Switching Faraday rotation on a molecular level

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ABSTRACT

In this work we present measurements of the switching of the Faraday effect in metal-organic compounds. Faraday rotation is the rotation of the plane of polarization of linearly polarized light under the influence of a magnetic field in the direction of propagation of the light. It is the magnetic equivalent of circular birefringence and is related to magnetic circular dichroism via the Kramers-Kronig transformation. The Faraday effect is used in optical isolators and magnetic sensors.

Faraday rotation and magnetic circular dichroism spectra have been calculated and measured for various nanoparticles, nanocomposites, magnetic fluids and metal-organic complexes. These measurements and calculations indicate that it is possible to change the magneto-optical response by changing the state of the molecule, such as a change in protonation or oxidation state. The molecular environment also influences the magneto-optical spectra of metal-organic complexes and organic molecules. Thus it is possible to change the Faraday rotation spectrum by modifying the molecular environment or the molecule itself. We have measured the reversible switching of the magneto-optical response by these principles. This easily induced reversible switching opens the possibility of new devices such as switchable optical isolators.

Keywords: Faraday rotation

1. INTRODUCTION

Faraday rotation is the rotation of the polarization of light due to magnetically induced circular birefringence, induced by a magnetic field parallel to the propagation of the light. It was discovered by M. Faraday,¹ and can be described by the formula

$$\theta = VBL \quad (1)$$

Where θ is the rotation of polarization, B is the amplitude of the magnetic field parallel to the propagation of light, L is the length of propagation through the magnetic field and V is the Verdet constant expressed in $\text{deg. T}^{-1}\text{m}^{-1}$, a material parameter.

Faraday rotation differs from naturally occurring optical rotation in a key aspect: non-reciprocity. Upon reflection through a sample, natural optical rotation is canceled because it is reciprocal. Faraday rotation on the other hand is non-reciprocal, and as such rotation accumulates upon multiple reflections through a sample. This advantage is important in the associated applications, and is a very useful feature for the measurement of Faraday rotation. By measuring the Faraday rotation after an even number of reflections through a sample, reciprocal effects cancel out, leaving only non-reciprocal effects such as Faraday rotation. Additionally, these effects are amplified in magnitude by the number of times light has traveled through the sample, facilitating the measurement and application of these effects.

Faraday rotation is employed in a broad range of applications such as optical isolators,² magnetic field sensors,³ current sensors⁴ and displacement sensors.⁵ It can also be used to acquire information on the structure of magnetic materials,⁶ quantum dots⁷ and semiconductors⁸ or to derive information about the structure of the universe;⁹ this is possible due to the relative simplicity yet high precision of the measurement of Faraday rotation.¹⁰ All of this knowledge and these applications rely on knowledge of the Verdet constant.

The Verdet constant, V , is a wavelength dependent material parameter. Organic materials have relatively small Verdet constants in regions far from resonance, typically hundreds of degrees per Tesla per meter in the

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visible wavelength region, displaying a quadratic decline towards longer wavelengths.^{11–14} In contrast to typically diamagnetic organic materials, para- and ferromagnetic inorganic materials such as iron oxide films, ferrofluids¹⁵ or iron garnet films¹⁶ display Verdet constants in the visible wavelength region on the order of millions of degrees per Tesla per meter.

Magnetic circular dichroism (MCD) is a difference in absorption between left- and right-hand circularly polarized light due to a magnetic field parallel to the direction of the propagation of light. While natural circular dichroism (NCD) requires a lack of inversion centers and mirror planes at a molecular level, MCD does not have these requirements and can be present in all materials. It is mainly used for characterization, providing an excellent fingerprinting capability. The main advantages of MCD compared to standard absorption spectroscopy are the bisignate nature of MCD and the more stringent selection rules, which provide greatly enhanced resolution.¹⁷ The disadvantages are that the material must contain magnetically active components. A recent example of MCD in analysis is the use of MCD to analyze quantum effects in single molecule magnets.¹⁸ Additionally it is frequently used to characterize and analyze metallo-proteins, amongst others providing indispensable information on the spin and oxidation states of heme groups.¹⁷

In this work we present measurements of the reversible switching of the magneto-optical response in solution. These data can be extended to further research on electro-chemical switching of magneto-optical response. This allows for novel, reversibly switchable magneto-optical devices.

2. EXPERIMENTAL DETAILS

The investigated solutions were made by dissolving $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, purchased from Sigma Aldrich, in MilliQ water. Acidification of the solution was achieved by adding 37m% HCl solution, and neutralization was achieved by adding KOH solution.

In order to spectrally measure both Faraday rotation and MCD, a laser driven light source (LDLS) was employed (Energetiq LDLS EQ-99). The generated light was focussed into a Cornerstone 260 1/4 m monochromator which was operated by a computer. The slits were chosen such that the resulting beam had a full width half maximum of approximately 2 nm. Subsequently the collimated beam was sent through a linear polarizer, followed by a photo-elastic modulator (PEM) with its axis oriented at 45° respective to the polarization of the light. The light then passed through a 2 mm optical quartz cuvette in a 1 Tesla DC magnet with magnetic field in the direction of the propagation of light. After passing through a polarizer which polarized the light perpendicular to the axis of the PEM, the light was collected by a photomultiplier tube (PMT). The electrical signal generated by the PMT was fed into two separate lock-in amplifiers. The operating frequency (approximately 50 kHz) of the PEM served as reference frequency in the lock-in amplifier (Stanford Research Systems SR830) for the circular dichroism measurements, and the second harmonic of the operating frequency served as the reference frequency in a second lock-in amplifier for the optical rotation measurements. The measured lock-in values were read in by a personal computer.

In order to analyze the resulting signal, it is necessary to analyze the Mueller matrices of the optical components. The derivation is beyond the scope of this paper but can be summarized by the fact that the signal at the reference frequency of the PEM is proportional to the circular dichroism present in the sample while the signal at the second harmonic of the PEM reference frequency is proportional to the optical rotation. By measuring both values for multiple discrete magnetic fields it is possible to extract the magnetic circular dichroism and the Faraday rotation.¹⁹ Dividing the Faraday rotation by the pathlength of the sample results in the Verdet constant.

With knowledge of either the Faraday or MCD spectrum of a material, it is possible to use the Kramers-Kronig relations in order to calculate the other spectrum.²⁰ This is only exact if one of the two magneto-optical spectra is known from $0 \rightarrow \infty$ nm, which is not the case here; as such both spectra were measured. Despite this it is possible to obtain qualitatively satisfactory spectra using correct boundary conditions.

Figure 1. Absorption, MCD and Faraday rotation spectra of a 0.42M aqueous solution of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$. Neutral is a solution in MilliQ water and Acid is a solution in 18.5m% HCl.

3. RESULTS - TODO MOLAR ELIPTICITY UNITS

Figure 1 displays the absorption, MCD and Faraday rotation spectra of a 0.42M aqueous acid and neutral solution of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ from 350 nm to 850 nm. These spectra respectively correspond to the spectra of the CoCl_4^{2-} ion and the $\text{Co}(\text{H}_2\text{O})_6^{2+}$ ion. While both of these ions are d7 systems, the first is present in a tetrahedral configuration and the second is present as an octahedral complex. Despite the fact that the CoCl_4^{2-} ion is distorted from a perfect tetrahedral configuration, the resulting splitting is sufficiently small to neglect in the further analysis of the spectrum.²¹

Four clear bands can be seen in the absorption spectrum of the solution acidified by addition of concentrated HCl, with another band appearing as a slight shoulder on the stronger bands at approximately 605 nm. While the strong band at approximately 525 nm is present in both complexes, all the other bands disappear upon complexation with water.²²

In order to explain the MCD spectrum of the CoCl_4^{2-} complex, it is necessary to analyze the energy diagram of the complex. This energy diagram is depicted in Figure 2.

Figure 2. Energy level diagram for CoCl_4^{2-} .

Figure 3. Demonstration of the reversible switching of Faraday rotation and MCD for a $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ solution. Left axis is the MCD at 690nm and right axis is the Faraday rotation at 710nm. The sample was switched from neutral to acid twice with concentrated HCl, returning to the original Faraday rotation and MCD values.

The observed MCD transitions, besides the band at 525 nm, can all be assigned to transitions to $^4\text{T}_{1\text{P}}$ in the CoCl_4^{2-} complex. The band at 690 nm corresponds to the $5/2 \text{ U'}$ transition and the band at 660 nm to the E'' transition. The band at 620 nm corresponds to both the $3/2 \text{ U'}$ and the E' transition, which can not be resolved with the employed experimental setup. Most of the measured MCD originates from a C term²³ which is associated with a degenerate ground state without spin-orbit coupling and an excited state with spin-orbit coupling.

The observed Faraday rotation can be ascribed to the same transitions that cause the MCD. However, the intensities of the transition are different, and can not be accurately predicted by using the pure crystal field theory employed to explain the MCD spectrum.²⁴ To fully explain the intensities it is necessary to include molecular orbital theory, which is beyond the scope of this paper which demonstrates preliminary results on the ability to switch the magneto-optical response of materials.

Finally, with the obtained understanding of the (magneto-optical) spectra of both complexes, it is possible to exploit the differences in their spectra for the purpose of switching magneto-optical response. This is demonstrated in Figure 3.

By changing the concentration of HCl in the solution, it is possible to change the predominant complex present. This changes the magneto-optical response of the solution correspondingly. The CoCl_4^{2-} complex shows strong magneto-optical response in the 690 nm to 710 nm range, while the $\text{Co}(\text{H}_2\text{O})_6^{2+}$ complex displays no magneto-optical response in this region. Addition of concentrated HCl changes the predominant complex to the CoCl_4^{2-} complex, resulting in stronger Faraday rotation at 710 nm and a strong MCD response at 690 nm. Neutralizing the solution returns the balance to the $\text{Co}(\text{H}_2\text{O})_6^{2+}$ complex, effectively removing the magneto-optical response in this wavelength range. Crucially, subsequent addition of HCl returns the magneto-optical response to the same magnitude it was before. This indicates that the switching is reversible, an important characteristic for applications. This reversible switching is present in both the MCD and Faraday response. While this simultaneous switching may be desirable in certain applications, it would be interesting in future research to use transitions that are mainly active in either absorption or optical rotation, allowing a separation of both magneto-optical effects.

4. DISCUSSION AND PERSPECTIVES

It is possible to change the magneto-optical response of a material by changing its state, such as a change in protonation, oxidation or complexation state. In this work we present measurements of the switching of the

Faraday effect and MCD in aqueous solutions of cobalt complexes. We have measured the reversible switching of the magneto-optical response of cobalt complexes by acidification of the solution and addition of chlorine ions, and conversely by neutralization of the solution. This easily induced reversible switching opens the possibility of novel devices such as switchable optical isolators. Such devices would allow the variation of optical isolation purely by changing the molecular environment or state.

We have used the acidity of the solution and chlorine concentration to switch the magneto-optical response of cobalt complexes. While interesting as a first step towards tunable magneto-optical response, this is not practical in a device/application context. However, it is possible to extend this methodology to redox reactions. Future work will focus on using redox chemistry to switch magneto-optical characteristics. Cobalt complexes are an excellent initial system to investigate. Cobalt can exist stably in solution in both the 2+ and 3+ oxidation state, depending on the solution characteristics. By applying an oxidative potential to a solution of Co^{2+} it can be oxidized to Co^{3+} . This oxidation can occur purely by applying an electric potential to the present electrodes, and does not require any physical handling. This is ideal for applications such as optical isolators, which cannot be moved during operation without detrimental effects for their application. An extra advantage to an electrochemical approach is that much previous research exists on switching metal-organic compounds and the resulting changes in (nonlinear) optical activity.²⁵ These compounds are known to have good nonlinear optical properties and excellent reversibility upon switching. The extended conjugated electrons, coupled to a magnetically active redox active center provide optimal conditions for observing and switching magneto-optical activity. Consequently, in the future, their nonlinear magnetic properties could be studied with magnetization-induced second harmonic generation²⁶ a broadly applicable technique²⁷ which is sensitive to magnetization down to a single magnetic monolayer²⁸ when carefully measured.²⁹

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