Optical Rotation and Ellipticity in Molecular and Nanomaterials
a spectroscopic investigation

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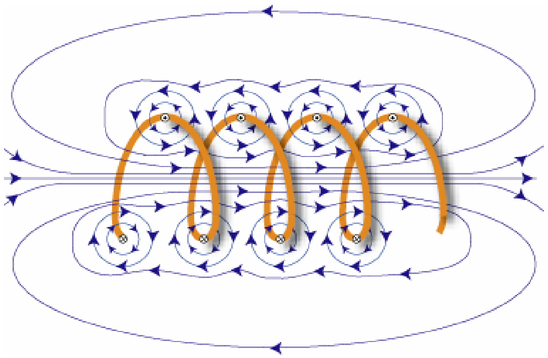
Overview

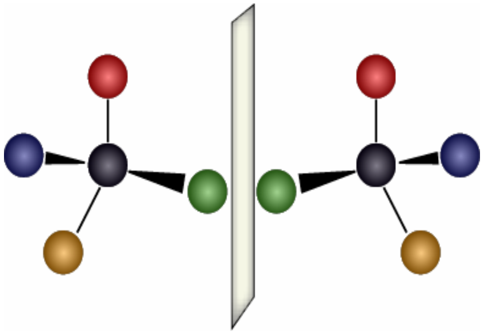
Part 1



Magnetism

in nanoparticles

Part 2



Chirality

in molecular films

Linearly polarized light

Linearly polarized light can be represented as a superposition of two opposite circularly polarized electromagnetic waves.

$$\psi(z,t) = A\cos(kz - \omega t)$$

When light encounters it interacts with its complex refractive index:

$$\tilde{n} = n + ik$$

Optical rotation and ellipticity originate in a different interaction with $\tilde{n}$ for left and right circularly polarized light.

Optical rotation

If one of the two circularly polarized waves travels with a slower phase velocity, the resulting linear polarization is rotated.

$$\phi = \frac{\pi\left(n^{+} - n^{-}\right)l}{\lambda}$$

Where l is the length of the material and λ is the wavelength of light.

$$\tilde{n} = n + ik$$

Ellipticity

If one of the two circularly polarized waves is more absorbed, the resulting linear polarization is follows an ellipse.

$$\theta = \frac{\ln 10}{4}\left(A^{+} - A^{-}\right)$$

$$\tilde{n} = n + ik$$

The need for a spectroscopic investigation

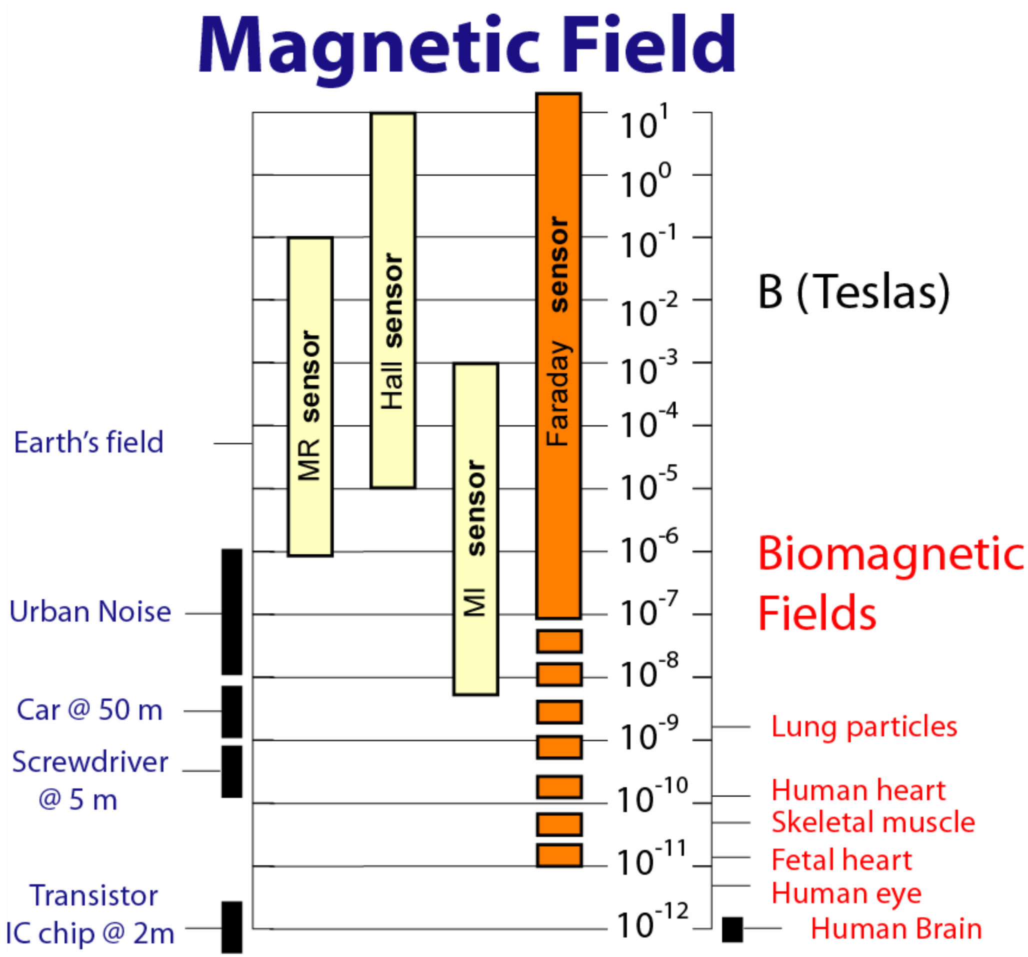
Optical rotation and ellipticity are related through the Kronig-Kramers relations.

$$\phi(\lambda) = \frac{1}{\pi} P \int_{-\infty}^{\infty} \frac{\theta(\lambda')}{\lambda' - \lambda} d\lambda'$$

$$\theta(\lambda) = -\frac{1}{\pi} P \int_{-\infty}^{\infty} \frac{\phi(\lambda')}{\lambda' - \lambda} d\lambda'$$

P is the Cauchy principal value

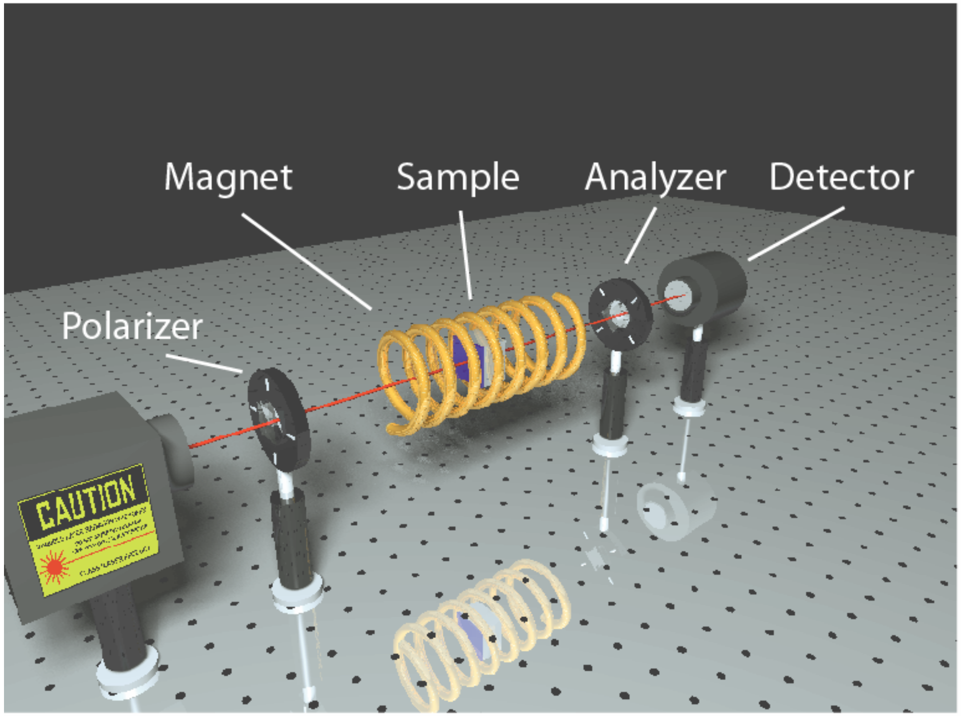
The Faraday sensor & biomagnetism



The study of biomagnetic fields is usually done by SQUID.

The Faraday Sensor could allow such studies to be done at room temperature!

A straightforward experimental technique



Faraday effect:
Under the influence of the magnetic field, the plane of polarization of the light is rotated.

$$\phi = V.B.l$$

ϕ is the angle of rotation

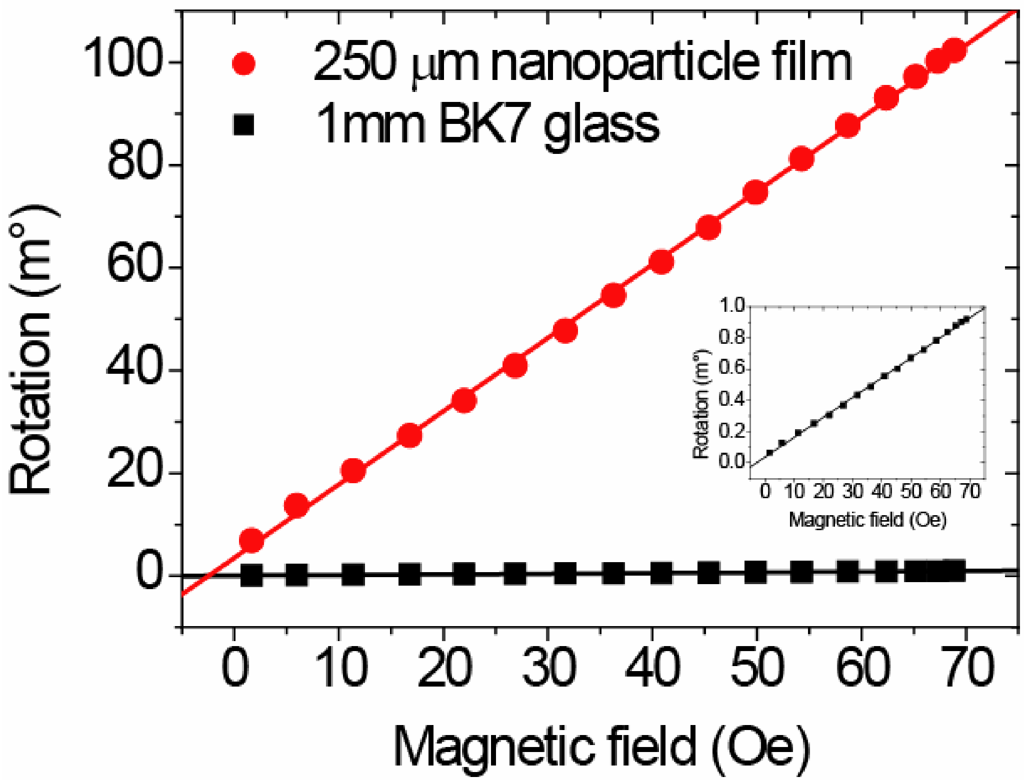
V is the Verdet constant

l is the sample thickness

B is the mag. flux density

Nanoparticles exhibit a large Faraday rotation

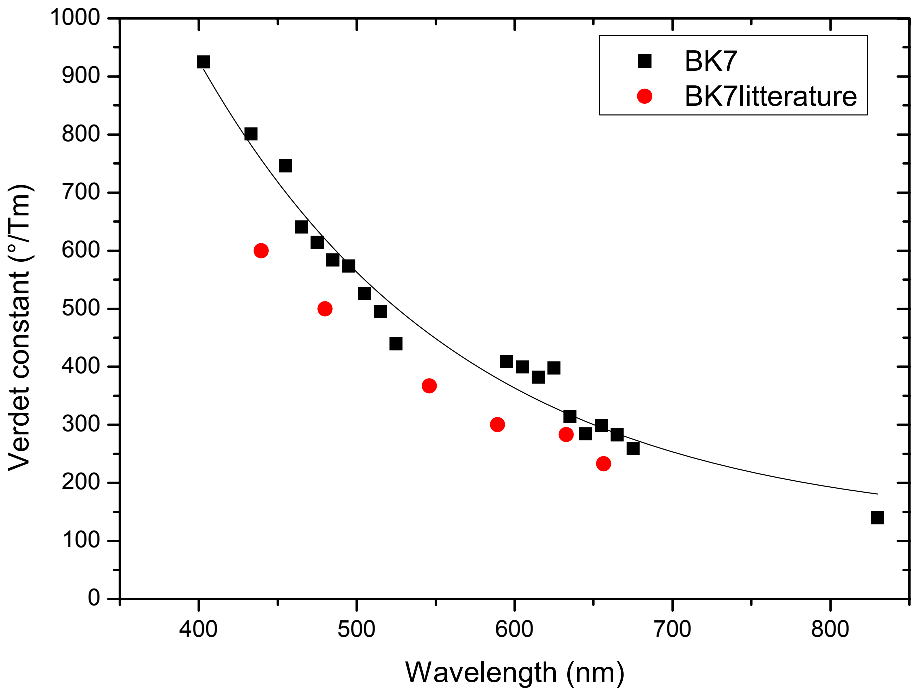
$CoFe_2O_4$ and Fe_3O_4 superparamagnetic nanoparticles, prepared chemically, were embedded in a polymer matrix (PMMA) and deposited on a 1mm BK7 glass plate.



- ease of preparation
- low cost

Accuracy within 1.5 µdeg./Oe

Selecting wavelength can further improve the sensitivity

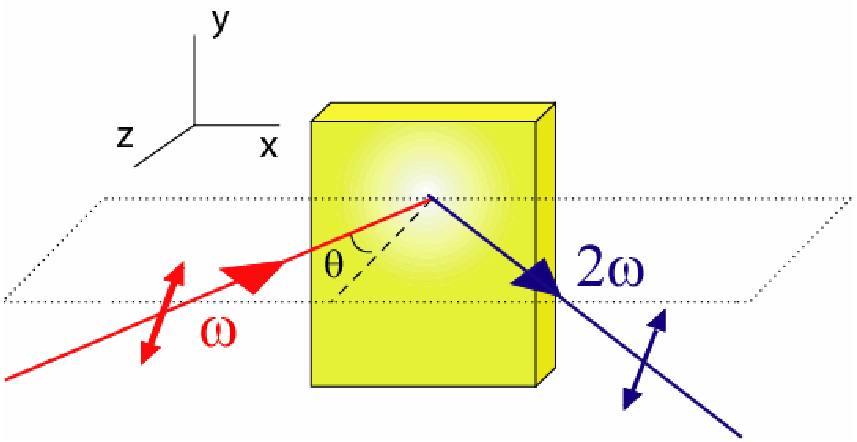


An experimental setup has been constructed for the measurements of Faraday rotation versus wavelength.

Faraday spectra of $CoFe_2O_4$, Fe_3O_4 and gold coated nanoparticles are under Investigation.

Second Harmonic Generation (SHG) requires symmetry breaking

In linear optics: $\mathbf{P} = \chi^{(1)} \cdot \mathbf{E}$



For more intense electromagnetic fields:

$$\mathbf{P} = \chi^{(1)} \cdot \mathbf{E} + \chi^{(2)} \cdot \mathbf{EE} + \chi^{(3)} \cdot \mathbf{EEE} + \ldots$$

The induced polarization contains higher harmonics:

$$\mathbf{P} = \mathbf{P}(0) + \mathbf{P}(\omega) + \mathbf{P}(2\omega) + \mathbf{P}(3\omega) + \ldots$$

where $\mathbf{P}_i(2\omega) = \chi^{(2)}_{ijk} \mathbf{E}_j(\omega) \mathbf{E}_k(\omega)$

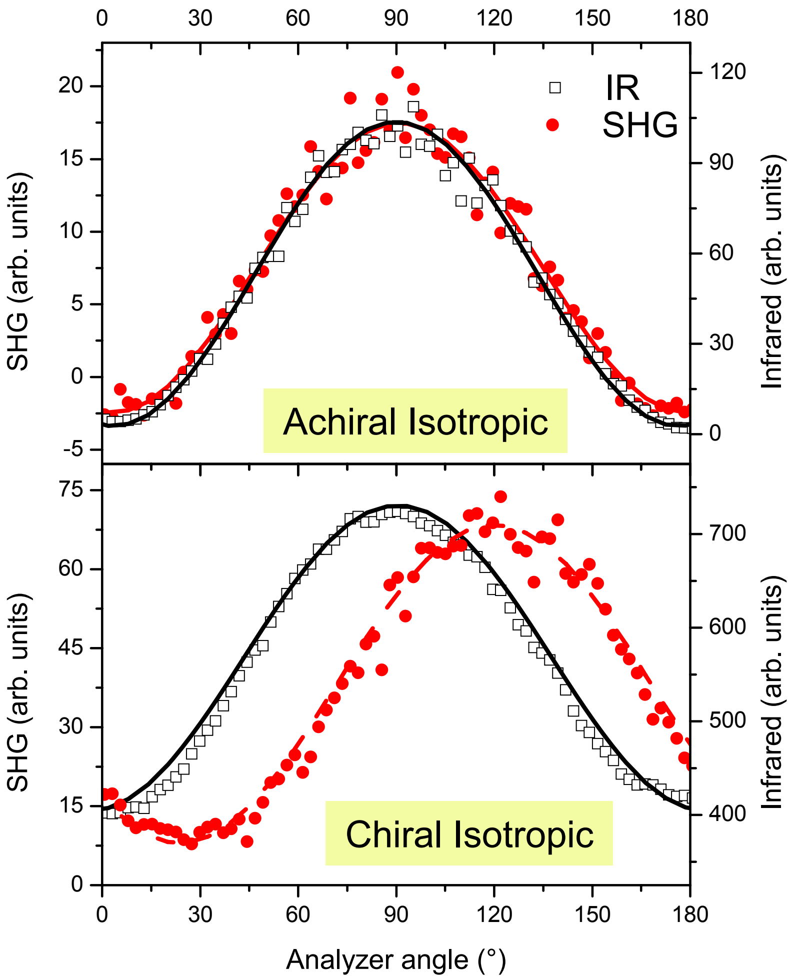
Within the electrical dipole approximation, <u>in centrosymmetric materials</u>:

$$-\mathbf{P}_i(2\omega) = \chi^{(2)}_{ijk}(-\mathbf{E}_j(\omega))(-\mathbf{E}_k(\omega)) \rightarrow \chi^{(2)}_{ijk} = 0$$

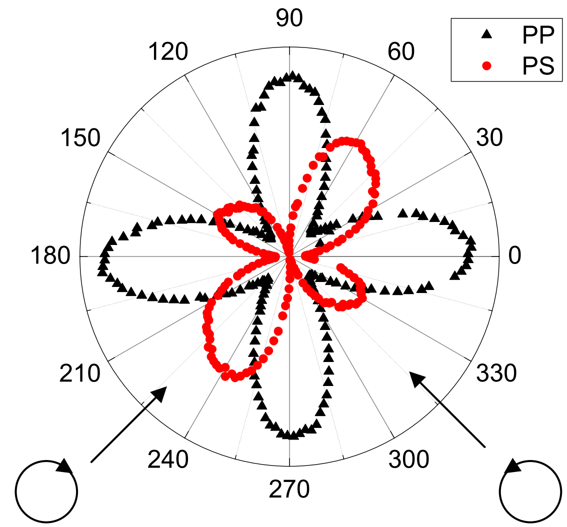
Spectroscopic SHG setup

Chirality with SHG

Fixed polarizer rotating analyzer:

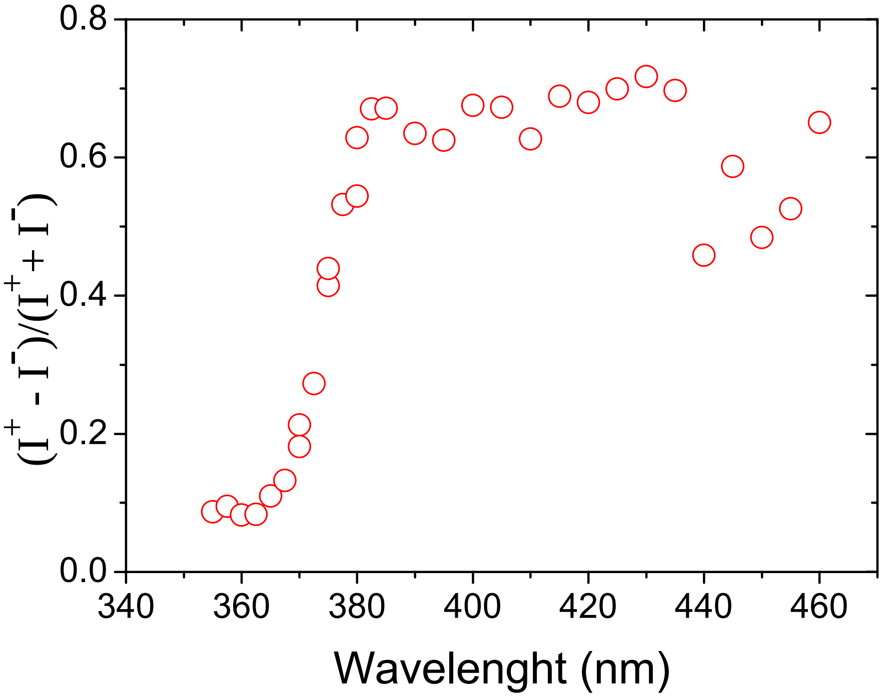


Fixed polarizer and analyzer, rotating a λ/4 wave plate:



Using different polarizer-analyzer combinations, we can successfully address the chiral tensor components of the nonlinear susceptibility.

SHG ellipticity at different wavelengths



SHG ellipticity is much more sensitive to chirality than linear processes.

Conclusions

– Nanoparticles exhibit a large Faraday rotation, which we can investigate spectroscopically.

– SHG ellipticity has been spectroscopically measured as part of a study on the Kroning-Kramers relationship between SHG ellipticity and SHG optical rotation.

– Besides their intrinsic interest, both Faraday and SHG spectra can provide valuable insight into the structures of molecular and nanomaterials.

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People involved