Excitation of Magnetic Dipole Transitions at Optical Frequencies

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We use the magnetic field distribution of an azimuthally polarized focused laser beam to excite a magnetic dipole transition in Eu3+ ions embedded in a Y2O3 nanoparticle. The absence of the electric field at the focus of an azimuthally polarized beam allows us to unambiguously demonstrate that the nanoparticle is excited by the magnetic dipole transition near 527.5 nm. When the laser wavelength is resonant with the magnetic dipole transition, the nanoparticle maps the local magnetic field distribution, whereas when the laser wavelength is resonant with an electric dipole transition, the nanoparticle is sensitive to the local electric field. Hence, by tuning the excitation wavelength, we can selectively excite magnetic or electric dipole transitions through optical fields.

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In the optical frequency regime, magnetic dipole transitions are orders of magnitude weaker than their electric dipole counterparts [1–3]. Because of this, magnetic dipole (MD) transitions are often neglected in optics, and the study of light-matter interactions becomes instead the study of interactions between electric fields and electric dipoles (ED). Perhaps the most well-known exceptions occur in the fields of metamaterials [4] and photonic crystal cavities [5,6], in which specially engineered structures can be produced to enhance interactions with the magnetic field. Nature, however, also provides materials with strong MD transitions, namely, rare earth ions. Many of their MD transitions are found within the visible spectrum, making them promising candidates for the optical excitation of MD transitions.

Much theoretical and experimental work has been done exploring the MD and ED contributions to spontaneous emission from Eu3+ and other trivalent rare earth ions [1,7–10]. Lifetimes and oscillator strengths have been studied as a function of local environment [11–14], ion concentration [15–17], and particle size [18–23]. But so far, research has focused solely on detecting and enhancing spontaneous MD emission, with no work done on selective excitation through magnetic fields. In 1939, Deutschbein first identified the MD character of the 7F0 → 5D1 transition in Eu3+ (c.f. Fig. 1(a)) by exploiting the birefringence of Eu(BrO3)3 · 9H2O and Eu(C2H8SO4)3 · 9H2O crystals [24]. He could deduce the MD or ED character of a transition by recording absorption or emission spectra for ordinary and extraordinary polarizations and comparing them to a spectrum taken along the c axis of the crystal. However, he could not selectively address individual transitions. Here, we report the direct and selective optical excitation of a MD transition in the rare earth ion Eu3+.

The light-matter interaction between a charge-neutral quantum system and an electromagnetic field can be represented by a multipole expansion of the interaction Hamiltonian

\[ H_{\text{int}} = -p \cdot E(t) - m \cdot \mathbf{B}(t) - |Q| \cdot E(t) - \cdots, \]

with \( p \) being the electric dipole moment, \( m \) the magnetic dipole moment, and \( Q \) the electric quadrupole moment (a tensor). The different terms of the interaction Hamiltonian lead to different selection rules, and their magnitudes depend on the size of the quantum system. For an atomic system, characterized by the Bohr radius \( a_0 \), the magnitude of the ED is \( p = ea_0 \) (\( e \) is the elementary charge) and the magnitude of the MD corresponds to the Bohr magneton

![FIG. 1 (color online). (a) Simplified energy level structure of Eu3+ with approximate energy scale on the left hand side. The excitation wavelength (blue arrows) is tuned to be resonant with either the 7F0 → 5D1 magnetic dipole transition at 527.5 nm or the 5F1 → 5D1 electric dipole transition at 532 nm. The emitted signal (red arrows) consists of several different transitions, primarily 5D0 → 7F2 and 5D0 → 7F1. (b) Topographic image taken with an atomic force microscope showing two spatially separated 60 nm Eu3+ nanoparticles.](image-url)
Individual Eu$^{3+}$ nanoparticles are then excited by an azimuthally polarized laser beam. The electric field intensity in the focal plane of a strongly focused azimuthally polarized beam forms a ring, or doughnut, around the optical axis, with an intensity null on axis. Figures 2(a) and 2(b) show the characteristic doughnut pattern of a tightly focused azimuthal beam together with a horizontal linecut through the center of the doughnut, demonstrating that the on-axis intensity of the electric field is equal to zero. The magnetic field of this beam, however, shows a different pattern. As seen in Figs. 2(c) and 2(d), the magnetic field distribution forms a circular bright spot, with maximum intensity on axis. Raster scanning a single Eu$^{3+}$ nanoparticle through the focus will map either the magnetic or the electric field intensity distribution, depending on whether the particle exhibits a MD or ED transition at the wavelength of the excitation beam. Since an azimuthally polarized beam has different magnetic and electric focal field distributions, it is straightforward to determine whether the nanoparticle is interacting with the electric or magnetic field, based on the fluorescence image formed when raster scanning the nanoparticle through the stationary excitation beam.

As illustrated in Fig. 3(a), single nanoparticles are excited by the focused light (NA = 1.3) from a tunable optical parametric oscillator (OPO). Before entering the objective lens, the OPO laser is converted to an azimuthally polarized beam by sending it through a liquid crystal polarization converter and then through a spatial filter. Spontaneous emission from single nanocrystals is collected using the same objective lens. A dichroic beam splitter (not shown) separates the collected signal from the excitation laser, and bandpass filters block any remaining light at the

\[ m = \frac{\hbar e}{2m} \]  

\[ c = \frac{\hbar}{mca_0} = 1/137 = \alpha \]  

\[ B = E/c \]  

\[ \alpha \text{ weaker than the ED interaction.} \]

\[ \text{To measure MD interactions, we require a large quantum system (replacing } a_0, \text{ ED forbidden transitions, and/or a zero electric field. Typically, the selection rules of the electric quadrupole interaction [third term in Eq. (1)] are identical to those of the MD interaction [25] and therefore we require a zero electric field to unambiguously excite a MD transition.} \]

Such a situation can be achieved with an azimuthally polarized laser beam [26,27] as used in this work.

In our experiments we used 60 nm particles of Y$_2$O$_3$ doped with Eu$^{3+}$ ions. The Eu$^{3+}$ concentration is $10^{22}$ ions/cm$^3$ (38% mol). Figure 1(a) shows the energy level structure of Eu$^{3+}$. We prepared the particles as a powder through a room temperature colloidal coprecipitation method developed by Gowd et al. [28]. The powder is then dissolved in water, ultrasonicated, and deposited on a glass coverslip by spin coating, resulting in spatially separated Eu$^{3+}$ nanocrystals [see Fig. 1(b)]. Prefabricated markers on the coverslip make it possible to locate the same particle in several different experiments.
The signal is detected using an avalanche photodiode or a spectrometer. Excitation-rate images are recorded by raster scanning a selected nanoparticle in the focal plane of the excitation beam and measuring the fluorescence intensity pixel by pixel. The detected signal arises from a combination of ED and MD transitions at lower energy than the excitation, primarily the \( ^5D_0 \rightarrow ^7F_2 \) and \( ^5D_0 \rightarrow ^7F_1 \) transitions in the spectral range of 603–635 and 580–603 nm, respectively [see Fig. 1(a)] [7,29].

For a plane wave in free space the magnetic field strength is related to the electric field strength by the speed of light \( B = E/c \). With an azimuthally polarized laser beam we can drastically increase the ratio of \( B/E \). In the center of the beam the magnetic field is zero and hence \( B/E \rightarrow \infty \). However, the signal-to-noise ratio in measurements also depends on the ratio of max \( |B| \) and max \( |E| \) evaluated in different spatial locations. While the magnetic field is maximum in the center of the beam, the electric field finds its maximum at the outer ring surrounding the focal point (cf. Fig. 2). In Fig. 3(b) we have evaluated the ratio of maximum field intensities as a function of focusing angle and find that with a NA of 1.3, the ratio of maximum magnetic and electric field intensities can be enhanced by a factor of 3.4 compared to a plane wave in free space. This implies an intensity ratio of \( c^2 \max \{ |B| \}^2 / \max \{ |E| \}^2 = 11.6 \) inside the nanoparticle (with \( n = 1.94 \) at 530 nm).

In Fig. 4, we show representative excitation rate images of an Eu\(^{3+}\) nanoparticle (bottom row) recorded at two different excitation wavelengths. For comparison, we also include typical excitation rate images of dye-doped polystyrene nanoparticles (fluospheres). The absorption spectrum of the fluospheres is dominated by ED transitions; that is, their excitation rate scales with the local electric field intensity. Therefore, the image formed by raster scanning a fluosphere through the focus shows a doughnut shape, reflecting the electric field intensity distribution in the focus of an azimuthally polarized beam, as shown in Figs. 4(a) and 4(c). The linecuts in Figs. 4(b) and 4(d) clearly show that the intensity in the center exhibits a minimum. Because of the finite size of the fluospheres, the intensity is not exactly zero at the center.

Single Eu\(^{3+}\) nanoparticles, however, show a markedly different behavior. Depending on whether the excitation wavelength is tuned into resonance with a MD or ED transition, an Eu\(^{3+}\) nanoparticle will map out the distribution of the magnetic or the electric field. At 532.0 nm excitation wavelength, the Eu\(^{3+}\) exhibits an ED transition corresponding to one of the \( ^7F_1 \rightarrow ^5D_1 \) transitions...
527.5 nm brings the Eu$^{3+}$ ion to the $^7F_0$ state, and hence an image taken with an azimuthally polarized beam tuned to 532.0 nm yields a doughnut-shaped intensity distribution with a characteristic circular bright spot in the center [Fig. 4(e)]. As shown in the linecut in Fig. 4(f), the intensity in the center is now a maximum, demonstrating that the particle responds primarily to the magnetic field at this excitation wavelength. Thus, by tuning a mere 5 nm in excitation wavelength, we can selectively excite either ED or MD transitions. Vice versa, using these transitions we can map out either local electric field distributions or local magnetic field distributions. We find that the maximum MD excitation rate in Fig. 4(f) is roughly 3.25 times larger than the maximum ED excitation rate in Fig. 4(h). Combining this information with the $c^2 \max |B|^2 / \max |E|^2$ ratio from earlier and a previously published value of the oscillator strength of the $^7F_0 \to ^5D_1$ transition [21], we can infer the value of the $^7F_1 \to ^5D_1$ oscillator strength to be $0.63 \times 10^{-6}$ in our nanocrystals. For details of this estimate, see the Supplemental Material [30]. We emphasize that while spontaneous MD emission from rare earth ions has been shown before [1,7–10], our work unambiguously demonstrates the selective excitation of a MD transition. Since excitation is a stimulated process, similar measurement techniques can be employed for demonstrating stimulated transitions from the excited state and achieving lasing through magnetic dipole transitions.

In the future, we hope to employ our technique to quantitatively measuring MD transitions in other Ln$^{3+}$ lanthanides. For instance, it is known that the $^5D_4 \to ^7F_3$ transition in Tb$^{3+}$ has a significant MD contribution, but to date there is no precise measurement or estimate. Since the relative strength between the on-axis magnetic field and the off-axis electric field of an azimuthally polarized beam is known (cf. Fig. 3), we can, in principle, calibrate our method to measure the relative MD contribution in different Ln$^{3+}$ transitions for which the precise MD proportion is unknown.

There are, however, a few limitations to our technique. First of all, it requires a high doping concentration to ensure the particles have no preferred dipole direction. Also, although many host materials (including various glasses [35] and crystals [36]) have been used for bulk samples, making highly doped stable nanoparticles from the same materials could prove challenging. Finally, to map out general magnetic field distributions, we require more effective suppression of residual ED transitions. This can be achieved, for example, by cryogenically reducing the population of the $^7F_1$ state in Eu$^{3+}$ or by considering quantum emitters that have a larger spectral separation between ED and MD transitions.

In conclusion, we have shown that MD transitions in Eu$^{3+}$ ions can be excited optically and can therefore be used to map local magnetic fields. Future work will focus on developing scanning probes with Y$_2$O$_3$; Eu$^{3+}$ particles attached for magnetometry applications. Recently published work has already shown the possibility of using Eu$^{3+}$ particles as local probes when attached to the ends of AFM tips [29]. Using Eu$^{3+}$ nanoparticles on AFM probes could potentially enable the direct mapping of magnetic fields at specific wavelengths. Eu$^{3+}$ and other rare earth ions exhibit many other MD transitions in the visible region, which opens the possibility of mapping magnetic fields at multiple frequencies in parallel and furthering our understanding of light-matter interactions in inhomogeneous environments.

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The Supplemental Material is available online [30].

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[30] See Supplemental Material at http://link.aps.org/supplemental/10.1103/PhysRevLett.114.163903, which includes Refs. [31 34], for the calculation of the relative strengths of ED and MD transitions and for the derivation of the $^7F_1 \rightarrow ^5D_1$ ED oscillator strength.