

# A C Faraday Rotation of Aqueous Iron (III) Chloride

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Despite the many applications of Faraday Rotation (FR) in optics and communications, the significance of this magneto-optic effect in chemical analysis has not been fully explored. This study seeks to assess the effectiveness of FR in learning about the principles of chemical equilibrium and reaction kinetics. The dependence of the Verdet constant on the concentration of FeCl<sub>3</sub> in aqueous solution was investigated at 633 nm using Alternating Current (AC) FR. The AC technique, which has been used in several other studies, utilizes lock-in detection which allows for the reliable determination of exceedingly small rotation angles, which in turn can be used to determine the Verdet constant of a given sample. The Raman spectra of each sample was also collected using an excitation wavelength of 785 nm. The FR results showed the solution changing from a diamagnetic state to a paramagnetic state, and identified the magnetic transition concentration to be about 1.5 M. The data also showed that the Verdet constant deviates slightly from a linear dependence on solution concentration, suggesting that the relative concentration of species is complex even for simple compounds. Basic Raman spectral analysis confirmed the growth of paramagnetic species, but was not able to detect nonlinearity as clearly as FR. We conclude that FR, when used in conjunction with a well-established technique such as Raman spectroscopy, has the potential to contribute useful complimentary data for chemical analysis.

## INTRODUCTION

The phenomenon of Faraday Rotation (FR) has been known for its technological and fundamental significance for a significant amount of time (Slack 1934). It is observed as the rotation of the electric field vector of a linearly polarized light beam as it propagates through a medium in a magnetic field, which is applied along the direction of propagation. It arises from magnetically-induced circular birefringence in which right-hand and left-hand circularly polarized optical field components propagate through the medium at different rates, due to differing indices of refraction. The result is a net rotation of the light's plane of polarization. The amount of rotation is given by

Equation 1

$$\theta = lBV$$

**Eq. 1:** The angle of rotation of the light's plane of polarization as it traverses the medium

where  $l$  is the length of the medium,  $B$  is the magnetic flux density, and  $V$  is a material-specific constant called the Verdet constant (Buckingham and Stephens 1966). This constant is strongly dependent on the optical wavelength, but at any given wavelength, it can vary widely depending on the magnetic properties of the medium.

Materials with a quantifiably large Verdet constant have varied applications as optical isolators, modulators, and magnetic

field sensors, among other uses. However, few studies have investigated FR in the context of the chemical environments of solutions. Using a pulsed magnetic field setup and an Alternating Current (AC) field technique, aqueous solutions of lanthanide(III) ion and iron(III) chloride as well as a number of organic solvents have been studied (Miyamoto et al. 2009; Aloke et al. 1999). Ferromagnetic solids, when investigated using FR, yield large rotations. Most chemical solutions, conversely, exhibit a predominance of paramagnetic and diamagnetic behavior, and the resulting rotation is relatively small for visible light far from absorbance peaks (non-resonant FR). In order to accurately measure such rotations, recent efforts have focused on a technique employing a resonant resistor, inductor, and capacitor (RLC) circuit driven by an AC signal (Aloke et al. 1999). Using this technique in conjunction with Raman spectral analysis, our novel study attempts to connect FR data to an established method of chemical analysis, and to explain results in terms of chemical equilibrium. In this study, we show that an AC FR technique can be used to precisely measure and distinguish between the Verdet constants of varying concentrations of aqueous FeCl<sub>3</sub>. As FeCl<sub>3</sub> concentration increases, we hypothesize to see evidence of a change in the solution's dominant magnetic behavior from diamagnetism (due to water molecules) to paramagnetism, characteristic of Fe<sup>3+</sup> ions. This evidence would be displayed as a change in the sign of the Verdet constant, because optical rotation through diamagnetic materials is in the opposite direction from rotation through paramagnetic materials. Further, we show that this technique has the potential to recognize changes in chemical speciation where Raman spectroscopy does not indicate differences as clearly. In our view, this strongly suggests that FR can play a useful role as a complimentary technique in chemical analysis.

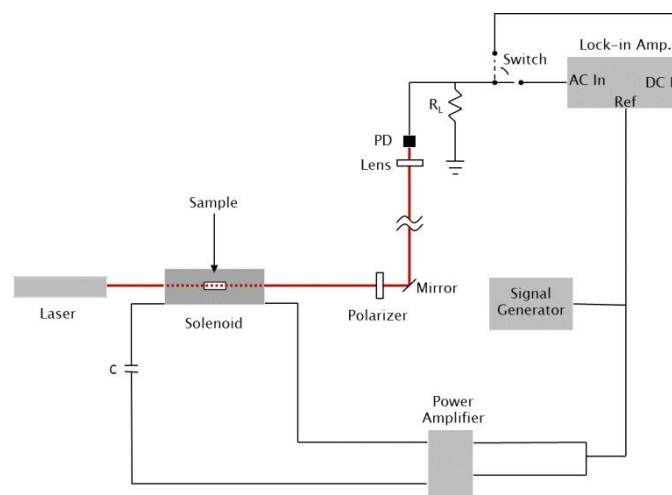
## METHODS AND MATERIALS

The experimental set-up for measuring FR is presented in Fig. 1. A polarized 1.5 mW He-Ne laser (JDS Uniphase) operating at 633 nm was directed at a sample resting in a 710-turn solenoid

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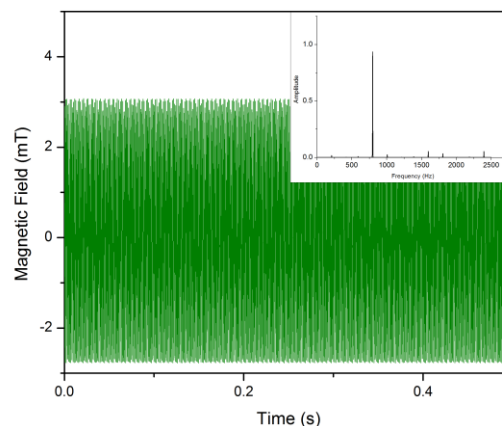
that was approximately 2.0 inches in diameter. The solenoid was part of a series RLC resonance circuit with a capacitance of 30  $\mu\text{F}$  and an inductance of 1.3 mH; thus, the magnetic field generated was oscillatory. The power curve for the circuit indicated a broad maximum of approximately 800 Hz. Hence, the circuit was driven close to 800 Hz by a sinusoidal signal from a function generator (Wavetek) amplified by a 120-watt power amplifier. The magnetic field was measured with a longitudinal Hall probe to verify that its frequency of oscillation matched that of the function generator. Fig. 2 displays a sample profile of the field taken over 0.5 seconds at a drive frequency of 798 Hz, and the inset provides a fast Fourier transform of the field data characterizing the field by a primary peak matching the drive frequency within  $\pm 0.1\%$ .



**Fig. 1** Experimental set-up used in measuring AC Faraday rotation. Oscillating the magnetic field at a high frequency lifted the rotation signal out of the background noise so that the lock-in amplifier could detect its amplitude. This method of detection requires the frequency of the driving signal, which the lock-in is using as a reference, to match the frequency of the signal being measured.

As light propagated through the sample, its polarization vector rotated according to Eq. 1, and because the magnetic field was oscillating, the direction of rotation also oscillated in response to the field. Next, a polarizer set at 45 degrees with respect to the laser's axis of polarization translated the oscillating rotation of the light into an oscillating intensity. This oscillating intensity signal was measured by a photo detector (Thorlabs, DET 110) as corresponding oscillating current amplitude. The signal was then sent to a lock-in amplifier (Model SR830 DSP) which could be configured to measure either the constant Direct Current (DC) component of the intensity or the Root mean square (RMS) amplitude of the AC component depending upon the position of a switch. Researchers have previously shown how the rotation amplitude can be calculated from the ratio of the signal's AC amplitude and DC component (Aloke et al. 1999). It should be noted that

measuring both the AC and DC components of current from the same instrument circumvents the issue of impedance mismatch between the lock-in and a separate DC meter. This mismatch can be resolved by utilizing a large resistor common to both the AC and DC detection circuits, so that net resistance in each circuit will be nearly the same. However, resistances that are too large become a source of thermal noise.



**Fig. 2** Magnetic field characterization taken over 0.5 sec for a drive frequency of 798Hz. Field strength is plotted against time to verify that it is oscillating with constant amplitude at the circuit's drive frequency. Inset: FFT analysis gives a primary peak at 797.1 Hz which matches the drive frequency to within 0.1%.

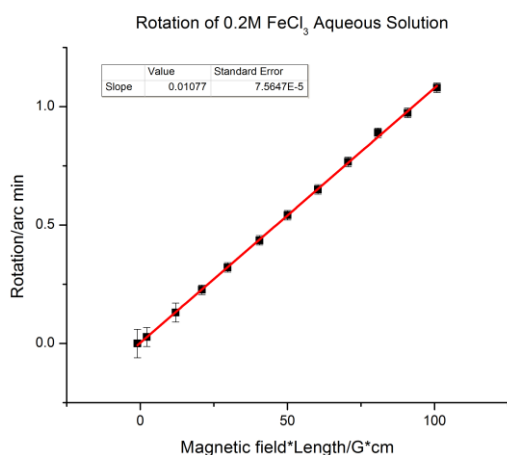
Seven aqueous  $\text{FeCl}_3$  solutions were measured using the set-up described above. They varied in concentration from 0 to 3.0 M, where the 0 molar solution was the water used as the solvent in the other solutions. High-purity water with a resistivity of 18 Mohm  $\cdot$  cm<sup>-1</sup> was used in all measurements. The Verdet constant of each solution was determined as the slope of the line formed when several rotation amplitudes were plotted against the product of magnetic flux density and sample length (slope of  $\theta$  vs.  $B l$ , as per Eq. 1). Fig. 3 shows a sample rotation plot for 0.2 M  $\text{FeCl}_3$ .

Raman measurements were performed with a spectrometer (Kaiser RAMANRX1<sup>TM</sup>) equipped with an MR Probe filtered probe head. The excitation wavelength was 785 nm (near-IR diode laser). Spectra of aqueous  $\text{FeCl}_3$  solutions were acquired using a laser power of 350 mW. Integration times were on the order of 10 s, and 30 to 50 spectra were averaged to provide a good signal-to-noise ratio.

## RESULTS

The Verdet constants of seven different molar concentrations of aqueous  $\text{FeCl}_3$  are shown in Fig. 4. The horizontal line marks the

point where the Verdet constant is zero, and the solution changes from diamagnetic to paramagnetic. Five Raman spectra were collected for the aqueous solutions of FeCl<sub>3</sub> of varying concentrations. Fig. 5 shows the band centered at ~314 cm<sup>-1</sup>, which is attributed to the FeCl<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub><sup>+</sup> octahedral species.



**Fig. 3** Optical rotation through a 0.2 M aqueous FeCl<sub>3</sub> solution is plotted against the product of magnetic field and the optical path length. From the relation  $\theta = lBV$ , the Verdet constant is the slope of this graph. This plot and most of the plots for other FeCl<sub>3</sub> concentrations give a Verdet constant with an uncertainty in the third or fourth significant digit.

## DISCUSSION

Over the range of concentrations studied, we expected to observe the magnetic behavior of these aqueous FeCl<sub>3</sub> solutions to change from diamagnetic to paramagnetic. This observation came in the form of a change in the sign of the Verdet constant in Fig. 4. This sign change occurs when FeCl<sub>3</sub> concentration is close to 1.5 M, exhibiting the same trend as in data published for FeCl<sub>3</sub> at 670 nm (Aloke et al. 1999). This switch from positive to negative Verdet constant occurs when the influence of the paramagnetic species in solution becomes stronger than diamagnetic effects of water.

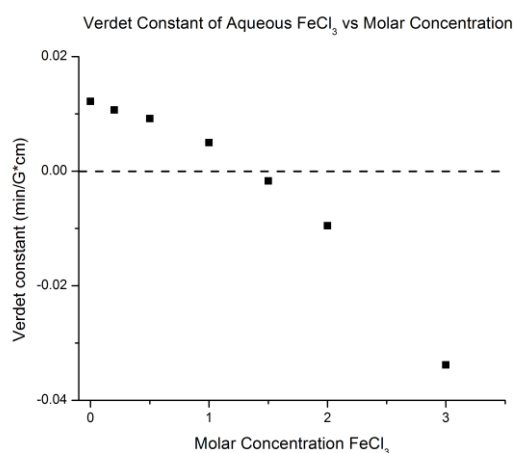
In a paper, Marston and Bush (1972) concluded that the predominant equilibrium of FeCl<sub>3</sub> in concentrated aqueous solution is represented as follows:



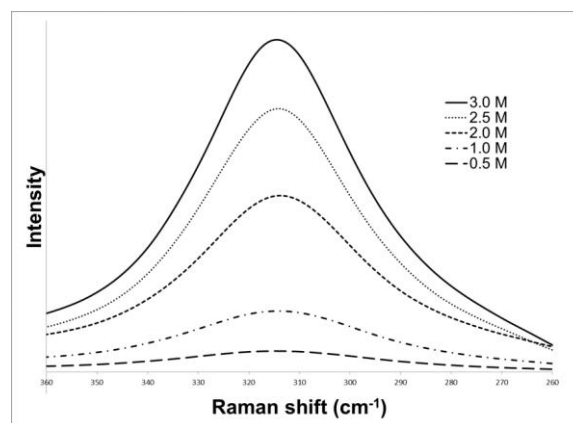
**Eq. 2:** The chemical equilibrium in aqueous iron (III) chloride solution

where  $n$  refers to the number of water molecules coordinating around the FeCl<sub>2</sub><sup>+</sup> ion (usually 2 to 4). Candidates for other species which may be present in lower numbers, but are not

expected to have much contribution to FR, include H<sub>3</sub>O<sup>+</sup> and Cl<sup>-</sup>. If Eq. 2 describes the equilibrium for solutions of any concentration of FeCl<sub>3</sub> and identifies the dominant species present, one would expect to see a linear change in the Verdet constant as more FeCl<sub>3</sub> is added. This expectation arises because even if the three species have differing magnetic properties, the ratio between them at a state of equilibrium remains the same for all molar concentrations of the starting materials. However, Marston and Bush also concluded that the relative presence of FeCl<sub>4</sub><sup>-</sup> ion may increase as more FeCl<sub>3</sub> is added, and their data suggests (although not conclusively) that by the time the solution reaches a concentration of 3.0 M, the equilibrium position has shifted towards the right-hand side of the equation.



**Fig. 4** The Verdet constant is plotted as a function of FeCl<sub>3</sub> concentration. The Verdet constant changes sign at around 1.5 M indicating a transition in the solution from diamagnetic to paramagnetic. Also, the decrease of the Verdet constant appears to be nonlinear, especially in the first half of the curve.



**Fig. 5** The Raman spectral band centered at ~314 cm<sup>-1</sup> for five concentrations of aqueous FeCl<sub>3</sub>. This band is attributed to the Fe(H<sub>2</sub>O)<sub>4</sub>Cl<sub>2</sub><sup>+</sup> octahedral species. The increase in peak intensities indicates an increase in the presence of Fe(H<sub>2</sub>O)<sub>4</sub>Cl<sub>2</sub><sup>+</sup>, but does not definitively show a deviation from a linear dependence on aqueous FeCl<sub>3</sub> concentration.

The left-hand side of Eq. 2 represents hydrated  $\text{FeCl}_3$ , a species that exhibits a weak diamagnetic behavior. We believe that this weak diamagnetism is a result of the water molecules coordinating around  $\text{FeCl}_3$  and suppressing iron's paramagnetic contribution. The same argument leads us to believe that  $\text{FeCl}_2(\text{H}_2\text{O})_n^+$  ion is also weakly diamagnetic, or at the very most, weakly paramagnetic. The species that contributes to the majority of the solution's magnetism is  $\text{FeCl}_4^-$  ion. Because  $\text{FeCl}_4^-$  does not have water molecules coordinating around it, the paramagnetism of the  $\text{Fe}^{3+}$  ion is expressed more strongly, making this species paramagnetic. Assuming a constant equilibrium, the net magnetic contribution of these species scales linearly with the concentration of aqueous  $\text{FeCl}_3$ . This accounts for the right half of the plot in Fig. 4, which depicts a negative linear trend in the Verdet constant with increasing concentration of aqueous  $\text{FeCl}_3$ .

Until an approximate concentration of 1.5 M, the Verdet constants in Fig. 4 appear to show a nonlinear decrease with concentration. This suggests that the relative concentration of species contributing to diamagnetic (mostly water) and paramagnetic behavior is not simple when the overall concentration of  $\text{Fe}^{3+}$  ions is low. One possible explanation we hypothesize is that below a concentration of 1.5 M, the equilibrium ratio between the species in Eq. 2 shifts to favor products as concentration increases. This would be consistent with the previous findings of Marston and Bush, and would result in an accelerated production of the paramagnetic  $\text{FeCl}_4^-$  ion, causing the Verdet constant to move towards negative values at an increasing rate. Because this nonlinearity disappears at an approximate concentration of 1.5 M, the equilibrium ceases to shift at this concentration, and the value of 3.0 M cited by Marston and Bush as the end of the equilibrium change can be revised to a value half as large.

Error in the Verdet constants presented in Fig. 4 arises from the uncertainty in the magnetic field, the cell length, and the DC and AC signal intensities. However, the same cell and magnetic field calibration was used for every sample, so the relative uncertainty between these Verdet constants can be seen as due to error in the DC and AC signal measurements. This uncertainty is determined from the error in the slope of the linear fit used to obtain each Verdet constant, and is typically on the order of one to three percent. Additionally, multiple measurements of identical samples have given Verdet constants which match within the uncertainty of the measurement.

The Raman spectral band in Fig. 5 indicates, through relative peak intensities, an increasing presence of  $\text{FeCl}_2(\text{H}_2\text{O})_4^+$  with increasing aqueous  $\text{FeCl}_3$  concentration. Taken in conjunction with the molar coefficients in Eq. 2, these peaks also show how the presence of  $\text{FeCl}_4^-$  ion is increasing, and help verify that its increase is linear over the linear region of Fig. 4. However, they do not clearly show the deviation from the linear trend that FR was able to detect. A band attributed to  $\text{FeCl}_4^-$  was not studied directly because  $\text{FeCl}_4^-$  is not Raman active at the excitation wavelength used.

Raman spectroscopy can be used to monitor band

intensities of various  $\text{Fe}^{3+}$  species in solution, which can provide information about the relative quantities of these species as the concentration of aqueous  $\text{FeCl}_3$  increases. Further studies using Raman spectroscopy to probe additional  $\text{Fe}^{3+}$  species in aqueous solution will provide a more complete picture of  $\text{Fe}^{3+}$  speciation with increasing  $\text{FeCl}_3$  concentration. FR data, on the other hand, clearly identifies, through their change in sign, the concentration at which the diamagnetic or paramagnetic transition takes place in aqueous  $\text{FeCl}_3$ . While a more quantitative analysis of the magnetic behavior of aqueous  $\text{FeCl}_3$  solutions would require an in-depth quantum model, these two studies taken together offer a consistent picture as well as quantitative results that will contribute to the building of such a model. This study sought to assess the effectiveness of FR in providing details about chemical transitions, and our results suggest that its ability to track subtle changes in magnetism make it a viable technique for chemical analysis when used in conjunction with a well-established method such as Raman spectroscopy.

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