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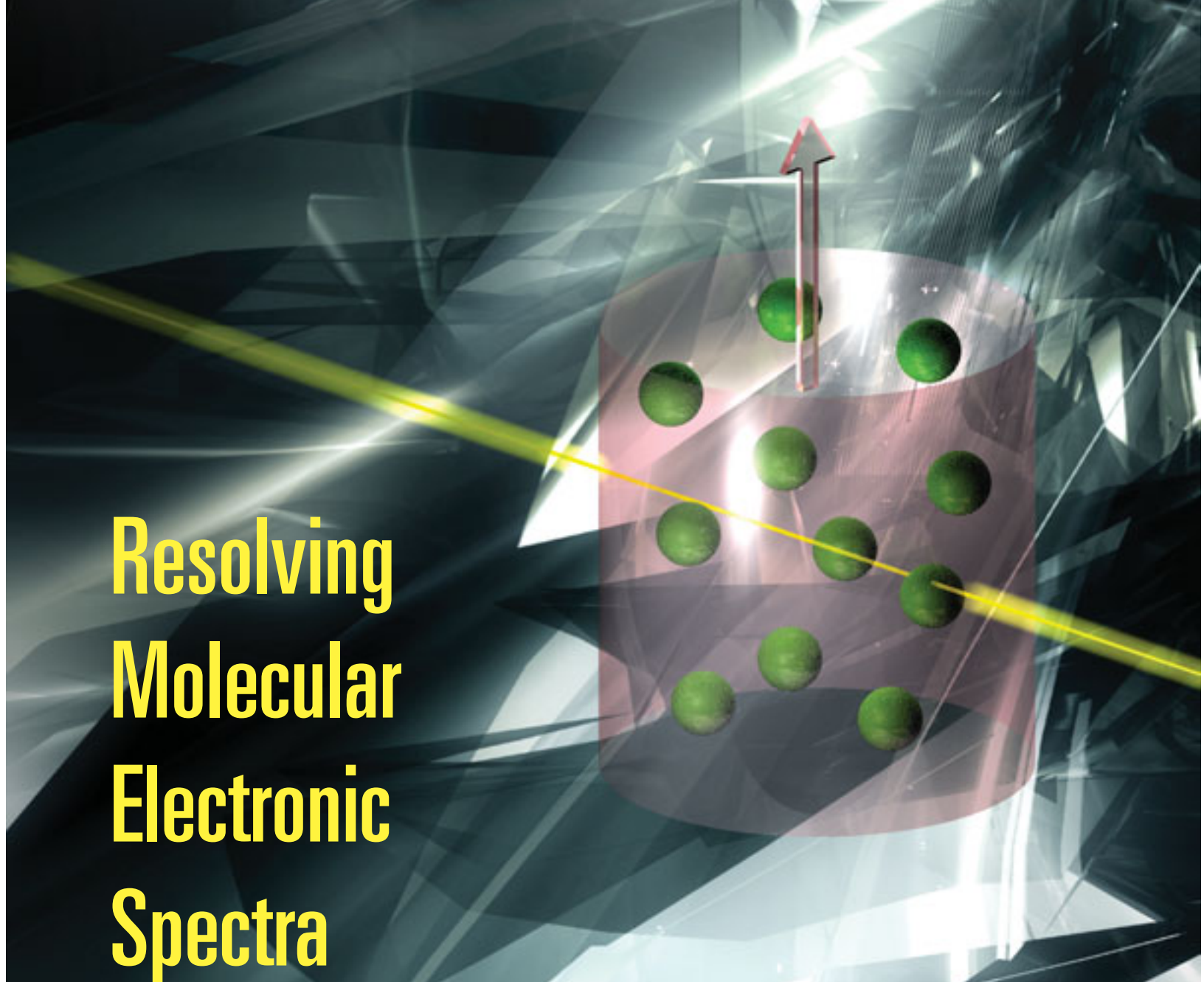
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Resolving Molecular Electronic Spectra

Using Magnetic Linear Dichroism

An old technique is rediscovered, but there is still much to be developed.

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Everybody reading this article is likely familiar with the principles of colorimetry, that is, quantitative determinations of molecular chromophores by electronic absorption spectroscopy. However, while analytically important, this remains a relatively trivial use of electronic spectroscopy—one can do a great deal better, although admittedly with more effort, in extracting the qualitative information inherent in an absorption spectrum. For example, the electronic spectra of transition-metal ions can provide important clues concerning the oxidation states, noncrystalline structures, number of discrete sites, and likely reactivities of the complexes, metalloproteins, and other materials in which they may be found. Furthermore, electronic spectroscopic methods are sensitive enough that the sites of interest need only be present in the
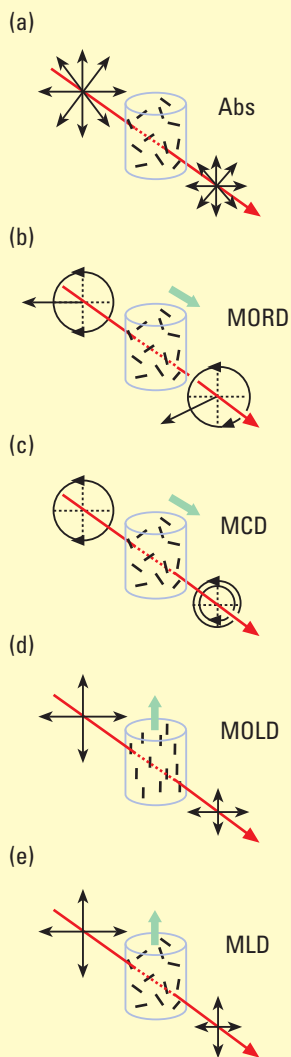
FIGURE 1. Relationship between various magneto–optical phenomena and electronic absorption spectroscopy.

Optical paths are indicated in red and, where appropriate, the direction of applied magnetic fields in green. Nonoriented and oriented chromophores in solution are represented by black rods in blue containers. (a) Absorption of randomly polarized ("unpolarized") light (Abs). (b) MORD is a rotation of the polarization plane of a linearly polarized light beam under the influence of a magnetic field that is parallel to the optical path. It is the only effect considered here that is observed throughout the spectrum, even in regions where the sample does not exhibit electronic transitions and results from a difference in the speeds of left and right circularly polarized light passing through the medium. (c) MCD is the difference in the absorption of left and right circularly polarized light induced by a magnetic field applied parallel to the light beam. (d) MOLD (also known as the Cotton–Mouton effect) occurs when a magnetic field is applied perpendicular to the light beam, causing alignment of the molecules in solution. This results in a difference in the absorption of light that is polarized perpendicular and parallel to the applied magnetic field. (e) MLD is also the differential absorption measured in a transverse applied magnetic field, but it arises from an ensemble of disoriented molecules. Rather than from molecular alignment, the true MLD (like MCD) is the result of a field-induced anisotropy in the electronic motions (Zeeman effect).

sample at trace levels, either as a constituent component, a contaminant, or a doped species deliberately introduced as a probe for some property of interest.

So, given these advantages, why for several decades has there been a gradual loss of interest and effort in this field, compared with virtually all other areas of spectroscopy? Although multiple answers to this question may exist, there has clearly been one seemingly insurmountable obstacle to progress. In general, chemically useful information, such as the site geometry or the nature of a derivative, is derived by analyzing the spectrum and identifying energies, relative intensities, and number of transitions under an observed spectral band. Such an analysis is often carried out implicitly by comparing the spectrum of the unknown with reference compounds in fingerprint fashion. Alternately, if suitable standard compounds are not available, the reference spectra may be constructed from theoretical considerations. The first approach is commonly used to identify unknown compounds by IR spectroscopy, whereas the second method is more likely to be applied when ^{1}H NMR is the primary analytical tool. Unfortunately, both approaches are of limited value with molecular absorption spectra, because these tend to exhibit broad bands, which are seldom rich in details that will reveal the underlying transitions.

It now appears that the general lack of resolution in molecular electronic absorption spectra can be overcome by the concerted application of magneto–dichroic methods. In such experiments, the difference between the absorptions of two alternating polarizations of a single light beam in an applied magnetic field is measured. There are two principal techniques, namely, magnetic circular dichroism (MCD) and magnetic linear dichroism (MLD). Note that MCD and MLD are properties of all matter and do not depend on special characteristics of the chromophore, such as asymmetry or orientation (required for natural CD and LD, respectively). Consequently, MCD and MLD are actually much more widely applicable than their nonmagnetic counterparts. Ironically, despite being just over a century old, MLD was ignored as a technique for molecular studies until recently. Indeed, some readers will already be familiar with the phenomenon as the basis of Zeeman background correction in electrothermal atomic absorption.

Historical perspective

In fact, a magnetic-field-induced LD can arise in molecular chromophores in one of two ways. Interestingly, these two phenomena are not really related, but have been confused in the literature. A short review of the relevant developments will serve to document the problem, explain the nature of the confounding effect, and introduce the basic experimental configurations (Figure 1).

1845: In September, Michael Faraday entered in his diary that he had spent the day passing a ray of polarized light through a piece of glass and had observed a rotation of the plane of polarization when he placed the two poles of a magnet on the same side of the ray. "And thus," he wrote, "magnetic force and light were proved to have relation to each other. This fact will most likely prove exceedingly fertile and of great value in the inves-

tigation of both conditions of natural force" (*1*). Today, we recognize this experiment as the first detection of a magnetic optical rotatory dispersion (MORD). This measurement, also known as magnetic birefringence, provides data directly related to MCD by mathematical transformation. Consequently, MCD experiments are often described as being performed in the "Faraday configuration", with the magnetic field aligned parallel to the light beam passing through the sample.

1875: The Kerr effect, which involves detecting field-induced birefringence with an applied field perpendicular to the light beam (*2*), was discovered. Although it is associated with an electric field, the effect of a perpendicular magnetic field was also subsequently examined, so we like to describe MLD experiments as being performed in the Kerr configuration.

Ca. 1900: Pieter Zeeman reported the magnetic circularly polarized and magnetic linearly polarized emissions of sodium atoms (*3, 4*). These experiments are simply the reverse of atomic MCD and MLD, respectively. Voigt published an early nonquantum mechanical theory of molecular MLD, drawing on the contemporary data of Majorana (*5–7*).

Cotton and Mouton demonstrated a magnetic orientational linear dichroism (MOLD) associated with certain colloids (*8, 9*). In this case, a magnetic field was used to align the samples, and the oriented colloidal particles exhibited a natural LD. They went on to show that Voigt's theory described a phenomenon that was either nonexistent or too weak to measure. It is important to realize that the Cotton–Mouton effect, or MOLD, is fundamentally different from the intrinsic MLD featured in this article. MLD is a consequence of the Zeeman effect and arises from nonoriented samples. Unfortunately, this distinction has been completely lost on many reviewers and writers of textbooks.

The 1960s: Interspersed between the end of Queen Victoria's reign and the arrival of *The Beatles,* several dozen studies of the Faraday effect in transition-metal ions and organic chromophores emerged. For technical reasons, these were mostly MORD rather than MCD measurements. Nevertheless, by this time, Buckingham and Stephens had already reviewed the existing literature and published a theoretical interpretation of molecular MCD (*10*).

An immediate surge in the number of reported MCD studies followed the publication of the Buckingham and Stephens theory—so much so that after only three years, Schatz and McCaffery felt the need to review the situation again (*11*).

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This pattern of reviewing the MCD literature every few years has been repeated up to the present. In sharp contrast, early papers reporting the MLD of lanthanide ions were only just beginning to appear (*12, 13*), trailing the parallel development of MCD and MORD spectroscopy by ~60 years.

1985: Almost 90 years after Zeeman first carried out emission measurements in Faraday and Kerr configurations, Vala used matrix isolation techniques to clearly show for the first time that the information contained in atomic MCD and MLD was different and complementary (*14*). It is very probable that the discouraging results and comments of Cotton and Mouton had much to do with the lack of MLD activity for so long.

1999: Unaware of much of the earlier literature, but inspired by the efforts of Vala and associates, our group investigated the feasibility of performing MLD measurements on molecular chromophores and started to develop the necessary theory to interpret the spectra. Finally, we obtained reproducible spectra from nonoriented, frozen solutions of hemoprotein derivatives and showed two specific examples in which the information content of molecular MCD and MLD was different and complementary (*15, 16*).

Principles

To understand the complementary nature of MCD and MLD, it is easiest to consider the case of an atomic transition from the ground-state ^{1}P to an excited-state ^{1}S (Figure 2). Notice that we are dealing with "spin singlets" (indicated by the superscripted prefixes), that is, all of the intrinsic electron spins remain paired during the transition to give a net spin of 0 in both states. However, although the circulating motions of the electrons in the excited state combine to produce an "orbital singlet" (S implies the system quantum number L is 0), the ground state is an "orbital triplet" (P implies L is 1, which, in the presence of a magnetic field, splits into three levels: $M_L = 1$, 0, and −1).

In other words, electrons can move in three distinct orbits with respect to an applied magnetic field in the ground state. This, in turn, results in three induced magnetic moments coupling with the applied field to produce three levels of differing potential energy. On the other hand, only one pattern of orbital motion is available to the excited-state electrons ($M_L = 0$ only).

For strong (electric-dipole-allowed) transitions, the relevant spectroscopic selection rules are $\Delta M_L = \pm 1$ for MCD and $\Delta M_L = 0, \pm 1$ for MLD (*15, 16*).
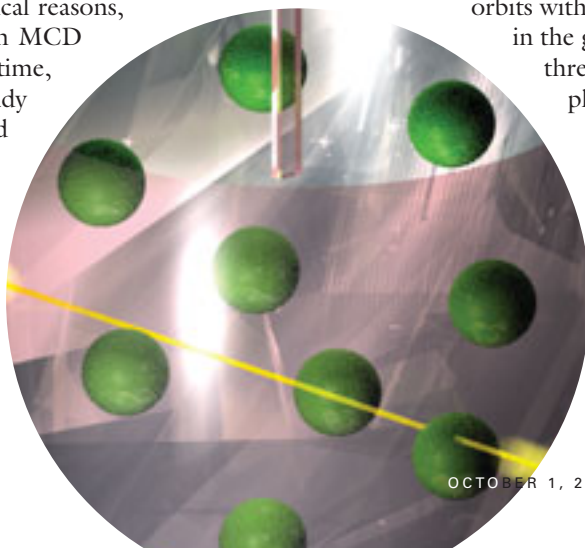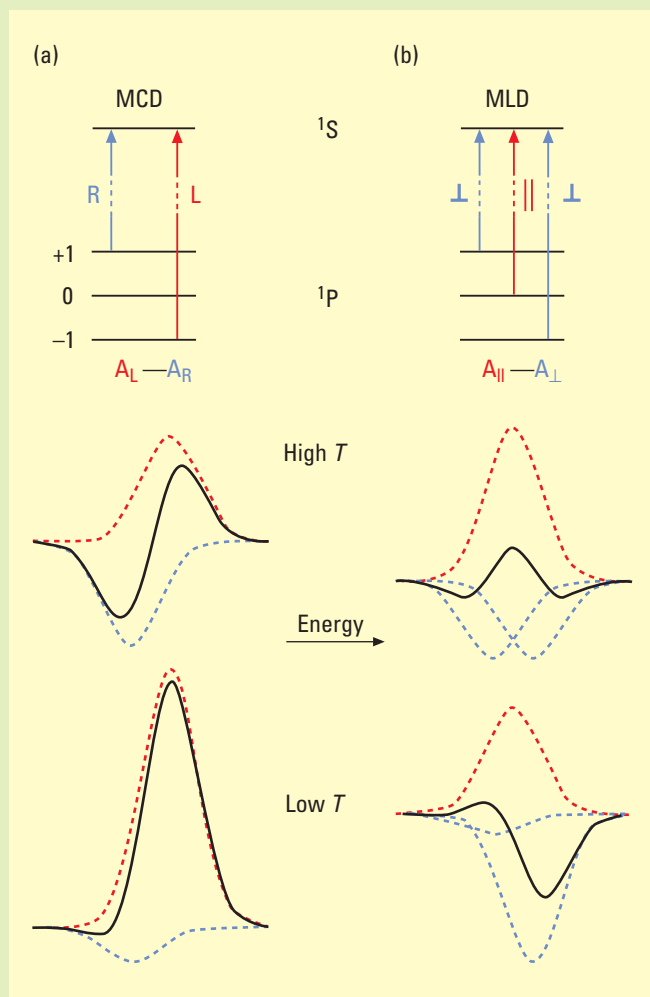
FIGURE 2. Simple atomic examples of (a) MCD and (b) MLD arising from an electric-dipole-allowed transition from an orbital triplet (P $\Rightarrow$ M_L = +1, 0, –1) to an orbital singlet (S $\Rightarrow$ M_L = 0 only).

The diagram is not to scale; the separation of the electronic ground and excited states is, in reality, orders of magnitude greater than the magnetic splitting between the ground-state magnetic sublevels. (a) Absorption of left circularly polarized light (A_L) corresponds to the transition where ΔM_L = +1, and absorption of right circularly polarized light (A_R) corresponds to the transition where ΔM_L = –1. Due to a Boltzmann distribution of the individual chromophores across the ground state, the signal $A_L - A_R$ will be a derivative at ambient temperatures and near Gaussian at cryogenic temperatures. (b) Absorption of parallel linearly polarized light ($A_\parallel$) corresponds to the transition where ΔM_L = 0, and absorption of perpendicular linearly polarized light ($A_\perp$) corresponds to the transition where ΔM_L = ±1. Due to a Boltzmann distribution of the individual chromophores across the ground state, the signal $A_\parallel - A_\perp$ will be a second derivative at ambient temperatures and approach a Gaussian band shape at cryogenic temperatures.

Thus, it can readily be seen in Figure 2 that more of the allowed transitions are incorporated into the MLD signal than are revealed in the MCD spectrum. Other very useful features of both types of spectra are the observed magnetic field and temperature dependencies. When the ground state is a manifold of split magnetic levels, it will be subject to a Boltzmann population distribution that depends on the temperature and magnitude of the applied magnetic field. Consequently, at ambient temperatures and typical present-day laboratory field strengths (<10 T), the sample will exhibit an approximately even population distribution in the ground state, leading to a first derivative-shaped MCD spectrum and a second derivative-shaped MLD spectrum (Figure 2). However, at cryogenic temperatures and strong fields (>1 T), most of the molecules in the sample will be in the lowest magnetic level, leading to near-Gaussian-shaped spectral bands in both cases.

In contrast to the energies of the orbitals belonging to the same shell in free atoms, the orbitals of the centers in molecular chromophores may differ quite considerably in energy. Under such conditions, the magnetic fields generated by the orbital motions of the electrons in molecules are smaller than those in atoms, an effect known as quenching, which leads to a weakening of the MCD and MLD signals. The quenching, however, is partly overcome by the large uncompensated magnetic fields generated by the unpaired electrons in molecules carrying intrinsic electronic spin, an effect called spin–orbit coupling. The theory that describes the magneto–optical properties of such systems is complex and beyond the scope of this article. However, the utility of the combined use of MCD and MLD spectroscopy in solving molecular problems can be demonstrated with the aid of two examples.

Relative sensitivities

In our group, the primary research thrust is the application of MCD and MLD for studying metalloproteins. We are usually confronted with samples that contain multiple, inseparable cofactors, most of which are involved in electron transfer and do not directly interact with substrates. Centers of this type tend to undergo single-electron transfers between two stable oxidation states, one diamagnetic (spin 0) and the other paramagnetic (spin 1/2). Chromophores with paramagnetic ground states (spin >0, i.e., with unpaired electrons) tend to exhibit strong signals at cryogenic temperatures due to an excess population in the lowest magnetic level.

Therefore, we invariably choose to work at ultralow temperatures if possible because of the considerable improvement in sensitivity. There is, however, a downside. Spin 1/2 chromophores, particularly oxidized cytochromes, yield such strong MCD spectra that they completely obscure signals from anything else. The problem is illustrated in Figure 3a, which shows the MCD spectra of ferricytochrome c (spin 1/2) recorded in the presence and absence of an equal concentration of deoxymyoglobin (spin 2). The spectrum of the ferricytochrome c clearly dominates.

We have demonstrated both experimentally and theoretically that paramagnetic chromophores with a single unpaired elec-

tron (spin 1/2) yield very weak MLD signals, compared with the MLD of systems with more than one unpaired electron (*16, 17*). This is particularly important because, quite often, substrate- or other ligand-binding centers in metalloproteins can be prepared in spin states >1/2, whereas the electron-transfer centers have spins 1/2. The significance of these observations is clarified in Figure 3b, which shows the MLD spectrum of deoxymyoglobin (spin 2) in the presence and absence of an equal concentration of ferricytochrome *c* (spin 1/2). Evidently, unlike MCD spectra, the MLD spectrum of the ligand-binding deoxymyoglobin completely dominates.

The spectra of Figure 3 illustrate the complementarity of MCD and MLD, each technique essentially detecting only one component of the sample. Unambiguous deconvolution of the electronic properties of substrate-binding sites in the presence of electron-transfer centers is thus clearly possible. A further noteworthy feature of the deoxymyoglobin MLD spectrum is that it was the first we ever measured for a molecular chromophore. Moreover, because the data were obtained at 4.2 K with a sample prepared as a frozen glass, chromophore reorientation under the influence of an applied magnetic field was precluded. Therefore, this spectrum conclusively demonstrates that the measured signals are not due to MOLD, but are due to intrinsic MLD, stemming from the Zeeman effect.

Improved resolution of electronic transitions

In addition to resolving the characteristics of individual chromophores, there is a need to resolve the set of transitions associated with each chromophore. When we were selecting a sample to test the resolution afforded by combining MLD with other electronic spectroscopies, we were intrigued by a crystallographically characterized compound containing iron in its tetravalent oxidation state. The presence of high-valent iron species is proposed in numerous biochemical and nonbiological catalytic oxidation cycles. However, most of the predicted intermediates are not well characterized, due partly to a paucity of studies with suitable model compounds. At the outset of this benchmark study, we had neither actual reference spectra, nor a very clear idea how they might be simulated.

The complex $[Et_4N][Fe^{IV}Cl(\eta^4\text{-MAC}^\star)]$ (Figure 4) has roughly square-pyramidal geometry with a single chloride in the apical position (*18, 19*). Its 4.2-K absorption spectrum exhibits overlapping transitions throughout the visible region (Figure 4, bottom). If the chloride is stripped by adding monovalent silver, or replaced with fluoride by metathesis, the visible bands are lost (not shown), indicating that chloride-to-metal charge-transfer transitions are responsible for the spectrum in this region. The MCD spectrum of the complex exhibits several strong features in the same range (Figure 4, middle). At 4.2 K, the MCD spectrum should approximate a series of overlapping positive and negative Gaussian bands, each centered close in energy to the maxima of the absorption spectrum.

Consequently, by straightforward inspection of the absorption and MCD spectral data, it seems clear that there are four resolved transitions at ~460 nm (21,700 cm^{-1}), 530 nm (18,900 cm^{-1}), 650 nm (15,400 cm^{-1}), and 740 nm (13,500
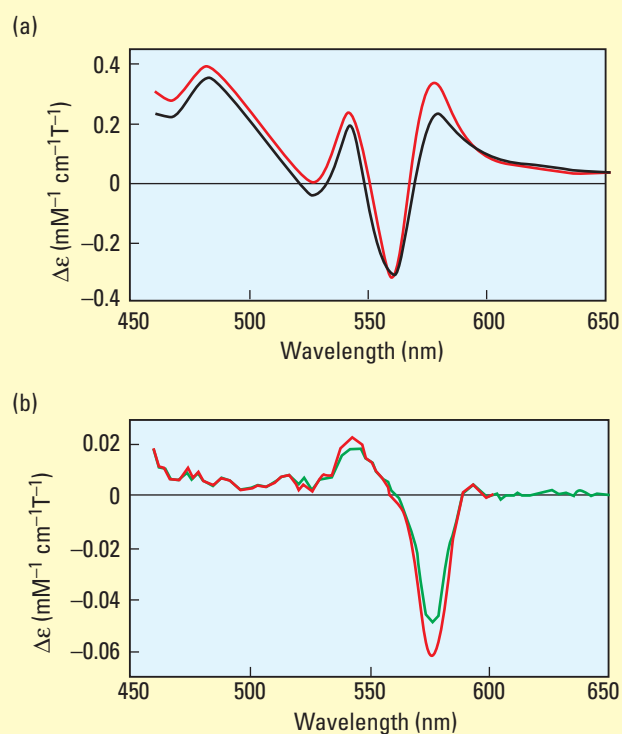

FIGURE 3. Magneto–optical spectra of ferricytochrome *c* (spin = 1/2) and deoxymyoglobin (spin = 2) recorded at 4.2 K and 5.0 T.

(a) MCD spectra of ferricytochrome *c* (black) and equal concentrations of ferricytochrome *c* and deoxymyoglobin (red). (b) MLD spectra of deoxymyoglobin (green) and equal concentrations of ferricytochrome *c* and deoxymyoglobin (red).

cm^{-1}). The presence of four halide-to-metal charge transfers can reasonably be expected in chromophores with 4-fold symmetry (*20*) if we apply the conventional wisdom of expecting any transitions from the $3p_z$ orbital (along the chloride–iron axis) to be in the UV region. So, in the absence of any additional information, the temptation is great to assume the system approximates 4-fold symmetry and take the data analysis no further. Indeed, this kind of simple symmetry-based approach is common in the assignment of electronic spectra of transition-metal complexes.

In fact, to simultaneously fit the absorption and MCD spectra of Figure 4, it is necessary to include a minimum of five Gaussian components (not shown). However, this procedure is also unsatisfactory for two reasons. First, the S/N of the present data set is much better than those normally obtained for less-characterized samples, where the chromophore is likely to be dilute. If the absorption and MCD spectra of Figure 4 ex-
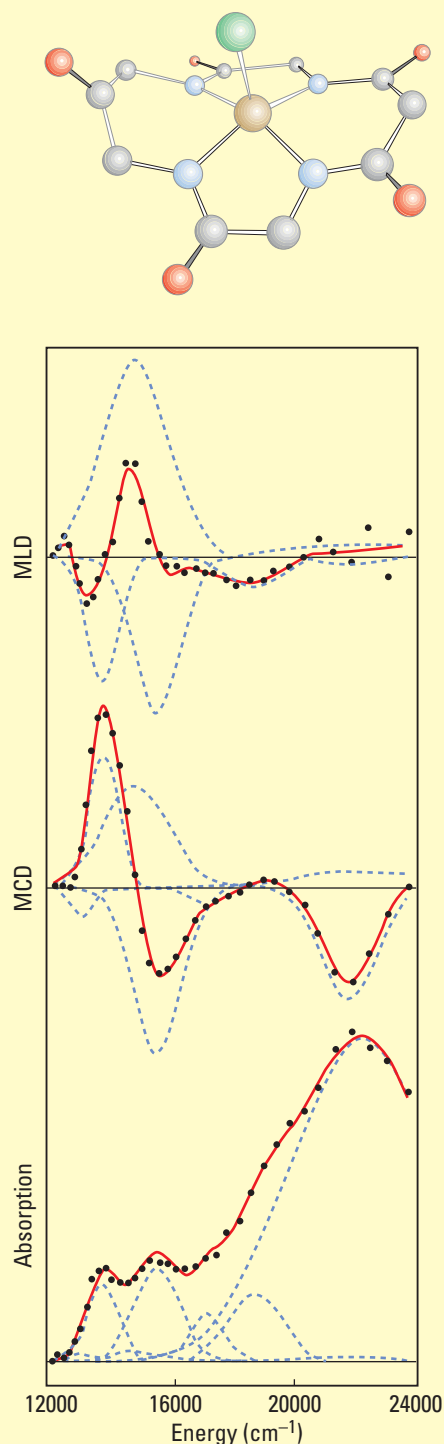
FIGURE 4. (bottom) Absorption (no magnetic field), (middle) MCD in a 1.0-T magnetic field applied parallel to the light path, and (top) MLD in a 5.0-T field applied perpendicular to the light path of (structure at the top) $[Et_4N][Fe^{IV}Cl(\eta^4\text{-}MAC^*)]$.

The three data sets were recorded at 4.2 K using the same sample dissolved in acetonitrile/propionitrile (50% v/v) with the instrumentation and methods described in Ref. 15. Experimental data are given by black symbols; the broken blue curves represent the Gaussian bands; solid red lines are simulations (best fits) constructed by summing eight Gaussian bands. The simulations are based on a simultaneous least-squares fit of the three spectra in which the energies, widths, and amplitudes of the individual Gaussian bands are treated as adjustable parameters. Gray represents carbon; green, chlorine; brown, iron; blue, nitrogen; red, oxygen.

hibited the experimental S/N typically encountered, we would be unable to distinguish between the qualities of theoretical fits using four or five Gaussian components. Second, it is a theoretical assumption that the electronic transitions under study will have Gaussian (or some other idealized) band shapes, whereas at some level of precision, this will not be valid.

Consequently, if the quality of any given fit is inspected in great enough detail, it should prove inadequate in some way. Unavoidably then, the acceptance or rejection of a particular fit can be a matter of personal bias that is determined to some extent by the individual spectroscopist's conviction concerning the validity of the theoretical approach used. Although eliminating all ambiguity may not be possible, it is clearly much less of an issue if there are strong spectral features such as peaks and troughs, rather than vague inflections or slightly distorted bands, to guide the fitting procedure.

Interestingly, the predominant feature in the MLD spectrum of $[Et_4N][Fe^{IV}Cl(\eta^4\text{-}MAC^*)]$ (Figure 4, top) is a peak centered at ~680 nm (14,700 cm^{-1}). This strong positive band is located between the two lowest-energy maxima of the absorption spectrum and corresponds to a position in the MCD spectrum where overlapping transitions almost completely cancel each other. It follows, therefore, that the MLD spectrum will yield information not reliably obtainable from the combined absorption and MCD data, even before any numerical fitting is attempted.

At cryogenic temperatures, the MLD spectrum is also expected to approximate a series of positive and negative Gaussian bands. All three spectra can thus be simulated as a single set of bands, differing only in their associated technique-specific coefficients. To simultaneously fit the three spectral envelopes using this method, it is necessary to take into consideration a minimum of eight transitions—an impressive increase in spectral resolution. The individual transitions (blue) and resulting simulations of the spectral envelopes (red) are given in Figure 4.

Other groups have reported convincing electronic spectral deconvolutions by the combined use of absorption, MCD, and sometimes natural CD data, but these studies were special cases in which few or unusually well-resolved transitions were involved (*21, 22*). Also, we do not mean to imply that other techniques like fluorescence, resonance Raman, and Stark spectroscopy do not have a role in electronic spectral assignment. The message is simply that, in the general case of multiple, broad, overlapping transitions in the visible region, particularly when the chromophores are paramagnets, the inclusion of MLD data in the protocol leads to a significant improvement in the number of transitions resolved.

Current problems, future directions

The major impediment to the rapid development of molecular MLD spectroscopy is lack of resources. Worldwide, the number of laboratories undertaking MCD measurements is still quite small, and apart from our own, we are aware of no others where visible-to-near-IR MLD is the major thrust. A few more interested groups are required to achieve a critical mass in the field. Our spectrometer, which uses conventional disper-

sive optics technology that has not changed for 40 years, was originally designed to meet the requirements of MCD measurements, and it does this very well. However, MLD yields significantly weaker signals than MCD, resulting in only a small number of exceptional chromophores being amenable to study with the existing equipment. It is now apparent that different technology will have to be developed to construct more sensitive MLD-specific spectrometers.

The next generation of instruments will, therefore, undoubtedly incorporate digital methods for recovering signal rather than the present ubiquitous lock-in amplifier-based analog technology. Alternatively, FT principles or laser optics can advantageously be used to construct spectrometers for some applications. In short, redesigning the spectrometer should lower present noise levels by orders of magnitude. For several reasons that are beyond the scope of this article, using higher magnetic-field strengths is of rather limited value, except in the case of diamagnetic chromophores for which the signal intensity increases with the square of the applied field.

To date, we have recorded preliminary MLD spectra associated with n-π^*, π-π^*, and d-d transitions and charge transfers of macrocycles and mononuclear complexes and clusters in both small model compounds and proteins. In most cases, MLD signals are clearly detectable, but intensities are close to the detection limit, compromising the reliability of the data. Consequently, with the anticipated improvements in instrumentation, we expect that combined MCD/MLD spectroscopy will, in the long term, prove to be a sought-after tool for deconvoluting overlapping spectra and assigning the underlying transitions of a great many chromophores in a wide range of samples.

In the foreseeable future, we do not envision routine analytical uses for this combination of techniques outside of specialist laboratories, but rather applications where there is no other method of extracting the desired information. The biomedical sciences appear to be a productive area in which to seek applications, especially as these methods do not suffer any loss of photometric accuracy (only precision) when dealing with scattering samples.

Past collaborative ventures with colleagues at dozens of universities worldwide suggest that many institutions with active research programs analyzing samples in which chromophores are embedded in complicated matrixes (e.g., metalloproteins) could benefit from an MCD/MLD facility. We do not perceive any lack of potential applications, only a shortage in the number of individuals with the knowledge to drive such operations. Recently, we have been forced to severely curtail the extent of our collaborations with other institutions, because now we produce almost all the samples we can process given the available instrument time in our own wet laboratories. The cost of the necessary equipment is presently comparable with that required for inductively coupled plasma MS, that is, somewhat less expensive than typical ^{1}H NMR instrumentation. However, once particular analytical applications have been identified, much less expensive, dedicated instruments can certainly be designed and constructed.

Emile L. Bominaar is a research scientist at Carnegie Mellon University. His scientific interests concern the electronic structure of transition-metal complexes and metal clusters in proteins, using spectroscopy and molecular quantum mechanics as investigative tools. Jim Peterson is currently assistant director of the Center for Molecular Analysis at Carnegie Mellon University. The application of spectroscopic and electrochemical methods to bioanalytical problems are his primary research interests, especially in the areas of nitric oxide biochemistry and mitochondrial pathology. Address correspondence to Peterson or Bominaar at Dept. of Chemistry, Carnegie Mellon University, 4400 5th Ave., Pittsburgh, PA 15213 (jamesp@andrew.cmu.edu or eb7g@andrew.cmu.edu).

References

(1) Faraday, M. *Entry dated 13th September, 1845;* G. Bell and Sons, Ltd.: London, 1933.

(2) Kerr, J. *Philosophical Magazine* **1875,** *50,* 337–348.

(3) Zeeman, P. *Philosophical Magazine* **1897,** *5,* 55–60.

(4) Zeeman, P. *Philosophical Magazine* **1897,** *5,* 255–259.

(5) Voigt, W. *Rendiconti Accademia dei Lincei* **1902,** *XI,* 505–507.

(6) Majorana, Q. *Rendiconti Accademia dei Lincei* **1902,** *XI,* 90–98.

(7) Majorana, Q. *Rendiconti Accademia dei Lincei* **1902,** *XI,* 531–539.

(8) Cotton, A.; Mouton, H. *Annales de Chimie et de Physique (8)* **1907,** *11,* 145–203.

(9) Cotton, A.; Mouton, H. *Annales de Chimie et de Physique (8)* **1907,** *11,* 289–339.

(10) Buckingham, A. D.; Stephens, P. J. *Annu. Rev. Phys. Chem.* **1966,** *17,* 399–432.

(11) Schatz, P. N.; McCaffery, A. J. *Quarterly Reviews* **1969,** *23,* 552–584.

(12) Argyle, B. E.; Suits, J. C.; Freiser, M. J. *Phys. Rev. Lett.* **1965,** *15,* 822–825.

(13) Boccara, A. C.; Ferré, J.; Briat, B.; Billardon, M.; Badoz, J. P. *J. Chem. Phys.* **1969,** *50,* 2716–2718.

(14) Vala, M.; Eyring, M.; Pyka, J.; Rivoal, J.-C.; Grisolia, C. *J. Chem. Phys.* **1985,** *83,* 969–974.

(15) Peterson, J.; Pearce, L. L.; Bominaar, E. L. *J. Am. Chem. Soc.* **1999,** *121,* 5972–5980.

(16) Bominaar, E. L.; Peterson, J. *J. Chem. Phys.* **1999,** *111,* 7512–7518.

(17) Bominaar, E. L.; Achim, C.; Peterson, J. *J. Chem. Phys.* **1998,** *109,* 942–950.

(18) Collins, T. J.; Kostka, K. L.; Uffelman, E. S.; Weinberger, T. L. *Inorg. Chem.* **1991,** *30,* 4204–4210.

(19) Kostka, K. L.; et al. *J. Am. Chem. Soc.* **1993,** *115,* 6746–6757.

(20) Lever, A. B. P. *Inorganic Electronic Spectroscopy;* Elsevier: Amsterdam, 1968.

(21) Solomon, E. I.; Pavel, E. G.; Loeb, K. E.; Campochiaro, C. *Coord. Chem. Rev.* **1995,** *144,* 369–460.

(22) Mack, J.; Stillman, M. J. *Inorg. Chem.* **2001,** *40,* 812–814.