Photon-assisted tunneling in a Fe$_8$ Single-Molecule Magnet

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The low temperature spin dynamics of a Fe$_8$ Single-Molecule Magnet was studied under circularly polarized electromagnetic radiation allowing us to establish clearly photon-assisted tunneling. This effect, while linear at low power, becomes highly non-linear above a relatively low power threshold. This non-linearity is attributed to the nature of the coupling of the sample to the thermostat. These results are of great importance if such systems are to be used as quantum computers.

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Molecular nanomagnets have attracted much interest in recent years both from experimental and theoretical point of view$^{[1-13]}$. These systems are organometallic clusters characterized by a large spin ground state with a predominant uniaxial anisotropy. These features yield a pronounced barrier for magnetization reversal and therefore a hysteretic behavior below a blocking temperature. The quantum nature of these systems makes them very appealing for phenomena occurring on the mesoscopic scale, i.e. at the boundary between classical and quantum physics. Up to now the most thoroughly investigated systems were a dodecanuclear mixed-valence manganese-oxo cluster with acetate ligands (hereafter Mn$_{12}$-ac)$^1$ and an octanuclear iron(III) oxo-hydroxo cluster of formula [Fe$_8$O$_2$(OH)$_{12}$](tacn)$_6$$^{18+}$ where tacn is a macrocyclic ligand, (hereafter Fe$_8$)$^2$, both having a ground spin state $S = 10$, but substantially differing in their anisotropy. Indeed, while the first is essentially tetragonal with a barrier of 67 K, the latter is orthorhombic with a barrier of 25 K, leading to an enhancement of the ground-state tunneling rate compared to Mn$_{12}$-ac.

Recently it has also been proposed that molecular nanomagnets could be used as quantum computers by implementing Grover’s algorithm$^{[14]}$. For this to occur it is necessary to be able to generate an arbitrary superposition of eigenstates of these systems. The suggested way to do this was through the use of multifrequency coherent magnetic radiation in the microwave and radiofrequency range. This would first introduce and amplify the desired phase for each $M$ state and this information could be finally read-out by standard magnetic resonance techniques. In this approach advantage is taken from the non-equidistance of the $M$ levels of the ground multiplet arising from the large axial anisotropy of these systems, which allows coherent populations of the different $M$ levels. A recent theoretical work pointed out that a very accurate control of pulse shape technique, both in amplitude, duration and choice of frequency is needed to fulfill the condition to design quantum computing devices in molecular nanomagnets$^{[15]}$. In addition to such basic difficulties, we will see below that the microwave power cannot exceed a critical value above which non-linear effects occur. In particular the phonons associated with spin relaxation are crucially influencing the dynamics of the system.

In order to investigate the feasibility of the proposed process any preliminary experiment should aim to understand the effects of microwave absorption on the spin dynamics of these systems at low temperature. The main issues addressed in this letter concern: (i) controlled increasing of excited state populations through the absorption of microwave radiation, (ii) mechanism of photon-assisted tunneling, and (iii) subsequent heating occurring after relaxation.

The measurements were performed on a new magne-
tometer, involving $10 \times 10 \, \mu m^2$ micro-Hall bars [16, 17] in a dilution refrigerator equipped with three coils allowing to apply a field in any direction, at sweeping rates up to 1 T/s. Continuous radiation, in the FIR region, was generated by a couple of Gunn diodes (Radiometer Physics GmbH), working at fundamental frequencies of 95 GHz and 115 GHz, and equipped with double and triple harmonic generators and calibrated attenuators. We irradiated the sample using a 6 mm waveguide equipped with infrared filters in order to reduce heating. The circular polarization, induced by filters, was maximized around 97%. The study was performed on a 0.1 mm Fe\(_8\) single crystal synthesized according to the standard procedure.

As schematically depicted in Fig. 1, microwave radiation with a frequencies of 115 GHz corresponds to the energy separation between the ground states $M = \pm S$ and the first excited states $M = \pm (S-1)$ of Fe\(_8\) in zero applied magnetic field [2, 10]. If the radiation is linearly polarized, the populations of the first excited states $(M = \pm (S-1))$ in both wells will be enhanced equally (equal transition probability for $\Delta M = \pm 1$). On the opposite, the use of circular polarization has the advantage to distinguish between $\Delta M = +1$ (left polarization, $\sigma^-\,$ photons) or $\Delta M = -1$ (right polarization, $\sigma^+\,$ photons) [18], and the population of only one of the two excited states will be enhanced (Fig. 1). An excess of tunneling from one well to the other is then expected. Therefore, circular polarization can help to distinguish between spin-phonons relaxation, and spin-phonons relaxation modified by the absorption of photons. The first equally affect the two sides of the barrier, i.e. the two branches of the hysteresis loop, while the second modifies the population of only one side of the barrier, i.e. one branch of the hysteresis loop. Any difference observed between the two branches of the hysteresis loop, has to be traced back to photon absorption.

Fig. 2a shows the hysteresis loops of a Fe\(_8\) single crystal with the easy axis parallel to the applied field, measured at 60 mK under irradiation. The tunneling transition near zero field is strongly enhanced for a radiation at 115 GHz. This is in agreement with a photon induced population transfer from $M = -10$ to $M = -9$, and agrees with earlier HF-EPR studies showing strong zero field absorption at about 116 GHz [2, 10]. Fig. 2a also shows the expected asymmetry of the hysteresis loops in the presence of circularly polarized radiation. In particular, the height of the zero-field step (first tunnel resonance, $n = 0$), obtained when sweeping the field from negative saturation, is much less affected than when sweeping from positive saturation. Besides, the effect of a radiation at 95 GHz (Fig. 2b) with no level matching is quite comparable to that of temperature (Fig. 2c) (heating induced by large power irradiation). These results establish clearly that tunneling is assisted by photons for the matching frequency of 115 GHz. Similar qualitative effects were also observed in a field of 0.22 T, corresponding to the second tunnel resonance ($n = 1$).

For the quantitative study of the power dependence of photons-induced tunneling, we first cooled the sample from 5 K down to 0.04 K in a field of $H_z = 1.4$ T yielding a positive saturated magnetization state. Then, in the presence of continuous microwave radiation at 115 GHz and power $\rho$, we swept the applied field at a constant rate over the zero field resonance transition and mea-
measured the fraction of molecules which reversed their spin. This procedure yields the total tunnel probability \( P(\rho) \). The photon induced tunneling probability \( P_{EPR}(\rho) \) was evaluated from:

\[
P_{EPR}(\rho) = P(\rho) - n_{10}P_{\pm 10}
\]

where the ground state tunnel probability \( n_{10}P_{\pm 10} \) was measured in the absence of radiation \[19\]. The obtained \( P_{EPR}(\rho) \) first increases linearly with \( \rho \) and then becomes highly non-linear (Fig. 3).

In order to give a simple explanation of the observed behavior, we developed a scenario in which the spin temperature increases rapidly with the absorbed microwave power. We used the generalized master equation formalism as described by Leuenberger and Loss \[20\] but with photon induced transition probabilities \( \Gamma_{RF} \) between the energy states \( M = \pm S \) and \( \pm (S - 1) \). At low temperature \( (T << 1 \text{ K}) \), it is sufficient to consider only the six lowest levels (Fig. 1) with occupation numbers \( n_{M} \) where \( M = \pm S, \pm (S - 1), \pm (S - 2) \). As initial condition we have chosen positive saturation of the sample, i.e. \( n_{S} \approx N \), where \( N \) is the number of molecules. We yield for small microwave power \( \rho \) and \( P_{EPR} << 1 \):

\[
P_{EPR} \approx \frac{2\Gamma_{RF}\Delta_{\pm 9}}{9g\mu_{B}\mu_{0}dH_{z}/dt} + \sum_{M = 9, S} \frac{\Delta_{\pm M}e^{-E_{10,M}/k_{B}T_{S}}}{\tau_{M}g\mu_{B}\mu_{0}dH_{z}/dt}
\]

where \( \tau_{M} \) is the lifetime of the excited level \( M \), \( E_{10,M} \) is the energy gap between the levels 10 and \( M \), \( \Delta_{\pm M} \) is the tunnel splitting of the levels \( \pm M \), and \( T_{S} \) is the spin temperature. All constants of this model were found by measuring the overall transition rate via excited spin levels \( P_{th}(T) \) due to thermal activation, as described in \[19\].

The spin temperature \( T_{S} \) were determined by mapping \( P_{EPR}(\rho) \) onto \( P_{th}(T) \) such as \( P_{EPR(\rho)} = P_{th}(T_{0} = T_{S}) \) (Fig. 4). We obtained a nearly linear variation of \( T_{S} \) versus \( \rho \) (inset of Fig. 3).

The energy transfer from the spin system to the thermostat involves contributions of the electromagnetic radiation bath, the phonon bath and the spin bath. However, at low temperatures \( (T < 1 \text{ K}) \) the phonon specific heat is vanishingly small and the photon bath completely negligible. The specific heat \( C_{S} \) of the spin bath is greatly influenced by weak dipolar fields giving a flat distribution of Schottky anomalies with a nearly constant specific heat \[21, 22\]. The electromagnetic power absorbed by the spin system, \( dW/dt = h\omega(1 - n_{S-1}/N)\Gamma_{RF} \approx h\omega\Gamma_{RF} \) \[18\], passes to the thermostat via spin–lattice and spin–spin relaxation. The effect of the latter should be more important due to their larger specific heat. Neglecting the phonon specific heat, the heat transfer equation can be written:

\[
dW/dt = C_{S}dT/dt + C_{S}(T_{S} - T_{0})/\tau_{S}
\]

where \( T_{0} \) is the cryostat temperature and \( \tau_{S} \) is a diffusion time for magnetic excitations. At equilibrium \( (dT/dt = 0) \), the spin-bath temperature is therefore \( T_{S} = T_{0} + h\omega\Gamma_{RF}T_{S}/C_{S} \). Because \( C_{S} \) is almost temperature independent between 0.3 and 0.8 K \[21, 22\], \( T_{S} \) increases nearly linearly with the microwave power which is in good agreement with our observation (inset of Fig. 3).

Finally, the microwave absorption at 95 GHz and for
\[ n = 1 \] at 115 GHz might be due to spin–spin interactions which broaden strongly the energy levels. Such a broadening has already been observed by EPR linewidth measurements\[10\] and spin–spin cross–relaxation measurements\[23, 24\].

In conclusion, the use of circularly polarized microwaves allowed us to show for the first time the phenomenon of photon-assisted tunneling in magnetism, using a single molecule magnet Fe\(_8\). In accordance with the selection rules for EPR spectroscopy\[18\], circularly polarized radiation promotes the transition \( M = -10 \) to \(-9\) with \( \Delta M = +1\), giving an effect of magnetic dichroism at millimeter wavelengths. At lowest microwave powers, the tunnel probability increases linearly with the power, whereas at higher powers we enter in a non-linear regime resulting from an increase of the spin temperature \( T_S \).

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[1] R. Sessoli, H.-L. Tsai, A. R. Schake, S. Wang, J. B. Vincent, K. Folting, D. Gatteschi, G. Christou, and D. N. Hendrickson, J. Am. Chem. Soc. 115, 1804 (1993).
[2] A.-L. Barra, P. Debrunner, D. Gatteschi, Ch. E. Schulz, and R. Sessoli, EuroPhys. Lett. 35, 133 (1996).
[3] L. Thomas, F. Lionti, R. Ballou, D. Gatteschi, R. Sessoli, and B. Barbara, Nature (London) 383, 145 (1996).
[4] J. R. Friedman, M. P. Sarachik, J. Tejada, and R. Ziolo, Phys. Rev. Lett. 76, 3830 (1996).
[5] S. M. J. Aubin, N. R. Dilley, M. B. Wemple, G. Christou, and D. N. Hendrickson, J. Am. Chem. Soc. 120, 839 (1998).
[6] N.V. Proko'ev and P.C.E. Stamp, Phys. Rev. Lett. 80, 5794 (1998).
[7] W. Wernsdorfer and R. Sessoli, Science 284, 133 (1999).
[8] J. Yoo, E. K. Brechin, A. Yamaguchi, M. Nakano, J. C. Huffman, A.L. Maniero, L.-C. Brunel, K. Awaga, H. Ishimoto, G. Christou, and D. N. Hendrickson, Inorg. Chem. 39, 3615 (2000).
[9] J. J. Alonso and J. F. Fernandez, Phys. Rev. Lett. 87, 097205 (2001).
[10] S. Hill, S. Maccagnano, Kyungwha Park, R. M. Achey, J. M. North, and N. S. Dalal, Phys. Rev. B 65, 224410 (2002).
[11] E. M. Chudnovsky and D. A. Garanin, Phys. Rev. Lett. 89, 157201 (2002).
[12] Julio F. Fernandez, Phys. Rev. B 66, 064423 (2002).
[13] M. Dressel, B. Goshunov, K. Rajagopalan, S. Vongtragoon, and A. A. Mukhin, Phys. Rev. B 67, 060405 (2003).
[14] M. N. Leuenberger and D. Loss, Nature 410, 789 (2001).
[15] B. Zhou, R. Tao, S.Q. Shen, and J. Q. Liang, Phys. Rev. A 66, 010301 (2002).
[16] A.D. Kent, S. von Molnar, S. Gider, and D.D. Awschalom, J. Appl. Phys. 76, 6656 (1994).
[17] L. Bokacheva, A.D. Kent, and M.A. Walters, Phys. Rev. Lett. 85, 4803 (2000).
[18] A. Abragam and B. Bleaney, Electron paramagnetic resonance of transition ions (Clarendon Press, Oxford, 1970).
[19] W. Wernsdorfer, A. Caneschi, R. Sessoli, D. Gatteschi, A. Cornia, V. Villar, and C. Paulsen, EuroPhys. Lett. 50, 552 (2000).
[20] M. N. Leuenberger and D. Loss, Phys. Rev. B 61, 12200 (2000).
[21] A.M. Gomes, M.A. Novak, R. Sessoli, A. Caneschi, and D. Gatteschi, Phys. Rev. B 57, 5021 (1998).
[22] F. L. Mettes, F. Luis, and L. J. de Jongh, Phys. Rev. B 64, 174411 (2001).
[23] R. Giraud, W. Wernsdorfer, A. M. Tkachuk, D. Mailly, and B. Barbara, Phys. Rev. Lett. 87, 057203 (2001).
[24] W. Wernsdorfer, S. Bhaduri, R. Tiron, D. N. Hendrickson, and G. Christou, Phys. Rev. Lett. 89, 197201 (2002).