Resonant photon absorption in the low spin molecule $V_{15}$

W. Wernsdorfer$^1$, A. Müller$^2$, D. Mailly$^3$ and B. Barbara$^1$

1 Laboratoire Louis Néel, associé à l’UJF, CNRS, BP 166, 38042 Grenoble Cedex 9, France
2 Facultät für Chemie, Universität Bielefeld, D-33501 Bielefeld, Germany
3 Laboratoire de Photonique et de Nanostructures, CNRS, 91460 Marcoussis, France

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Abstract. – Resonant photon absorption in the GHz range was observed via low temperature micro-SQUID magnetization measurements of the spin ground state $S = 1/2$ of the molecular complex $V_{15}$. A simple single-molecule interpretation is proposed. The line-width essentially results from intra-molecular hyperfine interaction. The results point out that observing Rabi oscillations in molecular nanomagnets requires well isolated low spin systems and high radiation power.

It is widely admitted that single-molecule magnets (SMMs) have a great potential for quantum computation [1], in particular because they are extremely small and almost identical, allowing to obtain, in a single measurement, statistical averages of a larger number of qubits. Each spin being carried by a big molecule of $\sim 1$ nm$^3$, these magnets are naturally diluted (with $10^{19} - 10^{20}$ molecules/cm$^3$), which is highly desirable to minimize dipolar interactions and thus preserve quantum coherence. Despite such natural dilutions, dipolar interactions remain rather important (0.1 – 0.5 K) in large spin SMMs such as Mn$_{12}$ or Fe$_8$ ($S = 10$) [2] displaying resonant quantum tunneling of magnetization [3, 4, 5, 6, 7, 8]. Reductions of dipolar interactions can easily be achieved by decreasing the value of the spin $S$. At a given concentration, the dipolar energy scales with the square of $S$. Thus, decreasing the spin from $S = 10$ to 1/2 leads to a reduction of dipolar energy by a factor of $(1/20)^2 \sim 10^{-3}$ [9]. At first glance, low spin systems seem more suitable for quantum computation than large spin systems.

In this paper we report the first study of the micro-SQUID response of a low-spin molecular system, $V_{15}$, to electromagnetic radiation. The advantages of our micro-SQUID technique in respect to pulsed electron paramagnetic resonance (EPR) techniques consist in the possibility to perform time-resolved experiments (below 1 ns) [10] on submicrometer sizes samples (about 1000 spins) [11] at low temperature (below 100 mK). Our first results on $V_{15}$ open the way for time-resolved observations of quantum superposition of spin-up and spin-down states in
SMMs. Other results obtained in similar systems but with large spins concern for example EPR measurements [12], resonant photon-assisted tunneling in a Fe₈ SMM [13] and non-resonant microwave absorption in a Mn₁₂ SMM [14].

The molecular complex V₁₅ forms a lattice with space group R₃c containing two molecules per unit cell [15, 16]. The third order symmetry axis of the unit cell is also the symmetry axis of the two V₁₅ clusters. In each molecule the fifteen V⁴⁺ ions (S = 1/2), are placed on a quasi-spherical layered structure formed of a triangle sandwiched between two non-planar hexagons. Each hexagon contains three pairs of strongly coupled spins and each spin at a corner of the inner triangle is coupled to two of those pairs (one belonging to the upper hexagon and one belonging to the lower hexagon) [16]. In principle, this molecule should be discussed in terms of the entanglement of the 15 spins 1/2, with a Hilbert space dimension of 2₁⁵. However, considerable simplifications occur at low temperature where the molecule can be described by a S = 1/2 spin ground state and a S = 3/2 excited state. The energy separation of both spin states of \( \approx 3.8K \) was accurately determined by susceptibility and high-field magnetization measurements [17] and by inelastic neutron scattering experiments [18]. Magnetization measurements performed down to 30 mK showed that the S = 1/2 spin ground state is split in zero field by \( \approx 80 \text{ mK} \) [9, 19]. The origin of this splitting for a half-integer spin is interpreted by the interplay between intra-molecular, hyperfine and Dzyaloshinskii-Moriya interactions [9, 19]. Inter-molecular interactions (dipolar or residual exchange interactions) can be evaluated from the low temperature Curie-Weiss law associated with the spin ground state, giving the Curie constant \( C = 0.686 \mu_B K/T \) and the paramagnetic temperature \( \theta_p \approx 12 \text{ mK} \), corresponding to a mean internal field of \( \approx 12 \text{ mT} \). This value, one order of magnitude larger than calculated dipolar interactions is nevertheless much smaller than usual super-exchange interactions; it is attributed to non-trivial exchange paths.

The measurements were made at a cryostat temperature of 40 mK using a 50 \( \mu \text{m} \) sized single crystal of V₁₅. The magnetic probe was a micro-SQUID array [20] equipped with three coils allowing to apply a field in any direction and with sweep rates up to 10 T/s.

Fig. 1. – Equilibrium magnetization curves measured with or without irradiation. The cryostat temperature was 40 mK. The electromagnetic radiation was pulsed with a period of 10 ms and a pulse length going from 0 (no radiation) to 3 ms.
Magnetization versus applied field curves \( M(B_0) \) were measured in the quasi-static regime with a field sweep rate slow enough (1 mT/s) to keep the system at equilibrium. The phonon-bottleneck regime has a characteristic spin-phonon relaxation time to the cryostat \( \tau_s \) of few seconds [9]. Ac radiation pulses of 0.1 to 0.3 ms were applied every 10 ms. Due to the large value of \( \tau_s \) the relaxation in the intervals between pulses is negligible. As a consequence the effects of each pulse are additive leading to an equilibrium magnetization after a time being larger than \( \tau_s \).

\( M(B_0) \) curves for several pulse lengths, measured at \( \nu = 14 \text{ GHz} \), are reported in Fig. 1. Two symmetrical dips are clearly visible at \( B_\nu = \pm 0.491 \text{ T} \). They result from resonant absorptions of photons associated with \( m_s = 1/2 \) to \( -1/2 \) spin transitions, as indicated in the inset of Fig. 2. Typical measurements at other frequencies are presented in Fig. 2. Apart of the resonant absorptions, a small absorption is also seen at all applied fields. In order to understand better the origin of this absorption, Fig. 3 presents the same data as in Fig. 1 but the magnetization \( M \) is converted into a spin temperature \( T_s \) using the equation [22]:

\[
M(T_s)/M_s = \tanh(g\mu_B S B_0/k_B T_s)
\]

with \( S = 1/2 \) and \( g = 2.02 \) (see below). Fig. 3 shows clearly the increase of the spin temperature \( T_s \) because of resonant absorptions and a nearly field independent increase of \( T_s \).

Before going into a deeper discussion, we show in Fig. 4 the experimental confirmation of the linear evolution of the resonant field with frequency \( \nu = \gamma B_\nu \) predicted by the inset of Fig. 2. The measured slope \( d\nu/dB_\nu = \gamma \approx 28.3 \text{ GHz/T} \) yields a gyromagnetic ratio \( g = 2h\gamma/\mu_B \approx 2.02 \), a value close to the one obtained by Ajiro et al. [23] in single-crystal EPR measurements at 2.4 K \( (g \approx 1.98) \).

In order to analyze the resonance lines we will consider the well known Rabi model for a
spin 1/2, which stipulates that the probability $P$ of finding the system in the state $m_s = -1/2$ at time $t$, if it was in the state $m_s = 1/2$ at $t = 0$, is given by [24, 22, 25]:

$$P = \frac{(\gamma B_{ac})^2}{(\gamma B - \nu)^2 + (\gamma B_{ac})^2} \sin^2(\omega_{\text{Rabi}} t)$$

(2)

where $\omega_{\text{Rabi}} = 1/2 \sqrt{(\gamma B - \nu)^2 + (\gamma B_{ac})^2}$, $B$ is total field seen by the spin, and $B_{ac}$ the
amplitude of the electromagnetic field. In the limit of long times, Eq. 2 becomes proportional to the time, \( P = \pi(\gamma B_{ac}/2)^2t\delta(\gamma B - \nu) \), and the transition rate \( \Gamma = dP/dt = \pi(\gamma B_{ac}/2)^2\delta(\gamma B - \nu) \) turns out to be a constant. Integrating \( \Gamma \) over a distribution of local fields \( F(B_L) \) and considering that \( B = B_0 + B_L \), where \( B_0 \) is the applied field, we obtain the field-dependent spin-photon transition rate:

\[
\Gamma_L = \frac{\pi}{4} \gamma B_{ac}^2 F(B_L = B - B_0)
\]

This expression shows that the field-dependence of the transition rate is given by the distribution function of local fields. Below, we analyze the results in terms of two limiting distributions, a Gaussian distribution and a Lorentzian one.

The measured magnetization dips corresponding to resonant power absorption (Figs. 1-3), result from the balance between the induced transition rate \( \Gamma = \Gamma_L + \Gamma_0 \) and \( \tau_s \). \( \Gamma_0 \) is taking into account small heating effect of the environment. \( \Gamma_\tau_s \) can be determined using the measured equilibrium magnetization with and without irradiation, \( M_{RF}(B_0) \) and \( M_0(B_0) \) respectively, and is given by [22]:

\[
\Gamma \tau_s = \frac{1}{2} \frac{M_{RF}(B_0)}{M_0(B_0)} - 1
\]

Fig. 5 shows \( \Gamma_L \tau_s \) obtained from the data in Figs. 1 and 2. Taking the example of the resonance at \( \nu = 14 \) GHz, \( B_0 = 0.491 \) T, we yield \( \Gamma_L \tau_s \approx 0.2 \) (Fig. 5). As mentioned above, \( \tau_s \approx 1 \) s is rather large due to the phonon bottleneck effect. This allows to obtain sufficiently large values of \( \Gamma_L \tau_s \) to observe significant radiation absorption even if the rate \( \Gamma_L \approx 0.2 \) s\(^{-1}\) is relatively small. Using expression (3) we yield \( B_{ac} \sim 1 \mu\)T. Similar values were obtained for all measured frequencies.
The resonant absorption lines of Fig. 5 were well fit with a Gaussian distribution:

\[ F(B_L) = \frac{1}{\sigma_L \sqrt{2\pi}} e^{-\frac{(B_0 - B_\nu)^2}{2\sigma_L^2}} \]

yielding \( \sigma_L \approx 35 \text{ mT} \) for frequencies between 2 and 20 GHz.

The Gaussian and Lorentzian distributions essentially differ when \( |B_0 - B_\nu| > \sigma_L \), that is the Gaussian distribution is more localized (non correlated fields) than the Lorentzian one (correlated fields). Our result suggests therefore that the line-broadening is due to fluctuations of non-correlated intra-molecular nuclear spins and not to correlated inter-molecular interactions.

This is confirmed by several features:

(i) \( \sigma_L \approx 35 \text{ mT} \) (Fig. 5) is much larger than the mean dipolar field seen by the molecules (< 1 mT);

(ii) \( \sigma_L \) is also larger than intermolecular interactions (12 mT);

(iii) \( \sigma_L \) is close to the hyperfine field of \( \text{V}_{15} \) (≈ 40 mT) [9, 17, 19]. This value is derived from the hyperfine field of 11.2 T/\( \mu_B \) obtained in different systems of \( \text{V}^{14} \) [26] and giving a field of about 20 mT for a single \( \text{V}^{14} \) spin;

(iv) finally, \( \sigma_L \) is very close to the level width (40 mK) obtained from magnetic relaxation experiments near the \( m_s = \pm 1/2 \) avoided level crossing. Its origin was mainly attributed to hyperfine and weak Dzyaloshinskii-Moriya interactions [9, 17, 19].

This hyperfine broadening of resonant absorption is consistent with theoretical investigations according which the main dephasing mechanism of magnetic molecules is connected with nuclear spins [27, 28, 29, 30, 31, 32].

The inset of Fig. 4 presents the field dependence of the quality factor \( G = B_\nu/\sigma_L \) that gives a lower bound of the precessional coherence of \( \text{V}_{15} \) molecule spins. A linear increase of \( G \) is observed reaching \( G = 20 \) at 0.7 T that is rather far from values of \( 10^4 \) needed for quantum computation.

Finally, we discuss the possibility of observing Rabi oscillations with the present set-up. Due to inhomogeneous broadening only a low bound of the coherence time can be estimated from the resonance lines: \( \tau_c^{-1} = \gamma \sigma_L \). The corresponding number of coherent flips of the spin system is given by \( N = \tau_c/\tau_{\text{Rabi}} = B_{ac}/(2\pi \sigma_L) \) (Rabi coherence). Using the values of \( B_{ac} \) and \( \sigma_L \) obtained from the fit of the resonance lines, we get \( \tau_c \approx 2 \text{ ns} \) (comparable to recent EPR measurements [33]) and \( N \approx 10^{-6} \), showing that there is no hope to see Rabi oscillations in the present conditions. In order to get \( N >> 1 \), it will be necessary to increase the radiation field \( B_{ac} \) by orders of magnitude. Note that \( \Gamma_{\text{L,Max}} \approx \gamma B_{ac}^2 / 4\sigma_L \) increases with electromagnetic power and decreases for broader distribution of local fields. An important consequence of intra-molecular inhomogeneous broadening is the possibility to significantly longer coherence times that can be evidenced using spin-echo techniques. This should lead to a transverse relaxation time \( \tau_2 >> \tau_c \) which will be necessary for quantum computation.

In conclusion, we presented a new technique for studying radiation absorption in the molecular system \( \text{V}_{15} \) constituting a first step towards the observation of Rabi oscillations in molecular magnets. The main results are the observation of relatively narrow resonant absorption lines that are dominated by hyperfine interaction. In order to observe Rabi oscillations in a magnetic system, an important requirement is a large ac field amplitude.

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