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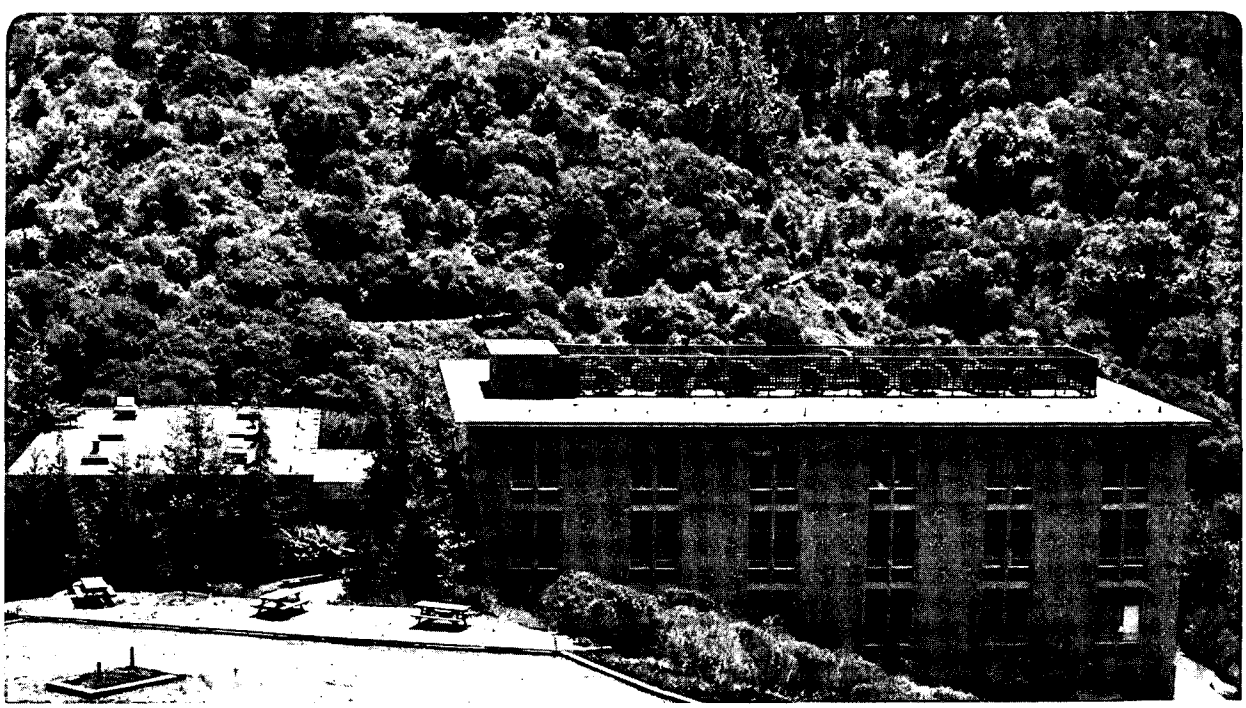
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An Introduction to MCD Spectroscopy: Some Theory and Applications

D.W. Ball

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An Introduction to MCD Spectroscopy: Some Theory and Applications

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ABSTRACT

This article describes the general theoretical basis for magnetic circular dichroism (MCD) spectroscopy. MCD is a powerful technique that combines some attributes of absorption spectroscopy and magnetic resonance spectroscopy. Under appropriate conditions, much more information can be deduced about atomic and molecular energy states with MCD as the single spectroscopic technique than most other types of spectroscopy. Some experimental data will be presented to illustrate how MCD is being utilized at the Lawrence Berkeley Laboratory to study the energy levels of lanthanide and actinide compounds.

Introduction

Researchers typically use several spectroscopic techniques to investigate the electronic energy levels in atoms and molecules: UV-visible, electron paramagnetic resonance (EPR), electron spin resonance (ESR), even infrared (IR) and near infrared (NIR). In all of these techniques, quantum mechanical or group theoretical selection rules dictate which energy levels will be accessed by an allowed transition. UV-visible and IR techniques are frequently augmented with linearly polarized light; simple group theory indicates that the selection rules usually become more specific, allowing one to further define the properties of the initial and final energy states.

Circularly polarized light (cpl) can be used instead of linearly polarized light (lpl). When using circularly polarized light, different selection rules are applied than when using linearly polarized light, so that transitions to some different excited states may be allowed. Hence, circularly polarized light spectroscopy is complimentary to linearly polarized light spectroscopy, since they can provide different spectroscopic information about the same species.

Cpl spectroscopy is especially useful in examining energy levels of high-symmetry species. Little information can be gleaned from singlet states or degenerate multiplet states; however, upon application of a magnetic field to the species, the multiplet states can split (the Zeeman effect). Cpl can be used to probe these now non-degenerate energy levels and extract data regarding the multiplicity and symmetry of the levels involved in the transition. The coupling of cpl spectroscopy and a magnetic field is called *magnetic circular dichroism* (MCD) spectroscopy. This article explores the theoretical background of MCD spectroscopy, describes necessary experimental apparatus, and discusses some experimental results that demonstrate the usefulness of MCD as compared to other spectroscopic techniques.

Optical Activity

Magnetic circular dichroism (MCD) spectroscopy is not really a new technique. It is an application of the Faraday effect, noted by Michael Faraday in 1846 [1,2]. The Faraday effect is simply the appearance of optical activity in a sample that has been exposed to a longitudinal magnetic field, *i.e.* one that is coincident with the propagation axis of the light. The Faraday effect should be differentiated from natural optical activity that can be present in the absence of a magnetic field.

The Faraday effect refers to optical activity using linearly polarized light, which can be thought of as a sum of circular polarized components. If the index of refraction n_+ for right circularly polarized (rcp) light is different than the index of refraction n_- for left circularly polarized (lcp) light, then as linear polarized light passes through a sample, one of its circularly-polarized components will be retarded -- that is, travel slower -- with respect to the other. The emerging combination of light will thus have a different resultant linear polarization (unless circumstances are such as to make the linear polarization the same or at a 180° angle from the incoming polarization) and will appear to have rotated upon passing through the sample.

In most naturally-occurring optically-active samples, $n_+ \neq n_-$ because of structural or stereochemical effects. Only certain substances will show natural optical activity. However, *in the presence of a magnetic field, $n_+ \neq n_-$ for all substances*; therefore, *all substances show the Faraday effect to some degree.* Generally, the Faraday effect occurs for all wavelengths of light.

In a region of the electromagnetic spectrum where the sample absorbs light, the index of refraction is expressed as

$$\hat{n} = n - i\,k \qquad (1)$$

where k is an absorption coefficient and i is the square root of -1. For rcp and lcp light, this can be express as

$$\hat{n}_{\pm} = n_{\pm} - i\, k_{\pm} \qquad (2)$$

If, in the region of absorption, $k_+ \neq k_-$, the sample is said to show circular dichroism (CD); if the CD is present only upon application of a magnetic field, it is said to show magnetic circular dichroism, or MCD. MCD is a consequence of the interaction of electronic energy levels with the magnetic field, and so is a measure of the Zeeman effect. Because MCD is dependent on the absorption coefficient $k_{\pm}$, it is nonzero only in regions of the spectrum where absorption of light occurs.

Theory of MCD

MCD is similar to Zeeman spectroscopy in that the sample is placed in a magnetic field and the split energy levels are examined. Since with most samples the splitting of the energy levels is usually much less than the spectroscopic linewidth, the magnet-field absorption is usually indistinguishable from the zero-field absorption when measured by conventional absorption spectroscopy. MCD is a method of measuring this minute change, using circular polarized light.

A sample that has all nondegenerate energy levels -- *i.e.* singlet states -- will show little or no quantifiable MCD, since the nondegenerate levels will not split in a magnetic field (however, they may mix -- see the discussion of $\mathcal{B}$ terms, below). In order to have degenerate energy levels, a system must either possess at least a three-fold symmetry axis or contain an odd number of electrons (Kramers degeneracy). These necessities suggests that only certain molecules will have an MCD spectrum. This is indeed the case, and simple group theoretical manipulations of their molecular point groups are crucial to the theoretical interpretation of an MCD spectrum.

Numerically, the magnitude of MCD is directly related to the difference between the absorption coefficients of lcp and rcp light:

$$MCD \propto k_- - k_+ \tag{3}$$

Another way of writing this is in terms of the circular polarized absorbances:

$$MCD \propto \Delta A_\pm \equiv A_- - A_+ \tag{4}$$

where the + and - refer to rcp and lcp light, respectively. MCD is hence a subtractive technique that can have both positive and negative features, depending on the relative magnitudes of A_+ and A_-.

The MCD spectrum can also be expressed mathematically in terms of the quantum mechanical description of energy level transitions in spectroscopy. For a single transition between two levels $G \rightarrow X$ in a system of local symmetry Σ, equation 4 can be rewritten as

$$MCD \propto \Delta A_\pm = K_1\left(|\langle G | m_- | X \rangle|^2 - |\langle G | m_+ | X \rangle|^2 \right) \tag{5}$$

where the first term on the right is the transition probability between the ground state having irreducible representation label G and an excited state with irreducible representation label X for lcp light, the second term is the transition probability between state G and state X for rcp light, $m_\pm$ is the electric dipole moment operator for right and left cp light, and K_1 is a spectroscopic constant. One can define a similar quantity for the *total* absorption of the same spectral transition $G \rightarrow X$:

$$A = K_2\left(|\langle G|m_-|X\rangle|^2 + |\langle G|m_+|X\rangle|^2 \right) \qquad (6)$$

where K_2 is also a spectroscopic constant. Experimentally, K_1 and K_2 are determined by measuring spectra of standards [3].

From equation 5, we see that MCD is defined as the difference between two transition moments. As was mentioned previously, this indicates that an MCD spectrum can be either positive or negative for an absorption. Moreover, we will find that some MCD signals can have derivative-type lineshapes. However, it should be pointed out that this is a fundamental consequence of subtraction, not derivation. An MCD spectrum is not a derivative spectrum like ESR or EPR. MCD is *differential*, not derivative.

At this point, various quantum mechanical and electrodynamical substitutions and approximations can be made in equations 5 and 6 to express them in terms of known or measurable terms. Such detail will not be given here; it is given elsewhere [4,5]. Here just the final result will be given (I follow the format of Piepho and Schatz, reference 5):

$$\frac{\Delta A_{\pm}}{\varepsilon} = \gamma\mu_B B\left[\mathcal{A}_1\left(-\frac{\partial f(\varepsilon)}{\partial \varepsilon}\right) + \left(\mathcal{B}_0 + \frac{\mathcal{C}_0}{kT} \right) f(\varepsilon) \right] \qquad (7)$$

where $\Delta A_{\pm}$ is the change in absorbance, ε is the light energy, γ is a spectroscopic constant, μ_B is the Bohr magneton, **B** is the magnetic field strength, k is the Boltzmann constant, and T is the absolute temperature. $f(\varepsilon)$ is a general lineshape function (*e.g.* Gaussian); equation 7 shows contributions from both the lineshape and the derivative of the lineshape. $\mathcal{A}_1$, $\mathcal{B}_0$, and $\mathcal{C}_0$ are parameters that define the amount of absorptive (the $\mathcal{B}_0 + \mathcal{C}_0/kT$ part) and derivative (the $\mathcal{A}_1$ part) signals in the MCD spectrum. Let us consider each parameter in turn. $\mathcal{A}_1$ is defined as

$$\mathcal{A}_1 = \frac{1}{|G|} \sum_{\alpha,\lambda} \left[\langle X\lambda|\mu_z|X\lambda\rangle - \langle G\alpha|\mu_z|G\alpha\rangle\right] \times \left[|\langle G\alpha|m_-|X\lambda\rangle|^2 - |\langle G\alpha|m_+|X\lambda\rangle|^2\right] \tag{8}$$

where G represents the irreducible representation of the ground state, X that of the excited state, μ_z is the magnetic moment operator, and m_+ and m_- are the electric dipole operators for rcp and lcp light, respectively. |G| is the degeneracy of the state G. α and λ are the components of the G and X representations (for example, a singly degenerate state, like an A state, has only one component (making the summation unnecessary), a doubly degenerate state like E has two components, a triply degenerate state like T has three components, *et cetera*).

The first set of bracketed terms on the right side of equation 8 is the magnetic splitting or Zeeman term; the second set of bracketed terms represent the circular dichroism. If both of the two states involved in the transition G → X show no splitting in a magnetic field, the $\mathcal{A}_1$ value will be identically zero (since both matrix elements in the first set of brackets are zero). This would be the case, for example, if both states were singlets, as in a $A_1 \rightarrow B_1$ transition. In order for $\mathcal{A}_1$ to be nonzero, either the ground state or the excited state must be degenerate and also Zeeman-split by a longitudinal magnetic field. If $\mathcal{A}_1$ is nonzero, the MCD spectrum is said to show an *$\mathcal{A}$ term*. Because of the derivative lineshape function associated with $\mathcal{A}_1$ in equation 7, $\mathcal{A}$ terms are characteristically sinusoidal.

Let us look at $\mathcal{C}_0$ next, as it is similar to $\mathcal{A}_1$. $\mathcal{C}_0$ in equation 7 is defined as

$$\mathcal{C}_0 = -\frac{1}{|G|} \sum_{\alpha,\lambda} \langle G\alpha|\mu_z|G\alpha\rangle \times \left[|\langle G\alpha|m_-|X\lambda\rangle|^2 - |\langle G\alpha|m_+|X\lambda\rangle|^2\right] \tag{9}$$

The variables are the same as described above for $\mathcal{A}$ terms. $\mathcal{C}_0$ is very similar to $\mathcal{A}_1$, except that only a ground state magnetic interaction or Zeeman term is present in the definition of $\mathcal{C}_0$. . There are two other major differences: (a) in equation 7, one sees that $\mathcal{C}_0$ describes

the amount (in part) of normal, absorptive lineshape signal in an MCD spectrum, and (b) the $\mathcal{C}_0$ parameter has a temperature dependence associated with it, meaning that its contribution to the absorptive MCD lineshape varies with absolute temperature. Note that if the excited state X is nondegenerate, $\mathcal{C}_0 = \mathcal{A}_1$. This kind of MCD signal, an absorptive signal that varies with temperature, is called a *C term*.

The parameter $\mathcal{B}_0$ has a more complicated definition:

$$\mathcal{B}_0 = \frac{2}{|X|}\mathcal{R}e\sum_{\alpha,\lambda}\left[\sum_{K\kappa,\,K\neq X}\frac{\langle X\lambda|\mu_z|K\kappa\rangle}{E_K - E_X}\times\left(\langle G\alpha|m_-|X\lambda\rangle\langle K\kappa|m_+|G\alpha\rangle - \langle G\alpha|m_+|X\lambda\rangle\langle K\kappa|m_-|G\alpha\rangle\right)\right.$$

$$\left. + \sum_{K\kappa,\,K\neq G}\frac{\langle K\kappa|\mu_z|G\alpha\rangle}{E_K - E_G}\times\left(\langle G\alpha|m_-|X\lambda\rangle\langle X\lambda|m_+|K\kappa\rangle - \langle G\alpha|m_+|X\lambda\rangle\langle X\lambda|m_-|K\kappa\rangle\right)\right] \qquad (10)$$

E_K, E_X, and E_G are the energies of the states with symmetry labels K, X, and G. |X| is the degeneracy of the excited state X. $\mathcal{R}e$ indicates that only the real portion of the complex value inside the brackets should be considered. The $\mathcal{B}_0$ parameter describes the amount of mixing of some third state K, with component(s) κ, into states X (the first summation over K) and G (the second summation over K) in the presence of the magnetic field. Since all quantum mechanical states will mix together to some extent in a magnetic field, all materials have nonzero $\mathcal{B}_0$ (this accounts for the universality of the Faraday effect). However, in systems where the energy levels are widely spaced, large values for $E_K - E_X$ and $E_K - E_G$ in the denominators of equation 10 suggest that $\mathcal{B}_0$ will be very small. This kind of signal is called a *B term* and is the temperature-independent part of the normal absorptive-type lineshape of equation 7.

A parameter $\mathcal{D}_0$ is also defined:

$$\mathcal{D}_0 = \frac{1}{2|G|} \sum_{\alpha,\lambda} \left[|\langle G\alpha | m_- | X\lambda \rangle|^2 + |\langle G\alpha | m_+ | X\lambda \rangle|^2 \right] \tag{11}$$

$\mathcal{D}_0$ is called the dipole strength, and now we can rewrite the total absorption from equation 6 as

$$\frac{A}{\varepsilon} = \gamma \mathcal{D}_0 f(\varepsilon) \tag{12}$$

where ε, γ, and $f(\varepsilon)$ have been previously defined.

Table I lists the types of terms defined for MCD spectroscopy, along with their energy dependence relative to their corresponding absorption lines and their temperature dependence. When performing MCD spectroscopy, the energy and temperature dependences allow one to assign the type of MCD terms that exist for each transition.

As an example, Figures 1 and 2 show simple energy level diagrams that illustrate the appearance of $\mathcal{A}$ and $\mathcal{C}$ terms. In Figure 1, when no magnetic field is present, the P term is triply degenerate and rcp light induces transitions at the same wavelength and intensity as lcp light; the difference between lcp and rcp light absorption is zero, as shown in the MCD spectrum at the bottom left. When a magnetic field is applied, the P term can split into its three components. Group theory shows that right circularly polarized light will induce a transition from the ground state to only one component of the excited state, while left circularly polarized light will induce a transition from the ground state to a different component of the excited state. Since the energy levels now occur at slightly different energies, A_+ and A_- are not equal versus energy, and a nonzero $\mathcal{A}$ term is present. Furthermore, the zero point between the extrema of the $\mathcal{A}$ term coincides with the maximum of the corresponding absorption. Again, remember that while the line shape is defined as derivative (*cf.* eq. 7), MCD itself is defined as differential (*cf.* eqs.3 - 5).

Figure 2 shows a similar diagram, only now with the P term as the ground state. In the presence of a magnetic field, the ground state splits and transitions occur only between certain levels for lcp and rcp light. However, if one assumes thermal equilibrium of the electronic states, Boltzmann statistics will determine the relative populations of the lower states; at low temperatures and with large enough splittings, only the lowest state will be populated. This means that the negative peak in the MCD spectrum of Figure 2 will be practically nonexistent and the MCD signal will look like an absorption, indicating the existence of a nonzero $\mathcal{C}$ term. Moreover, this absorptive MCD peak will have its maximum at the same energy as the absorption maximum. Figures 1 and 2 show simplified energy level diagrams; real systems are usually more complex.

$\mathcal{B}$ terms are difficult to display. Ideally, the value of $\mathcal{B}_0$ depends on all of the electronic energy levels K, which are infinite. Practically, only levels very close to the energy levels involved in the transition will induce $\mathcal{B}$ terms to any great extent, so there are usually only a few non-negligible terms in the sum. But for most cases, it is difficult to predict the appearance of $\mathcal{B}$ terms accurately on an *a priori* basis.

Equations 8 - 11 may appear so complex so as to make predicting numerical values for $\mathcal{A}_1$, $\mathcal{B}_0$, $\mathcal{C}_0$, and $\mathcal{D}_0$ next to impossible. With the exception of $\mathcal{B}_0$ (as mentioned in the previous paragraph), this is not the case. The use of group theory provides enormous simplification of these expressions, and for oriented systems an exact theoretical value for the parameters $\mathcal{A}_1$, $\mathcal{C}_0$, and $\mathcal{D}_0$ can be determined by simply evaluating the matrix elements in equations 8 - 11. In fact, group theory shows that many of the matrix elements in the summations are identically zero! Matrix elements can be simplified or evaluated using the Wigner-Eckhart theorem:

$$\left\langle G\alpha \left| \hat{O}^f_\phi \right| X\lambda \right\rangle = \begin{pmatrix} G \\ \alpha \end{pmatrix} \begin{pmatrix} G^* & f & X \\ \alpha^* & \phi & \lambda \end{pmatrix} \left\langle G \left\| \hat{O}^f \right\| X \right\rangle \qquad (13)$$

where $\hat{O}^{f}_{\phi}$ is the operator which transforms as symmetry fϕ (analogous to Gα and Xλ), $\begin{pmatrix} G \\ \alpha \end{pmatrix}$ is a *2j symbol*, $\begin{pmatrix} G^* & f & X \\ \alpha^* & \phi & \lambda \end{pmatrix}$ is a *3jm symbol*, and $\langle G \| \hat{O}^{f} \| X \rangle$ is a *reduced matrix element*. G* and α* indicate the complex conjugate of the symmetry labels G and α (which in almost all cases are real, so G* = G and α* = α). 2j and 3jm symbols are tabulated in terms of symmetry labels [5] or angular momentum quantum numbers [6], and so can be looked up. Reduced matrix elements can sometimes be evaluated [5] and sometimes not. However, in cases where they can be evaluated, the simplifications of the matrix elements in equations 8 - 11 by applying the Wigner-Eckhart theorem are obvious and are an important aspect to the theoretical prediction of MCD spectra.

Moreover, taking ratios like $\mathcal{A}_1/\mathcal{D}_0$ and $\mathcal{C}_0/\mathcal{D}_0$ sometimes yields cancellation of certain reduced matrix elements that cannot be evaluated, leaving behind dimensionless numerical values which can be derived experimentally. Unfortunately, determining the ratio $\mathcal{B}_0/\mathcal{D}_0$ is not always helpful because the reduced matrix elements generally will not cancel. In many cases, it can also be shown that the ratios $\mathcal{A}_1/\mathcal{D}_0$ and $\mathcal{C}_0/\mathcal{D}_0$ are directly related to the magnetic *g* values of the states involved in the transition, although *g* values so derived are not as precise as when derived from EPR or ESR spectroscopy. Procedures and derivations for doing these reductions have already been given [5]. The ability to apply group theoretical techniques to calculate the MCD parameters -- especially $\mathcal{A}_1$ and $\mathcal{C}_0$ -- in an *a priori* fashion is a fundamental reason for the power of MCD to provide symmetry assignments for energy states.

Finally, it should be mentioned that the above relatively simple expressions for $\mathcal{A}_1$, $\mathcal{B}_0$, $\mathcal{C}_0$, and $\mathcal{D}_0$ are applicable to *oriented* systems. For systems having isotropic symmetry (like T_d and O_h), the equations for these parameters are identical if the species is randomly oriented. However, for non-isotropic species, the equations are different when the sample is randomly oriented. While the same general procedures are followed to derive these

equations, they are summations of several terms because of the inequality of the space-oriented x, y, and z axes. Because of this, such non-oriented systems are harder to analyze, and ratios like $\mathcal{A}_1/\mathcal{D}_0$ and $\mathcal{C}_0/\mathcal{D}_0$ may not be as useful.

Experimental Apparatus

MCD spectroscopy is very similar to normal, dispersive UV-visible spectroscopy. The main difference is that the monochromatized light is circularly polarized. This is done with a photoelastic modulator, or PEM, which takes light linearly polarized at 45° and converts it into circularly polarized light by passing it through a stressed silica crystal (for other regions of the spectrum, different crystals can be utilized in PEMs). A good description of the theory behind the PEM has already been published [7,8]. The PEM generates rcp and lcp light alternatively at a frequency of about 50 kHz; if a sample shows circular dichroism, the detector will see a fluctuation in the signal intensity at that 50 kHz frequency. This AC signal can be fed into a lock-in amplifier, which can detect very small differences in signal intensities. The ability of the lock-in amplifier to detect such small signals makes circular dichroism spectroscopy a very sensitive technique.

Because polarized light is being used, there is a special requirement so that the sample does not give spurious MCD spectra: that the sample and sample holder (*i.e.* a cuvette or deposition rod) not change the polarization of the incoming light due to structural effects. This requires that the sample and sample holder be structurally isotropic, cubic, or uniaxial; if uniaxial, the appropriate crystal axis must be oriented colinear with the direction of light propagation. With biaxial and improperly oriented uniaxial samples, structural effects will induce a polarization change in all wavelengths and independent of any circular dichroism; these effects will have to be known and analytically eliminated before study of the true MCD can be attempted. An interesting example of this requirement is the use of sapphire as a sample holder for vaporized samples in an MCD experiment. Crystalline Al_2O_3 is uniaxial and must be specially cut so that the unique axis is coincident with the

propagation direction of the circularly polarized light; otherwise, it will act as a birefringent plate and introduce extra, nonzero CD into the spectrum.

Implicit in the above requirement is that curved surfaces cannot be used in the optical train of the spectrometer after the cp light has been generated; *e.g.* after the PEM. Therefore not only are lenses contraindicated, but round cuvettes or tubular sample holders cannot be used; they will act as birefringence sources and will alter the polarization of the cp light.

A typical MCD spectrometer is shown in Figure 3. Again, it is very similar to a dispersive UV-vis spectrometer except for the polarizer P and the photoelastic modulator PEM. A magnet surrounds the sample, oriented so that the direction of the magnetic field H is coincident with the propagation of the light.

Figure 4 shows a block diagram of the MCD spectrometer. The major difference between an MCD and a UV-vis spectrometer is illustrated here: the lock-in amplifier that will detect and amplify any alternating signal at the same frequency as the PEM, or ~50kHz; existence of such a signal indicates circular dichroism. Notice that the detector is connected to the lock-in and directly to the data collection point (a computer, in this case), allowing for simultaneous measurement of MCD and absorption spectra.

Details of MCD spectrometer construction have been given in the literature [9].

Because of the dual-input capability of our spectrometer, an MCD spectrum can be measured simultaneously with a single-beam absorption spectrum. In our system, the MCD signal is directly proportional to the $\Delta A_{\pm}$ of the sample; the single beam absorption spectrum must be ratioed against a background and the logarithm of the ratio must be taken to get a spectrum proportional to the absorbance. Once this is done, areas under the peaks can be measured in an attempt to evaluate values for $\mathcal{A}_1$, $\mathcal{C}_0$, and $\mathcal{D}_0$ [5].

Examples of MCD

Although MCD had its birth in the mid 19th century, MCD as an analytical tool did not mature until the mid 1960s, when Stephens [10] and Schatz *et al.* [11] applied group theory to identify the symmetries of the states in the MCD spectra of $Fe(CN)_6^{3-}$, MnO_4^-, and CrO_4^- in aqueous solution. In doing so, the researchers were able to assign unambiguously the symmetries of the states of some transitions. The assignments were made by determining the theoretical sign of the $\mathcal{A}$ and C terms for the expected symmetries of the excited states and comparing these with experiment, and by evaluating the ratios $\mathcal{A}_1/\mathcal{D}_0$ and $C_0/\mathcal{D}_0$ theoretically and comparing these with experimentally determined ratios. These appear to be the first cases where symmetry assignments, previously in doubt, could be determined with certainty.

MCD has been coupled with the technique of matrix isolation spectroscopy to study the MCD of atoms and molecules isolated in cryogenic inert gas matrices [12]. Samples that have been studied include metal atoms [12,13] and dimers [14], high temperature species like TiO [15], and phthalocyanide molecules and complexes [12]. MCD has also been used to probe the weak $^3\Sigma_g^- \rightarrow {}^3\Delta_u$ transition of O_2. In this report, the advantages of MCD over very-long-pathlength spectroscopy was pointed out [16].

At the Lawrence Berkeley Laboratory, we are interested in using MCD to probe the electronic energy levels of lanthanide and actinide atoms and ions. For example, we have measured the UV-vis and MCD spectra of UCl_4 in cryogenic inert gas matrices. The UV-visible spectrum and energy level calculations of matrix-isolated UCl_4 have been previously published [17], but no magnetic spectroscopy was performed. Part of the UV-vis and MCD spectra of UCl_4 in solid N_2 at 11K is shown in Figure 5. The UV-vis spectrum agrees with the earlier work [17].

Our initial interpretation of the UCl_4 spectrum differs from the one given in reference 17, however, because of the MCD spectrum. One section of the UCl_4 spectra is shown in more detail in Figure 6. The absorption spectrum shows two resolved peaks at

15840 and 15851 cm^{-1}; note also the low energy shoulder on the 15840 cm^{-1} absorption. Reference 17 assigns these signals to a single transition, split by solid state effects. However, the MCD spectrum suggests a different interpretation. The extrema of the MCD spectrum coincide almost exactly with the absorption maxima; furthermore, the MCD signals have opposite signs. If these absorption signals were due to the same transition, one would expect the MCD peaks to have the same sign and the same relative intensity, as the absorption and MCD of the multiplet at 16184 cm^{-1} in Figure 5. (Note that the MCD signal of the pair of peaks may be an $\mathcal{A}$ term due to its apparent sinusoidal lineshape and the absorption may in fact be a single site-split absorption, but other evidence does not support this assumption.) The conclusion is that the peaks at 15840 and 15851 cm^{-1} are in fact two separate but nearly degenerate absorptions.

Additionally, measuring the MCD spectrum between 11 and 30K shows no definitive temperature effect. Thus it is concluded that the MCD of UCl_4 is dominated by $\mathcal{B}$ terms! The fact that all transitions show $\mathcal{B}$ terms suggests that at least one mixing state K (*cf.* equation 10) is interacting with the ground state.

Using these extra clues from MCD, tentative energy level assignments and a parametric crystal field fitting were deduced for UCl_4 that differ substantially from those in reference 16. A D_{2d} basis set was assumed, which gave a much better fit than a T_d basis (which was adopted by reference 17). The old crystal field calculations are compared with the new, tentative crystal field calculations in Table II. The absolute energy deviation of the new tentative fit is about 95 cm^{-1}, which is similar to those of several other U^{4+} systems which have been published [18-20]. Reference 17 gives an energy deviation of 105 cm^{-1}.

The reason for mentioning the tentative fit now is to illustrate how the information provided by MCD can contribute to a better understanding of UCl_4: by presenting more exact information about the existence of electronic energy levels, a new (and presumably better) theoretical understanding of the electronic structure of a molecular species can be achieved.

To illustrate the existence of a temperature dependent C term, Figure 7 shows the MCD spectrum of $NdCl_3$ in a nitrogen matrix. That the MCD signal decreases with increasing temperature is direct evidence for a C term, which in turn indicates the existence of a degenerate ground state. Such a conclusion is warranted when one realizes that Nd^{3+} is an odd electron system; hence all electronic energy levels will be at least doubly degenerate (Kramers doublets).

Conclusions

MCD is a powerful spectroscopic technique, and can in some cases yield immediate information about ground and excited state symmetries. Analysis of MCD signals can give g values similar to magnetic resonance spectroscopy, although less precise. It has been shown that MCD spectra can also be used to estimate the magnitude of spin-orbit coupling [21] as well as Jahn-Teller effects in high symmetry systems [22]. MCD is to be one of the most informative of spectroscopic techniques, and circular dichroism spectroscopy appears to be gaining adherents as its usefulness is continually demonstrated.

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Figure Captions

Figure 1. An energy level diagram showing the appearance of an $\mathcal{A}$ term. The upper part shows an S ground state and a P excited state that is triply degenerate when the magnetic field is zero and split when H is nonzero. Underneath each energy level diagram is the MCD spectrum expected for the transitions shown. The right MCD spectrum is consistent with a positive value for $\mathcal{A}_1$.

Figure 2. An energy level diagram showing the appearance of a $\mathcal{C}$ term. In this case, the P state is the ground state and the S state is the excited state. *Cf.* Figure 1. The MCD spectrum shown is consistent with a positive value for $\mathcal{C}_0$.

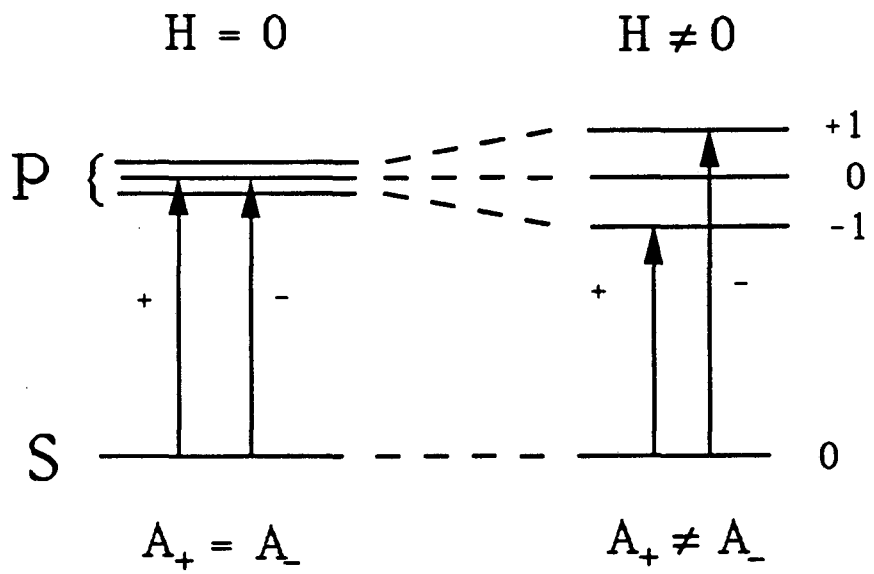
Figure 3. A diagram of a typical magnetic circular dichroism spectrometer.

Figure 4. A block diagram showing the major spectroscopic and electronic components of an MCD spectrometer. *Cf.* Figure 3.

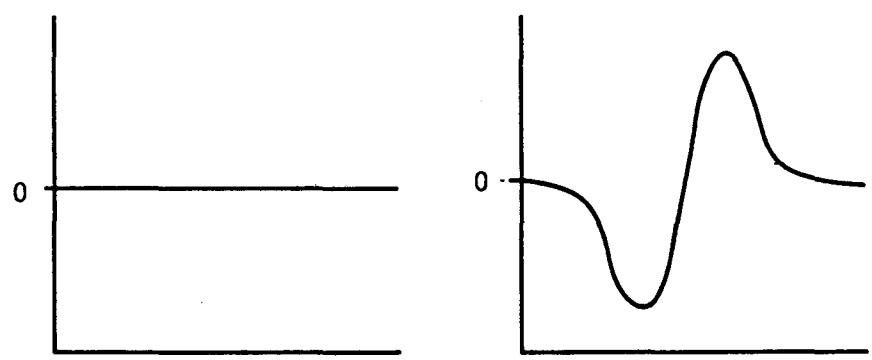
Figure 5. The absorption and MCD spectra of UCl_4 isolated in a cryogenic nitrogen matrix at ~11K.

Figure 6. An expanded view of the absorption and MCD spectra of UCl_4 in solid N_2 at ~11K.

Figure 7. MCD spectra of $NdCl_3$ in a cryogenic nitrogen matrix at various temperatures. The decreasing signal with increasing absolute temperature indicates a $\mathcal{C}$ term.

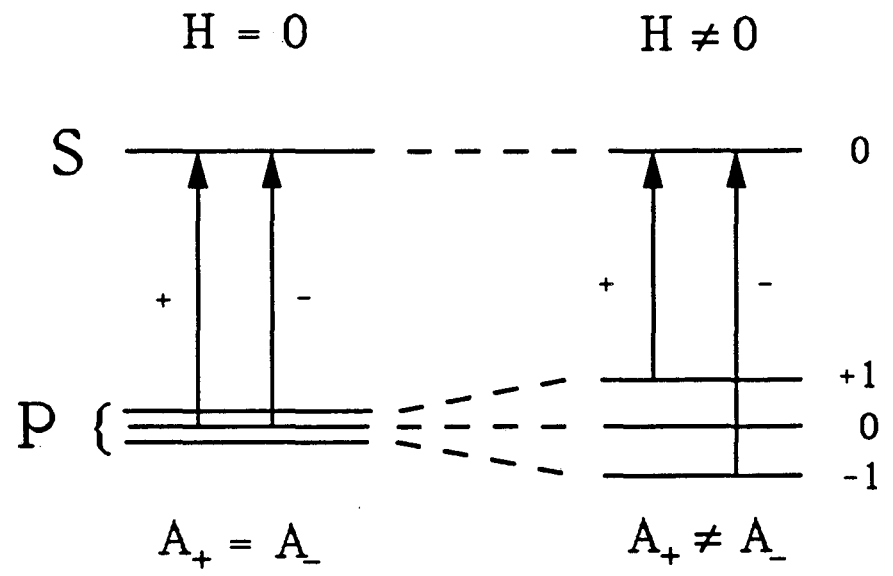


MCD:



$\mathcal{A}$ term

Figure 1



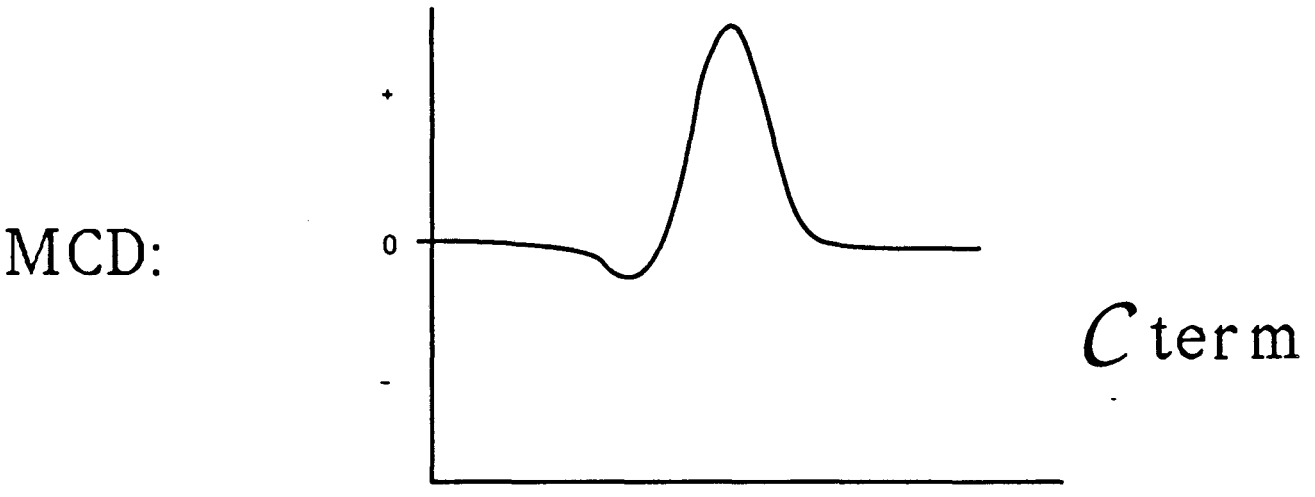
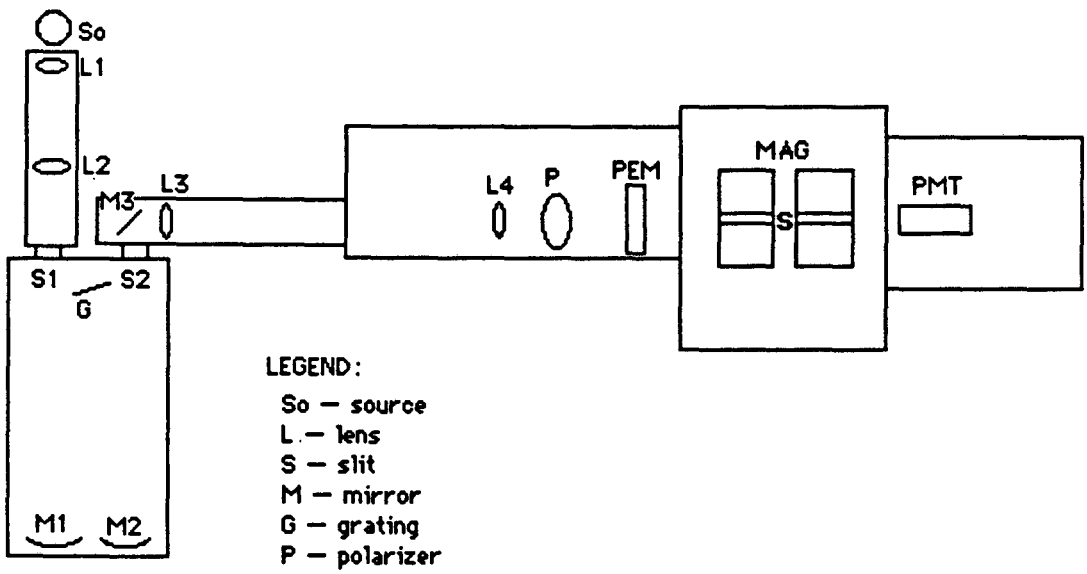


Figure 2



LEGEND:

So — source
L — lens
S — slit
M — mirror
G — grating
P — polarizer
PEM — photoelastic modulator
MAG — magnet
PMT — photomultiplier tube
S — sample

Figure 3

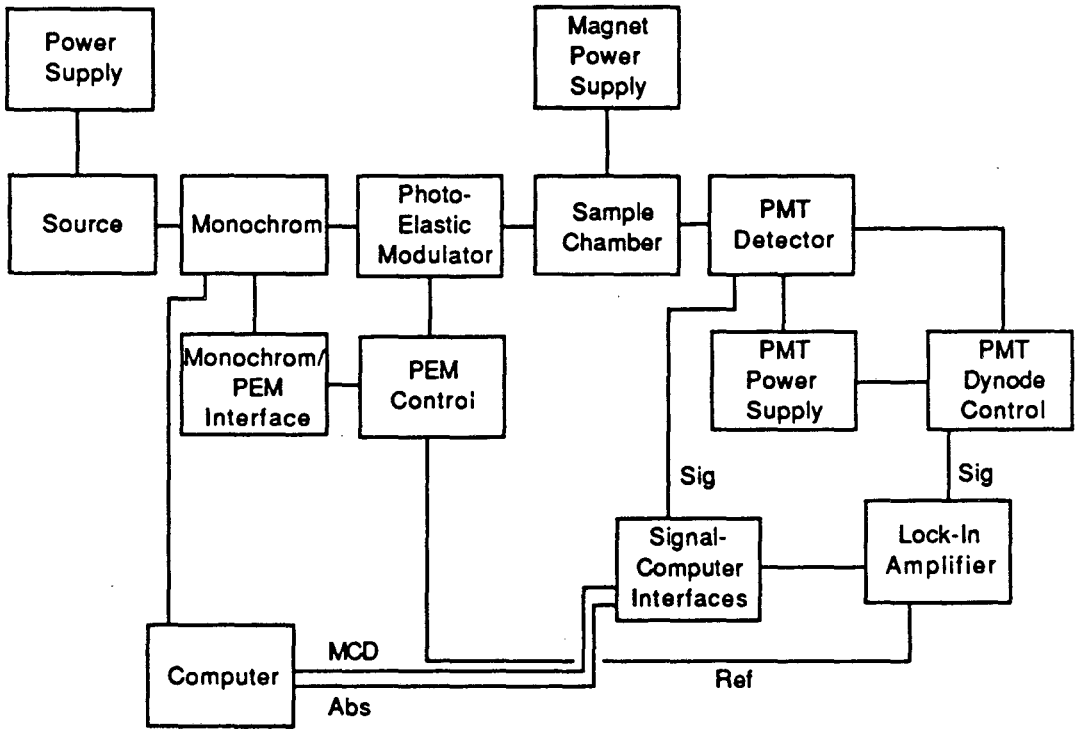

Power Supply
Magnet Power Supply
Source
Monochrom
Photo-Elastic Modulator
Sample Chamber
PMT Detector
Monochrom/ PEM Interface
PEM Control
PMT Power Supply
PMT Dynode Control
Sig
Sig
Signal-Computer Interfaces
Lock-In Amplifier
Computer
MCD
Abs
Ref

Figure 4

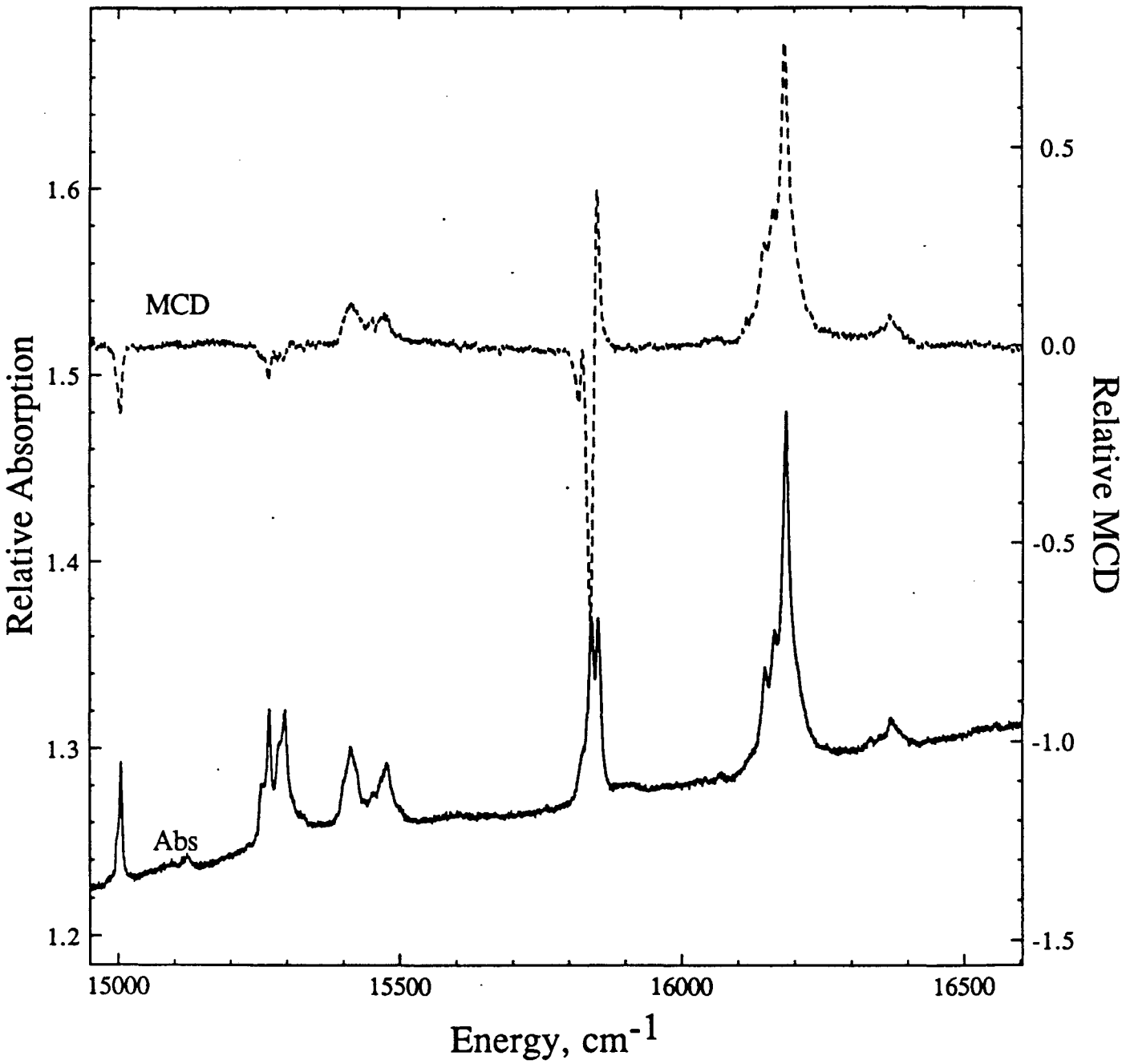

Relative Absorption
Relative MCD
MCD
Abs
1.6
1.5
1.4
1.3
1.2
0.5
0.0
-0.5
-1.0
-1.5
15000
15500
16000
16500
Energy, cm-1

Figure 5

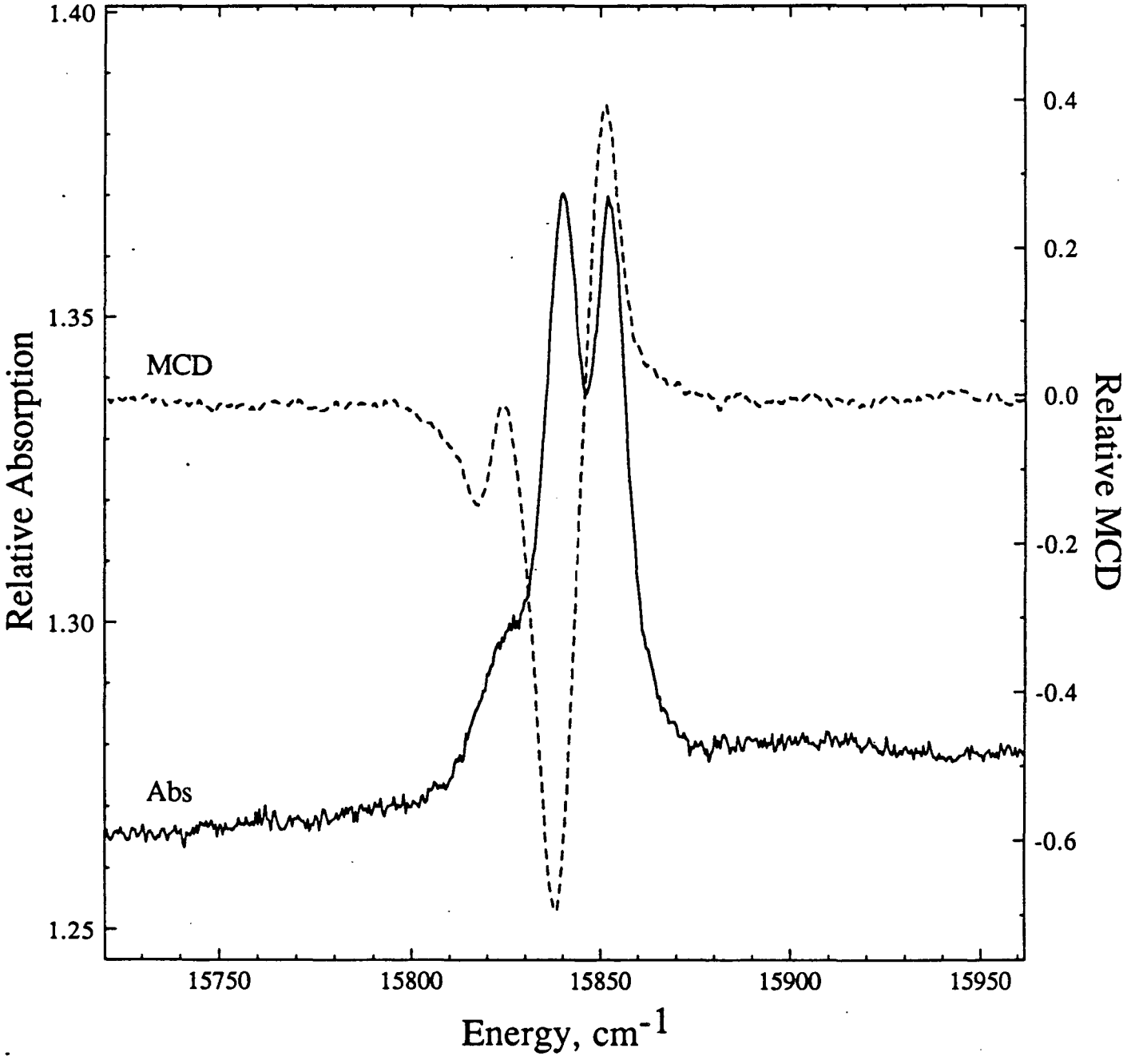

1.40
1.35
1.30
1.25
Relative Absorption
MCD
Abs
0.4
0.2
0.0
-0.2
-0.4
-0.6
Relative MCD
15750
15800
15850
15900
15950
Energy, cm-1

Figure 6

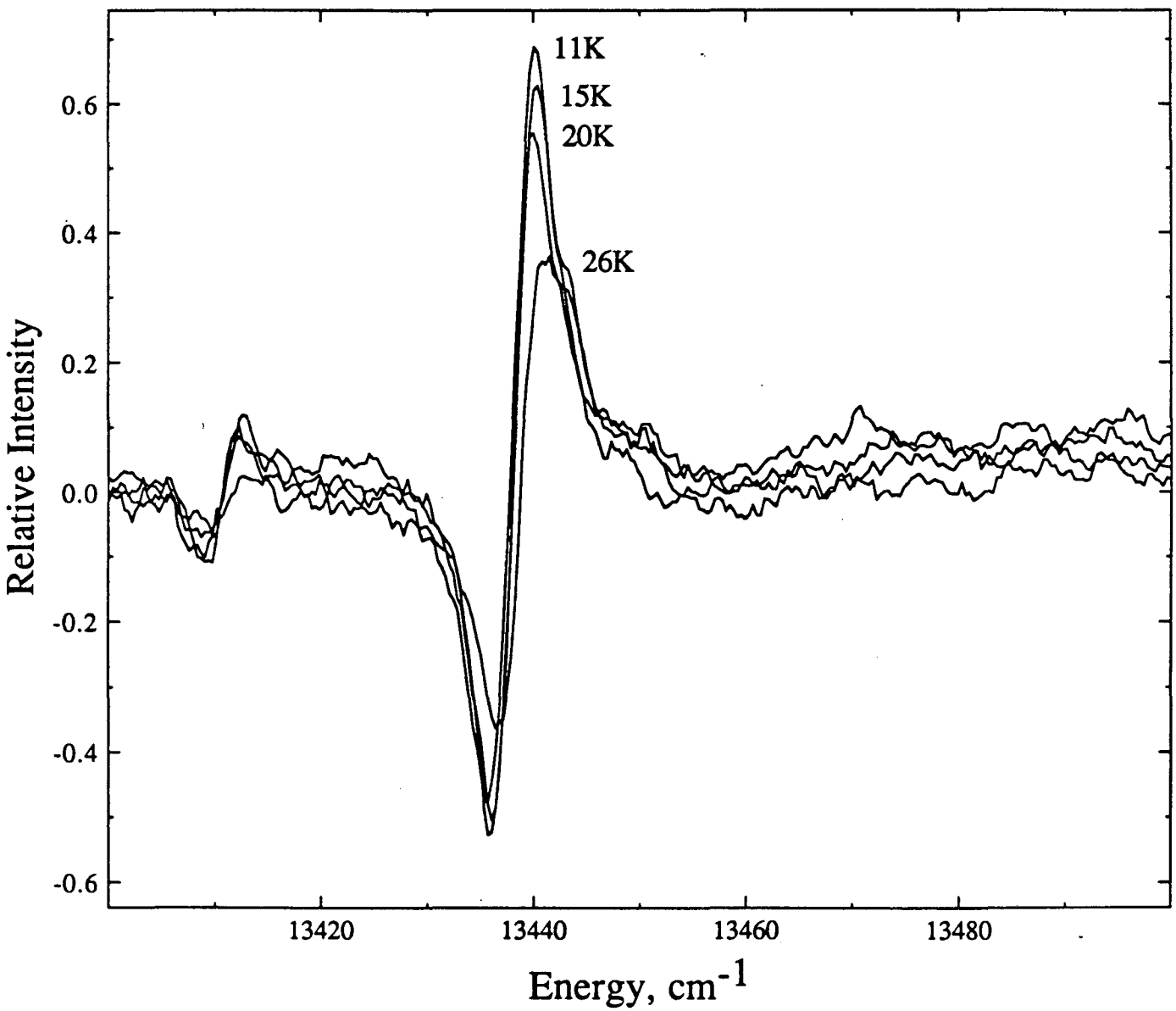

11K
15K
20K
26K
Relative Intensity
0.6
0.4
0.2
0.0
-0.2
-0.4
-0.6
13420
13440
13460
13480
Energy, cm-1

Figure 7

Table I: Types of MCD Signals and Their Dependence on Energy and Temperature

Type of MCD Signal	Energy Dispersion Relative to Absorbance	Temperature Dependence
$\mathcal{A}$ term	Negative Derivative Relationship	None
$\mathcal{B}$ term	Directly Related	None
$\mathcal{C}$ term	Directly Related	Inversely Related

Table II

Comparison of Calculated[a] and Observed Energy Levels For Matrix-Isolated UCl_4: UV-Visible *vs.* UV-Visible-MCD Spectra

UV-Visible Spectra [17]		MCD Spectra	
Calculated[b], cm^{-1}	Observed, cm^{-1}	Calculated[c], cm^{-1}	Observed, cm^{-1}
14982	15001	14888	15005
15128	15265	15160	15269
		15209	15297
		---	15414
15152	15408	15501	15477
15746	15834	15855	15840
		15883	15851
16048	16178		
16349	16364	16383	16185
		---	16372
---	16902	16990	16911
		18701	18447
20655	20671	20492	20679
---	21709	21705	21718
		---	23075
23219	23219	23202	23221

[a] Both calculations involved a symmetry-dependent parametric least squares fitting to a semi-empirical Hamiltonian.

[b] T_d basis set; 6 parameters used in fitting.

[c] D_{2d} basis set; 9 parameters used in fitting.

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