Ultrafast quantum spin-state switching in the Co-octaethylporphyrin molecular magnet with a terahertz pulsed magnetic field

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Molecular spin crossover switches are the objects of intense theoretical and experimental studies in recent years. This interest is due to the fact that these systems allow one to control their spin state by applying an external photo-, thermo-, piezo-, or magnetic stimuli. The greatest amount of research is currently devoted to the study the effect of the photoexcitation on the bi-stable states of spin crossover single molecular magnets (SMMs). The main limitation of photo-induced bi-stable states is their short lifetime. In this paper we present the results of a study of the spin dynamics of the CoOEP molecule in the Low Spin (LS) state and the High Spin (HS) state induced by applying the magnetic pulse of 36.8T. We show that the spin switching in case of the HS state of the CoOEP molecule is characterized by a long lifetime and is dependent on the magnitude and duration of the applied field. Thus, after applying an external stimuli the system in the LS state after the spin switching reverts to its ground state, whereas the system in the HS state remains in the excited state for a long time. We found that the temperature dependency of magnetic susceptibility shows an abrupt thermal spin transition between two spin states at 40K. The proposed here theoretical approach opens the way to create modern devices for spintronics with the controllable spin switching process.

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I. INTRODUCTION

Spin engineering mostly concentrates on the manipulation of spin degrees of freedom in various magnetic materials and the exploration of their potential applications in spintronics. Current examples for the applications of spin engineering in magnetic nanostructures and devices are increasingly ample, ranging from the development of single molecular magnet as qubits. Therefore, the spin engineering in magnetic nanostructures, including theoretical modeling, experimental demonstration, and device design for applications, is demanding multidisciplinary backgrounds of knowledge and technology which create great challenges for researchers.

Magnetic or spin logic appears as an appealing alternative due to its nonvolatile character, which can boost up switching on/off, its possibility to reduce the size of the element down to the several-atoms scale on/off spin per atom instead of one elementary charge per 10⁴ atoms in semiconductors, and speed increase as a secondary size effect. The modern experiments are promising, they still move in the micrometer regime, thus not fully exploiting the possible quantum nature of molecular magnetism. In other hand, small molecules perform logic operations using as input cation concentrations. The latter is fast with respect to the logic operation but slow with respect to repeatability. Thus a need for magnetic-logic devices on the molecular scale emerges. At the same time the experimental evidence of laser-driven ultrafast magnetic/spin manipulation in the antiferromagnetic materials motivates the design of a cluster with more than one spin center which allows for spin manipulation.

The problem of the gigahertz magnetization/spin switching speed of todays magnetic logic and a magnetic memory devices into the terahertz regime underlies the entire field of information processing. The physics of present-day devices imposes serious limitations on this technological transformation, so we must invent new paradigms based on the quantum spin dynamics in the picosecond regime. This challenge could be met by a simulation of the quantum spin switching in a picosecond pulsed magnetic field. Currently, no easily accessible method is available to generate intense sub-picosecond magnetic pulses localized at the nanoscale. However in the work, show that bimetallic nanorings can act as nanoscale sources of intense ultrashort magnetic pulses. In this instance rely on the enhanced light absorption associated with the plasmons of metallic rings to generate transient thermoelectric currents that in turn produce sub-picosecond pulses with magnetic fields as high as a few tenths of a Tesla in the vicinity of the rings. The ability to generate strong magnetic fields localized on the nanoscale is of interest for elucidating spin and magnetization dynamics at sub-picosecond time and nanometer...
length scales, and it holds great potential for materials characterization, terahertz radiation generation, and magnetic recording.

Magnetic molecules have been intensively studied so far because of their potential technological applications and for the possibility they offer to investigate fundamental properties of matter at the nanoscopic scale. An intensively studied class of magnetic molecules is constituted by the so-called single molecule magnets or molecular nanomagnets. These systems are characterized by a slow relaxation of magnetization at low $T$ and give rise to magnetic hysteresis. This is one condition for storing information in a molecule. Therefore, since a SMM represents an isolated magnetic entity, it might be considered as the smallest practical unit for magnetic memories. The studying of a possibility of the switching of the spin states would incredibly increase the amount of information storable with respect to current devices. In order to have a deeper understanding of fundamental features and a major control on technological aspects, the time-dependent spin dynamics constitutes the key point. The micromagnetic model describes appropriately the dynamics of the magnetization(spin) in a magnetic nanostructures. In this model the magnetization(spin) is assumed to be a spatial- and time-dependent continuous function. The magnetization(spin) dynamics are described by the Landau-Lifshitz-Gilbert (LLG) equation including the energy contributions of the anisotropy, the exchange interaction, the magnetostatic interaction, and the Zeeman energy. The microscopic result of the quantum modeling is the cluster spin models, which have been proved to be a powerful tool for approaching the extreme phenomenology of the ultrafast magnetization(spin) dynamics. Ab initio models for the general spin Hamiltonian can be efficient in providing insight on the local atomic scale values such as the local magnetic moment $\mu_s$, the local anisotropy $D_i$, or a pairwise exchange $J_{ij}$ in the magnetic molecule. The parameters of the theory, the exchange integrals and the anisotropy, are usually fitted to experiments or calculated from static density functional theory (DFT).

Switching between the LS and HS states can be done by varying the temperature, applying pressure or by light irradiation. In the first and the second case the population of the LS and HS states is fully determined by thermodynamic equilibrium and such transitions are called temperature- and pressure-induced spin crossover transitions. In the case of light-induced spin crossover, after initial excitation to d-states or to metal-to-ligand charge transfer states, the system undergoes a complex cascade of intermediate transitions and eventually gets trapped in a non-equilibrium metastable state. The whole process is called light-induced excited spin state trapping (LIESST). The details of the LIESST process are still under debate.

We report here the possibility of a commutation of the CoOEP SMM between the two states of a spin-crossover system by a pulsed magnetic field. Choosing a cobalt-based spin-crossover system follows the idea that cobalt(II)[CoOEP] materials, as well as iron(III) ones have metal-ligand bonds shorter than those in iron(II) materials, leading to faster relaxation dynamics between the HS and LS states. The molecule cobalt(II) ([Ar]3d7 4s2) may be either in the LS state ($\uparrow\downarrow\uparrow\uparrow\uparrow\uparrow\uparrow S = 1/2$) or in the HS state ($\uparrow\downarrow\downarrow\uparrow\uparrow\uparrow S = 3/2$), both of which are paramagnetic.

II. THEORETICAL ASPECTS

A. The spin-dynamics simulations

The dynamic behavior of a spin is determined by the equation of motion, which can be derived from the quantum theory with the general spin Hamiltonian $\hat{H}_{\text{spin}}$ that calculated the spin structure of a magnetic molecule with Hamiltonian

$$\hat{H}_{\text{spin}} = \hat{H}_{\text{ex}} + \hat{H}_{\text{an}} + \hat{H}_{\text{ZEE}} + \hat{H}_\text{a}(t).$$

The first term $\hat{H}_{\text{ex}}$ is the Heisenberg-Dirac Hamiltonian, which represents the isotropic exchange interaction, $\hat{H}_{\text{an}}$ is the exchange Hamiltonian the term due to the axial single-ion anisotropy, and $\hat{H}_{\text{ZEE}}$ is the interaction between the spin system and the external magnetic field. In order to give a theoretical description of a magnetic molecule we exploit the irreducible tensor operator technique. For the study of the CoOEP magnetic properties, it is a good approximation to treat the electrons of one Co-atom as a single atomic spin which is interacting with its surroundings. Thus, one can be content with $\hat{H}_{\text{spin}}$ without the first term $\hat{H}_{\text{ex}}$. We will consider an approximate treatment, restricting ourselves to the simplest, but very useful, approximation, known as mean field theory. This "mean field" Hamiltonian, which describes the interaction of the spin $\hat{S}$ with the external magnetic field, given by its flux $\hat{H}_{\text{eff}}$, can be expressed as:

$$\hat{H}_{\text{spin}} = -\gamma \hat{H}_{\text{eff}} \hat{S}.$$  \hspace{1cm} (2)

The generally shaped formula is

$$\hat{H}_{\text{eff}} = -\frac{\partial \hat{H}_{\text{spin}}}{\partial \langle \hat{S} \rangle}.$$  \hspace{1cm} (3)

Here the effective magnetic field $\hat{H}_{\text{eff}}$ is an external magnetic field $H_z$, the anisotropy fields $\hat{H}_{\text{an}}$, the exchange interaction $\hat{H}_{\text{ex}}$ and external magnetic pulse field $H_{\text{pulse}}(t)$. We use the "mean field" approximation for $\hat{H}_{\text{eff}} \Rightarrow H_{\text{eff}}$ with replacement $\hat{S} \Rightarrow M_s = \gamma \langle \hat{S} \rangle$. We call "mean" the mean field. (Historically it was often called the "molecular field"). It includes the average effect of the neighbors but neglects correlations between the spin and its neighbors. Since we have the one magnetic atom, this approach us quite suitable. Use (2) we
Using this expression one can evaluate the magnetization effective magnetic field with specifying the interactions spin equation for a system of the spins precessing in a magnetic field of the magnetic field. Thus we can consider the external of the anisotropic system do not depend on the direction of a molecule will be only scalar, the magnetic properties heat. Since in further researches the anisotropic part magnetic properties of the system as the magnetization, Hamiltonian, we can evaluate a different thermodynamic properties of the system as the magnetization, Hamiltonian using a so-called "g tensor" is used to account for the anisotropy of the Zeeman response to an applied magnetic field, an "effective" Zeeman Hamiltonian \( \hat{H}_{\text{spin}} \), which stay we diagonalized \( \hat{H}_{\text{spin}} \).

A spin structure is defined only proceeding from the spin model of a molecule. Here we use to calculate a spin structure by the ITO method within the generalized spin Hamiltonian \( \hat{H}_{\text{spin}} \).

Once we have the energy levels of the spin-Hamiltonian \( \hat{H}_{\text{spin}} \), we can evaluate the different thermodynamic properties with given total spin protection and the double exchange contributions (index \( s \))

\[
\langle \partial_t \rangle = \frac{1}{1 + \lambda^2} (\hat{S}) \times \mathbf{H}^\text{mean} - \frac{\lambda}{1 + \lambda^2} (\langle \hat{S} \rangle \times \mathbf{H}^\text{mean})
\]

The effective magnetic field \( \mathbf{H}^\text{mean} \) is given by the free magnetic energy variational with magnetization:

\[
\mathbf{H}^\text{mean}_{\text{eff}}(M_s, t) = -\frac{\delta F}{\delta M_s}
\]

where \( F \) is the free energy of the magnetic nanosystem

\[
F = -Nk_B T \ln Z(H_z)
\]

with the partition function

\[
Z(H_z) = \sum_{M_z, \mu} \exp[-\epsilon_\mu(M_s)/kT] \sum_{M_s} \exp[-g_s M_s H_z / k T] \exp[\mu(M_s + g_s M_s H_z)/kT]
\]

Here we have the energy levels \( \epsilon_\mu(M_s) \) of the spin-Hamiltonian \( \hat{H}_{\text{spin}} \), which stay we diagonalized \( \hat{H}_{\text{spin}} \).

The ZFS Hamiltonian is given by

\[
\hat{H}_{\text{ZFS}} = \hat{S} \cdot \mathbf{D} \cdot \hat{S}
\]

where \( \hat{S} \) is the vector operator for the effective spin of Co atom, and \( \mathbf{D} \) is the second-order anisotropy tensor. After diagonalization in the magnetic axis frames, the Hamiltonian becomes

\[
\hat{H}_{\text{ZFS}} = D \hat{S}_z^2 + E (\hat{S}_y^2 - \hat{S}_z^2)
\]

The parameter \( D \) is called the axial ZFS parameter and \( E \) is the rhombic ZFS parameter, which vanishes for high symmetry molecules. Parameter \( D \) has to be negative for the magnetic bistability associated with SMs. When a molecule is placed in a magnetic field \( \mathbf{H} \), the electron's energies will depend on its magnetic moment value \( M_s \). To account for the anisotropy of the Zeeman Hamiltonian using a so-called "g tensor" is used

\[
\hat{H}_{\text{ZEE}} = \mu_B \mathbf{H} \cdot \mathbf{g} \cdot \hat{S} = \mu_B \begin{bmatrix} H_x & H_y & H_z \end{bmatrix} \begin{bmatrix} g_x & 0 & 0 \\ 0 & g_y & 0 \\ 0 & 0 & g_z \end{bmatrix} \begin{bmatrix} S_x \\ S_y \\ S_z \end{bmatrix}
\]

The g-tensor was calculated in a spin-orbit coupled spin unrestricted relativistic ZORA approach. The degenerate perturbation theory was used with the external magnetic field as perturbation.
III. RESULTS AND DISCUSSION

The most important aspect to the establishment of real devices based on SMMs, e.g. high density rewritable memories, is to achieve such conditions under that externally driven system could be switched between two stable LS and HS spin states and would remain in each of these states for a certain period of time. The LS/HS bi-stability is connected with small energy ($\Delta E_{HS-LS}=2.133$ meV ) magnitudes involved in the switching between these two spin states (Figure 1a). Much research is currently focused on the study of photo-switching mechanism between LS and HS states, changes in the geometric and electronic structure of molecules in these states, the magnetic properties of SMMs. However, we found no studies on the time-dependent spin dynamics of spin-crossover systems. In this paper we focus on the behavior of the spin of the molecules under the influence of external stimuli and finding the conditions under which the system would be able to stay in one of the bistable states arbitrarily long time. Since the photo-induced states of SMMs are characterized by a short lifetime, we effect on the system being studied by a short magnetic pulse of high amplitude. In the experimental study $^{18}$, it was shown that the application of an external magnetic field of 32T to spin-crossover solid system $\text{Co(O}_{2}\text{H}_{2}\text{(fsa)$_2$en})(\text{py})_2$ takes place an irreversible and quasicomplete transition from the HS to the LS state. This also means that after applying a perturbation the system can remain in HS state for a long time. In this paper, we have developed an approach for the study of the spin dynamics of spin-crossover systems and apply it to one of the intensively studied objects from a number of SMMs the CoOEP molecule. The chemical structure of CoOEP molecule is exhibited in Fig. 1(c). Fig 2 shows the magnetic susceptibility plotted as the product $\chi T$ versus temperature for the CoOEP molecule. The temperature variation of the magnetic susceptibility $\chi T$ showing the abrupt of the thermal spin transition with the jump between two spin states occurs at temperature of $T_{1/2}=40K$.

By irradiating LS molecules with visible light, HS molecule can be generated because of the efficient electronic decay of excited state via Inter System Crossing towards metastable HS state. This effect is now referred as LIIESST (Light Induced Electronic Spin State Trapping) in the literature. Once irradiation is stopped, the system relaxes to the thermal equilibrium state LS. One important LIIESST-result is the decoupling of different degrees of freedom during the electronic spin state trapping and the transfer of excess energy to molecular vibration modes. Contrary to the LIIESST, here considered in some detail the quantum dynamics of the HS spin state trapping and impacts on it of a short magnetic pulse.

We present here a theoretical approach to the organic magnetic CoOEP-molecule in terms of numerically solvable the time-dependent LLG-model with a general spin Hamiltonian in the context of the ITO model. In practice, these models apply to the quantum spin-state switching in the Co-octaethylporphyrin molecular magnet with a picosecond pulsed magnetic field and provide an understanding of a spin-crossover phenomenon in these molecule. In the calculations by LLG-method was used the next parameters: $T_{\text{pulse}}=0.17ps$ (ultrashort THz pulse); time of start pulse is 37.4ps; the height of
The magnetic susceptibility product $\chi T$.

The spin dynamics for the CoOEP molecule with magnetic pulse (S=1/2).

The spin dynamics for the CoOEP molecule without magnetic pulse (S=1/2).

The spin dynamics for CoOEP molecule without magnetic pulse (S=3/2).

The magnetic pulse is 36.8T. We solved the LLG equation for two different states $S=1/2$, $t_{2g}^{1}e_{g}^{1}$ (LS) and $S=3/2$, $t_{2g}^{2}e_{g}^{2}$ (HS). Under the influence of the constant Zeeman magnetic field 0.1T, after a certain period of time, which is determined in case of a single molecule by the size of ZFS, the time-dependent spin structure is formed. In the time of "saturation" of the system we apply the external stimuli of a magnetic pulse. The system in the LS state behaves classically without the application of the pulse. Under the influence of the 36.8T pulse a spin switching on the pulse duration of 100fs is happened, after which the system returns to the ground state (Fig 3). In the case of the HS state of the system the situation is changing drastically. Under the influence of the pulse a spin switching occurs as well, but the system remains in this state for a long time (Fig 4). With increasing magnetic field up to 36.8T a spin switch occurs and the $H_{eff}$ sign is changed. In our approach $H_{eff}$ is the $\langle \hat{S} \rangle$ derivative of the spin-Hamiltonian. In our case, the Hamiltonian (1) has no $H_{ex}$ term, because there is only one transition metal atom in CoOEP molecule and, accordingly, the spin-spin interaction is absent. Thus, the anisotropic $H_{an}$ term is only a nonconstant one, which is quadratic in $\langle \hat{S} \rangle$ (2) and, therefore, $H_{eff}$ is proportional to $H_{eff}$ is the $\langle \hat{S} \rangle$. Qualitatively, the $H_{eff}$ behavior is the same as the $\langle \hat{S} \rangle$, which is seeing from the Fig 3 and 4.
molecule in the LS and HS states. We found that the spin-crossover CoOEP molecule undergo the spin switching between LS and HS states after applying the external stimuli of a short magnetic pulse of 36.8T. The temperature dependency of magnetic susceptibility shows an abrupt thermal spin transition between two spin states at 40K. We also found the difference in the spin dynamics for two spin states of CoOEP molecule. Thus, after the spin switching under the magnetic pulse the system in the LS state reverts to its ground state, whereas the system in the HS state after the spin switching remains in the excited state for a long time. This behavior gives us the possibility to assign such system as an appropriate candidate for the SMM and opens a way to realize a controlled spin switching in real devices for spintronics.

FIG. 6: (Color online) The spin dynamics for the CoOEP molecule with magnetic pulse (S=3/2).

IV. CONCLUDING REMARKS

In the paper we present the results of the theoretical study of the spin behavior in the CoOEP molecule under influence of high magnetic pulse. Based on the LLG equation we described the spin dynamics of the

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1 F. Troiani and M. Affronte, Chem.Soc.Rev. 40, 3119 (2011).
2 A. P. de Silva and S. Uchiyama, Nat. Nanotechnol. 2, 399 (2007).
3 W. Hübner, S. Kersten, and G. Lefkidis, Phys. Rev. B 79, 184431 (2009).
4 D. A. Allwood, G. Xiong, M. D. Cooke, C. C. Faulkner, D. Atkinson, N. Vernier, and R. P. Cowburn, Science 296, 2003 (2002).
5 B. Ferguson and X.-C. Zhang, Nat. Mater. 1, 26 (2002).
6 M. Tonouchi, Nat. Photonics, 1, 97 (2007).
7 C. Vicario, C. Ruchert, F. Ardana-Lamas, P. M. Derlet, B. Tudu, J. Luning, and C. P. Hauri, Nat. Photonics, 7, 720 (2013).
8 C. Vicario, B. Monoszlai, and C. P. Hauri, Phys. Rev. Lett. 112, 213901 (2014).
9 R. Wieser, E. Y. Vedmedenko and R. Wiesendanger, Phys.Rev.Lett. 106, 067204 (2011).
10 O.V.Farberovich, V.L.Mazalova, A.V.Soldatov, [arXiv:1410.1658v1 [cond-mat.mes-hall]] 7 Oct.2014.
11 A. Tsiatmas, E. Atmatzakis, N. Papasimakis, V. Fedotov, B. Luk’yanchuk, N.I. Zheludev and F. Javier Garcia de Abajo, [arXiv:1303.6072v1 [cond-mat.mes-hall]] 25 Mar.2013.
12 A. Kirilyuk, A.V. Kimel and T. Rasing, Rev. Mod. Phys. 82, 2731 (2010).
13 W. Linert and M. Verdaguer, eds., Molecular Magnets (Springer-Verlag, Wien, 2003).
14 B. Guo and S. Ding, Landau-Lifshitz equations (World Scientific, Singapore, 2008).
15 V.V.Maslyuk, I. Mertig, O.V. Farberovich, A. Tarantul and B. Tsukerblat, Eur.J.Inorg.Chem. 2013, 1897 (2013).
16 Spin-Crossover Materials, edited by M. Halicrow (Wiley, West Sussex, 2013).
17 M. Cammarata, R. Bertoni, M. Lorenc, H. Cailleau, S. Di Matteo, C. Maurici, S.F. Matar, H. Lemke, M. Chollet, S. Ravy, C. Laulh, J.-F. Llardi and E. Collet, Phys. Rev. Lett. 113, 227402 (2014).
18 A. Bousseksou, K. Boukheddaied, M. Goiran, C. Consejo, M-L. Boillot and J-P. Tuchagues, Phys. Rev.B 65, 172412 (2002).
19 M. Bernien, X-ray absorption spectroscopy of Fe complexes on surfaces. PhD Thesis, Freie Universitt Berlin (2010).
20 J.J. Borras-Almenar, J.M. Clemente-Juan, E. Coronado and B.S. Tsukerblat, Inorg.Chem.38, 6081 (1999).
21 D.A. Garanin, Phys. Rev.B 55, 3050 (1997).
22 R. Wieser, [arXiv:1302.1985v1 [cond-mat.mes-hall]] 8 Feb 2013.
23 G. te Velde, F. M. Bickelhaupt, S.J.A. van Gisbergen, C. Fonseca Guerra, E.J. Baerdens, J.G. Snijders and T. Ziegler, J. Comput. Chem. 22, 931 (2001).
24 ADF2014, SCM, Theoretical Chemistry, Vrije Universiteit, Amsterdam, The Netherlands, http://www.scm.com
25 E. van Lenthe, A. E. Ehlers and E. J. Baerdens J. Chem. Phys. 110, 8943 (1999).
26 S.F. Matar, Ph. Guionneau and G. Chastanet, Int. J. Mol. Sci., 16, 4007 (2015).