (a) At high temperature, the Raman process due to phonons resulted from broadening of a vibrational mode dominates the relaxation, characterizing an exponential relation with energy of the mode as the relaxation barrier. (b) A vibrational mode with lower energy and weaker spin-phonon coupling could be dominant when temperature is reduced, and turns the relaxation barrier to a lower one.

understanding. As discussed above, however, the Orbach regime may not be the best for practical application. The direct tunneling regime provides a better trade-off between long relaxation time and high temperature, and could be our major concern. Besides, because only the ground state doublet is involved in this regime, it makes a clear two state qubit. As for reducing the rate of direct tunneling, we may use SMMs with large spins and small transverse magnetic anisotropy E , and design more rigid backbones for the magnetic center.

The first principle can be understood with perturbation theory. For a spin with $E = 0$, the ground states are two degenerated states consisting of $|\pm S\rangle$. Quadratic spin terms cannot yield any transition for $S > 1$. The direct tunneling becomes possible, when $E(S_x^2 - S_y^2)$ mixes state $|m\rangle$ ($-S < m < S$) into the ground state doublet, with mixing proportions $\propto E^{(m \mp S)/2}$ for $|\pm S\rangle$. As a result, increasing S leads to exponential reduction of the tunneling rate. It is this small tunneling rate that gives rise to the broad magnetic hysteresis in those large spin ($S = 15/2$) dysprosium SMMs [7–9]. As these molecules almost reach the limit of atomic angular momentum, reducing the E value is a direction for further progress. Besides those magnetic engineering, enclosing the magnetic center with more rigid backbones may better screen the spin from the acoustic phonons, and moreover, make the vibrational modes harder to access.

In conclusion, we have demonstrated how the direct tunneling between the ground state doublet gives rise to the observed temperature dependences of magnetic relaxation time. In particular, we found that the tunneling due to a vibrational mode can yield exponential temperature dependence, raising a relaxation barrier characterized by energy of the mode. Reasons for the slowness and hysteresis are systematically clarified and suggestions for improvements are provided. We proceeded with the problem of magnetic relaxation based on the microscopic Hamiltonian and the density operator. This theory is fully quantum and may apply to describe general magnetic decoherence processes. The formulations are readily amenable for *ab initio* calculation for diverse quantum magnetic systems such as magnetic impurities, molecules, and atoms.

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Refs. [25,49–51], and the explanation to why barrier reduction due to phonons' finite lifetime has limited effectiveness for the underbarrier relaxation, which includes Refs. [47,52].

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