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Near infrared light absorption in magnetic nanoemulsion under external magnetic field

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ABSTRACT

We study the magnetic field dependent near infrared photon absorption behavior in a magnetically polarizable oil-in-water emulsion of droplet radius ~110 nm. The absorption of near infrared photons in magnetic nanoemulsion is found to be dependent on the volume fraction and applied magnetic field, which is attributed to the variation in the Mie absorption efficiency during the structural transitions of nanoemulsion droplets in dispersion. Also, the absorption linearly increases with incident near infrared photon energy up to certain external magnetic field. The imaginary part of the refractive index (k_1) of magnetic nanoemulsion obtained from the near infrared absorption profile in the Rayleigh regime is found to vary with external magnetic field and the sample volume fraction (ϕ). The measured k_1 follows a power law increment with sample volume fraction ($k_1 \sim \phi^p$, where p is the exponent). The exponent (p) decreases with external magnetic field implying that the structural transition of nanoemulsion droplets increases k_1. After a critical magnetic field (beyond Rayleigh regime), field induced absorption of near infrared photons decreases because of the increase in the aspect ratio of the chain like aggregates and interchain spacing which in turn reduces the Mie absorption efficiency.

1. Introduction

Absorption is the study of interaction of waves with matter, which is probably the most widespread and precise analytical technique used to study isolated atoms, molecules, small clusters in gas, condensed phases, bio-molecules, and the structures and dynamics of quantum systems from atomic domain to natural proteins [1–3]. Infrared absorption spectroscopy is a powerful technique for in-situ analysis of chemical, bio-medical and nano-fluidic systems [4–6]. Aggregation processes of dielectric and metal nanoparticles were also studied using infrared absorption spectroscopy [7,8]. Saito et al. measured the optical attenuation constants of magnetic nanofluid at infrared region during field induced aggregations of magnetic nanoparticles in dispersion [9].

Recently, optical properties of nanofluids have been a topic of intense research due to their fascinating properties and interesting applications [10–15]. Among nanofluids, magnetic nanocolloids possess the unique property of tunability of particle interaction by external magnetic field, which makes an attractive candidate for fundamental research [16–18] and have potential applications in optical sensors [19,20], defect sensors [21,22], tunable optical filter [23], magneto-controllable photonic device [24,25], miniature 'smart' cooling [26,27], probing of weak molecular forces [28], etc. The external magnetic field induced structural evolution due to aggregation and de-aggregation process in the magnetic colloidal system has been studied by small-angle neutron scattering (SANS), small-angle X-ray scattering (SAXS), light scattering, optical microscopy with digital image analysis, confocal scanning laser microscopy, etc. [29–32]. Liu et al. first demonstrated the field induced aggregation in ferrofluid emulsions [33]. Recently it has been shown that the light scattering through such aggregates gives rise to enhanced transmitted field with a Fano shape profile [25]. Extinction coefficient of magnetic fluids has been studied in detail using the spectral transmittance approach and molecular dynamics simulation where it has been shown that the extinction coefficient increases with increasing particle volume fraction and particle diameter (for a fixed volume fraction) [34,35]. The heterodyne interferometry technique has also been used for studying low field induced tiny variations in the complex refractive index for anisotropic and opaque magnetic fluid thin film specimen [36]. It was also shown that the field induced aggregation and de-aggregation process in magnetic nanofluids can alter the propagation of light waves leading to exciting optical phenomena which are of fundamental interests and have practical applications [10,37].

In this paper, we study the behavior of near infrared (IR) photons absorption by a magnetically polarizable oil-in-water emulsion (here after referred as nanoemulsion), with droplet diameter ~220 nm, in presence of an external magnetic field.

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We probe the near infrared absorption as a function of sample volume fraction and external magnetic field. Also, using the near infrared absorption profile in the Rayleigh regime, we evaluate the imaginary part of the refractive index (k_1) of magnetic nanoemulsion that depends on the sample volume fraction and external magnetic field.

2. Materials and experimental setup

Magnetic nanoemulsion, used in the experiment, is a dispersion of octane oil droplets (average diameter, $d = 220$ nm; polydispersity $< 5\%$) in water. Each of these oil droplets contains oleic acid coated magnetic (Fe_3O_4) nanoparticles (diameter, $a = 8$ nm). The oil droplets are electrostatically stabilized with an anionic surfactant: sodium dodecyl sulfate ($CH_3(CH_2)_{10}CH_2SO_4^- Na^+$). Fig. 1 shows a schematic of the experimental setup used in the present study. The magnetic nanoemulsion is taken in a cuvette of path length, $l = 1$ mm, which is kept inside the cuvette holder. The cuvette holder is placed inside a solenoid in such a way that the direction of the light passing through the sample is along the direction of the external magnetic field. The magnetic field is varied by changing the current passing through the coil using a DC programmable power supply. A standard fiber optic spectrometer (AvaSpec-2048, Avantes, USA), with a tungsten halogen light source, is used to record the absorption spectra. The spectrometer has a usable wavelength (λ) range of 200–1100 nm and the absorption spectra is recorded in the near infrared range ($\lambda = 800-1100$ nm; energy, $E = 1.55-1.12$ eV). The detector is a CCD linear array with 2048 pixels, with a signal to noise ratio of 200:1. The resolution of the spectrometer is 0.04 nm. The integration time and ramp rate are optimized to record the exact absorption spectrum for each external magnetic field.

3. Results and discussions

Fig. 2a–e shows the phase contrast microscopic images of magnetic nanoemulsion observed at different external magnetic fields (0–220 G). The direction of the applied magnetic field is shown by the arrow. It can be seen that at zero external magnetic field the nanoemulsion droplets are randomly oriented and as the magnetic field increases, the droplets orient themselves along the direction of the external magnetic field leading to a chain like structure. Fig. 2f shows the schematic of a magnetic nanoemulsion droplet. In magnetic nanoemulsion, oil droplets are electrostatically stabilized with sodium dodecyl sulfate (SDS) (Fig. 2f). When the droplet double layer is very thin ($\kappa a_1 < 5$), the electrostatic force profile is as follows:

$$F_r(r) = 4\pi\varepsilon_1\zeta_0^2 a_1{}^2\left[\frac{\kappa}{r}+\frac{1}{r^2}\right]\exp[-\kappa(r-2a_1)],$$

where a_1 ($= d/2$) is the droplet radius, r is the droplet separation distance, ε_1 is the dielectric permittivity of the suspending medium, ζ_0 is the electrical surface potential and κ is the inverse Debye length that essentially depends on the electrolyte concentration (C_s) and can be represented as

$$\kappa^{-1} = \left(\frac{1}{4\pi}\right)\left[2L_B^2C_s\right]^{-0.5},$$

where 'L_B.' is the Bjerrum length [38,39].

Fig. 2g shows the schematic of magnetic nanoemulsion droplets dispersed in water in the absence of any external magnetic field where the nanoemulsion droplets are in the random Brownian motion. When the magnetic coupling constant

$$\Lambda = \frac{\pi\mu_0 d^3\chi^2H^2}{72k_BT}$$

(χ and k_BT are the effective susceptibility of an individual nanoparticle and thermal energy, respectively), which is the ratio of the dipolar interaction strength to thermal energy, is much greater than one ($\Lambda \gg 1$), the nanoemulsion droplets in dispersion undergo an disorder–order transition, i.e. Brownian to a linear chain-like structures with head-on aggregation along the external magnetic field direction (Fig. 2b–e and h) [25,33,40]. Such field induced aggregation and formation of chainlike structure has been verified experimentally [30,41] and by using computer simulations [42].

Fig. 3a shows the absorption of near infrared photons by the magnetic nanoemulsion with photon energy for the volume fractions of $\phi = 0.0014$, 0.0019, 0.0022, and 0.0067 in absence of external magnetic field. Here, the absorption linearly increases with photon energy and higher volume fractions show more absorption which indicates that absorption increases with the number density (ρ_n) of nanoemulsion droplets in the dispersion ($\phi = \rho_n\upsilon$, where υ is the droplet volume [43]).

Here the nanoemulsion droplet size ($d \sim 220$ nm) is much smaller than the wavelength of the infrared photons ($\lambda = 800-1100$ nm) and according to the Rayleigh scattering theory ($d < \lambda$), the absorption cross-section (C_{abs}) is given by the relation: $C_{abs} = \alpha\upsilon$, where $\alpha = 4\pi k_1/\lambda$ is the absorption coefficient, k_1 is the imaginary part of the refractive index ($m = n_1 + ik_1$) of nanoemulsion, and υ is the droplet volume [44]. The real part of the refractive index (n_1) of magnetic nanoemulsion indicates phase speed and the imaginary part (k_1) signifies absorption losses during the propagation of an electromagnetic wave through the medium [44]. The absorption cross-section is related to the incident photon energy (E) as

$$C_{abs} = \frac{4\pi\upsilon\, k_1}{hc} \times E \quad (1)$$

where h is the Plank constant. It is clear from Eq. (1) that C_{abs} increases linearly with the increasing photon energy (E) in the Rayleigh regime. It is evident from Fig. 3a that the higher energy infrared photon causes more absorption for all the four volume fractions ($\phi = 0.0067$, 0.0022, 0.0019, and 0.0014) of the nanoemulsion samples. It must be noted that, Fig. 3a actually shows that absorption (A) increases with volume fraction (ϕ) and the relation between absorption (A) and absorption coefficient (α) is [45]

$$\alpha = \frac{2303A\rho}{\phi\ell} \quad (2)$$

where ρ is the density of the nanoemulsion droplet and ℓ is the optical path length (~ 1 mm). From Eqs. (1) and (2) it is evident that absorption (A) is directly proportional to the absorption coefficient (α) and absorption cross-section (C_{abs}).

Fig. 3b shows the absorption coefficients (α) as a function of incident photon energy (E) for the nanoemulsion specimens of four different volume fractions. Absorption coefficient values are obtained from the absorption values (Fig. 3a) using Eq. (2). It can be seen from Fig. 3b that the absorption coefficient increases with

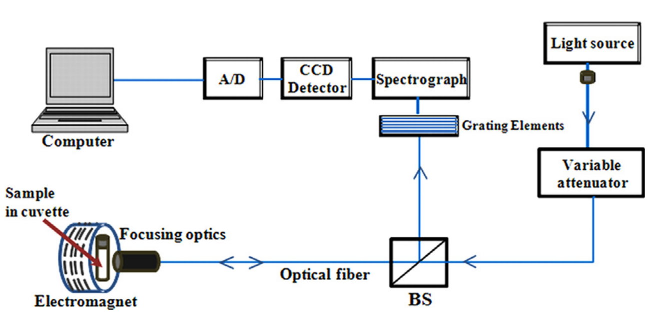

Fig. 1. Schematic of experimental setup to study the external field induced near infrared photons absorption by magnetic nanoemulsion.