

Radio-frequency spectroscopy of the low-energy spectrum of the magnetic molecule $\text{Cr}_{12}\text{Cu}_2$

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We present tunnel diode oscillator (TDO) measurements of dynamic magnetic susceptibility, inelastic neutron-scattering (INS) measurements, and theoretical predictions based on quantum Monte Carlo (QMC) calculations for a magnetic molecule system, $\text{Cr}_{12}\text{Cu}_2$. The TDO measurements show not only ground-state level crossings (as can also be observed in low-temperature dc magnetization measurements) but also clear evidence of crossings between certain excited energy levels. These TDO results are in excellent agreement with our theoretical predictions for a Heisenberg Hamiltonian and are further confirmed by our INS measurements. Our present findings demonstrate that the TDO technique is a valuable magnetic spectroscopic tool for studying magnetic molecules, and that the QMC method is a valuable tool for predicting properties of computationally demanding systems such as $\text{Cr}_{12}\text{Cu}_2$.

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Crystal samples of magnetic molecules have the striking feature that they can be successfully analyzed in terms of the discrete magnetic energy spectrum of an individual molecule, originating from intramolecular exchange interactions between the magnetic ions.¹⁻⁴ This is due to the circumstance that the magnetic interactions between molecules are generally ignorable as compared to the intramolecular interactions, and thus they play no role except in a range of suitably low temperatures. Put differently, for investigating laboratory samples the task is reduced to that of developing a successful model of the individual magnetic molecule. The need to increase the number of spectroscopic and theoretical tools available to study magnetic molecules is thus a major priority. In some cases (e.g., proposals that molecular nanomagnets could be used in quantum information processing⁵⁻⁷) it is vital to have a detailed and accurate picture of the energy spectrum of the molecules and to know how the spectrum develops in a magnetic field. More generally, as the size and complexity of magnetic molecules that are synthesized continues to grow, traditional techniques such as susceptibility measurements no longer suffice to characterize the materials adequately. In an effort to address this need, we show that tunnel diode oscillator (TDO) measurements reveal not only changes in the ground state with magnetic field but also provide compelling evidence for transitions between excited states in the immediate vicinity of level crossings. We also demonstrate that the quantum Monte Carlo (QMC) method is a valuable tool for developing a successful theoretical model of a computationally demanding system.

Our results are obtained for the $\text{Cr}_{12}\text{Cu}_2$ (“hour-glass”) magnetic molecule⁸ which can serve as a valuable model system as we are able to provide several clear theoretical predictions which are directly compared with our TDO measurements. Specifically, our QMC calculations provide predictions for the low-temperature magnetization versus magnetic field, as well as certain excitation energies, and our

TDO measurements are in excellent agreement with these predictions. Furthermore, our inelastic neutron-scattering (INS) measurements provide an independent experimental validation of the excitation energies as obtained from the QMC calculations and the TDO spectroscopy.

The magnetic properties of $\text{Cr}_{12}\text{Cu}_2$ are determined by the interactions between 12 Cr^{3+} ions (spins $3/2$, $g_{\text{Cr}}=1.98$) and two Cu^{2+} ions (spins $1/2$, $g_{\text{Cu}}=2.1$), arranged as shown in Fig. 1, where g_{Cr} and g_{Cu} refer to the spectroscopic splitting factors. To achieve a theoretical description of this system, we have used an isotropic Heisenberg model with three exchange constants, which we treat as three adjustable param-

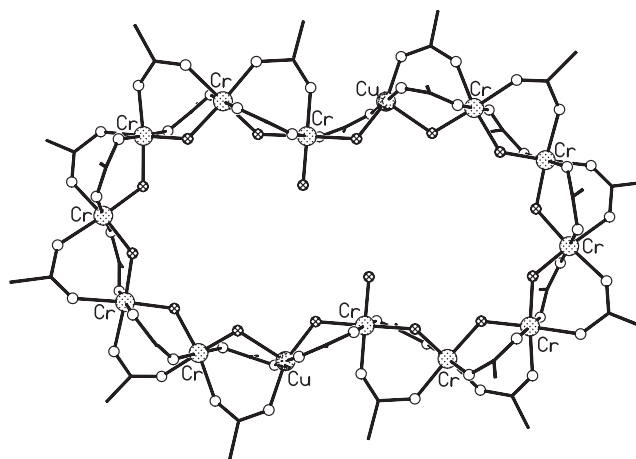


FIG. 1. Chemical structure of the $\text{Cr}_{12}\text{Cu}_2$ magnetic molecule. Cr^{3+} ions are shown as dotted circles and Cu^{2+} ions as heavily shaded circles. The compound has inversion symmetry and the metal centers within the molecule lie within a plane. The metal-metal edges are bridged by fluoride (crossed circles) and carboxylate ligands (oxygen open circles and carbon as lines). There are two ethyl-di-*iso*-propylammonium cations at the centers of each lobe of the hour glass which are not shown.

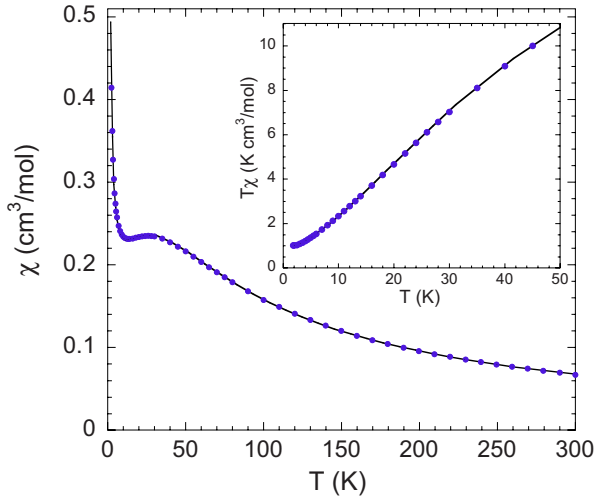


FIG. 2. (Color online) Low-field dc magnetic susceptibility, $\chi=M/H$, versus temperature for $H=0.1$ T showing both experiment (symbols) and theory (solid line). The values of the exchange constants are given in Ref. 9. Inset: the same data ($T < 50$ K), plotted as $T\chi$ versus T . The low-temperature limiting value, $T\chi \approx 1$ K cm³/mol, is consistent with an $S=1$ ground state.

eters whose values are determined by optimizing the fit to the measured weak-field magnetic susceptibility, $\chi(T)$. (One of the exchange constants, J_1 , describes the Cr-Cr interactions, and due to asymmetries of the ligands, the Cr-Cu interactions are distinct from the Cu-Cr interactions. These are described by exchange constants J_2 and J_3 .⁹) The Hilbert-space dimension of $\text{Cr}_{12}\text{Cu}_2$, $D \approx 6.7 \times 10^7$, is so large as to make matrix diagonalization of the Heisenberg Hamiltonian not feasible so we have instead carried out our calculations using the QMC algorithm that was introduced in Ref. 10. This procedure allows us to entirely avoid the computational challenges associated with large matrices, and it has recently been demonstrated to be a very useful tool for studying magnetic molecules.^{8,11-19} For the present system, the speed of the QMC method allowed us to survey the entire three-dimensional parameter space and to identify a unique set of parameters that provide an excellent fit to the measured $\chi(T)$ as shown in Fig. 2.

Having determined the values of the exchange constants, we used the QMC method to calculate the low-temperature differential susceptibility, dM/dH , versus magnetic field H . The model predicts that for $H < 8.15$ T the ground state of the system has total spin $S=1$, while in the field intervals (8.15, 11.9 T) and (11.9, 16.2 T), the ground state has total spin $S=2$ and 3, respectively. Using these values of the ground-state level-crossing fields,²⁰ the zero-field excitation energies of the lowest $S=2$ and $S=3$ multiplets are 0.94 and 2.32 meV (as measured relative to the $S=1$ zero-field ground state). We note that our QMC calculations also provide all other ground-state level-crossing fields²¹ up to the saturation field of 80.7 T, but only those crossings occurring with $H < 14$ T are of relevance to the present measurements.

The real part χ' of the radio-frequency susceptibility was measured by using a sensitive TDO technique. The design and capabilities of a TDO as applied to the study magnetic materials are discussed at length elsewhere.²² Briefly, an LC

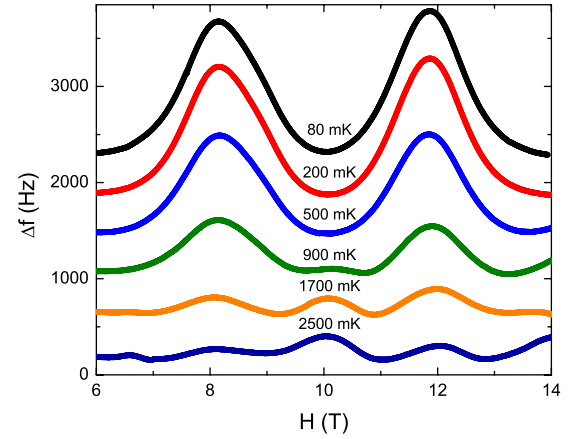


FIG. 3. (Color online) TDO frequency shift as function of magnetic field for different temperatures, from 80 mK to 2.5 K. Note the development of the intermediate peaks at elevated temperature.

tank circuit is driven by a tunnel diode properly biased to the region of the negative resistance of its IV characteristic. As a result, the circuit self-oscillates at the resonant frequency and the excitation magnetic field is very low (~ 20 mOe). A properly designed and stabilized circuit allows one to measure changes in susceptibility on the order of a few parts per billion. When a nonconducting sample is inserted into the coil, the resonant frequency changes by $\Delta f = -4\pi\chi'\Delta f_0$, where $\Delta f_0 = f_0 V_s / 2V_c$, f_0 is the frequency of an empty resonator, V_s is the sample volume, and V_c is the volume of the coil. The measurements were performed in a Kelvinox MX-400 dilution refrigerator. For each experimental run, the temperature was kept constant and an external field was slowly swept at a rate of 10 Oe/s. No hysteresis was observed between ascending and descending branches of $\Delta f(H)$ measurements.

By subtracting the smooth and reproducible background contribution of the empty resonator, the field dependence of χ' for the sample was obtained up to a calibration constant, Δf_0 , so the results presented are for the relative frequency shift, and the amplitude is not important for the present work. These data are shown in Fig. 3 for six different temperatures for magnetic fields up to 14 T. For the lowest three temperatures two peaks are observed. These three temperatures are sufficiently low that χ' reduces to dM/dH so the two peaks correspond to two steps in the magnetization. The field values at which the steps occur are $H=8.1$ and 11.9 T, in excellent agreement with the theoretical values (given above) of the first two ground-state level-crossing fields for our model of this system.

As the temperature is increased to 900 mK and above, additional peaks progressively become visible, as seen in Fig. 3. As discussed in the Appendix of Ref. 11, these additional peaks signify resonances in the temperature- and field-dependent dynamical susceptibilities that are inaccessible to dc measurements. Such resonances occur when the energy difference between two levels is of the order of $\hbar\omega$ (where $\omega = 2\pi f$ is the angular frequency of the TDO magnetic field) but only if there is significant thermal occupation of the pair of intersecting levels. (Below 900 mK the crossing of a pair of excited levels is of no consequence because there is neg-

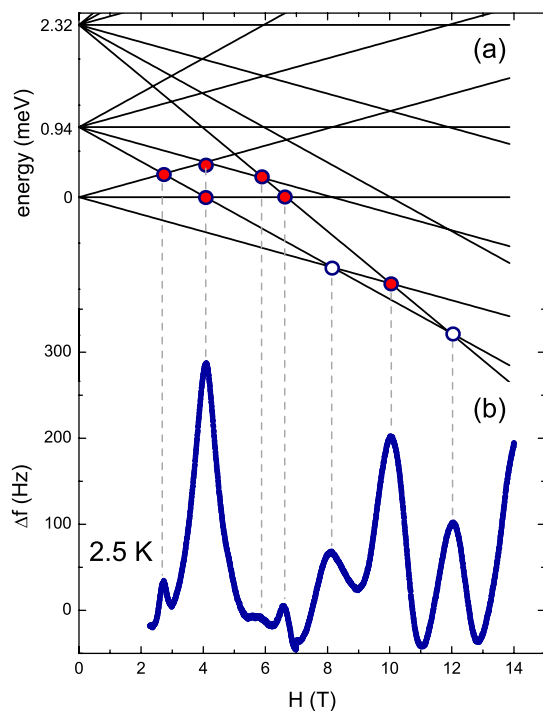


FIG. 4. (Color online) (a) Zeeman splitting of predicted energy levels. (b) TDO measurements versus magnetic field for 2.5 K (directly below the energy levels, with dashed lines to emphasize the agreement between peaks and crossings).

ligible thermal occupation of these excited levels so the two visible peaks in χ' are associated exclusively with ground-state level crossings.) Highlighted in Fig. 4(a) are those energy levels of the Heisenberg model which undergo level crossings within approximately $k_B T$ of the ground-state energy at that particular field. For 2.5 K there are five crossings involving excited levels with appreciable thermal occupation. These occur for fields of 2.7, 4.1, 5.95, 6.6, and 10 T. Note that these theoretical field values are in excellent agreement with the values of the measured resonance fields, shown in Fig. 4(b).

To provide independent confirmation of some of our results, INS measurements were performed on the FOCUS spectrometer²³ of the Swiss spallation neutron source SINQ, Paul Scherrer Institute, Villigen, Switzerland. Neutron spectra have been recorded in zero field with an incident neutron wavelength of 4.4 Å at 1.5 and 6 K. The spectra are vanadium normalized and empty canister corrected. The spectra summed over all scattering angles are shown in Fig. 5, where several peaks are clearly visible. Using the quantum number assignments for the various levels from our QMC calculation, we are able to identify the peaks that are labeled as I and II in Fig. 5 as corresponding to transitions from the $S=1$ ground state to the lowest $S=2$ state (INS peak at 0.96 meV) and from the lowest $S=2$ state to the lowest $S=3$ state (INS peak at 1.32 meV), respectively. The corresponding excitation energies, measured from the $S=1$ ground state, are 0.96 and 2.28 meV, and it will be noted that the values from all three methods (QMC, TDO, and INS) are in close agreement. In addition to these two transitions several other peaks are present in the INS spectrum, corresponding to transitions

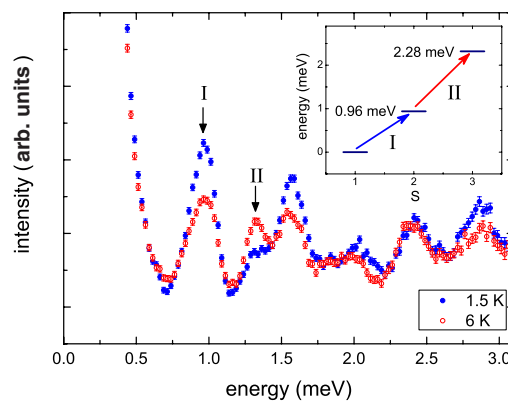


FIG. 5. (Color online) INS spectra with a 4.4 Å incident neutron setting for $\text{Cr}_{12}\text{Cu}_2$ at 1.5 K (blue, full symbols) and 6 K (red, open symbols) totaled for all scattering angles, with the zero-field energy-level diagram shown as an inset, with arrows identifying transitions.

to states with larger excitation energy. There is currently insufficient information to uniquely determine the quantum numbers of these other excited states so a detailed analysis of these data will be presented elsewhere.

Our present results demonstrate how the use of three complementary methods (QMC, TDO, and INS) is able to provide an accurate description of the low-lying energy spectrum of the $\text{Cr}_{12}\text{Cu}_2$ magnetic molecule. The QMC method is used to determine values for the exchange constants and to provide predictions for the energies of the three lowest ($S=1, 2, \text{ and } 3$) states; the TDO method is used to confirm these theoretical predictions, as well as provide a spectroscopic means of observing field-induced excited-state level crossings; and INS measurements independently confirm both the QMC calculations and the TDO spectroscopy. The present outstanding agreement between theory and experiment down to 80 mK confirms the legitimacy for the present system of building a theoretical model of an individual magnetic molecule, in particular where the role of intermolecular magnetic interactions is explicitly ignored. It is also remarkable that although we have assumed a strictly isotropic Heisenberg Hamiltonian all of these measurements are in excellent agreement with the theoretical model. Although nonisotropic mechanisms are often important for magnetic molecules, similar successes of a purely Heisenberg model have also been recently observed in other systems.^{11,24}

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- ²¹The full list of predicted ground-state level-crossing fields (in Tesla) is 8.15, 11.9, 16.2, 19.8, 24.1, 27.6, 31.7, 35.15, 39.3, 42.6, 47.1, 50.1, 55.2, 57.65, 64.3, 65.5, and 80.7.
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