Influence of the Dzyaloshinskii-Moriya exchange interaction on quantum phase interference of spins

W. Wernsdorfer\textsuperscript{1}, T.C. Stamatatos\textsuperscript{2}, and G. Christou\textsuperscript{2}

\textsuperscript{1}Institut Néel, CNRS and Université J. Fourier, BP 166, 38042 Grenoble Cedex 9, France
\textsuperscript{2}Department of Chemistry, University of Florida, Gainesville, Florida 32611-7200, USA

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Magnetization measurements of a Mn\textsubscript{12}mda wheel single-molecule magnet with a spin ground state of $S = 7$ show resonant tunneling and quantum phase interference, which are established by studying the tunnel rates as a function of a transverse field applied along the hard magnetization axis. Dzyaloshinskii-Moriya (DM) exchange interaction allows the tunneling between different spin multiplets. It is shown that the quantum phase interference of these transitions is strongly dependent on the direction of the DM vector.

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Single-molecule magnets (SMMs), sometimes called molecular nanomagnets, consist of an inner magnetic core and a surrounding shell of organic ligands\textsuperscript{[1]} that can be tailored to bind onto surfaces or into junctions. SMMs come in a variety of shapes and sizes and permit selective substitution of the ligands in order to alter the coupling to the environment. It is also possible to exchange the magnetic ions, thus changing the magnetic properties without modifying the structure and the coupling to the environment. SMMs combine the classic macroscale properties of a magnet with the quantum properties of a nanoscale entity. They display an impressive array of quantum effects that are observable up to higher and higher temperatures due to progress in molecular design, ranging from quantum tunnelling of magnetization\textsuperscript{[2,3,4]} to Berry phase interference\textsuperscript{[5,6,7,8]} and quantum coherence\textsuperscript{[9,10]} with important consequences on the physics of spintronics devices\textsuperscript{[11]}.

Up to now, the spin system of an SMM has mainly been described by a single spin $S$, and the associated tunneling processes were transitions inside the multiplet of $S$\textsuperscript{[1]}. Recent studies in the field of molecular magnetism go beyond this giant-spin approximation, describing the molecule as a multi-spin system\textsuperscript{[12]}. In this case, the total spin $S$ of the molecule is not fixed, but several multiplets with different total spins appear and the number of allowed tunnel transitions and relaxation paths of the spin system increase considerably. For a simple multi-spin description with symmetric exchange coupling between spins, tunneling between different multiplets is forbidden. However, antisymmetric exchange coupling between spins, that is the Dzyaloshinskii-Moriya (DM) interaction, can lift the degeneracy of energy level crossings belonging to different spin multiplets, and tunneling and interference between these levels become allowed\textsuperscript{[12,13,14,15]}. DM interactions result in general from pairwise interactions of neighbouring spins, which do not have an inversion centre. This condition is fulfilled most of the time in SMMs even when the entire molecule has an inversion centre\textsuperscript{[14,16]}.

We present here resonant quantum tunneling measurements of a Mn\textsubscript{12}mda wheel\textsuperscript{[17]}, which is a member of the $\text{[Mn}_{12}\text{(O}_2\text{CMe})_{14}\text{(R-mdap)]}_8$ family of loops, all with the same core and metal topologies but with R-substituted mda\textsuperscript{2−} groups\textsuperscript{[18]}. We show that this compound exhibits quantum phase interference effects at all observed tunnel resonances and that the phase of interference depends strongly on the direction of the DM vector $\vec{D}_{1,2}$.

The Mn\textsubscript{12}mda ($R = \text{Me}$) wheel was prepared by the reaction of Mn(O$_2$CMe)$_2$4H$_2$O and N-methylidethanolamine (mdaH$_2$) in the presence of the organic base NEt$_3$, and crystallizes as dark red plate-like crystals in triclinic space group $P\bar{1}$. Full details of the synthesis, crystal structure and magnetic characterization were presented elsewhere\textsuperscript{[17]}, establishing a ground state spin $S = 7$ that the wheel consists of alternating Mn$^{2+}$ and Mn$^{3+}$ ions, and therefore all subunits consisting of two neighboring Mn ions must lack an inversion centre, justifying therefore the possibility of DM interaction even though the complete molecule has an inversion centre\textsuperscript{[14,16]}. Although our Mn\textsubscript{12}mda wheel is very similar to those in\textsuperscript{[13,18]}, the hysteresis loops show resonant tunneling steps that are much more narrow, allowing us to study in detail the quantum effects involved.

The magnetization measurements were performed by using a micro-SQUID setup\textsuperscript{[19]} on top of which a single crystal of Mn\textsubscript{12}mda wheels was placed. The field was aligned with the easy axis of magnetization using the transverse field method\textsuperscript{[20]}.

Fig. 1\textsuperscript{a} shows the temperature dependence of the hysteresis loops of Mn\textsubscript{12}mda wheels. The loops display a series of steps, separated by plateaus. As the temperature is lowered, the hysteresis increases because there is a decrease in the transition rate of thermally assisted tunneling\textsuperscript{[2,3]}. The hysteresis loops become temperature independent below 0.3 K, demonstrating quantum tunneling at the lowest energy levels\textsuperscript{[4]}. Apart from the major steps, these hysteresis loops reveal fine structure in the thermally activated regime. In order to determine
to be described. Each spin conclusion about the influence of the DM interaction employed does not affect the generality of the obtained discussion of the observed tunnel rates. The simple model the lowest energy levels, and allows a qualitative dis-

FIG. 1: (Color online) (a) Hysteresis loops of single crystals of Mn$_{12}$mda wheels at different temperatures and a constant field sweep rate of 8 mT/s. (b) Minor hysteresis loops at 0.04 K. The magnetization was first saturated at 1 T. After ramping the field to zero at 0.14 T/s, the field was swept three times back and forth (between ±0.07) over the zero-field resonance $k = 0$ with a sweep rate of 0.28 T/s. Then, the field is quickly swept back to 1 T at the indicated field sweep rates leading to resonant tunneling at the transitions $k = 1S, 1A,$ and 2. The corresponding field values are used to find the spin Hamiltonian parameters $D$ and $J$.

precisely the resonance positions, we used the minor loop method described in [21]. A typical example is presented in Fig. 1.

In order to explain the observed tunnel resonances and tunnel probabilities, and to study the influence of DM interaction on quantum phase interference, we model the 12-spin-system with a simple dimer model of two ferromagnetically coupled spins $S_1 = S_2 = 7/2$ [13, 17]. Although this model can be questioned [14, 22], it represents a useful simplification that keeps the required calculations manageable, has been found to describe well the lowest energy levels, and allows a qualitative discussion of the observed tunnel rates. The simple model employed does not affect the generality of the obtained conclusions about the influence of the DM interaction to be described. Each spin $S_i$ is described by the spin Hamiltonian:

$$\mathcal{H}_i = -DS_{i,x}^2 + E(S_{i,x}^2 - S_{i,y}^2) + \hat{O}(4) - g\mu_B\mu_0 S_i \cdot \vec{H}$$

where the first term describes the isotropic Heisenberg exchange interaction with exchange constant $J$, and the second term is an antisymmetric DM interaction between the two spins and the DM vector $\hat{D}_{1,2}$.

Exact diagonalization of the total spin Hamiltonian $\mathcal{H} = \mathcal{H}_1 + \mathcal{H}_2 + \mathcal{H}_{\text{ex}}$ and use of $J = -0.435$ K and $D = 0.985$ K lead to the energy spectrum shown in Fig. 2. The lowest lying spin states belong to the $S = 7$ and $S = 6$ multiplets. Due to the ferromagnetic exchange, the first excited spin multiplet’s $|S = 6, M_S = \pm 6\rangle$ doublet is located at about 8.8 K above the ground state doublet $|S = 7, M_S = \pm 7\rangle$ in zero magnetic field. Using $D = 0.985$ K and $J = -0.435$ K, we can reproduce well the 6 observed tunnel transitions. The resonances $k = 0$, $1S$, and $2$ correspond to transitions between the states of the $S = 7$ multiplet, whereas $k = 1A$, $1E$, and $2E$ correspond to transitions between the $S = 7$ and $S = 6$ multiplets. The latter ones are not allowed unless the antisymmetric DM interaction between the two spins is introduced (Eq. 2).

In order to get more insight into the tunnel process, we studied the tunnel resonances as a function of
of a transverse field and used the Landau-Zener (LZ) method [6, 23, 24]. We first placed a crystal of the Mn$_{12}$-unda wheel in a high negative field $H_z$ to saturate the magnetization at 40 mK. We then swept the applied field at a constant rate $dH_z/dt$ over the $k = 0$ resonance transition and measured the variation of magnetization using a micro-SQUID. For the other transitions, we used the minor loop method [21] (Fig. 1b). The fraction of molecules that reversed their spin was deduced from the step height, giving the LZ tunnel probability $P_k$ between two quantum states $m$ and $m'$. We deduced the corresponding tunnel splitting $\Delta_k$ using the LZ equation:

$$P_k = 1 - \exp \left[ -\frac{\pi \Delta_k^2}{2\hbar\mu_B|m - m'|\mu_0 dH_z/dt} \right]$$  (3)

Its validity can be tested by plotting $\Delta_k$ as a function of $dH_z/dt$ [23, 24]. We found that the LZ method is only applicable in the region of high sweep rates where $\Delta_k$ is independent of the field sweep rate. For the $k = 0$ resonance, this region is achieved for about $\mu_0 dH_z/dt > 0.1$ T/s. The deviations from the LZ equation at lower sweep rates have been studied in detail [24, 22] and are mainly due to reshuffling of internal fields [26]. Note that $\Delta_k$ obtained at lower sweep rates always underestimates the real $\Delta_k$; it can therefore be used only as a lower-limit estimation [14].

Fig. 3 shows $\Delta_k$ as a function of a transverse field $H_{tr}$, applied approximately along the hard axis of magnetization (x axis) and measured at $\mu_0 dH_z/dt = 0.56$ T/s. The observed oscillations can be explained by quantum phase interference of two tunnel paths [2] and has been observed in other SMMs [6, 13, 21, 14]. We used the period of oscillation to determine the transverse anisotropy parameter $E = 0.19$ K (Eq. 1). At $\mu_0 dH_z/dt = 0.56$ T/s, the LZ method is applicable only for $k = 0$ and approximately for $k = 1S$. However, for $k = 1A$ the sweep rate was too slow to apply the LZ method and we therefore plot only the tunnel probability in Fig. 3c.

Fig. 3d and 3e shows the tunnel probabilities for excited state tunnel transitions $k = 1E$ and 2E. Here, phonons first excite the spin from the ground state $|S, M_S > = |7, -7 >$ to the first or second excited spin states $|7, -6 >$ or $|6, -6 >$. Then, during the LZ field sweep, the spin tunnels to $|6, 6 >$ or $|7, 5 >$, respectively. Although this method can yield the activation energies and level lifetimes [24], the tunnel splittings are difficult to deduce. Nevertheless, the tunnel probabilities $P_k$ can be found and studied as a function of transverse field (Fig. 3d-e), showing clearly oscillations of $P_k$.

In multi-spin systems, transitions between different multiplets can be allowed by DM interactions, that is, the observation of tunneling at $k = 1E$, 2E, and 1A establishes the presence of a DM interaction in Mn$_{12}$unda wheels. A very interesting observation is that the oscillations of the tunnel probabilities are not symmetrical with respect to the sign of the transverse field ($P_k(H_{tr}) \neq P_k(-H_{tr})$). This is in clear contrast to transitions between states of the same multiplet ($k = 0$ and 1S, see Fig. 3a-b). Numerical diagonalization of the total spin Hamiltonian $H$ shows that the phase of the oscillation depends strongly on the orientation of the DM vector $\vec{D}_{1,2}$ (Eq. 2). Expressing $\vec{D}_{1,2}$ in terms of the modulus $|\vec{D}_{1,2}|$ and the usual polar angles $\theta_{DM}$ and $\varphi_{DM}$ defined with respect to the $z$ axis, we found that (i) for small values of $|\vec{D}_{1,2}|$, $\Delta_k$ does not depend on DM interaction for a transition within a spin multiplet; (ii) $\Delta_k$ depends strongly on $|\vec{D}_{1,2}|$ and $\theta_{DM}$ for a transition between spin multiplets, whereas it hardly depends on $\varphi_{DM}$. $\Delta_k$ is nearly proportional to $|\vec{D}_{1,2}|$ and the period of oscillation is close to those for transitions within a spin multiplet.

Figs. 4 and 5 show a few examples of $\Delta_k$ calculated with the Hamiltonian parameters given above, $|\vec{D}_{1,2}| = 0.03$ K, and several $\theta_{DM}$ values. We find the best agreement for $\theta_{DM} \approx 10^\circ$.

We would like to point out two deviations between the measurements and the dimer model, which we believe are due to the approximate nature of the latter.
First, the experimental values of $\Delta_k$ for $k = 0$ and 1S are about one order of magnitude smaller than the calculated ones. This discrepancy, also observed for a similar molecule [13, 14], can be reduced by introducing $\mathcal{O}(4)$ terms but it seems impossible to reproduce simultaneously the periods of oscillation and the values of $\Delta_k$. Second, the tunnel rates for $k = 1E$, 2E, and 1A can be adjusted with the values of $|D_{1,2}|$ and the phase of oscillation with $\theta_{\text{DM}}$. However, we did not manage to find a $\theta_{\text{DM}}$ value that fits simultaneously the phases of all three transitions. These deviations should motivate more theoretical work on the subject, as well as extensions to more sophisticated models for the Mn$_{12}$ wheel involving two sets of six independent Mn spins.

In conclusion, we have shown for the first time how the DM interactions can affect the tunneling transitions and quantum phase interference of a SMM. Of particular novelty and importance is the phase-shift observed in the tunnel probabilities of some transitions as a function of the DM vector orientation. Such observations are of importance to potential applications of SMMs that hope to take advantage of the tunneling processes that such molecules can undergo.

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