Superradiation from Crystals of High-Spin Molecular Nanomagnets

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Abstract

Phenomenological theory of superradiation from crystals of high-spin molecules is suggested. We show that radiation friction can cause a superradiation pulse and investigate the role of magnetic anisotropy, external magnetic field and dipole-dipole interactions. Depending on the contribution of all these factors at low temperature, several regimes of magnetization of crystal sample are described. Very fast switch of magnetization’s direction for some sets of parameters is predicted.

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I. INTRODUCTION

Comparatively recently discovered\textsuperscript{1,2,3,4} molecular nanomagnets of high-spin molecules are prospective from the point of view of practical application of the superradiation (SR) phenomena in electron spin resonance (ESR) frequency region. These are crystals of organic molecules which consist of about 10 atoms of transitional metals. They are bounded in the molecule with indirect exchange interaction, as a result, each molecule possesses spin $S \approx 10$.

One of the manifestations of SR phenomena is the radiation intensity approximately proportional to the number of radiators squared\textsuperscript{5}. The properties of such coherent effects in optics have been extensively studied. Similar effects exist in the radiofrequency region (SR in spin systems was observed in several experiments, see Refs. \textsuperscript{6,7}), but although these and optical phenomena are similar in some aspects, the physics governing SR in spin systems is very different. It is natural and rather helpful to use magnetic resonance methods to describe SR in such systems\textsuperscript{8,9}.

Let us return to high-spin molecular nanomagnets. The molecules interact mostly through dipole forces. In macroscopic terms, the motion of the magnetic moment of a crystal composed of such molecules leads to the radiation of electromagnetic waves, whose feedback influence creates radiation friction force (Lorentz force). At low temperature, when the time of transverse relaxation $T_2$ (most usually due to spin-spin interactions) is large, relaxation by means of radiation friction can serve as the main cause of SR. Pure electromagnetic radiation mechanism (with $T_2^{-1} = 0$) was proposed recently\textsuperscript{10} (see also discussion in Ref. \textsuperscript{11}). Both of the relaxation mechanisms mentioned above are taken into account in the approach we elaborate in this work for molecular nanomagnets. Electromagnetic radiation is described in terms of the retarded potential expansion; for the transverse relaxation a regular magnetic resonance description is used. Recently we applied similar description for nuclear and electron SR in solids\textsuperscript{13}.

First, give some qualitative estimations. The characteristic relaxation time due to radiation from a spin system in constant external magnetic field $H_0$ is $T_R \sim \frac{c^3}{\omega_0 M}$, where $M$ is a magnetic moment of the sample, $\omega_0 = \gamma H_0$. $\gamma$ is gyromagnetic ratio. This time is obtained by the expansion of the radiation field in powers of $1/c$ (see, for instance, Ref. \textsuperscript{12}). The time $T_2$ due to dipole-dipole interactions can be estimated (for simplicity assume
paramagnetic with regular structure) via the second moment of resonance line, $M_2$. This time is about $1/\sqrt{M_2}$, where $M_2 \sim \gamma^2 n^2 \mu^2 \left(1 - L^2 \left(\frac{\nu H_0}{\mu H_0}\right) - \frac{2T}{\mu H_0} L \left(\frac{\nu H_0}{\mu H_0}\right)\right)$ for large spin (see Ref. 13, where this formula was discussed). Here $n$ is concentration of spins (number of spins over number of lattice nodes in crystal), $\mu$ is the magnetic moment of spin, $T$ is the temperature, $L(x)$ is the Langevin function. If $T \to 0$, then $T_2 \sim \frac{H_0}{\gamma n T}$. We discuss the situation when radiation friction is the main relaxation mechanism, thus $T_R \ll T_2$. Relaxation must be slow in comparison with spins rotation about the field $H_0$, $\omega_0 \gg \frac{1}{T_R}$. Also, the sample size should be smaller than the radiating wavelength, $\frac{\omega_0 V^{1/3}}{c} \ll 1$ ($V$ is the volume of the sample), then the phase of emitted photons is the same throughout the sample and the process of radiation becomes coherent. In typical EPR experiments, $\omega_0 \sim 10^{12} s^{-1}$ and $T \sim 0.1K$, and for linear size of a sample about 0.01cm all these conditions may be satisfied. The temperature can be higher for bigger $\omega_0$ and smaller sample size. Thus, the need for SR situation when radiation damping prevails over transverse relaxation is quite realistic for ESR.

Considering the high-spin molecule as a single paramagnetic particle, a crystal sample is a super-paramagnet with strong magnetic anisotropy. For example, the molecules $\text{[Mn}_{12}\text{O}_{12}(\text{CH}_3\text{COO})_{16}\text{(H}_2\text{O})_4] \cdot 2\text{CH}_3\text{COOH} \cdot 4\text{H}_2\text{O}$ have spin $S = 10$ and strong single-site anisotropy barrier about 70K. This temperature corresponds to magnetic energy of such a spin in a field of about $10^5$G (in this field $\omega_0 \sim 10^{12} s^{-1}$) that leads to a shift of the resonant frequency due to $M_z$ variations.

II. EQUATION OF MOTION

Equation of motion of the magnetic moment $M$ of the sample of spherical shape can be written as follows:

$$\dot{M} = \gamma M \times \left(H_0 + \beta \frac{M_z}{V} \hat{z} - \frac{1}{2c^2 V^{1/3}} \lambda_{ij} \ddot{M}_j + \frac{2}{3c^3} \dddot{M}\right) + R \tag{1}$$

where $H_0$ is constant magnetic field, directed along the anisotropy axis Oz, $\hat{z}$ is the unit vector along this axis, $\beta$ is the anisotropy coefficient, $\lambda_{ij}$ is the tensor (which in general is determined by the shape of the sample), $R$ is the term describing the transverse Bloch relaxation. The second term in the brackets is the anisotropy field (like in Landau — Lifshits equation), third and fourth terms appear as expansion of the retarded potential by powers
of \( \omega_0 V^{1/3}/c \). The third term gives a small shift of the resonance frequency, \( \Delta \omega_0 \ll \omega_0 \). It does not lead to any noticeable physical effect and can be neglected. The fourth term describes the electromagnetic friction.

Consider the case when the field \( H_0 \) and the anisotropy field are large compared to all other fields in the crystal. Thus, the rotation of \( \mathbf{M} \) around the effective field \( H_0 + \beta \frac{M_z}{V} \hat{z} \) is the fastest motion and all other effects are comparatively slow. Then, the zero-th order approximation is

\[
\dot{\mathbf{M}} = \gamma \mathbf{M} \times \left( H_0 + \beta \frac{M_z}{V} \hat{z} \right).
\]

Using (2) repeatedly, one can obtain

\[
\ddot{\mathbf{M}} = \gamma^2 \left( \mathbf{M} \cdot \left( H_0 + \beta \frac{M_z}{V} \hat{z} \right) \right) - \mathbf{M} \cdot \left( H_0 + \beta \frac{M_z}{V} \hat{z} \right)^2,
\]

Substitute these expressions in (1) and then average equation (1) over the fast frequency \( H_0 + \beta M_z/V \). Finally we obtain:

\[
\rho^2 + n_z^2 = 1 + \frac{1}{K \xi} \left[ \frac{1}{(1 + K n_z)^2} - \frac{1}{(1 + K n_z(0))^2} \right],
\]

\[
\dot{n}_z = \xi (1 - n_z^2) (1 + K n_z)^3 + \frac{1}{K} \left[ 1 + K n_z - \frac{(1 + K n_z)^3}{(1 + K n_z(0))^2} \right].
\]

Here \( n_{x,y,z} = M_{x,y,z}/M(0) \) are normalized components of the magnetic moment, \( \rho^2 = n_z^2 + n_y^2 \), \( K = \frac{\beta M(0)}{V H_0} \) is the dimensionless coefficient of anisotropy, \( \xi = T_2/T_R \) is the ratio of the characteristic time of transverse relaxation and the characteristic time of longitudinal relaxation due to radiation friction, \( T_R = \frac{3c^3}{2 \gamma_0 \omega_0 M(0)} \), \( n_z(0) = \cos \theta(0) \) where \( \theta(0) \) is the angle of the initial deviation of \( \mathbf{M} \) from the \( Oz \) axis. Note, that we measure the dimensionless "time" in the units of \( T_2 \). We neglect spin-lattice interaction here.

The intensity of dipole radiation\(^{17} \) is \( I = \frac{2}{3c^3} \dot{\mathbf{M}}^2 \). The biggest contribution in \( \dot{\mathbf{M}} \) is due to rotation about \( H_0 \), i.e. due to \( \dot{M}_z \) and \( \dot{M}_y \). Using formulae (3) for these quantities, we obtain

\[
I = \frac{2M^2(0)}{3c^3} \omega_0^4 (1 + K n_z)^4 \rho^2.
\]

It is seen that \( I \) is proportional to the second power of the number of molecules, \( N \), in the sample which is \( N \) times the incoherent radiation. This is the manifestation of Dicke’s superradiance for molecular nanomagnets. Using the same parameters as in the Introduction,
one can see that $I$ can be as large as $10^9$ erg/s for the concentration of molecules in crystal $n \approx 4 \cdot 10^{20}$ cm$^{-3}$. It is rather big quantity, although this radiation splashes only during about $10^{-9}$ s (because the amount of energy released during a flip of the magnetic moment in the field $H_0$ is about 1 erg). It is questionable whether such a short signal can be detected, however, the flip of a total magnetic moment makes a direct experimental observation of the phenomena possible.

### III. REGIMES OF MOTION

Let us consider first the SR when transverse relaxation can be completely neglected compared to radiation relaxation, i.e. when $\xi \to \infty$. This situation can be realized at low temperatures. Fig.1 shows how the final (in the equilibrium state) $z$-component of polarization, $n_z(t \to \infty)$, depends on the coefficient of anisotropy, $K$. The evolution of $n_z(t)$ and $I(t)/I(0)$ for big but finite $\xi$ (the value $\xi = 100$ was chosen) and several values of parameter $K$ is shown in Fig.2. We want to attract attention to the case when the value of $K$ is slightly less than 1, in this situation the magnetization switches its direction rapidly from the unequilibrium state causing a very sharp and high SR pulse. This can be obtained directly from equation (5) that gives the evolution of the $z$-component of the total magnetization. Introduce the quantity $\epsilon(t) = \cos(\pi/2 - \theta(t))$ where $\theta(t)$ is the angle between vector $n$ and the $z$ axis. If initially vector $n$ had only a small deviation from positive or negative directions of the $Oz$ axis, then $\epsilon(0) \equiv \epsilon_0 \ll 1$. Substituting $n_z(t) = \pm 1 \mp \epsilon(t)$ into (5), for $K = 1$ and $\xi \gg 1$, we obtain

$$\epsilon(t) = \frac{\epsilon_0}{(1 - 6\epsilon_0^2 \xi^3 t)^{1/3}}$$

when $n$ was directed (approximately) against $H_0$, and

$$\epsilon(t) = \epsilon_0 e^{-16\xi t}$$

if $n$ was directed (approximately) along $H_0$. Thus, in unequilibrium case, the magnetic moment begins to deviate very slowly from the negative direction of the $Oz$ axis and then, at some moment, makes a very quick flip producing a short powerful splash of SR. Note, that the final value of $|n_z|$ is smaller than $|n_z(t = 0)|$ due to transverse relaxation.

The value of $K$ depends on the external field and, therefore, can be tuned. The peak of SR exists in the region $0 \leq K \leq 1$ (anisotropy of the type "easy axis") and in the region
$K < 0$ ("easy plane"). For the values of $K \ll -1$, the initial $z$-component of polarization generally is not big, that makes the SR effect weaker. If $K > 1$, no SR pulse appears.

When a relative contribution of the transverse relaxation increases, the SR effect becomes smaller. Fig.3 is the 3-D plot of the final polarization $n_z(t \to \infty)$ as function of $K$ and $\xi$ (for the initial polarization $n_z(t = 0) = -0.9$). Values of $n_z(t \to \infty)$ close to $-1$ mean that $\mathbf{M}$ did not flip; values close to 1 indicate that $\mathbf{M}$ had changed its initial direction to the opposite. It is seen that strong transverse relaxation (small values of $\xi$) destroys the SR completely.

IV. CONCLUSION

The usual way to obtain a SR pulse from spin system is to place a sample in a tuned resonant coil. A feedback from the coil creates a coherent relaxation from the initially un-equilibrium state. However, for crystals of high-spin molecules a strong magnetic anisotropy makes this mechanism not effective because of the significant variations in the resonant frequency\cite{11}.

In this paper we give a rigorous (phenomenologically based) description for SR phenomena in crystals of high-spin molecules. The main mechanism for the SR is an interaction of spin magnetic moments with the cooperative radiated electromagnetic field acting on an entire sample. Contrary to this, the transverse relaxation changes phases of spins rotation chaotically. As a result, the radiation field can switch the direction of $\mathbf{M}$ and produce the SR pulse, while the usual relaxation just dissipates the total magnetization.

The equations of motion predict a very strong SR pulse for the value of anisotropy parameter $K = \frac{\beta M(0)}{V H_0}$ close (but smaller) to 1. Such a scenario is presented in Fig.2 for $K = 0.9$. The delay time is long enough to make the experimental observation of SR possible.
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FIG. 1: The dependence of the final $z$-component of polarization on $K$ for $T_2^{-1} = 0$. The value $n_z(t = 0) \approx -1$. 
FIG. 2: Evolution of $n_z(t)$ and $I(t)/I(0)$. Parameter $\xi$ is 100, the values of parameter $K$ are $-1.5$, $-0.5$, $0.9$, $1.1$ (up-to-down).
FIG. 3: The dependence of $n_z(t \to \infty, \xi, K)$ on $\xi$ and $K$ for $n_z(t = 0) = -0.9$. 