Magnetism of isolated Mn_{12} single-molecule magnets detected by magnetic circular dichroism: Observation of spin tunneling with a magneto-optical technique

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We report magnetic and magneto-optical measurements of two Mn_{12} single-molecule magnet derivatives isolated in organic glasses. Field-dependent magnetic circular dichroism (MCD) intensity curves (hysteresis cycles) are found to be essentially identical to superconducting quantum interference device magnetization results and provide experimental evidence for the potential of the optical technique for magnetic characterization. Optical observation of magnetic tunneling has been achieved by studying the decay of the MCD signal at weak applied magnetic field.

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Individual molecules that act as magnets are appealing from both fundamental scientific and technological points of view, especially given their potential as quantum computing components.[1] Much attention has focused on the family of molecules based on a dodecamanganese core, denoted generally as $[Mn_{12}O_{12}(O_2CR)_{16}(H_2O)_x]S_x$ (R=substituent, $x=3-4$, S=solvent). These systems behave as single-molecule magnets (SMM's),[2] but the vast majority of the previous studies on them have centered on crystalline materials. It is an intriguing and important challenge to investigate these molecules when they are isolated from each other, but since this is not currently feasible, we have chosen, in the interim, to study ensembles of molecules isolated from each other in inert matrices. On the other hand, the development of methods for measurement of magnetic and spin properties of isolated molecules is important when the detection limits of traditional superconducting quantum interference device (SQUID) instruments are reached. Key questions include what techniques can be used to study these phenomena and whether tunneling can be observed in isolated molecules using these other techniques. In order to answer these questions we have used two techniques, magnetic susceptibility and magnetic circular dichroism (MCD), and we will show that the magnetic and optical responses are essentially identical.

To a first approximation, the effective spin Hamiltonian for a Mn_{12} SMM is

$$H=-DS_z^2-g\mu_B\mathbf{S}\cdot\mathbf{H}+H', \tag{1}$$

where $D=0.55$ K is the zero-field splitting parameter for the ground-state manifold and $S=10$. H' contains terms that do not commute with S_z and are responsible for tunneling between different M_S states.

Isolated molecules of $Mn_{12}Ac$ ($R=CH_3$) and $Mn_{12}Bz$ ($R=C_6H_5$) can be obtained by dissolving them in noncoordinating organic solvents.[3] MCD requires optical isotropy and transparency, so the solvents were selected according to their facility for forming strain-free, transparent glasses at cryogenic temperatures.[4] Two mixtures were employed: (1) CH_2Cl_2:toluene (1:1 by volume) and (2) CH_3CN:dmf (where dmf=N,N'-dimethylformamide, 1:2 in volume). The molecular magnetic moments are so small that the torque imparted by applied magnetic fields up to 5×10^4 Oe is not enough to orient the molecules, which therefore remain randomly oriented in the frozen glass.

Magnetic measurements were performed using a commercial rf-SQUID magnetometer (MPMS2), with applied magnetic fields up to 5×10^4 Oe. Samples of 0.06 ml of 6-g/l solution were placed in a cylindrical Teflon container, which was sealed with a screw-on lid. The field dependencies of the magnetization for $Mn_{12}Ac$ and $Mn_{12}Bz$ in a glass of CH_2Cl_2:toluene ($Mn_{12}Ac/CH_2Cl_2$:tol and $Mn_{12}Bz/CH_2Cl_2$:tol) at $T=1.8$ K are shown in Figs. 1(a) and 1(b), respectively (gray curves). The lack of orientation prevents in this case observation of the steplike behavior in the magnetization hysteresis cycles seen at certain resonant fields and characteristic of tunneling.[5]

A quantitative description of the dynamics of the magnetization for a single molecule depends on the angle θ between the applied magnetic field and the molecule's easy axis of magnetization and can be expressed in terms of the differential equation

$$\frac{dM}{dH}=\frac{(H,T,\theta)}{\alpha}[M-M_{\mathrm{eq}}(H,T,\theta)]\sin\theta, \tag{2}$$

where $\alpha=dH/dt$ is the magnetic field sweeping rate, $M_{\mathrm{eq}}(H,T,\theta)$ is the equilibrium magnetization, and $\Gamma(H,T,\theta)$ is the relaxation rate that can be written as $\Gamma=\nu_0\exp(-U_{\mathrm{eff}}/k_BT)$. Here, ν_0 is the attempt frequency and U_{eff} is the effective potential-energy barrier, which includes the conditions of resonance that also depend on θ. At very low temperatures, when only the $M_S=\pm10$ levels are significantly populated, the equilibrium magnetization is closely approximated by

$$M_{\mathrm{eq}}=M_{\mathrm{sat}}\left[\tanh\left\{\frac{g\mu_B|S|H\cos\theta}{k_BT}\right\}+\frac{H\sin\theta}{H_a}\right]. \tag{3}$$

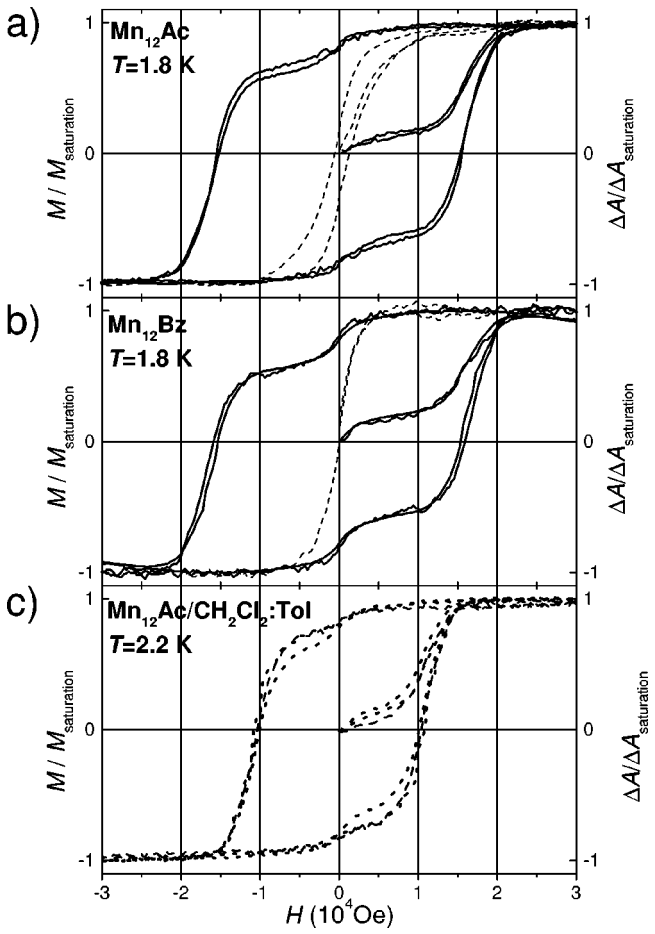

FIG. 1. Field dependence of SQUID magnetization (gray curves) and MCD at 21 200 cm^{-1} (black curves) for $Mn_{12}Ac$ (a) and $Mn_{12}Bz$ (b). In (a) and (b), the black solid curves indicate the magnitude of the MCD in 1:1 CH_2Cl_2:tol glasses, while the dashed lines correspond to the relevant SMM in a 1:2 CH_3CN:dmf glass. For (c), the gray dotted curve indicates the magnetization of $Mn_{12}Ac/CH_2Cl_2$:tol, while the black curves represent MCD measurements at 21 200 cm^{-1} (dotted line) and 19 700 cm^{-1} (dashed line).

The first term inside the brackets of Eq. (3) confers the tanh dependence that is typical paramagnetic behavior of an isolated pair of Zeeman levels, which is a good approximation for the low-temperature limit. The second (linear) term arises from misalignment of the easy axis of magnetization of the particles with the field, which causes mixing of states that differ by ± 1 in their M_S values. In order to simplify the analysis of the data, the linear contribution to the magnetization has been subtracted from the results shown in Fig. 1. The remaining part is sensitive to relaxation mechanisms and, at temperatures below the blocking temperature, gives rise to hysteresis.

The steps seen near zero field in Fig. 1 were observed at all temperatures between 1.8 and 3 K. They are consistent with the existence of two molecular species with different effective energy barriers and therefore different relaxation rates and blocking temperatures. While the species with the higher temperature barrier is blocked in this temperature range, the other remains superparamagnetic and thus undergoes a rapid change of magnetization near zero field. This hypothesis is confirmed by the presence of two frequency dependent peaks in both components of the ac-magnetic susceptibility of $Mn_{12}Ac/CH_2Cl_2$:tol and $Mn_{12}Bz/CH_2Cl_2$:tol.[6] The high-temperature blocking peak is usually placed between 3.5 and 6 K, while the low-temperature peak appears around 2 K. The low-temperature peak has also been observed in certain Mn_{12} derivatives, where it is ascribed to Jahn-Teller distortions of the core.[7] The height of the zero-field step depends on the fraction of molecules that undergo the fast relaxation mechanism, which is calculated from the ac-susceptibility peaks to be about 15% for $Mn_{12}Ac/CH_2Cl_2$:tol and 20% for $Mn_{12}Bz/CH_2Cl_2$:tol. Another contribution to the zero-field step arises from the fact that all molecules undergo resonant tunneling between spin states at zero field, irrespective of their orientation (see below), but this is very small in comparison with the superparamagnetic contribution seen here, and thus it can be considered as irrelevant.

MCD is the differential absorption of left and right circularly polarized light by a sample in longitudinal magnetic field,[8] and can be written as $\Delta A = A_L - A_R$. It provides a powerful tool for studying molecular systems with degenerate electronic states. For orbitally nondegenerate paramagnetic species, the intensity of the MCD associated with a given transition depends on the degree of spin-orbit coupling and varies with magnetic field and temperature in a manner that is determined by the ground- and excited-state parameters, including g factors and zero-field splittings (ZFS).[9] An analysis of MCD of $Mn_{12}Ac$ has been published recently,[10] wherein a quantitative description of the polarization of each optical transition is given. We have investigated the MCD of Mn_{12} SMM's using a spectrometer that is described elsewhere.[11] We show here that this spectroscopic technique is not only related with magnetization but permits effectively the same measurements as SQUID magnetometry, as it can be inferred by comparision of quantitative description of MCD shown by McInnes *et al.* with Eqs. (2),(3).

MCD spectra at $T = 4.2$ K are shown in Fig. 2. Four bands are observed for both $Mn_{12}Ac/CH_2Cl_2$:tol and $Mn_{12}Bz/CH_2Cl_2$:tol, but the change of solvents leads to significant differences. In CH_3CN:dmf the $\sim$19 700-cm^{-1} band almost disappears and there is a relative enhancement of the band at $\sim$21 100 cm^{-1}. McInnes *et al.*[10] have described the MCD spectra for Mn_{12} SMMs in the low-temperature limit with a simple model comprising B and C terms.[8] B terms are linearly proportional to the field and are associated with diamagnetism in either the ground or excited state of the electronic transition. C terms are associated with ground-state paramagnetism and, in the limit of a two-level Zeeman system assuming that equilibrium thermal populations are maintained, have the same tanh dependence on the applied magnetic field as the magnetization shown in Eq. (3).

The magnetic-field dependencies of the MCD signals at 21 200 cm^{-1} are shown in Figs. 1(a) and 1(b) for $Mn_{12}Ac$ and $Mn_{12}Bz$ in both CH_2Cl_2:tol and CH_3CN:dmf glasses. Measurements were made using the same experimental conditions as for the SQUID magnetization loops. The MCD signal was measured continuously while changing the field at

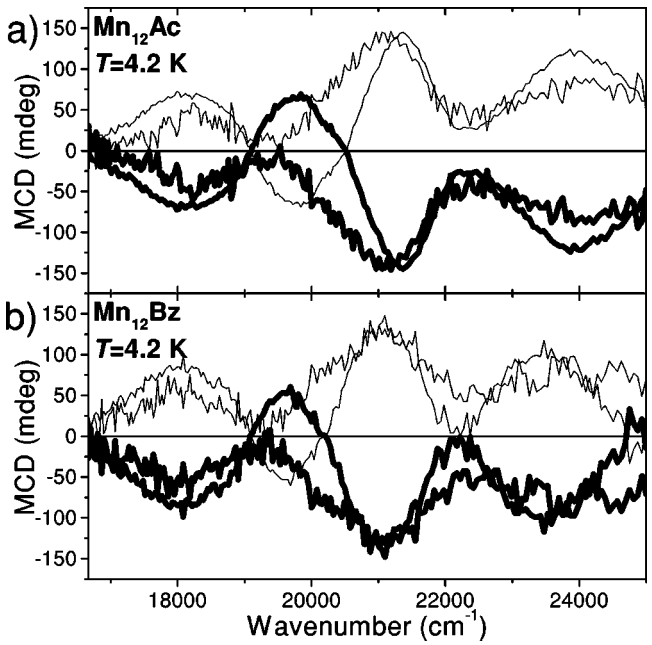

FIG. 2. MCD spectra for the relevant SMM in CH_2Cl_2:tol 1:1 (black lines) and CH_3CN:dmf 1:2 (gray lines) at $H=10^4$ Oe (thick lines) and $H=-10^4$ Oe (thin lines).

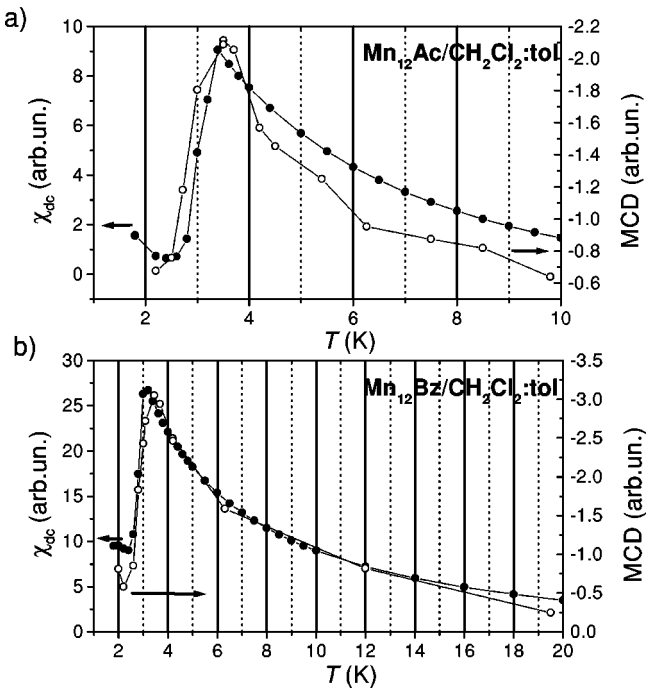

FIG. 3. ZFC measurements of (a) $Mn_{12}Ac$ and (b) $Mn_{12}Bz$ in 1:1 glasses of CH_2Cl_2:tol, with an applied magnetic field of $H=10^3$ Oe. Solid circles indicate SQUID measurements (referred to the left axis) and open circles stand for MCD measurements (referred to the right axis).

a rate of $\alpha=19.6$ Oe/s. By subtracting the linear B-term contributions, the MCD results can be directly compared with the SQUID magnetization data. As seen in Fig. 1, the hysteresis loops measured by the two methods are essentially identical. Moreover, as shown in Fig. 1(c), the MCD cycle measured for the 19 700-cm^{-1} band of $Mn_{12}Ac/CH_2Cl_2$:tol (which has been assigned polarization properties significantly different from those of the 21 200-cm^{-1} band[8]) is superimposable on the 21 200-cm^{-1} curve of the same sample after the linear contributions have been subtracted.

Comparing the MCD hysteresis cycles measured at the same wavelength for $Mn_{12}Ac/CH_2Cl_2$:tol and $Mn_{12}Ac/CH_3CN$:dmf [Fig. 1(a)], we see that, for the latter, there is a huge increase of the zero-field step. In addition, the remnant magnetization at zero field is reduced to about 30% of the saturation value, reproducing the previously reported results for the same system.[4] As noted above, the magnitude of the zero-field step should be correlated with the relative intensity of the low-temperature blocking peak of the in-phase component of the ac-magnetic susceptibility, both being determined by the proportion of molecules that undergo the fast relaxation mechanisms. Thus, it appears that there is a clear influence of the environment on the blocking barriers of these SMM's; the CH_3CN:dmf glass induces a much greater proportion of fast-relaxing molecules than is the case for CH_2Cl_2:tol mixture. These results are confirmed by ac-magnetic susceptibility measurements, where an increase of the high- or low-temperature blocking peak is observed for the glasses. For $Mn_{12}Bz$ the increase of fast-relaxing molecules due to the change of solvent is even greater [Fig. 1(b)], and for $Mn_{12}Bz/CH_3CN$:dmf there is no hysteretic behavior, even down to 1.7 K.

MCD spectroscopy can also be used for zero-field-cooled (ZFC) experiments and the measurements of tunneling phenomena. ZFC dc susceptibility data obtained for $Mn_{12}Ac/CH_2Cl_2$:tol and $Mn_{12}Bz/CH_2Cl_2$:tol using the SQUID and by MCD spectroscopy at 21 200 cm^{-1} are shown in Figs. 3(a) and 3(b). Results obtained for both techniques are in close accord. They show the blocking temperature peak at 3.5 K and the same Curie-Weiss $[\sim(T-T_c)^{-1}]$ behavior at higher temperatures. The low-temperature blocking peak is not clearly seen for these dc measurements because is out of the working temperature range.

The determination of information about tunneling in glasses is limited by the random orientation of the molecules. However, evidence of tunneling can be obtained by comparing the relaxation rates at zero field with those at small, nonzero fields. If relaxation resulted only from classical thermal effects, the highest energy barrier, and thus the slowest relaxation rate, should occur at zero field. When tunneling effects are significant, their contributions to relaxation will be greatest when conditions of resonance are attained between states of different M_S. For a sample of randomly oriented SMM's, the only resonance that occurs simultaneously for all molecules is at zero field, which should therefore correspond to a local maximum of the relaxation rate.

Decay measurements of the MCD signal where performed at 21 200 cm^{-1} for $Mn_{12}Ac/CH_2Cl_2$:tol at 2.2 K. A field of -2.5×10^4 Oe was applied to saturate the sample, then rapidly changed to zero or other weak positive fields. After an initial rapid decrease of signal due to the superparamagnetic

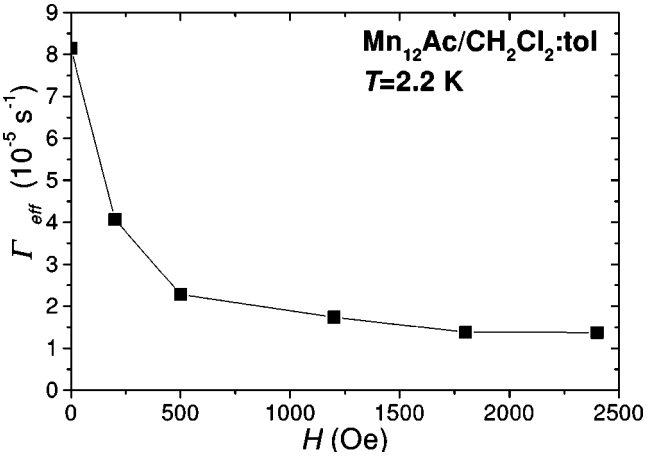

FIG. 4. Magnetic field dependence of the MCD decay rate.

particles, the decay curves could be accurately fitted with the equation $\Delta A(t)=\Delta A_{eq}+(\Delta A_{sat}-\Delta A_{eq})\exp(-\Gamma_{eff}t)$ where Γ_{eff} represents an effective decay rate for the entire randomly oriented ensemble. The field dependence of Γ_{eff} for $Mn_{12}Ac/CH_2Cl_2$:tol is shown in Fig. 4. The maximum at zero field clearly confirms the presence of tunneling. To our knowledge, this is the first observation of spin tunneling with a magneto-optical method.

To summarize, we have shown that MCD is a powerful technique for magnetic characterization of SMM's. The MCD signal is directly proportional to magnetization, reproducing the magnetometry experiments and can be accurately described through Eqs. (2), (3). Measurements performed on Mn_{12} SMM's at visible wavelengths have permitted determination of properties from blocking temperatures to quantum tunneling. Further development of optical methods for magnetization measurements has a special appeal with regard to quantum computing applications.

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[6] See EPAPS Document No. E-PRBMDO-69-023401 for ac magnetic susceptibility for microcrystalline powder of $Mn_{12}Bz$ in Araldit and in a 1:1 glass of CH_2Cl_2:toluene. A direct link to this document may be found in the online article's HTML reference section. The document may also be reached via the EPAPS homepage (http://www.aip.org/pubservs/epaps.html) or from ftp.aip.org in the directory /epaps/. See the EPAPS homepage for more information.

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