Mechanisms of Spin-Mixing Instabilities in Antiferromagnetic Molecular Wheels

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The microscopic theory of field-induced spin-mixing instabilities in antiferromagnetic molecular wheels CsFe_8 is proposed. The basic features of magnetic torque measurements [O. Waldmann *et al.*, Phys. Rev. Lett. **96**, 027206 (2006)] are well explained by the interplay of three basic ingredients: the spin-mixing vibronic interaction with field-dependent vibronic constants, cooperative elastic interactions, and spin-mixing interactions independent from vibrations. The main contribution to spin mixing comes from second-order zero-field splitting mechanisms. At variance with previous interpretations, we find that the observed anomalies are not associated with a phase transition.

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Antiferromagnetic (AFM) molecular wheels have recently been the subject of intense research because of their ability to display new mesoscopic quantum phenomena, including the possibility of their use in quantum computation [1]. In these systems the lowest spin states are closely spaced so that a sufficiently strong magnetic field can induce level crossings (LC). Close to LC the levels are quasidegenerate and molecular properties become sensitive to weak interactions, which thereby can be experimentally probed in this regime. Among the experimental techniques, torque magnetometry has proved very successful in probing novel phenomena in magnetic molecules at LC [2]. In particular, an experimental study [3] of the magnetic torque (τ) dependence on applied magnetic field (B) for a single crystal of the AFM wheel $\{\text{CsFe}_8[\text{N}(\text{CH}_2\text{CH}_2\text{O})_3]_8\}\text{Cl}$ [4] has been recently reported, showing characteristic anomalies below a critical temperature $T_c \approx 0.7$ K. For B almost perpendicular to the wheel uniaxis z ($\phi \approx 90^\circ$), the authors observed quasilinear step-like behavior of $\tau(B)$ in proximity of singlet-triplet LC between the ground $S = 0$ and the first excited $S = 1, M = -1$ levels, for $B = B_0$ (Fig. 1). They interpreted this as a signature of a field-induced magnetoelastic instability, caused by the vibronic mixing of these levels. The region of existence of this instability, also supported by recent NMR results [5], was interpreted in terms of a phase diagram [3]. It consists of a dome-shaped curve elongated at T_c^{max} by a cusplike feature (jump of $\partial T/\partial B$ at B_0 ; see Fig. 2, curve c).

A description of the observed spin-mixing [6] instabilities in CsFe_8 has been given in [3,7] within a single-molecule two-level model. The vibronic origin of the spin mixing was correctly addressed, but the model itself does not give a finite critical temperature because cooperative interactions have not been included. Also, a microscopic theory of spin-mixing interactions is lacking. Given the novelty of the discussed phenomena and their relevance for the interplay of quantum nanosystems with their environment, the insight into the underlying mechanisms will be of broad interest. In this Letter we present a microscopic

theory of spin-mixing instabilities in AFM wheels, describing the key experimental facts and elucidating the basic mechanisms responsible for spin mixing.

We describe the molecular spectrum in terms of the lowest exchange multiplets split to first order after zero-field splitting (ZFS), $H_{\text{ZFS}} = D \sum_{k=1}^8 s_{k,z}^2$. In vicinity of LC the lowest intersecting Zeeman components are practically of the $|S, -S\rangle$ and $|S+1, -S-1\rangle$ type, with spin projections defined with respect to the quantization axis along the applied field (Fig. 1). The basic interactions involving the two lowest levels on the wheels are

$$H = \sum_n H^{(n)} + \sum_{\langle nm \rangle} V Q_n Q_m,$$

$$H^{(n)} = -\frac{\hbar^2}{2M} \frac{\partial^2}{\partial Q_n^2} + \frac{1}{2} K Q_n^2 + W Q_n \sigma_y^{(n)} + \mu_B (B_0 - B) \times [(2S+1)\sigma_0^{(n)} + \sigma_z^{(n)}], \quad (1)$$

where n, m number the CsFe_8 molecules, W is the vibronic constant describing the mixing of $|S, -S\rangle$ and $|S+1, -S-1\rangle$ levels.

FIG. 1 (color online). Calculated energy spectrum of CsFe_8 as function of field, for $\phi = 90^\circ$ and: $J = -18 \text{ cm}^{-1}$, $D = -0.38 \text{ cm}^{-1}$ [3] (J has been fitted to reproduce the observed B_0). Vertical dashed lines delineate the region of spin-mixing instability and the arrows specify the dominant W_{-2} vibronic mixing mechanism (3).

FIG. 2 (color online). The field-temperature diagram delineating the region of quasilinear steplike behavior of the magnetic torque in CsFe₈ close to the singlet-triplet LC, for $\phi = 93.6^\circ$ (as in experiment [3]). The diagrams were calculated with (a) cooperative magnetoelastic contribution only, and adding the (b) real and (c) imaginary permanent coupling.

$-S - 1\rangle$ states on sites by the active nuclear coordinates Q_n (intramolecular vibrational modes which lower the symmetry of corresponding molecules [8]), and $\sigma_i^{(n)}$ are Pauli matrices acting in the space of the two states on site n . Without loss of generality, a pure imaginary vibronic coupling has been chosen here. The intermolecular elastic interaction is described by a single force constant V , given the high symmetry of the environment of each CsFe₈ site [4,9]. Having in mind that the Jahn-Teller stabilization energy on sites and the considered temperature domain are both much smaller than the vibrational quantum $\hbar\omega$, $\omega = \sqrt{K/M}$, we can average Eq. (1) on the lowest vibrational states on sites. The resulting Hamiltonian was used for the mean-field treatment of the structural ordered phase [8] characterized by the order parameter $\langle Q_n \rangle$, the average

distortions on the wheels along the Q_n coordinates. Because all CsFe₈ molecules are equivalent in the crystal, they are characterized by the same equilibrium distortion in the ordered phase, $\langle Q_n \rangle \equiv \langle Q \rangle$. Since the vibronic coupling on sites is the driving force for the distortions, the average value of the $S/S + 1$ mixing on sites, characterized by the average off diagonal element of the density matrix $\langle S, S + 1 \rangle$ [10], is $\sim \langle Q \rangle$. Thus, the region of spin-mixing instability is bounded by the region of structural phase transition $\langle Q \rangle \rightarrow 0$.

The calculated phase diagram for the singlet-triplet mixing is shown in Fig. 2, curve *a*. It is important to stress that if cooperative effects are neglected ($V = 0$), no phase diagram is obtained; i.e., $\langle Q \rangle = 0$ for all $T \neq 0$. The critical parameters of the calculated diagram are obtained as follows:

$$\frac{\tilde{\Delta}_{\max}}{2} = k_B T_c^{\max} = \mu_B (B_c^{\max} - B_0) = \frac{2z|V|}{K - z|V|} E_{JT}, \quad (2)$$

where $\tilde{\Delta}_{\max}$ is the energy gap at LC and $T = 0$ K, $E_{JT} = W^2/2K$ is the Jahn-Teller stabilization energy of isolated CsFe₈ molecules at the degeneracy point ($B = B_0$), and $z = 8$ is the number of nearest neighbors. Equation (2) gives a fixed ratio between critical parameters, which compares well with experiment. However, the absolute values of these parameters are reproduced for a wide range of K , V , and W . For instance, taking $\hbar\omega = 100$ cm⁻¹ and $M = 14$ as suggested in Ref. [3] gives $K = 484$ meV Å⁻², which for $V = 57$ meV Å⁻² gives $W = 1.5$ meV Å⁻¹. With these values we obtain $T_c^{\max} \approx 0.9$ K and $\Delta B_c^{\max} \approx 3$ T, in good agreement with the measured critical values, leading to an energy gap $\tilde{\Delta}_{\max} \approx 1.8$ K, which compares very well with the gap measured for this molecule via NMR experiments ($\tilde{\Delta}_{\max} \approx 2$ K) [5]. The derivative $\partial\tau/\partial B$ displays a region of linear dependence on B delimited by two vertical walls at the position of critical fields, at all $T < T_c^{\max}$. According to Eq. (2), this linear dependence can arise only if *both* cooperative effects ($V \neq 0$) and vibronic coupling on site ($W \neq 0$) are considered.

Since within this basic approximation no cusplike feature can be reproduced, we update the model by including a vibration-independent (permanent) $S/S + 1$ coupling term $W_0 \sin\phi$ in $H^{(n)}$, where ϕ is the angle between B and the wheel uniaxis. The presence of permanent spin-mixing interaction was supposed to be responsible for avoided crossings observed in other wheels, like NaFe₆ [11], but no definite conclusion of their importance in CsFe₈ was drawn from torque measurements [3]. The permanent coupling can in general be partitioned into real and imaginary contributions, so that the additional term in Hamiltonian (1) reads $\text{Re}(W_0)\sigma_x + \text{Im}(W_0)\sigma_y$. If only the real part is taken into account, we obtain an overall shrinking of the phase diagram, but no cusplike feature arises (Fig. 2, curve *b*). Also, the presence of such a term decouples the $S/S + 1$ mixing from the structural phase transition: solutions $\langle Q \rangle \neq 0$ are obtained only below some critical tempera-

FIG. 3. Calculated torque for $\phi = 93.6^\circ$ as function of applied field for the field-independent (a) and the field-dependent (c) vibronic constants at $T = 0.25$ K. Plot (b) and (d) are the first derivatives of functions (a) and (c), respectively.

ture, whereas $\langle S, S+1 \rangle$ will be nonzero for any temperature and field. Also, $\partial\tau/\partial B$ shows the same qualitative behavior as in the previous case.

On the other hand, the inclusion of $\text{Im}(W_0)$ in (1) leads to $\langle Q \rangle \neq 0$ and $\langle S, S+1 \rangle \neq 0$ for any temperature and field, which means that no phase transition occurs anymore. Accordingly, instead of looking for the phase transition criterion, we calculate τ and $\partial\tau/\partial B$ and, following the experimental methodology [3], define two critical fields for each temperature as end points of the flat portion of $\partial\tau/\partial B$ [Fig. 3(b)]. Curve c in Fig. 2 shows the B - T diagram thus obtained, which now outlines the region of quasilinear steplike behavior of the torque function [Fig. 3(a)] rather than a real thermodynamic phase. The cusplike feature on the diagram is clearly present now, the qualitative agreement with the shape of the experimental diagram being achieved already for a small value of $\text{Im}(W_0) = 0.009 \text{ cm}^{-1}$. As seen in Fig. 3(b), in this case the region of quasilinear regime of $\partial\tau/\partial B$ is not delimited by vertical walls anymore, which is also in agreement with experiment [see Fig. 2(a) of Ref. [3]]. Hence, at variance with the interpretation proposed in [3], we find that the cusp feature appearing in the experimental B - T diagram demonstrates that no phase transition is associated to the torque anomalies in the CsFe_8 AFM wheel, despite the fundamental role played by cooperative effects in the underlying magnetoelectric instabilities. Notice that $\partial\tau/\partial B$ in Fig. 3(b) displays a *negative* constant slope within the critical field values, whereas the experimental plots reported in [3] show a slightly *positive* slope. We could only invert the slope of the calculated torque by introducing magnetic field dependence of the vibronic constant, $W(B) = W(B_0) + W_1(B_0 - B)$. For the value of $W_1 = -0.1 \text{ cm}^{-1} \text{ T}^{-1}$ we were able to invert the slope of the calculated $\partial\tau/\partial B$ function [Fig. 3(d)] to match the experimental behavior. Hence, the proposed thermodynamic model highlights three fundamental facts that need to be included in any reliable theory of the observed torque anomalies: cooperative effects, the existence of both vibronic and vibration-independent singlet-triplet coupling, and the magnetic field dependence of the effective singlet-triplet vibronic coupling constant.

With this in mind, let us turn now to the microscopic mechanisms of $S/S+1$ mixing and consider the Dzyaloshinsky-Moriya (DM) antisymmetric exchange first. We choose here a coordinate system in which B lies in the zy plane, resulting in real DM spin-mixing coupling constants. The condition for them to be nonzero is the alternation of the neighbor DM vector components along z , $d_{k,k+1;z}$ [11], a possibility supported by the C_4 symmetry of CsFe_8 [4]. Hence, the DM interaction provides a viable vibration-independent singlet-triplet coupling mechanism in CsFe_8 . For $\phi \approx \pi/2$ one obtains $|W_0| \approx 1.07\Delta d$. Using the estimation $|\Delta d| \approx 0.01J$ for NaFe_6 from Ref. [11], for the current value of J we obtain $|W_0| \approx 0.2 \text{ cm}^{-1}$, which compares well with the value assumed in the simulations reported in Fig. 2.

However, the DM mechanism is not expected to be relevant for the vibronic spin mixing. An inspection of the structure of CsFe_8 [4] shows that the static variations in the bridging geometries of nearest-neighbor pairs are already larger (they are not related by any symmetry operation) than any expectation for $\langle Q \rangle$, so that $W\langle Q \rangle$ will not exceed W_0 . Note that according to our simulations the former should be 1 order of magnitude larger. Furthermore, there are no reasons to suppose that the DM interaction can result in field-dependent vibronic constants in low orders of perturbation theory.

Consider now the effect of ZFS interaction on the iron sites (in the chosen coordinate system it will give rise to imaginary coupling constants). At first let us suppose the local anisotropy axes are parallel to z . Simple angular momentum addition arguments suffice to rule out ZFS as a viable mechanism to couple directly a singlet and a triplet, neither vibronically nor permanently, although it can lead to direct coupling at higher LC, between S and $S+1$ states with $S > 0$. However, it is still possible to conceive ZFS-based indirect coupling pathways between singlet and triplet, mediated by excited spin multiplets. H_{ZFS} ($\equiv H$) can in fact couple the singlet ground state with the quintet excited state; the quintet in turn can be coupled to the triplet first excited state via H . Thus, four different singlet-triplet coupling mechanisms involving the quintet multiplet can be identified as $W_{M_S} = (1/2)i(H)_{0M_S}(H)_{M_S,-1}[1/(E_0 - E_{M_S}) + 1/(E_{-1} - E_{M_S})]$, corresponding to $M_S = 0, -2, 1$ and -1 , and evidently displaying magnetic field dependence via the energy denominators. In proximity of LC we obtain

$$W_{M_S} \approx i \frac{(H)_{0M_S}(H)_{M_S,-1}}{\Delta E_{0M_S}^0} \left[1 - \frac{(2M_S - 1)}{\Delta E_{0M_S}^0} \mu_B(B - B_0) \right], \quad (3)$$

where $\Delta E_{0M_S}^0$ corresponds to the exchange energy gaps corrected to first order in ZFS (Fig. 1).

It turns out that if the local anisotropy axes are exactly parallel to z , for nearly perpendicular orientation of B the ZFS coupling becomes extremely small, since no spin polarization can be induced along these axes [12]. We consider therefore a simple and yet realistic modification of our model, in which the local anisotropy axes are tilted by angles $(-1)^k\theta$ in corresponding tangential planes. In this case, within the dimer approximation [13], the matrix elements in Eq. (3) are given by $(H)_{0M_S}(H)_{M_S,-1} = g(\theta)f_{M_S}(\phi)\Delta_0\lambda_0$, with $\Delta_0 = (2s-1)^2(Ns+3)[80(Ns-1)]^{-1}\sqrt{3Ns(Ns+2)/6}$; g and f are angular factors depending on the specific mechanism, and λ_0 is defined below. For a wheel in which all ZFS constants on sites are equal, $D_k = D$, we obtain $W_{M_S} = 0$. Accordingly, ZFS mediated singlet-triplet coupling can only occur (i) if the actual C_4 symmetry of the molecule entails a static dimerization distortion implying $D_k = D + (-1)^k\Delta D$ and $\lambda_0 = D\Delta D$, and (ii) if we invoke coupling to some normal mode

of vibration, which for the particular choice of local anisotropy axis orientation made here can be shown to be of the general form $Q = 1/2 \sum_{k=1}^8 \exp(i2\pi nk/N) q_\theta^{(k)}$, $n = \pm 1, \pm 2$, and $N/2$, where $q_\theta^{(k)}$ is a local, e.g., tetragonal distortion on site. This implies $\lambda_0 = D(\partial D/\partial Q)$. Note that if local anisotropy axes are parallel to z , only the dimerization mode ($n = N/2$) can be active.

As we have seen, in the present setting ZFS (DM) gives rise to pure imaginary (real) contributions both to vibronic and to permanent singlet-triplet coupling. Accordingly, if ZFS is the mechanism responsible for vibronic coupling, it must also contribute to permanent coupling, and the same holds true for the DM mechanism. However, the plots of $\partial\tau/\partial B$ (Fig. 3) indicate that vibronic coupling must be field-dependent, a requirement which only the ZFS mechanism can fulfill. From (3) we obtain the estimation $W_1/W \approx -0.12$ to be compared with $W_1/W \approx -0.06$ derived from our simulations. It is thus reasonable to claim that ZFS is the dominant mechanism ruling vibronic coupling in CsFe_8 .

For $\phi \approx \pi/2$ only mechanisms involving the $M_S = 0$ and $M_S = -2$ components of the quintet will be active. In particular, at LC and for $\theta = 80^\circ$, we obtain from (3) $W = 0.26\lambda_0$. An estimation of λ_0 can be obtained as follows. In Ref. [14] the variation of ZFS in complexes of Fe^{3+} in octahedral environment in function of ligand-field parameters was calculated. Taking the typical R^{-5} dependence of ligand-field parameters on the iron-oxygen distance R [15], we obtain for a tetragonal distortion q_θ [8] the following estimation: $\partial D_k/\partial q_\theta^{(k)} \approx 12 \text{ cm}^{-1} \text{ \AA}^{-1}$. Taking e.g. $Q = 1/2 \sum_{k=1}^8 \sin(4\pi k/N) q_\theta^{(k)}$, we obtain $\partial D/\partial Q = 6 \text{ cm}^{-1} \text{ \AA}^{-1}$. Taking into account the tilting of anisotropy axes on sites, one should divide the fitted value of D [3] by $(3\cos^2\theta - 1)/2$, which gives $D = 0.86 \text{ cm}^{-1}$. From these estimates we derive $\lambda_0 \approx 5.16 \text{ cm}^{-2} \text{ \AA}^{-1}$ and $W \approx 0.17 \text{ meV \AA}^{-1}$. The estimated vibronic coupling constant is about 9 times smaller than the value required by the simulations in Fig. 2. We note however that in contrast to DM mechanism, where only the dimerizing mode is active, several modes are active in the ZFS mechanism (5 within the present approximations) and will always add up to an enhanced vibronic coupling.

In the inelastic neutron scattering spectrum of CsFe_8 [1] an inhomogeneous broadening of $\approx 0.1 \text{ meV}$ of the lowest singlet-triplet transition was associated with the distribution of J values among the molecules, which would result in a distribution of B_0 of $\sim 0.5 \text{ T}$. This would broaden the B - T diagram in Fig. 2(c) along the field axis, making the cusplike feature less sharp. On the other hand, this broadening alone cannot be the reason for the discussed spin-mixing anomalies, since it does not have a critical behavior with temperature and field [1].

In conclusion, we proposed here a microscopic theory of spin-mixing instabilities, fully accounting for the main features of torque experiments in the AFM wheel CsFe_8 .

It indicates three basic interactions: (i) spin-mixing vibronic coupling with field-dependent vibronic constants, (ii) intermolecular elastic interaction, and (iii) vibration-independent spin-mixing interactions. The first one gives the main contribution to spin-mixing instabilities and mainly originates from second-order ZFS mechanisms. The direct consequence of the presence of a permanent spin-mixing term is that the observed magnetoelastic instabilities are not related to a phase transition. We also find that the deviation of the local anisotropy axes from the wheel uniaxis plays a crucial role in the spin-mixing mechanisms. These findings will serve as a basis for general understanding of magnetoelastic instability phenomena, a rapidly growing field of molecular magnetism.

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