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Circularly Polarized Luminescence Spectroscopy

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I. Introduction

Circularly polarized luminescence (CPL) spectroscopy is based on the differential *spontaneous* emission of left and right circularly polarized radiation by luminescent systems. The primary observables in CPL spectroscopy are the emission circular intensity differential (ECID)

$$\Delta I(\lambda) = I_L(\lambda) - I_R(\lambda) \qquad (1)$$

and the emission dissymmetry factor

$$g_{em}(\lambda) = 2\Delta I(\lambda)/I(\lambda) \qquad (2)$$

where $I(\lambda) = I_L(\lambda) + I_R(\lambda)$ and I_L and I_R denote respectively the intensities of the left (L) and right (R) circularly polarized components of the emitted radiation. The total luminescence observed in a CPL experiment is, in general, elliptically polarized, so the major measurement task is to either measure the generally small difference between I_L and I_R or to separate and measure the I_L and I_R components independently.

Differential emission of left and right circularly polarized radiation can be observed for both atomic and molecular systems under a variety of conditions, and it can originate from a variety of radiative relaxation processes. In this review, however, we shall confine our attention to the CPL associated with *electronic* transitions in molecular systems (including coordination compounds and ions in crystals), considering molecular vibrational motions only insofar as they affect the radiative transition probabilities of electronic transitions via vibronic coupling interactions. Molecular rotational motions are considered only in the context of how they may determine the orientational distribution of the electronic transition moments (in the excitation and emission processes), and in this context they are considered classically.

Electronic CPL spectroscopy is the emission analogue of electronic circular dichroism (CD) spectroscopy. The primary observables in the latter,

$$\Delta\epsilon(\lambda) = \epsilon_L(\lambda) - \epsilon_R(\lambda) \qquad (3)$$

and

$$g_{abs}(\lambda) = \Delta\epsilon(\lambda)/\epsilon(\lambda) \qquad (4)$$

where $\epsilon(\lambda) = [\epsilon_L(\lambda) + \epsilon_R(\lambda)]/2$, are related directly to the CPL observables defined in eq 1 and 2. CPL and CD depend on the same general aspects of molecular structure, but they differ insofar as CD reflects the structural properties of the ground electronic state of a system, whereas CPL reflects the structural properties of the luminescent excited states. The essential requirement for each is that the electronic transition re-

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sponsible for the observed circular intensity differential (ΔI or $\Delta\epsilon$) must occur in the presence of a chiral force field (*excluding* the radiation field).[1-3] For inherently chiral systems (i.e., *naturally* optically active systems), the chiral force fields are intrinsic to the structures of the systems and, therefore, CPL and CD may be observed in the absence of any externally applied force fields. For achiral systems, CPL and CD may be *induced* by application of a static magnetic field along the direction of light propagation (in the CPL experiment, this is the direction of emission detection). These magnetic-field-induced phenomena are generally referred to as magnetic circularly polarized luminescence (MCPL) and magnetic circular dichroism (MCD).[4,5] In MCPL and MCD, the chiral force field is provided by the externally applied static magnetic field.

In this review, we shall concentrate almost entirely on the CPL of naturally optically active systems in the absence of any externally applied fields. In general, natural CPL and magnetic CPL are used to investigate quite different aspects of molecular structure. So far, natural CPL has proved to be the more useful for eliciting sterochemical, conformational, and other 3-dimensional structural information about molecules, whereas magnetic CPL has been used primarily to probe the electronic structure of emitting states (with emphasis on state symmetries, degeneracies, and magnetic properties). Throughout the remainder of this article, we shall refer to magnetic CPL as MCPL and use CPL to refer to the zero-field natural phenomenon.

It was pointed out above that electronic CD and CPL depend upon the same aspects of molecular structure, so questions arise concerning why, and under what circumstances, one technique or the other (*or both*) should be used. Recalling that the CD process originates with the molecules in their thermally equilibrated electronic *ground* state and that CPL processes originate from vibrationally relaxed electronic *excited* states, it is immediately obvious that the information obtained from CD and CPL spectra is redundant only if the ground state and emitting state molecular geometries are identical. Applying the Franck–Condon principle to the respective absorptive and emissive electronic transitions, it is clear that CD will reflect the structure of a molecule in its ground electronic state, whereas CPL will reflect the structure of a molecule in its luminescent (excited) electronic states. Consequently, CD and CPL can be considered as complementary probes of molecular structure.[6-9]

The measurement of CPL, in many cases, has some advantages over the measurement of CD as well as some inherent limitations. The most serious limitation is, quite obviously, that the optically active molecule under study must contain a luminescent chromophore with a reasonable quantum yield. Although this severely limits the range of possible applications of CPL, it does result in a specificity and selectivity that is not present in CD/absorption experiments. Some of the more important advantages of the technique are listed below:

(1) CPL provides a direct probe of the chirality of molecular excited states (more specifically, the emitting states).

(2) Comparative CPL/CD studies can yield specific information concerning geometry differences between ground and excited states.

(3) CPL is uniquely suited for the study of emissive transitions that do not terminate in a thermally accessible ground state. These states cannot be studied by ordinary CD/absorption experiments.

(4) In many instances it is possible to observe CPL from excited states that are only weakly accessible via direct absorption processes from the ground electronic state and therefore only weakly observable in CD. This can be accomplished by populating the emitting state indirectly either by intermolecular or intramolecular radiationless energy transfer or by efficient radiationless decay from a higher excited state that has a larger absorption coefficient.

(5) In condensed media it is usually the situation that emission, if present, is observed from only one excited state. This is in contrast to absorption experiments where overlapping bands are usually observed. In the application of spectra–structure correlations this se-

lectivity afforded by CPL is extremely important.

(6) In large molecular systems it is quite common to have a number of electronically similar, but structurally distinct, chromophores. In these kinds of systems it is generally found that emission occurs from only one of the chromophores. This selectivity is again important in interpretation of spectra.

(7) Since, in general, the orientational distribution of molecules that one observes in emission is different than in absorption, CPL also provides information concerning the excited-state dynamics and energetics from the initial absorption event to emission.

In this review we shall emphasize the applications of CPL and some related experimental techniques that have been reported over the eight years since the last general review[4] as well as progress made in theoretical areas that relate to the development of more useful spectra–structure correlations. The reader is referred to our 1977 review article[4] for a more complete discussion of developments in this field prior to 1977 and for a more complete literature survey covering work published before 1977. It is important to keep in mind that what we are calling circularly polarized luminescence (CPL) has at various times been referred to in the literature as circularly polarized emission (CPE), circular emission (CE), emission circular intensity differentials (ECID), circularly polarized fluorescence (CPF), and circularly polarized phosphorescence (CPP). As used here, CPL refers to the differential spontaneous emission of left and right circularly polarized light by systems undergoing an electronic (or vibronic) transition, and no differentiation is made between fluorescent vs. phosphorescent emission processes.

II. Theory

The theoretical development of circularly polarized luminescence spectroscopy quite naturally has as its roots the extensive theoretical work concerning optical rotation and circular dichroism.[1-4,10] Emeis and Oosterhof[6,7] were the first to demonstrate that in the limit that the orientational distribution of emitting molecules is isotropic, there is a more-or-less direct analogy between the theoretical expressions relating the CD and CPL observables to molecular properties. In this limit, for a given electronic transition ($i \leftrightarrow j$), both $\Delta\epsilon$(CD) and ΔI(CPL) can be expressed in terms of a single molecular electronic parameter, the *rotatory strength*, defined by[1-4]

$$R_{ij} = Im\langle i|\mu|j\rangle\cdot\langle j|\mathrm{m}|i\rangle \tag{5}$$

where μ and m are the electric and magnetic dipole moment operators, respectively. The magnitude, and even the sign, of R_{ij} may differ in absorption (CD) vs. emission (CPL) since, in general, the $|i\rangle$ and $|j\rangle$ state vectors will have different compositions for the molecular ground state vs. emitting state geometries. In fact, by comparing the ΔI and $\Delta\epsilon$ spectra obtained in the $\mathrm{n} \leftrightarrow \pi^*$ transition region of an optically active ketone, Emeis and Oosterhof[6,7] were able to calculate the relative magnitudes of $R_{\mathrm{n}\pi^*}$(emission) and $R_{\mathrm{n}\pi^*}$(absorption) and from this deduce geometry differences between the ground and excited ($^1\mathrm{n}\pi^*$) states of the carbonyl chromophore.

As described below, an isotropic orientational distribution of emitting species (molecules or chromophores) must be considered as a special case in CPL spectroscopy, even when one is dealing with fluid samples of homogeneous composition. In general, the sample is excited along just one direction, and this results in the selective excitation of molecules with particular orientational distributions.

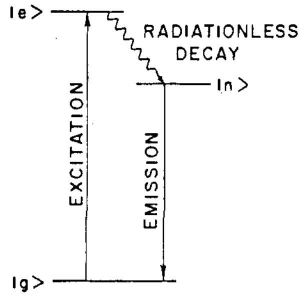

Figure 1. Generalized energy-level diagram for an emission experiment.

A. General Theoretical Formalism

As mentioned above, CPL spectroscopy probes molecular structure appropriate to a luminescent state at the time of the emission of the partially circularly polarized radiation. The population of an emitting state depends upon the orientation of the absorption transition dipole moment with respect to the polarization of the incident exciting beam, molecular conformation at the time of absorption, and the rate and efficiency of decay from the final state in absorption to the initial state in emission. A generalized energy level diagram is presented in Figure 1.

The formal relationship between the so-called "steady-state" differential emission intensity and the relevant molecular properties is given by

$$\Delta I(\lambda) = \int \Delta I(\lambda,t)\,\mathrm{d}t \tag{6}$$

where

$$\Delta I(\lambda,t) = (hc/\lambda)f_{\mathrm{CPL}}(\lambda)\int \langle N_n(\Omega,\gamma,t)\Delta W(\Omega,\gamma)\rangle\,\mathrm{d}\gamma \tag{7}$$

In this equation Ω and γ denote respectively the orientation of the emitting molecule with respect to laboratory coordinates and the conformation of the molecule. Both of these quantities may be time-dependent, and we have assumed for simplicity that conformation and orientation can be considered separately. $N_n(\Omega,\gamma,t)$ describes the time-dependent population of the emitting state n, which may be different from the final state in the initial absorption process. (See Figure 1.) $\Delta W(\Omega,\gamma)$ represents the appropriate differential transition rate as described below. The pointed brackets in this equation denote an average over allowed orientations, and the integral is over allowed conformations. The function $f_{\mathrm{CPL}}(\lambda)$ is an appropriately normalized lineshape function.

The differential transition rate, $\Delta W(\Omega,\gamma)$, is defined as the transition probability for emission of a left circularly polarized photon minus the transition probability for emission of a right circularly polarized photon. This quantity depends explicitly on both the molecular conformation at the time of emission and the orientation of the appropriate molecular transition moments relative to the direction of emission detection. The

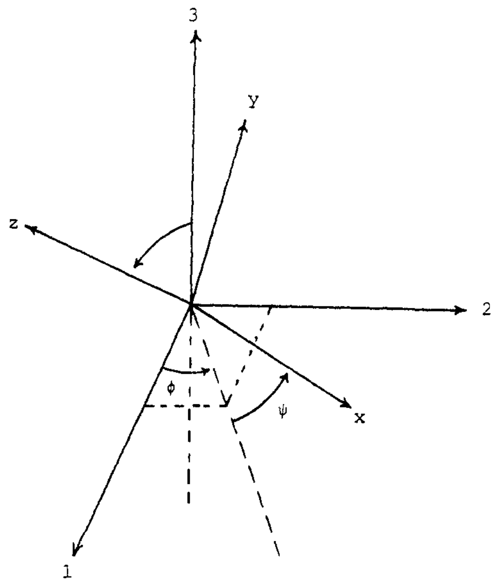

Figure 2. Relationship between the laboratory axes (denoted by **1**, **2**, and **3**) and the molecular axes (**x**, **y**, and **z**), as defined by the (Euler) angles of transformation (θ, ϕ, and ψ).

differential transition rate for an emissive transition, $g \leftarrow n$, is related to the rotatory strength as follows[11]

$$\Delta W(\Omega,\gamma) = K(\lambda^3)R_{gn} \qquad (8)$$

where $K(\lambda^3)$ is a constant. The rotatory strength, R_{gn}, is a fundamental molecular property that depends on molecular orientation through the Euler relationships connecting molecular and laboratory coordinate systems[12] and on molecular conformation through the wave functions for states $|n\rangle$ and $|g\rangle$.

During the lifetime of the emitting state, the molecule of interest may reorient or change conformation. Specific emitting-state conformations or distributions of conformations must be treated in the calculation of the rotatory strength. In some cases, for example, it may be that the dominant source of optical activity is the skewed arrangement of coupled chromophores. In this case the dihedral angle between the chromophores is the important conformational variable. Molecular reorientation is most easily treated by defining a function $G(\Omega_0;\Omega,t)$ as the probability that a molecule with orientation $\Omega_0(\theta_0,\phi_0,\psi_0)$ at time $t = 0$ has an orientation Ω at time t. The angles θ, ϕ, and ψ are defined with respect to the laboratory coordinate system (1, 2, and 3 axes), as illustrated in Figure 2. It follows that

$$N_n(\Omega,\gamma,t) = \int \mathrm{d}\phi_0 \int \mathrm{d}\psi_0 \int \sin\theta_0\, \mathrm{d}\theta_0 N_n(\Omega,\gamma,0)G(\Omega_0|\Omega,t) \qquad (9)$$

where $N_n(\Omega,\gamma,0)$ is the number of molecules in state $|n\rangle$ at time $t = 0$ with orientation Ω_0 and conformation γ.

If one assumes that decay to the emitting state is faster than other processes that may be occurring, then we can express $N_n(\Omega,\gamma,0)$ as

$$N_n(\Omega,\gamma,0) = \eta_e N_e(\Omega,\gamma,0)\exp(-k_e t) \qquad (10)$$

η_e and k_e represent respectively the efficiency and rate of decay of the initial population of molecules prepared in the excited state $|e\rangle$ at time $t = 0$. $N_e(\Omega,\gamma,0)$, the population of state $|e\rangle$ at time $t = 0$, is calculated from the intensity and polarization of the incident beam and the appropriate absorption transition moments.

The emission dissymmetry factor for the $g \leftarrow$ n transition can be written as

$$g_{\mathrm{em}}(\lambda) = \frac{4(hc/\lambda)f_{\mathrm{CPL}}(\lambda)K(\lambda^3)\int\int\langle N_n(\Omega,\gamma,t)R_{gn}\rangle\, \mathrm{d}\gamma\, \mathrm{d}t}{(hc/\lambda)f_{\mathrm{TL}}(\lambda)K(\lambda^3)\int\int\langle N_n(\Omega,\gamma,t)D_{gn}\rangle\, \mathrm{d}\gamma\, \mathrm{d}t} \qquad (11)$$

where $f_{\mathrm{TL}}(\lambda)$ denotes a normalized line-shape function for the total luminescence, which may or may not be the same as $f_{\mathrm{CPL}}(\lambda)$ and D_{gn} is the dipole strength of the emissive transition. The factor of 4 results from different multiplicative factors in the $\Delta I(\lambda)$ and $I(\lambda)$ expressions. Simplifying eq 11 yields the result

$$g_{\mathrm{em}}(\lambda) = \frac{4f_{\mathrm{CPL}}(\lambda)\int\int\langle N_n(\Omega,\gamma,t)R_{gn}\rangle\, \mathrm{d}\gamma\, \mathrm{d}t}{f_{\mathrm{TL}}(\lambda)\int\int\langle N_n(\Omega,\gamma,t)D_{gn}\rangle\, \mathrm{d}\gamma\, \mathrm{d}t} \qquad (12)$$

Application of this equation requires that one develop a model for molecular reorientation. The simplest approximation is to assume that the molecule is approximately spherical, so that molecular rotation can be described by a single exponential factor. In general, for an asymmetric molecule, five exponentials are necessary to describe the reorientation.[13] Two important limiting cases are when the reorientation is very rapid compared to emission, so that the orientation distribution of emitting molecules is isotropic, and when the reorientation is very slow compared to emission, so that the orientational distribution of emitting molecules can be calculated directly from the polarization and direction of the exciting radiation and the absorption transition dipole direction.

The final formal relationship between the experimental measurement and the appropriate molecular parameters follows from a time, spatial, and orientational average, as implied in eq 12. In Table I we have summarized results for luminescent molecules with one fixed emitting state conformation. Given in this table are expressions for g_{em} corresponding to a number of common experimental situations. Included are results for when the exciting radiation is unpolarized, linearly polarized, and circularly polarized. Expressions appropriate for the two limiting orientational distributions described above are also presented.

The consequences of generating nonisotropic orientational distributions of excited molecules for certain excitation geometries and polarizations in CPL experiments has been considered by Riehl and Richardson[5,11] and Tinoco et al.[14] In principle, for randomly oriented molecular systems, it is always possible to select an experimental geometry such that one generates an orientational distribution of emitting species that is isotropic with respect to the laboratory direction of emission detection. This is important for experimental reasons, as described below, since it is necessary to ensure that there is no linearly polarized component in the emission. As will be seen later in this review, if the species of interest is essentially a spherical emitter, as in the case of lanthanide ions, no special experimental setups are necessary.

The use of circularly polarized exciting light in CPL experiments has also been investigated. Beginning with the early work of Eaton[15] and Kokke,[16] it was recognized

TABLE I. Emission Dissymmetry Factors for Selected Experimental Situations[a]

exptl conditions	$g_{em}(\lambda) = 4f_{CPL}(\lambda)/f_{TL}(\lambda) \times$
Unpolarized Excitation	
frozen sample	
0° excitation[b]	$\dfrac{3\mu_x^{gn}m_x^{gn} + 3\mu_y^{gn}m_y^{gn} + 4\mu_z^{gn}m_z^{gn}}{3\lvert\mu_x^{gn}\rvert^2 + 3\lvert\mu_y^{gn}\rvert^2 + 4\lvert\mu_z^{gn}\rvert^2}$
90° excitation[b]	$\dfrac{7\mu_x^{gn}m_x^{gn} + 7\mu_y^{gn}m_y^{gn} + 6\mu_z^{gn}m_z^{gn}}{7\lvert\mu_x^{gn}\rvert^2 + 7\lvert\mu_y^{gn}\rvert^2 + 6\lvert\mu_z^{gn}\rvert^2}$
isotropic sample	$\mu^{gn}\cdot\mathbf{m}^{gn}/\lvert\mu^{gn}\rvert^2$
Linearly Polarized Excitation	
frozen sample: 90° excitation[b]	
0° polarization[b]	$\dfrac{3\mu_x^{gn}m_x^{gn} + 3\mu_y^{gn}m_y^{gn} + 4\mu_z^{gn}m_z^{gn}}{3\lvert\mu_x^{gn}\rvert^2 + 3\lvert\mu_y^{gn}\rvert^2 + 4\lvert\mu_z^{gn}\rvert^2}$
90° polarization[b]	$\dfrac{2\mu_x^{gn}m_x^{gn} + 2\mu_y^{gn}m_y^{gn} + 4\mu_z^{gn}m_z^{gn}}{2\lvert\mu_x^{gn}\rvert^2 + 2\lvert\mu_y^{gn}\rvert^2 + 4\lvert\mu_z^{gn}\rvert^2}$
Circularly Polarized Excitation	
isotropic sample[c]	$\dfrac{\mu^{gn}\cdot\mathbf{m}^{gn}}{\lvert\mu^{gn}\rvert^2} \times g_{abs}/2$

[a] We have used the notation $\mu_j^{gn} = \langle g|\mu_j|n\rangle$, where $\theta = x, y,$ or z (the molecule-fixed axes). [b] Defined relative to the direction of emission detection. [c] Neglecting any racemization or energy transfer processes in the excited state.

that if the incident excitation was circularly polarized, it might then be possible to observe CPL from a racemic mixture. This is, of course, true only if the differential population of excited molecules prepared by the circularly polarized excitation beam is maintained during the lifetime of the emitting state. Dekkers, Emeis, and Oosterhof[17] were the first to measure CPL in this manner from a racemic solution of *trans*-β-hydrindanone. More recently, Dekkers and Schippers[18] have observed CPL from several different racemic solutions, and partially resolved systems, and have reported the first attempts at determining enantiomeric purity by this technique.[19] Hilmes and Riehl[20,21] have reported the first example of CPL from racemic solutions of Tb(III) and Eu(III) with both chiral and achiral ligands.

Hilmes and Riehl[22] have formally treated the use of circularly polarized excitation in CPL of racemic mixtures and included explicitly the possibility of excited-state racemization and excited-state energy transfer. In this case, the differential emission intensity depends on the differential absorption, i.e., the CD at the excitation wavelength. In analogy with eq 7, we have

$$\Delta I^{\pi}(\lambda,t) = (hc/\lambda)f_{CPL}(\lambda)\int\langle\Delta N_n^{\pi}(\Omega,\gamma,t)\Delta W(\Omega,\gamma)\rangle\,d\gamma \quad (13)$$

where π denotes the incident circular polarization (left or right) and $\Delta N_n^{\pi}(\Omega,\gamma,t)$ describes the *differential* population of excited molecules in the emitting state.

B. Spectra–Structure Relationships

Although much useful structural information has been obtained from CPL measurements in recent years, there have not been many attempts at developing the kind of generalized spectra–structure correlations that have been one of the primary goals of circular dichroism (CD) and optical rotatory dispersion (ORD) for the last 25 years.[1] Parallel work in theory and experiment has led, since the early 1960s, to empirical "sector rules" in CD spectroscopy, which enable one to determine with variable reliability the stereochemistry of related compounds. There are several problems associated with the development of similar rules in CPL spectroscopy, including the fact that one has, at best, only indirect evidence concerning the geometry of a molecule in the emitting state.

There has been some effort devoted to examining model systems[22,23] in order to map out results to be expected for different molecular geometries and motions and different optical activity mechanisms. This kind of study has some utility in determining molecular structural changes, particularly when coupled with experimental results from CD spectroscopy so that the number of unknown quantities is reduced. In general, comparative CD and CPL studies are very useful and have been applied to a number of situations in which structural changes between the ground and emitting state are of primary interest.

For situations in which the luminescent chromophore of interest can be treated as more or less isolated from excited-state/ground-state structural changes, "sector rules" or their equivalent may be developed and applied by comparison with CD results. Particularly appropriate are transitions that have already been well studied in absorption. In this regard, Schippers and Dekkers[24] have developed a so-called "chirality rule" for the n $\leftrightarrow$ π^* transitions in β,γ-enones based upon an admixture of electric dipole intensity from the $C_\gamma{=}C_\beta$ bond to the intrinsic magnetic dipole transition of the carbonyl group. By examining a number of rigid compounds, they observed a cos a dependence of the rotatory strength, where a is the angle between the C=O bond and the C=C bond. This rule has then been applied[25] to CPL results, and differences between CPL and CD have been attributed to specific structural changes involving the C=O moiety.

As described in section IV.A, there has been some effort devoted to the calculation of rotatory strengths for intraconfigurational 4f–4f transitions in lanthanide coordination systems. These calculations are, however, difficult and cannot generally be used to determine absolute configuration in an unambiguous way from CPL data. Richardson[26] has been able to derive a set of selection rules for lanthanide optical activity that are useful in predicting the relative magnitudes of the 4f–4f

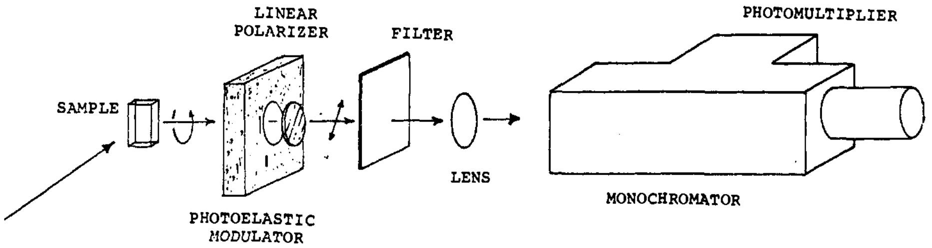

Figure 3. Schematic diagram for the optical components of a CPL spectrophotometer. The excitating light may be unpolarized, linearly polarized, or circularly polarized. The direction of emission detection is assumed to lie along the laboratory 3 axis.

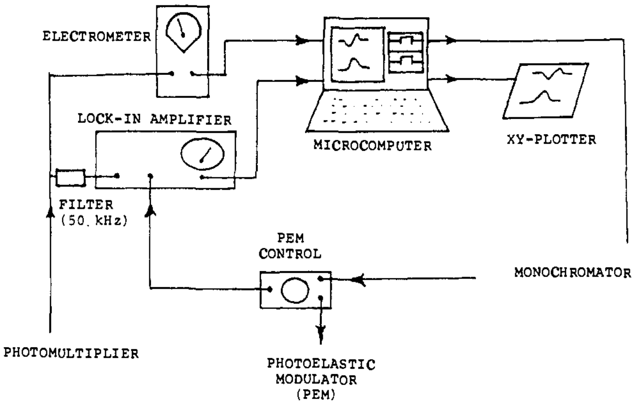

Figure 4. Schematic diagram for phase-sensitive detection of differential emission intensity in a CPL experiment.

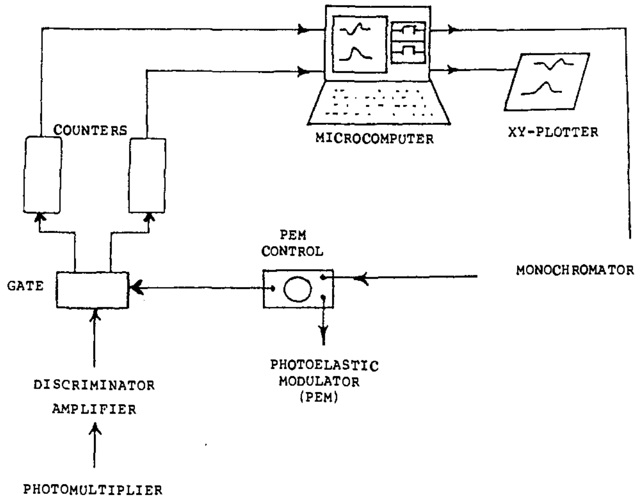

Figure 5. Schematic diagram for the differential photon-counting method of detection in a CPL experiment.

rotatory strengths in chiral lanthanide complexes.

III. CPL Measurement Techniques

All CPL measurements are currently being made on spectrometers constructed in individual research laboratories. The basic optical design of a CPL experiment is depicted in Figure 3. The incident excitation beam may be linearly polarized, circularly polarized, or unpolarized. The usual experimental configuration is to excite the sample of interest either at 0° or 90° from the direction of emission detection. The emitted light passes through a circular analyzer, which is comprised of a photoelastic modulator (PEM) followed by a linear polarizer oriented at 45° with respect to the crystal axis of the modulator. The modulator is driven at a frequency f_m (usually $\sim$50 kHz) and acts as an oscillating quarter-wave plate. On alternate cycles of the modulator oscillation, the PEM is acting as a quarter-wave-advancing or quarter-wave-retarding element. This results in right and left circularly polarized light being converted to the appropriate linear polarization, selected by the linear polarizer, and subsequently wavelength resolved by the emission monochromator and detected by the photomultiplier.

Until the recent work of Schippers, van den Beukel, and Dekkers[27] on the development and use of a photon-counting CPL spectrometer, all experimental measurements have used the phase-sensitive detection scheme reported by Steinberg and Gafni.[28] The latter design is depicted schematically in Figure 4. The output of the photomultiplier is input to a lock-in amplifier, whose reference signal is supplied by the PEM. Any f_m component in the generated photocurrent will be proportional to ΔI. The total emission intensity is monitored separately, either by directing the photomultiplier output through an electrometer or by mechanically chopping the emitted beam at a much lower frequency and using a second lock-in amplifier for phase-sensitive detection of the total photocurrent.[29] Signals proportional to I and ΔI are then input to a microcomputer for data manipulation, storage, and plotting, or simply directed to a two-pen recorder.

A schematic diagram of the photon-counting detection system of ref 27 is shown in Figure 5. In this case, the leading edge of the reference signal from the PEM is used to generate a synchronization signal that alternately directs the photon pulses into two separate counters, corresponding to the total and differential photon count. Data are collected over a variable time period (window), which is chosen to be shorter than $1/f_m$. The window is centered around the maximum and minimum in the sinusoidally varying modulation cycle. The counter readings over a finite number of modulation cycles at a fixed emission wavelength yield in a very direct way the luminescence dissymmetry ratio by simple division.

A. CPL Calibration and Standards

Because of the difficulties inherent in determining absolute emission intensities, the commonly reported experimental quantity is g_{em} (sometimes referred to as g_{lum}). When the phase-sensitive detection scheme is employed to measure CPL, some method of calibration must be used to relate the lock-in reading for ΔI and the electrometer (or lock-in) reading for I to g_{em}. Steinberg and Gafni[28] have reported a procedure for calibrating a CPL spectrometer in which a quarter-wave plate and an optical flat are used to generate continuous degrees of elliptical polarization. Reasonably good results can be obtained with a simpler procedure in which one simply determines the resultant signals for "pure" circularly polarized light by using a quarter-wave retardation plate and assuming that for a given total emission intensity, the disymmetry factor is linear with the lock-in reading.[30] Another method is to allow an initially unpolarized light beam to pass through a solution of known CD at the appropriate wavelength.[31] One of the principal advantages of the photon-counting detection scheme is that one has explicit counts for I and ΔI, so that if the instrument is working properly, no calibration procedure is necessary.

There has been some effort in recent years to develop reliable standards in CPL spectroscopy. Brittain[32] has suggested the use of tris(3-trifluoroacetyl-*d*-camphorato)europium (III), $Eu(facam)_3$, a commonly used NMR shift reagent that is commercially available in high purity. This species can be excited either by a UV source around 350 nm, or by an argon ion laser at 466 nm. The choice of this complex as a possible standard is based upon the fact that three different transitions are observed in a relatively narrow spectral region (575–635 nm), both positive and negative values of ΔI are present, and g_{em} values varying over an order of magnitude are measured. In addition, because the CPL spectrum is relatively insensitive to room temperature variations the complex can be prepared in sufficient purity without extensive drying procedures.[27]

Another possible choice for a CPL standard could be sodium uranyl acetate, which crystallizes in enantiomerically distinct crystals. The luminescence from individual crystals, which are easy to prepare and are very stable, is highly circularly polarized.[33] The only difficulty is that one needs to determine the absolute configuration of the crystal chosen.

B. Artifacts in CPL Measurements

In most applications of CPL, the circularly polarized components of the emitted light represent only a small fraction of the total emitted light intensity (usually $<10^{-2}$). CPL spectrometers are generally capable of determining g_{em} with a sensitivity of approximately 1 part in 10^4–10^5, depending on the total light intensity. One of the problems in CPL measurements is the fact that it is not possible to reliably determine CPL results if the emitted light is also partially linearly polarized.

Linear polarization in emission results from a distribution of emitting molecules that is not isotropic. As described above, even for molecular systems which have random orientational distributions in the ground state, the distribution of emitting molecules may not be random due to photoselection by the incident excitation beam.

The problem associated with the measurement of CPL in the presence of linearly polarized luminescence was first recognized by Steinberg and Gafni,[28] who demonstrated that even if the emitting sample was achiral, an apparent CPL signal was detected if the emission was linearly polarized. In principle, if the PEM is assumed to behave ideally, linearly polarized light cannot contribute to the f_m signal. Linearly polarized light will, in fact, result in a modulated signal at a frequency of $2f_m$. The PEM is supplied with a reference signal at this frequency for this purpose. For many molecular systems the linear polarization can be quite substantial, and it has been suggested[34] that the source of the artifact is an electronic problem associated with the use of a lock-in amplifier to detect a small f_m signal in the presence of a strong $2f_m$ signal. This conclusion has been disputed by Steinberg et al.[35]

This problem has very recently been addressed by Shindo and Nakagawa[36] and by Dekkers et al.[37] These authors conclude that the most likely source of the artifact signal in many cases is small inherent birefringence in the modulator itself. Dekkers et al.[37] have presented some experimental results that support their conclusion and demonstrated experimentally that the artifact, if present, and a true CPL signal are additive.

It is, obviously, possible to eliminate the artifact by ensuring that there is no linearly polarized component in the emission. This can be accomplished either by using unpolarized exciting light oriented at 0° or 180° with respect to the direction of emission detector or, when linearly polarized excitation is used, by aligning the beam direction at 90° and orienting the linear polarization parallel to the emission detection direction. It is also possible to choose so-called "magic angle" configurations to accomplish this purpose.[11]

It should be noted that the artifact one detects when linear polarization is present is difficult to distinguish from true circularly polarized emission. Very small realignments of the optical components can yield apparent signals of opposite signs and variable magnitudes. It is extremely important when CPL experiments are performed to check for linear polarization in the emission by looking for a signal at $2f_m$. If this is present, an f_m signal does not then necessarily indicate the presence of CPL.

IV. Applications of CPL Spectroscopy

A. Lanthanide and Actinide Complexes

The intraconfigurational f–f electronic transitions of lanthanide and actinide complexes are particularly well suited for chiroptical measurement techniques. These transitions generally exhibit relatively narrow spectral lines in both solution and solid-state media, and for the lanthanide complexes, nearly all of the transition intensity is observed in electronic *origin* lines (as opposed to vibronic lines). Furthermore, many of these transitions are predominantly magnetic-dipole in nature and are expected to exhibit relatively large rotatory strength to dipole strength ratios (R/D). As illustrated in eq 12, a large $|R/D|$ associated with a sharp emission line will yield a large $|g_{em}|$ within the frequency interval of that line, thus optimizing one of the intrinsic molecular conditions for CPL measurement.

Circularly polarized luminescence spectra have been reported for a large number of terbium and europium complexes in solution[20,21,32,38-94] and for several complexes in the solid (crystalline) state.[95,96] In each of these cases, the luminescence derives from f–f electronic transition processes. The theory of f–f optical activity (in emission and absorption) has been addressed by Richardson and co-workers,[26,97-98] and much of the experimental work carried out in this field prior to 1983 has been reviewed recently by Brittain.[99] The CPL of a uranyl compound in its crystalline state has also been reported.[33,100] In this case the luminescence is associated with spectroscopic processes localized on the UO_2^{2+}

(uranyl) ion, but these processes are not intraconfigurational f–f transitions.

Among lanthanide complexes, those of Eu(III), Gd(III), and Tb(III) generally exhibit the largest luminescence quantum yields. One-photon excitation of Gd(III) luminescence requires excitation energies >32 000 cm^{-1}, and the principal Gd(III) emission ($^6P_{7/2} \rightarrow {}^8S_{7/2}$) generally occurs in the 32 000-cm^{-1} spectral region. In contrast, one-photon excitation of Eu(III) and Tb(III) luminescence may be accomplished by using radiation in the visible region of the spectrum, and under these excitation conditions most of the Eu(III) and Tb(III) emissions occur in the visible and near-infrared spectral regions. A few Gd(III) CPL spectra have been measured (Foster and Richardson, unpublished results), but none have yet been reported in the literature. All of the lanthanide CPL measurements reported so far in the literature[20,21,32,38–96] have been for Eu(III) and Tb(III) complexes. The latter have been favored because of their relatively high luminescence quantum yields in a wide variety of solution media and because their emissions occur in easily accessible spectral regions.

1. Luminescence Properties of Eu(III) and Tb(III) Complexes

The lowest energy multiplets associated with the $4f^6$ electronic configuration of Eu(III) and the $4f^8$ electronic configuration of Tb(III) are shown in Figure 6 (each labeled according to its principal $^{2S+1}L_J$ Russell–Saunders components). Most CPL spectra recorded in the literature for Eu(III) complexes have been for emissions associated with the $^5D_0 \rightarrow {}^7F_J$ (J = 0–6) transition manifolds. The strongest emissions are invariable observed in the $^5D_0 \rightarrow {}^7F_{1,2,4}$ transition regions, with the $0 \rightarrow 2$ emission intensity exhibiting a *hypersensitivity* to the ligand environment (as characterized by donor-atom types, coordination number, and coordination geometry).[101–104] The largest $|g_{em}|$ values are invariably observed within the $0 \rightarrow 1$ emission region, reflecting the predominantly *magnetic-dipole* character of the $^5D_0 \rightarrow {}^7F_1$ transition vs. the predominantly *electric-dipole* character of the $^5D_0 \rightarrow {}^7F_J$ ($J \neq 1$) transitions.[26,95,97,98,105] In Eu(III) CPL studies, the best *probe* transitions are those occurring within the $^5D_0 \rightarrow {}^7F_1$ emission region (~16 700–17 100 cm^{-1}). The CPL signals (ΔI) may in many cases be larger within the $^5D_0 \rightarrow {}^7F_2$ emission region (~15 900–16 400 cm^{-1}), but the $|g_{em}|$ values will be larger within the $^5D_0 \rightarrow {}^7F_1$ emission region.

Most CPL spectra reported in the literature for Tb(III) complexes have been for emissions associated with the $^5D_4 \rightarrow {}^7F_J$ (J = 0–6) transition manifolds. The strongest emission is invariably observed within the $^5D_4 \rightarrow {}^7F_5$ transition region (~18 000–18 500 cm^{-1}), and the largest $|g_{em}|$ values are observed within the $^5D_4 \rightarrow {}^7F_5$ region *and* the $^5D_4 \rightarrow {}^7F_3$ region (~16 000–16 300 cm^{-1}). Both the $^5D_4 \rightarrow {}^7F_5$ and the $^5D_4 \rightarrow {}^7F_3$ transitions are calculated to have strong magnetic-dipole character, and these transitions may be considered as the best *probe* transitions in Tb(III) CPL studies.

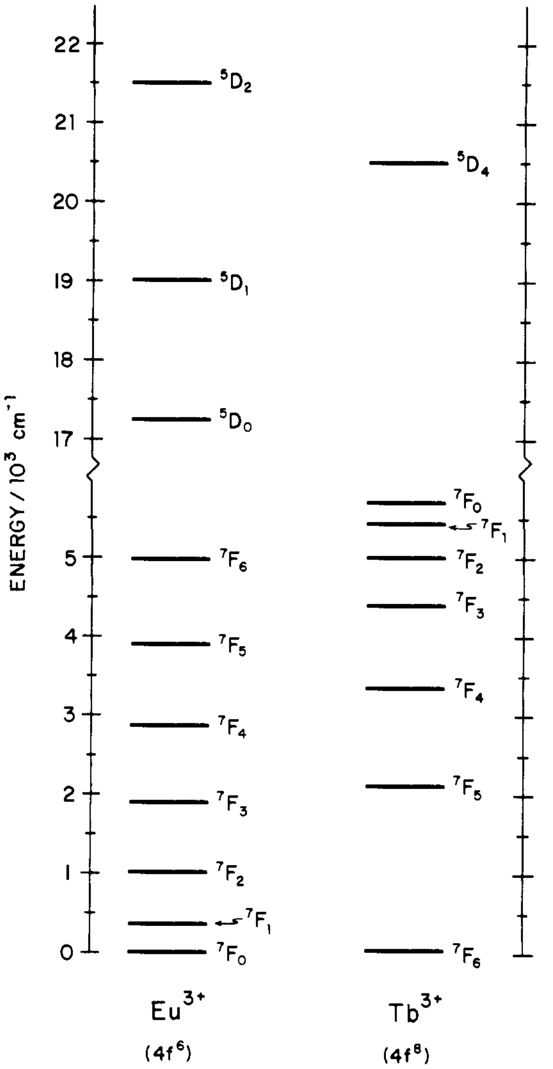

Figure 6. Energy-level diagram depicting the approximate locations of baricenters for the lowest energy multiplet levels of Eu^{3+} ($4f^6$) and Tb^{3+} ($4f^8$). Each level is labeled according to its principal $^{2S+1}L_J$ Russel–Saunders component.

The $^5D_0 \rightarrow {}^7F_1$ CPL/emission spectra of Eu(III) complexes are considerably easier to interpret than the $^5D_4 \rightarrow {}^7F_{3,5}$ CPL/emission spectra of Tb(III) complexes. The former can display (at most) only three crystal-field components (per complex or per site), whereas the latter may exhibit many more components (the number of which may be temperatue-dependent).[95,96] In contrast, one can almost always achieve higher quantum yields for Tb(III) $^5D_4 \rightarrow {}^7F_J$ emissions than for Eu(III) $^5D_0 \rightarrow {}^7F_J$ emissions. Therefore, in cases where CPL detection sensitivity is a problem, Tb(III) may be preferred over Eu(III) as the probe luminophore. In cases where detailed intepretations of spectra are of paramount interest, Eu(III) would be the luminophore of choice.

Examples of Eu(III) and Tb(III) CPL/emission spectra are shown in Figures 7 and 8. These are *axial* spectra obtained on single crystals of the compound $Na_3[Ln(ODA)_3]\cdot 2NaClO_4\cdot 6H_2O$ in which Ln = Eu^{3+} or Tb^{3+} and ODA = oxydiacetate. These crystals belong to the trigonal space group $R32$, the $Ln(ODA)_3{}^{3-}$ complexes have trigonal dihedral (D_3) symmetry, and the Ln^{3+} ions reside at sites with D_3 point-group symmetry.[95,96] The reader is referred to ref 95 and 96 for interpretations of these spectra and for detailed descriptions of the experimental conditions under which these spectra were obtained.

2. Types of Lanthanide Complexes Studied by CPL

The general types of lanthanide complexes for which CPL results have been reported in the literature are

TABLE II. Types of Lanthanide Systems Studied by CPL Spectroscopy

type	complexes[a,b]		ref
1	Ln(β-diketonate)$_n$(β-diketonate*)$_{3-n}$ chelates (n = 0, 1, or 2)	solutions using either neat or mixed nonaqueous solvents	44, 48, 55, 67, 73, 80, 84, 89
2	Ln(β-diketonate)$_3$/substrate* adducts	nonaqueous solutions with variable [chelate]:[substrate] concentration ratios	45, 53, 58, 66, 77, 78, 90
3	Ln(β-diketonate)$_3$/solvent*	solutions using neat optically active (chiral) solvents	48, 56
4	Ln(L)$_n$(L*)$_m$ (n = 1, 2, or 3; m variable)	(1) aqueous solutions under alkaline pH conditions (2) variable [Ln]:[L]:[L*] concentration ratios (3) L is an achiral, multidentate ligand which forms strong Ln(L)$_n$ complexes in aqueous solutions, and L* is an optically active (chiral) ligand	32, 54, 57, 59, 61, 64, 65, 68, 69, 71, 72, 74–76, 79, 81, 83, 85–88, 92
5	Ln/carboxylic acids*	(1) aqueous solutions under variable pH conditions (2) variable [Ln]:[ligand] concentration ratios	38, 41, 43, 49, 62–65, 82, 86, 91
6	Ln/carbohydrates* (simple and complex), nucleosides*, and nucleotides*	(1) aqueous and nonaqueous solutions (2) variable [Ln]:[ligand] concentration ratios	52, 70, 93
7	Ln/polyether ionophores* (cyclic and noncyclic)	(1) aqueous and nonaqueous solutions (2) various [Ln]:[ligand] concentration ratios	62, 94
8	Ln/proteins*	aqueous solutions under variable [Ln]:[ligand], ionic strength, and pH buffer conditions	39, 40, 42, 46, 47, 50, 51, 60, 70
9	Ln(ODA)$_3^{3-}$ in Na$_3$[Ln(ODA)$_3$]·2NaClO$_4$·6H$_2$O[c]	(1) axial spectra of single crystals (2) sample temperature was varied between 10 and 295 K	95, 96

[a] Asterisks denote inherently optically active constituents of the overall system. Note that these species are not necessarily coordinated *directly* to the lanthanide ion. [b] In all of the studies referenced here, Ln = Eu(III) or Tb(III) (i.e., either europium or terbium in its trivalent state). [c] The Ln(ODA)$_3^{3-}$ complex is inherently dissymmetric in single crystals of this compound. ODA = oxydiacetate ligand.

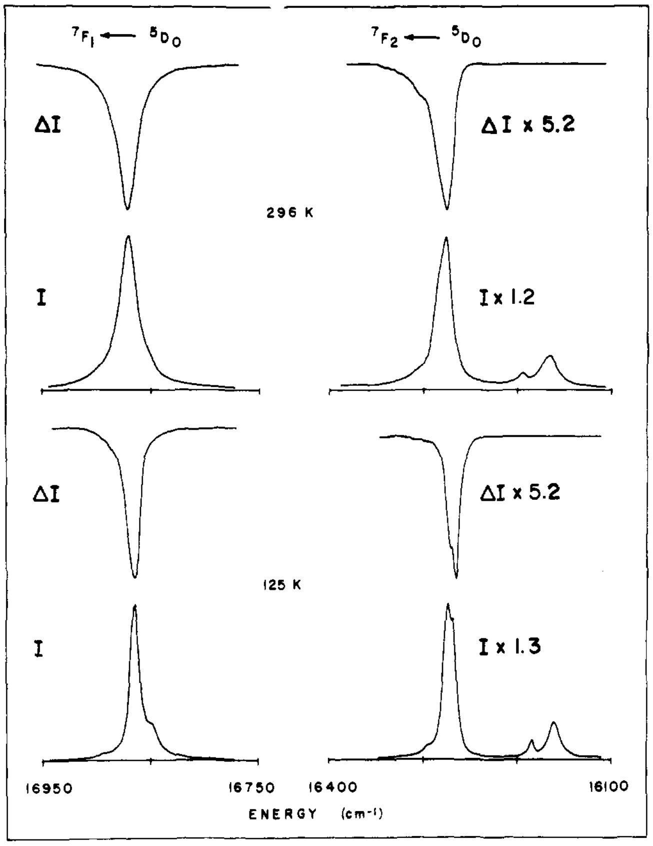

Figure 7. *Axial* CPL (Δ*I*) and total luminescence (*I*) spectra recorded at T = 296 and 125 K in the $^7F_1 \leftarrow {}^5D_0$ transition region of Eu^{3+} in Na$_3$[Eu(ODA)$_3$]·2NaClO$_4$·6H$_2$O. See ref 95 for the experimental details.

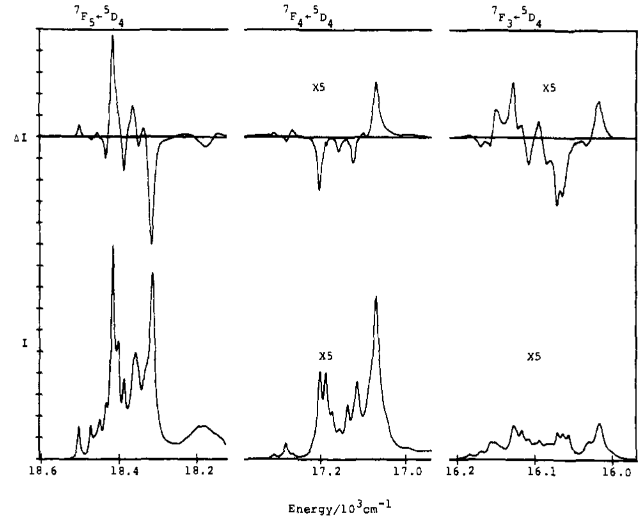

Figure 8. *Axial* CPL (Δ*I*) and total luminescence (*I*) spectra obtained in the ^7F_J (J = 5, 4, 3) $\leftarrow {}^5D_4$ transition regions of Tb^{3+} in Na$_3$[Tb(ODA)$_3$]·2NaClO$_4$·6H$_2$O at T = 125 K. Note the different intensity scales for the different transition regions. See ref 96 for the experimental details.

summarized in Table II. The relevant literature citations for each type of complex are also identified in Table II. For all of the systems classified as type 1, 5, 6, 7, or 8, the lanthanide (f–f) optical activity is induced by the presence of at least one *inherently* optically active ligand in the inner coordination sphere of the lanthanide ion. This may also be the case for many of the systems classified as type 2, 3, or 4; but alternatively the f–f optical activity in many of these systems may be attributable to *chiral perturbations* on inherently optically inactive complexes by optically active solvent molecules or molecules bound in an outer coordination sphere. Although it is possible that these chiral perturbations act *directly* on the lanthanide f^N-electron distributions, it is more likely that their major influence is to effect a chiral configuration of the atoms and molecules residing within the inner coordination sphere of the complex which will then present a chiral ligand field to the f^N electrons.

The mechanisms responsible for the induction of lanthanide f–f optical activity remain unclear, and detailed spectra–structure correlations are fraught with uncertainties. However, Dr. Harry G. Brittain of Seton Hall University has been remarkably successful in using Eu(III) and Tb(III) CPL/emission results to elicit important information about the binding constants, stoichiometries, coordination geometries, and chelate–substrate interactions for a wide variety of systems in solution.[32,53–59,64–69,71–93,99] Although many of Brittain's conclusions regarding detailed spectra–structure cor-

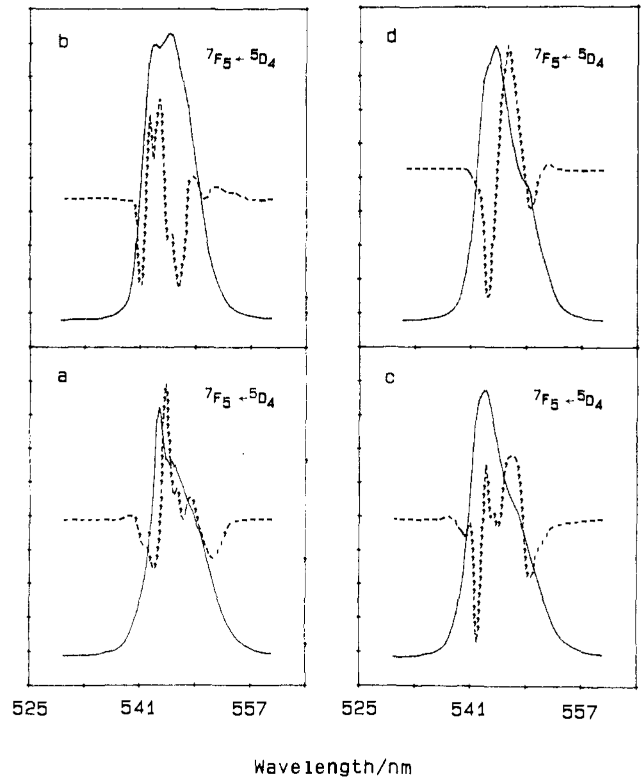

Figure 9. Total luminescence (—) and CPL (---) spectra for (a) 1:3 Tb(III)/D(−)ribose in aqueous solution at pH 6.0; (b) 1:3 Tb(III)/D(−)ribose in DMF; (c) 1:3 Tb(III)/D(+)mannose in aqueous solution at pH 5.6; (d) 1:3 Tb(III)/D(+)mannose in DMF. Tb(III) concentration = 0.01 M and λ_{exc} = 488 nm.

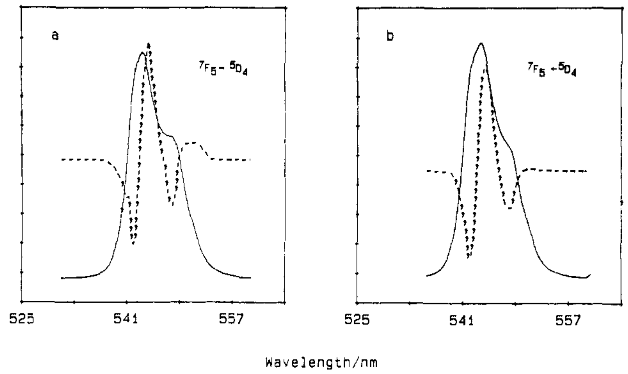

Figure 10. Total luminescence (—) and CPL (---) spectra for (a) 1:3 Tb(III)/D(−)arabinose in DMF and (b) 1:3 Tb(III)/β-D-(−)fructose in DMF. Tb(III) concentration = 0.01 M and λ_{exc} = 488 nm.

relations must be considered speculative, most of them provide useful "working hypotheses" for sorting out lanthanide complexation phenomena in solution media. It is clear that Eu(III) and Tb(III) CPL spectra contain structural information not obtainable from other types of spectroscopic measurements, but the methodologies for extracting this information are not yet fully developed and reliable.

As has been noted previously in this review, CPL spectroscopy combines the stereochemical sensitivity and specificity of natural optical activity and the measurement sensitivity inherent to optical emission techniques. The latter permits studies to be done at low concentrations, and the former ensures that small structural changes in the ligand environment about a lanthanide luminophore can be detected and monitored. One of the most useful applications of CPL in lanthanide solution studies has been to detect and monitor the interactions of Eu^{3+} and Tb^{3+} ions with very weakly coordinating ligands.[70] Many examples of this kind of application can be found in the references listed in Table II for the types **2**–**7** systems.

Illustrations of CPL induced in the $^5D_4 \rightarrow {}^7F_5$ transition region of terbium by several sugars and nucleosides in aqueous and nonaqueous solutions are shown in Figures 9–13. Neither the sugars nor the nucleosides have strongly coordinating donor moieties, yet their interactions with terbium in solution produce substantial f–f emission optical activity. Furthermore, the CPL signatures given by the various sugars and nucleosides are *distinct*, illustrating that the mechanisms responsible for the induced f–f optical activity are quite sensitive to the (chiral) structural details inherent to the different ligands. The theory of lanthanide f–f optical

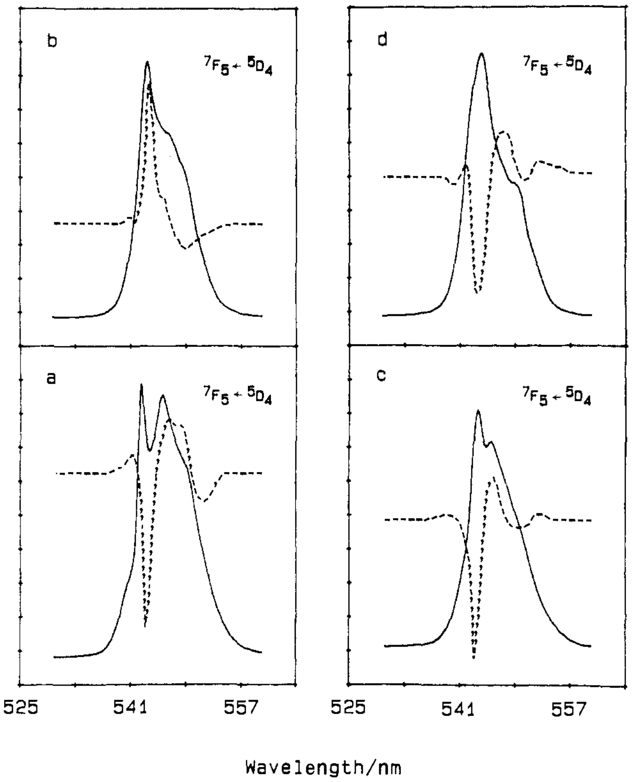

Figure 11. Total luminescence (—) and CPL (---) spectra for (a) 1:3 Tb(III)/cytidine in aqueous solution at pH 6.8; (b) 1:3 Tb(III)/cytidine in DMF; (c) 1:3 Tb(III)/uridine in aqueous solution at pH 7.5; (d) 1:3 Tb(III)/cytidine in DMF. Tb(III) concentration = 0.01 M and λ_{exc} = 488 nm.

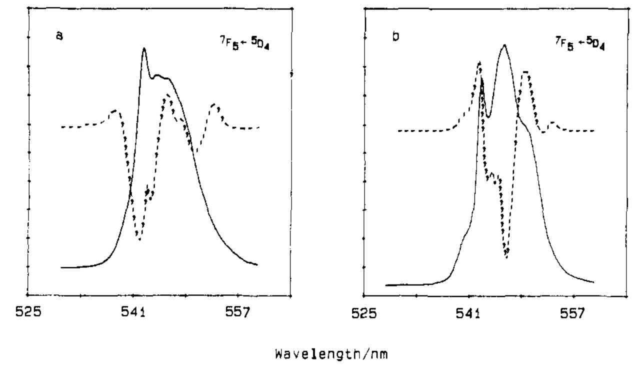

Figure 12. Total luminescence (—) and CPL (---) spectra for (a) 1:3 Tb(III)/inosine in aqueous solution at pH 9.0; (b) 1:3 Tb(III)/7-methylguanosine in aqueous solution at pH 8.1. Tb(III) concentration = 0.01 M and λ_{exc} = 488 nm.

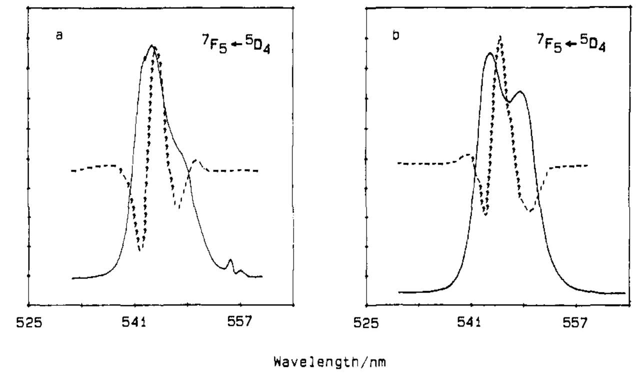

Figure 13. Total luminescence (—) and CPL (- - -) spectra for (a) 1:3 Tb(III)/adenosine in DMF [Tb(III) concentration = 0.02 M], and (b) 1:3 Tb(III)/1-methyladenosine in DMF [Tb(III) concentration = 0.01 M]. λ_{exc} = 488.0 nm.

activity is not yet sufficiently refined to permit a detailed interpretation of the CPL spectra shown in Figures 9–13 (*nor* of the analogous europium CPL spectra).[106] However, even without such an interpretation, these spectra have utility as qualitative probes (or monitors) of differentiated interactions between the lanthanide ions and a set of weakly coordinating and structurally similar ligand molecules in solution.[52,70,107,108]

Among the types of complexes listed in Table II, only the $Ln(ODA)_3^{3-}$ in $Na_3[Ln(ODA)_3]\cdot 2NaClO_4\cdot 6H_2O$ have been examined in the solid (crystalline) state. Furthermore, these are the only systems that contain no inherently optically active ligands. The optical activity of these systems is due to the dissymmetric arrangement of the oxydiacetate (ODA) ligands about the lanthanide ion. The $Ln(ODA)_3^{3-}$ complexes have tristerdentate chelate structures with trigonal dihedral (D_3) symmetry, and the LnO_9 coordination polyhedron for each complex is a *distorted* tricapped trigonal prisms with D_3 symmetry. Single crystals of $Na_3[Ln(ODA)_3]\cdot 2NaClO_4\cdot 6H_2O$ have the space group $R32$, with three $Ln(ODA)_3^{3-}$ complexes (of *like* absolute configuration, either or Δ) per unit cell. The Eu(III) and Tb(III) CPL/emission spectra for these crystals have been investigated in some detail, and these spectra provide the basis for the most thorough theoretical studies reported to date for lanthanide f–f optical activity.[95,96]

3. Lanthanide CD vs. CPL Measurements

Lanthanide–ligand interactions are generally expected to be essentially identical for all spectroscopic states split out of a $4f^N$ electronic configuration. Therefore, the stereochemical and other structural properties of a lanthanide complex are expected to be the same for the ground and excited $4f^N$ states, and the absorbing species will have structures identical with the emitting species. The absence of vibrational progressions in the electronic (f–f) absorption and emission spectra of lanthanide complexes supports this view. This being the case, circular dichroism (CD) and circularly polarized luminescence (CPL) measurements will yield identical structural information. The choice of CD vs. CPL, then, will depend on which technique can afford the greatest measurement sensitivity. For Eu(III), Tb(III), and (perhaps) Gd(III) complexes, CPL will most often be the best chiroptical technique to use. For other members of the lanthanide series, CD will most often be the chiroptical technique of choice.

4. Actinide CPL

The earliest reported measurements of actinide CPL were by Samoilov (in 1948).[100] who observed circular polarization in the emission lines of sodium uranyl acetate crystals at liquid helium temperature. In that same study, Samoilov also observed circular dichroism in the lines of the $Na[UO_2(CH_3COO)_3]$ crystals. More accurate and detailed CD measurements on the sodium uranyl acetate system have been carried out more recently by Denning et al.[109] and Palmer and Richardson,[110] and more complete CPL measurements on this system have been carried out by Murata et al.[33] and Palmer and Richardson.[110] This is the only actinide system for which CPL spectra have been reported in the literature.

$Na[UO_2(CH_3COO)_3]$ is cubic with four molecules per unit cell.[111] The space group is $P2_13$, providing the possibility of two enantiomeric forms. Each UO_2^{2+} ion is coordinated to three acetate ions via bidentate chelation modes, with the "mean" plane of the six acetate donor atoms (oxygens) being nearly perpendicular to the O–U–O axis. However, each of the four-membered chelate rings is slightly canted out of this equatorial plane, with one donor atom of each ring lying ~0.04 Å above the plane and the other lying ~0.04 Å below the plane. Furthermore, the U–O bond distances for these two donor atoms are slightly different (2.51 Å vs. 2.47 Å). Thus the point-group symmetry of each $UO_2(CH_3COO)_3^-$ complex in the crystal is C_3, and the site symmetry of each U atom is also C_3. The intrinsic chirality of each complex derives entirely from the very small twists of the chelate rings out of the equatorial plane of the UO_2^{2+} ion. The cubic crystallographic structure of the $Na[UO_2(CH_3COO)_3]$ system along with the rather subtle chirality in the $UO_2(CH_3COO)_3^-$ complexes make this system particularly interesting for optical activity studies.

Circularly polarized luminescence spectra have been recorded throughout the 15 600–21 250-cm^{-1} region for $Na[UO_2(CH_3COO)_3]$ at temperatures ranging from 4.2 to 296 K.[33,110] All of the luminescence observed in this spectral region can be assigned as originating from a single electronic excited state (Π_g) of the UO_2^{2+} moiety and terminating in the Σ_g^+ ground state. [Note that in the C_3 symmetry group of the $UO_2(CH_3COO)_3^-$ complexes Π_g transforms as E and Σ_g^+ transforms at A.] The total (unpolarized) emission spectra exhibit at least five long progressions in the O–U–O symmetry stretching vibrational mode (~850 cm^{-1}), one of which is based on the electronic origin (0–0) line and the remainder of which are based on "false" origins associated with one-phonon vibronic lines. The CPL spectra, in contrast, exhibit just *one* long progression in the O–U–O symmetry stretching mode, and it is based on the true electronic origin (0–0) line. This interesting observation most likely reflects the relative distributions of magnetic-dipole strength vs. electric-dipole strength among the 0–0 and 0–1 (phonon-assisted) transitions. The 0–0 line for the $\Pi_g \rightarrow \Sigma_g^+$ transition in the UO_2^{2+} moiety is expected to be predominantly magnetic-dipole in character, whereas the 0–1 (phonon-assisted) lines will have predominantly electric-dipole character. At low temperatures, the strongest lines observed in the CPL spectra have $|g_{em}|$ lines as large as 0.6.[33]

B. Transition-Metal Systems

Only two reports of CPL from optically active transition-metal complexes have appeared in the literature since our last review.[4] Peacock and Stewart[112] have reported the CPL from $Cr(en)_3^{3+}$ in uniaxial single crystals of $2Rh(en)_3Cl_3 \cdot NaCl \cdot 6H_2O$ at temperatures below 200 K. They were able to measure CPL not only from the electronic origin at 14900 cm^{-1} corresponding to the $^4A_2 \rightarrow {}^2E$ transition but also the CPL from a number of vibronic lines associated with this origin. These authors also report that at 40 K a second set of emission lines appear, which are attributed to a different site in the host crystal. This complex is, in fact, the only transition-metal complex whose CPL spectrum had been previously reported.[113]

Gafni and Steinberg[114] have reported the CPL from resolved $Ru(bipyridine)_3^{2+}$. The transitions observed for this complex in the visible part of the spectrum are known to be of the charge transfer type. These authors observe a variation of g_{em} across the emission band (520–700 nm) and interpret this result as an indication of a singlet–singlet as well as a singlet–triplet transition in the emission.

C. Organic Systems

The first measurement of molecular CPL by Emeis and Oosterhof[6] involved *trans-β*-hydrindanone (*trans*-bicyclo[4.3.0]nonan-8-one), and since then ketones have been the class of organic molecules most studied by the CPL technique. The primary reasons for this emphasis are the same reasons that have made the n → π* carbonyl transition one of the most widely studied transitions in CD spectroscopy, namely, that the transition is electric dipole forbidden, but magnetic dipole allowed in the *local* C_{2v} symmetry of the carbonyl chromophore. The transition picks up electric-dipole intensity from the perturbations due to the rest of the molecule, resulting in large dissymmetry ratios. In addition, this transition is usually located in a spectral region (~300 nm) isolated from other transitions. This latter characteristic is particularly important in any attempt at developing useful spectra–structure correlations.

Steinberg, Gafni, and Steinberg[35] have reported circular polarization in the phosphorescence of optically active camphorquinone and of benzoquinone in which the optical activity is induced by the presence of L-menthol in solution. These experiments were carried out in frozen glasses to increase the phosphorescence intensity. The dissymmetry ratio for D-camphorquinone phosphoresence ($\lambda > 550$ nm) was determined to be $(1-2) \times 10^{-3}$. This is an order of magnitude less than that of the fluorescence and reflects the fact that the electronic states involved are different. No evidence was found for any ground-state/excited-state structural changes in the dicarbonyl moiety. The induced CPL in the benzophenone phosphorescence was appreciable and is consistent with the formation of a 1:1 complex with L-menthol.

Schippers and Dekkers[18] have measured the CPL from the n → π* transition of *cis*-bicyclo[4.3.0]nonan-8-one and two trans-3,4 bridged cyclopentanone derivatives in an effort to detect CPL from conformational isomers of cyclopentanone itself through excitation with circularly polarized light. No CPL was detected in this latter experiment for a range of temperatures, and it was concluded from the sensitivity of their instrument that interconversion of the enantiomeric twist conformers must be occurring with a rate $>2 \times 10^9$ s^{-1}. Schippers et al.[25] have also studied a series of rigid unsaturated *β,γ*-enones, e.g., (1*S*,3*R*)-4-methyleneadamantan-2-one, and interpreted the measured circular polarization in terms of specific excited-state structural changes.[24] A number of other substituted monoketones and diketones have been studied by these authors.[19,115]

Barnett, Drake, and Mason[31] have reported circularly polarized luminescence from calycanthine. The spectra in the region of the π ↔ π* transition were interpreted in terms of aniline dimers. The authors were able to determine the absolute configuration from the frequency order of the oppositely signed CPL doublet, and this conclusion was in agreement with the previously determined crystal structure. In a related study, Schippers[116] has reported the CPL spectrum of (*R*)-(−)-[6,6]vespirene in an attempt to determine absolute configuration. In this case, however, the CPL and CD spectra did not show the simple couplet behavior characteristics of dimers or "pairwise excitons", and, therefore, were not amenable to a simple interpretation.

Brittain et al.[117] have reported CPL from (+)-1-(1-hydroxyhexyl)pyrene and its enantiomer in methanol at several concentrations. No measurable CPL was found for sample concentrations less than 1×10^{-4}; however, at higher concentrations a large signal was observed at wavelengths corresponding to excimer emission.

Pollman, Mainusch, and Stegemeyer[118] have measured circular polarization in the fluorescence from a number of achiral dye molecules dissolved in cholosteric liquid crystals. The CPL was analyzed in terms of helically oriented chromophores. The sign and magnitude of the CPL was shown to change sign as a function of temperature as the liquid crystal underwent a phase transition from an *l*-helix to a *d*-helix. It should be noted that g_{em} for these liquid crystal systems can be quite large (>0.02). These measurements were, in fact, made without the aid of a photoelastic modulator. The emission, measured nearly parallel to the helix axis of the liquid crystal, was simply allowed to pass through two static circular analyzers and recorded independently. Additional measurements on other achiral dyes have been reported by Stegemeyer, Stille, and Pollman.[119]

Sisido, Takeuchi, and Imanishi[120] have reported the circular polarization in the fluorescence from less than 1 mol % cholesteryl 3-(1-pyrenyl)proprionate in a mixed cholosteric liquid crystal of cholesteryl nonanoate (35%) and cholesteryl chloride (65%). The fluorescence in this case originates from the monomer. The circular polarization is intense and is observed to oscillate rapidly between positive and negative values, as the temperature is varied above and below the nematic point (43 °C). In a related study[121] involving a series of cholosteryl ω-arylalkanoates, these same authors observed large circular polarization in the excimer fluorescence from the cholesteric liquid crystals (g_{em}(max) = 0.15–0.30) but no circular polarization in the spectral region corresponding to monomer fluorescence. The intense CPL from these systems leads these authors to conclude that the excimer fluorescence transition moment is oriented nearly perpendicular to the optic axis of the cholesteric liquid crystals that were studied.

Brittain[122] has examined the achiral dye fluorescein dissolved in an optically active β-cyclodextrin solution and interpreted the results in terms of a preferential conformation of the fluoescein molecule. These solvent-induced CPL measurements involving fluorescein have been questioned,[36] since the emission has been shown to be partially linearly polarized.

CPL from a series of aromatic poly(α-amino) acids has recently been reported by Sisido et al.[122] CPL was observed at wavelengths corresponding to monomer emission for poly(9-anthrylmethyl L-asparatate) but not for poly(1- and 2-naphthyl-L-alanine), indicating that in these latter species there is no delocalization or exciton formation along the polymer chain. Large CPL signals were observed for excimer fluorescence from the 9-anthrylmethyl and 2-naphthyl-L-alanine aspartates.

D. Biochemical Systems

The measurement of circularly polarized luminescence has found considerable use as a structural probe in biochemical systems. This work has been pioneered by Professor I. Z. Steinberg and his research group at the Weizmann Institute. Their efforts have included both intrinsic fluorescence from biochemical systems as well as the chemical attachment of fluorescent probes. Of particular interest in these research efforts has been the measurement of CD and CPL and the interpretation of differences in terms of structural changes between ground and emitting states.[124]

Gafni[125] has recently investigated the CD and CPL of reduced nicotinamide adenine dinucleotide (NADH) in solution and bound to several dehydrogenase systems. Differences between the CD and CPL in these systems yielded information regarding the rigidity of the enzyme–coenzyme complex. Observed differences in the CPL among the different hydrogenases were interpreted in terms of structural changes around the active site of the enzyme as it binds to different substrates. Gafni[126] has also used CPL to probe age-related modifications in rat muscle glyceraldehyde-3-phosphate dehydrogenase. Comparison of spectra from enzymes isolated from old and young animals shows that the CPL from bound NADH is the same; however, CPL from the fluorescent 1,N^6-ethanoadenine dinucleotides were very different, thus pointing out regions of structural change.

Burtnick and Schaar[127] have measured circular polarization in the fluorescence of actin-bound ϵATP. The fluorescent ϵATP displays no CPL in solution. Information was obtained concerning the stability of the ϵATP-G-actin complex, as well as the stability of the G-actin complex itself. Steinberg, Wachtel, and Gafni[128] have studied conformational changes in tRNA through the measurement of circular polarization in the phosphorescence of native 4-thiouridine base units. Several different species were examined, each showing a distinctive dependence of g_{em} on salt concentration.

Tran and Drake[129] have reported CPL from bilirubin bound to human serum albumin, and Tran and Beddard[130,131] have reported CPL from bilirubin bound to bovine serum albumin. The spectroscopic results, along with lifetime studies, indicate that the Z-E, E-Z, and E-E isomers are present as photoproducts and contribute to the fluorescence.

In a different kind of study, Wynberg et al.[132] have reported the first observation of circularly polarized *bioluminescence.* They examined live firefly larvae and observed that the right and left lanterns of the larvae emitted light of opposite polarizations. It was proposed that the circular polarization is not molecular in origin but is due to the passage of linearly polarized light through a birefringent medium. The medium in this case is the surrounding membrane structure. The orientation of the emitted linear polarization with respect to the birefringent (membrane) axis of the left lantern must necessarily be enantiomeric to that of the right lantern.

V. Related Emission Phenomena

A. Fluorescence-Detected Circular Dichroism

Fluorescence-detected circular dichroism (FDCD) involves the measurement of differences in total fluorescent intensity when an optically active sample is excited with left and right circularly polarized light.[133] This technique probes the ground-state chirality of the system under study, since the discrimination takes place in absorption. The usefulness of this measurement technique rests on the fact that one is monitoring the differential absorption through the more sensitive and more selective measurement of emission intensity.

FDCD has, as yet, not found widespread applications as a stereochemical probe, even though potentially, it offers many of the same advantages as does CPL. One of the primary reasons for this is that accurate measurements are difficult, due to the difficulty of generating exactly equal amounts of left and right circularly polarized exciting light. It should also be mentioned that this technique is not suitable for studying systems with long-lived emitting states in the manner of CPL techniques described in section III, since in this application the emission must be occurring on a time scale faster than the PEM frequency (which is usually ~50 kHz). If instead of the PEM a Pockels cell is used to generate the circularly polarized exciting light, slower emission processes can be studied.

Many of the experimental problems associated with FDCD measurements have been overcome by Lobenstine and Turner,[134] who were able to improve the incident circular polarization by precise alignment of a Pockel's cell modulator and the use of an accurate high-voltage square wave for polarization switching. In addition, in order to minimize artifacts due to linear polarization, they have employed a two-photomultiplier detection scheme, modeled after the design of Hug,[135] who used it to overcome a similar artifact in the measurement of Raman optical activity. Lobenstine et al.[136] proceeded to use their instrument to measure FDCD for specific fluorescent tryptophans in a number of different proteins. Values for the dissymmetry range from -1×10^{-3} for human serum albumin to $+1.65 \times 10^{-3}$ for monellin. This is to be compared to a value of 4×10^{-4} for free tryptophan, demonstrating the sensitivity of the FDCD technique.

Although not described as such, Tran and Fendler[137] have reported experiments on tryptophan and dansyl-L(and D)-tryptophan that are essentially FDCD measurements. The primary goal in this work was the demonstration of stereoselective energy transfer (i.e., a difference in energy-transfer rates for the two enantiomeric systems). That these results are in error was pointed out by Lobenstine and Turner,[138] who repeated the measurements on tryptophan with due regard to experimental artifacts.

B. Magnetic Circularly Polarized Luminescence

As was mentioned in section I of this review, the measurement of magnetically induced circular polarization in the luminescence of molecular systems is much more suitable for studies aimed at a fundamental understanding of the electronic structure of the system under study, as opposed to molecular structure, which is the primary goal in natural CPL spectroscopy. The theoretical formalism for MCPL follows directly from that developed for natural CPL, the only modification being that the initial and final eigenstates are derived in the presence of the magnetic field. In most respects the resultant theoretical expressions appropriate for relating the measurement of MCPL to details of electronic structure resemble very closely those previously developed for MCD.[5,139]

In all but one of the existing published MCPL work, the solution or solid was studied in the presence of an externally applied static magnetic field. In the only exception, Muller et al.[140] have measured the circular polarization in the thermal emission from the (100) surface of a single crystal of *ferromagnetic* iron from 0.6 to 2.5 μm at temperatures just below the Curie point (950–1150 K). The material had been magnetically saturated in an external field of 1.5 T.

Foster et al. have used MCPL from a number of europium β-diketonate complexes in nonaqueous solutions[104] and several nine-coordinate europium complexes in aqueous solution[103] as an aid in studies aimed at elucidation of the solution structure of these species. The MCPL results in most cases clearly showed the magnetic sublevels involved in the complex multiplet–multiplet transitions in these species. These room temperature studies were the first examples of MCPL from solutions, and they illustrate the kind of unique information that can be obtained from this kind of an experiment.

Manson and Shah[141] have reported the measurement of circular polarization in vibrational sidebands of the $^2E_g \rightarrow {}^4A_{2g}$ transition in MgO:V^{2+} and MgO:Cr^{3+} at 1.6 K. The impurity ions occupy sites of cubic symmetry in MgO. The goal of this work was to use the Zeeman selection rules as a measure of the relative strengths of the T_{1u} vs. T_{2u} vibrations in coupling to the d electronic states and in promoting d–d electric dipole intensity. It was concluded that for V^{2+} the electric-dipole intensity arose predominantly from the T_{1u} vibration, whereas for Cu^{3+} the situation was reversed. Edel et al.[142] have recently observed magnetic induced circular polarization in the emission from F and F_A centers in CaO. Richardson and co-workers have reported MCPL results for a number of trivalent lanthanide ions (Ln^{3+}) in the cubic $Cs_2NaLnCl_6$ and Cs_2NaYCl_6:Ln^{3+} systems.[143-145] These results were obtained at high resolution under variable-temperature conditions, and their analysis revealed considerable information about the $4f^n$ electronic structure of the lanthanide ions.

VI. Summary

Though the measurement of circularly polarized luminescence is still limited to a small number of research laboratories, it is becoming an important spectroscopic tool in a variety of chemical and biochemical research problems. In the past several years important technical advances have been made in instrumentation, particularly in the development of the differential photon-counting method of detection[27] and in an understanding of the sources of experimental artifacts and how they can be minimized.[36,37] These advances should lead to the possibility of performing time-resolved CPL studies, as well as allowing for experimental work on weakly fluorescent systems and on systems that emit only at low temperatures. The high stability of the photon-counting technique should also enable one to measure CPL from dilute microscopic samples.

Applications of CPL to date have for the most part been concentrated in a relatively limited number of molecular systems. Areas that have been particularly exploited are the use of Eu(III) and Tb(III) in studies aimed at the elucidation of the structure of lanthanide complexes, in the use of these same species, as well as intrinsic fluorescence, as luminescent probes of biochemical structure, and in studies of $n\pi^*$ emissive transitions in ketones. Extensions of CPL spectroscopy to other luminescent systems will be greatly facilitated by continued theoretical progress. In particular, the development of reliable theories (or models) that are capable of relating the CPL observables to details of molecular structure or molecular dynamics is extremely important.

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