The Evolution of Magnetic Circular Dichroism as a Spectroscopic Method

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In the mid-19th century Faraday demonstrated that optical activity could be induced in matter by applying a magnetic field. Over the next 80 years, Faraday’s discovery was treated mostly as a curiosity rather than a useful tool for gathering information about a chemical species. By the 1930’s, quantum theory had advanced to the level where both the optical activity in a magnetic field and the observed Magnetic Circular Dichroism (MCD) effect could be qualitatively explained.\(^1\) It was not until the middle of the 20th century, however, that quantum theory was sufficiently sophisticated to be able provide quantitative expressions for MCD absorption spectra.\(^2\) As a result, MCD spectroscopy started to gain acceptance as a method to provide precise descriptions of the electronic structure of the ground and excited states of molecules. More recently there has been a shift away from the traditional absorbance MCD and toward X-ray Magnetic Circular Dichroism (XMCD). XMCD has the advantages of element specificity and minimal sample size required.\(^3\)

Fundamentally, MCD is similar to the circular dichroism exhibited by optically active molecules where right- and left-circularly polarized light are absorbed to different extents, resulting in an elliptically polarized wave. The difference in absorption, \(\Delta A\), is what is traditionally measured in circular dichroism spectroscopy. This differential absorption is also the key feature of MCD spectra. The distinct advantage of MCD over circular dichroism is that it does not require the absorbing material to be optically active. Instead, the application of a magnetic field splits the energy levels of the ground and excited states into their Zeeman sublevels. These split Zeeman levels provide the differential absorption characteristic of MCD, making it a universal phenomenon.\(^4\) This Zeeman splitting, combined with field-induced mixing of zero-field wavefunctions and the Boltzmann population of each sublevel, forms the full MCD spectrum. These three contributions to an MCD spectrum are generally evaluated separately; \(A_1\) terms are associated with Zeeman splitting, \(B_0\) terms with mixing of wavefunctions, and \(C_0\) terms are a temperature dependent measure of the Boltzmann distributions. Figure 1 provides examples of each type of MCD term and their associated absorption band shape. \(A_1\) terms are readily recognized by their derivative shape. Whereas \(B_0\) and \(C_0\) terms have similar shapes, they can be distinguished by the temperature dependence of \(C_0\) terms.

![Figure 1. Characteristic shapes of the three MCD band terms (top) and their associated absorption bands (bottom). From left to right: \(A_1\) term, \(B_0\) term, \(C_0\) term.\(^4\)](image-url)
Applications in Diamagnetic Compounds

One of the convenient aspects of MCD over more traditional absorbance spectroscopy is its ability to characterize molecules that are stable only in a solid matrix. An early example of MCD in this vein was the isolation of the Na\(^{−}\) ion in a solid NH\(_3\) matrix by Schatz and co-workers.\(^5\) By 1986 it had become widely accepted that Na\(^{−}\) did not exist in the purely monoanionic form in liquid NH\(_3\).\(^6\) The MCD spectrum of the solid matrix showed clear evidence of an A\(_1\) term, consistent with the formation of Na\(^{−}\). Computational analysis of the variable-temperature MCD spectrum provided further evidence that the observed transition was indeed from an isolated Na\(^{−}\) anion and not from other species, such as the Na\(^{+}\) -- e\(_{(s)}\) ion pair.

The first recorded MCD spectrum that confirmed the theoretical prediction that an A\(_1\) term could devolve into two B\(_0\) terms of opposite sign was provided by Mason in 1988 when he performed field-dependent MCD studies on mercury vapor.\(^7\) The theory that two B\(_0\) terms could arise from one A\(_1\) term was based on the relationship between the bandwidth of a given transition and the energy difference of the Zeeman split sublevels. At low applied fields (0.44 T) the spectrum of mercury vapor consists of one broad absorption band that coincides with a characteristically derivative-shaped A\(_1\) term in the MCD spectrum. As the applied field is increased (up to 6.16 T in this case) the energy difference between the Zeeman sublevels become sufficiently large such that the single absorption band splits into two symmetric bands with the corresponding appearance of two B\(_0\) terms of opposite sign in the MCD spectrum.

One of the most powerful capabilities of MCD arises from the dual-sign nature of the spectrum. This discriminating power allowed Jaw and Mason to confirm the absolute electronic structure of Pt\(_3(\mu\text{-CO})_3(P(\text{-}Bu)_3)_3\) in 1990.\(^8\) Extended Hückel calculations had provided a general picture of the electronic structure of this platinum complex but electronic absorption spectroscopy had been unable to provide concrete confirmation of these calculations. By calculating the expected sign of the MCD spectrum based on the proposed electronic structure Jaw and Mason were able to provide convincing evidence that the ordering of molecular orbitals proposed by the Hückel calculations was indeed correct.

Applications in Biological Systems

The ability of MCD to provide detailed information about the electronic structure of molecules has also been applied to biological systems. There are numerous reports of the use of MCD to verify the proposed electronic structure of various porphyrin systems.\(^9\) One of the more interesting reports comes from a study of the cis and trans isomers of an N-confused porphyrin encapsulating a copper atom (Figure 2).\(^10\) These porphyrins are considered confused because two of the pyrrole rings in the molecule are rotated such that a carbon atom coordinates to the metal center instead of the nitrogen atom. Upon recording the MCD spectra of these copper N-confused porphyrins it was observed that the MCD signal had a distinct positive to negative sign change when proceeding from low to high energy. This was opposite to what was observed in “non-confused” porphyrin systems where the sign of the MCD spectrum is negative for the lowest energy transitions and becomes positive for transitions of higher energy. Computational analysis of the frontier orbitals in both

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**Figure 2.** *cis*-N-confused copper porphyrin. R = C\(_6\)F\(_6\), R' = OEt.\(^10\)
confused and traditional porphyrin systems revealed an unusual $\Delta$HOMO-$\Delta$LUMO configuration in the confused porphyrin systems. By using this unusual electronic configuration, subsequent computations successfully reproduced the observed MCD spectrum, further confirming the ordering and degeneracy of the frontier orbitals in these porphyrin systems.

The high sensitivity of MCD has allowed, for the first time, detailed investigation of one of the intermediate species in the catalytic cycle in a Dimethyl Sulfoxide Reductase (DMSOR) active site in its fully intact enzyme form instead of in a truncated model compound. Coupled with EPR and computational studies, the MCD spectrum of the Mo(V) intermediate in the active site of DMSOR in *Rhodobacter sphaeroides* has allowed investigators to better understand the catalytic cycle that allows this enzyme to convert DMSO to dimethyl sulfide, a process that is important in the ecological cycle of many marine algae species.

**Applications in Magnetic Materials**

Recently, XMCD was used to explain the magnetic properties of a family of erbium metallofullerenes. The ability to tune the incident X-ray energy in XMCD experiments allows single-element selectivity, which was vital to this investigation. Previous investigations of paramagnetic metallofullerenes using more mainstream methods such as SQUID magnetometry were of limited use in characterizing these materials. The combination of very small quantities of samples available for testing and the large diamagnetic contribution from the fullerene cages made interpretation of the available data problematic. The combination of element selectivity and the intense synchrotron X-ray source allowed the contributions to the overall magnetic moment from the erbium atoms and the fullerene cage to be separated into their individual components. The investigation of the family of erbium metallofullerenes Er$_2$@C$_{82}$ (Figure 3), Er$_2$C$_2$@C$_{82}$, ErYC$_2$@C$_{82}$, and Er@C$_{82}$ revealed that there was no magnetic exchange between the Er$^{3+}$ ions enclosed in the dimetallofullerene cages. The antiferromagnetic interactions observed in Er@C$_{82}$ were attributed to exchange interactions between the unpaired spins that exist on the fullerene cage in the monometallic fullerene.

In summary MCD, and by extension XMCD, is a powerful spectroscopic tool that can be used to characterize a wide variety of compounds, from diamagnetic systems to complex proteins to magnetically dilute metallofullerenes. The sensitivity of MCD allows for the accurate determination of the electronic structure, and hence the physical properties, in cases where traditional electronic absorption spectroscopy cannot provide a clear answer. As access to synchrotron radiation has become more commonplace, the element-specific nature of XMCD has provided valuable insight into the electronics of systems that were difficult or impossible to study by more routine methods.

**References:**