

Circular Dichroism and Optical Rotation†

JOHN A. SCHELLMAN

Department of Chemistry, University of Oregon, Eugene, Oregon 97403

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I. Introduction

For well over a hundred years optical activity was regarded primarily as a refractive property of transparent media which was strongly, but obscurely, dependent on the configuration and conformation of the constituent molecules.¹ More recently in roughly three stages, the study of optical activity has entered into the realm of molecular spectroscopy. These stages were the establishment of the behavior of optical activity within absorption bands by Cotton² and later by Kuhn,³ the realization that the isolated optical activity of a single band is much simpler to interpret than optical activity at a single wavelength,^{4,5} and, finally, the availability of commercial equipment which converts the study of optical activity into a direct and accurate measurement of differential absorption of right and left circularly polarized light.

This essentially inverted development of the field has led to a peculiar structure to the theory as it exists in the literature. An analogous situation would be if the theory of the electronic absorption of atoms and molecules had been approached from the point of view of the refractive index. The result is that experimental workers in the field at the present time place most weight on the measurement and interpretation of circular dichroism (CD) but, on seeking theoretical guidance, find that the literature is mostly concerned with the optical rotatory dispersion (ORD) of line spectra. These remarks apply only to theoretical discussions at the elementary level. From a more advanced point of view, the topic has been covered in a very satisfactory manner by a number of writers (for example, ref 6-9).

What seems to have been bypassed in the literature is a discussion of circular dichroism at the minimum level of complexity, i.e., straightforward, time-dependent perturbation theory with simple electric and magnetic dipole interaction with the radiation. Though lacking the power and generality of other approaches to this problem, this

method is capable of producing a quite accurate representation of the theory of optical activity. As pointed out by Dirac,¹⁰ the use of the quantum theory of radiation adds nothing to the discussion for an absorptive process at low densities of radiation. The electric and magnetic dipole terms are all that are required for isotropic systems containing molecules small compared to the wavelength of light. By developing the absorptive property, CD, rather than the dispersive property, optical rotation, the accent is placed on the spectroscopic character of optical activity in agreement with current experiment and interpretation.

In this paper, the theory of optical activity will be developed following the program outlined above. Since the primary concern is the relationship of experimental data with quantum mechanical matrix elements, it will be necessary to consider real absorption bands with complex shapes. To do this, an empirical distribution of absorptive intensity will be used which is a generalization of a discussion by Kauzmann.¹¹ Optical rotation and, in particular, Rosenfeld's equation for optical rotation are generated from the CD expressions via the Kronig-Kramers transform.

II. Extinction Coefficient

In differential form the Beer-Lambert law is given by $\delta I/I = -2.303\epsilon C \delta z$, where ϵ is the extinction coefficient, C the concentration, δz the thickness of the thin layer of sample on which the light is impinging normally, I the intensity of the radiation in ergs $\text{cm}^{-2} \text{sec}^{-1}$, and δI the intensity lost in passage through the layer of thickness δz by the absorption of the molecules therein. δI is equal to the number of molecules in the layer, δN , times w , the average energy absorbed per molecule per second. $\delta I = w \delta N$. If the unit of concentration is moles per liter, $\delta N = (NC/1000)\delta z$ because l is defined in terms of unit cross-sectional area and

$$\epsilon = \frac{N}{2303} \frac{w}{l} \quad (1)$$

where N is Avogadro's number. Note that if w is not proportional to l , the extinction coefficient will depend on the intensity of radiation. From an examination of the units it can be seen that w/l is the cross section in cm^2 per molecule for the absorption process.

Linear dichroism and circular dichroism are defined in terms of differences in extinction coefficients as follows:

linear dichroism

$$\Delta\epsilon = \epsilon_x - \epsilon_y = \frac{N}{2303} \frac{w_x - w_y}{l} \quad (2)$$

circular dichroism

$$\delta\epsilon = \epsilon_- - \epsilon_+ = \frac{N}{2303} \frac{w_- - w_+}{l} \quad (3)$$

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TABLE I. Polarization Vectors for Circularly Polarized Light

	Electric	Magnetic
rcpl	$\mathbf{e}_+ = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ i \end{pmatrix}$	$\mathbf{h}_+ = \frac{1}{\sqrt{2}} \begin{pmatrix} -i \\ 1 \end{pmatrix}$
lcpl	$\mathbf{e}_- = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ -i \end{pmatrix}$	$\mathbf{h}_- = \frac{1}{\sqrt{2}} \begin{pmatrix} i \\ 1 \end{pmatrix}$

The subscripts x and y designate extinctions with linearly polarized light parallel to arbitrarily selected orthogonal axes. The subscripts $-$ and $+$ refer to extinctions obtained with left and right circularly polarized light. In eq 2 and 3, it is assumed that the pairs of extinctions were measured at the same intensity I .

III. Classical Description of Radiation

In a transparent, isotropic medium of refractive index n , electromagnetic radiation may be described in terms of perpendicular electric and magnetic fields E and H . E , H , and the direction of propagation of the radiation k are mutually orthogonal and have the same relation to one another as the x , y , and z axes of a right-handed coordinate system. In the Gaussian system, E and H have the same dimension and are related by $|\mathbf{H}| = n|\mathbf{E}|$.

If the z axis is defined as the direction of propagation in the medium, the electric and magnetic fields may be represented by two-dimensional vectors in the xy plane (Jones vectors¹²). The electric field may then be written

$$\mathbf{E} = \{v_e E_0 e^{i\psi}\} \quad (4)$$

where v_e is a normalized unit vector describing the state of polarization of the electric field, and E_0 and ψ are the amplitude and phase of the wave, respectively. $\psi = \omega t - nkz = 2\pi(\nu - z/\nu)$, where ω is the circular frequency $2\pi\nu$, κ is $2\pi/\lambda$, and ν is the velocity c/n . It is to be understood that the electric field is given by the real part of the complex expression. Braces will be used to mean the real part of any vector. Thus if \mathbf{v} is real, $\mathbf{E} = v_e E_0 \cos \psi = \{v_e E_0 e^{i\psi}\}$. For linearly polarized light, v_e may be written as a column vector

$$\begin{pmatrix} \cos \alpha \\ \sin \alpha \end{pmatrix}$$

where α is the azimuth of polarization relative to the x axis.

The magnetic vector may be obtained from the electric vector by multiplication by n and a rotation of 90° according to the right-hand rule stated above. This rotation is accomplished with the rotation matrix

$$\mathbf{R}(90^\circ) = \begin{bmatrix} 0 & -1 \\ 1 & 0 \end{bmatrix}$$

Thus, $\mathbf{H} = n\mathbf{R}\mathbf{E}$. \mathbf{R} only operates on the polarization vector \mathbf{v} . For the linearly polarized case

$$\mathbf{v}_h = \mathbf{R}\mathbf{v}_e = \begin{pmatrix} -\sin \alpha \\ \cos \alpha \end{pmatrix}$$

$$\mathbf{H} = \{n v_h E_0 e^{i\psi}\} = v_h H_0 \cos \psi$$

For circularly polarized light (cpl) the electric polarization is most conveniently represented by the vectors

$$\mathbf{e}_+ = 1/\sqrt{2} \begin{pmatrix} 1 \\ i \end{pmatrix} \text{ and } \mathbf{e}_- = 1/\sqrt{2} \begin{pmatrix} 1 \\ -i \end{pmatrix}$$

for right and left cpl, respectively. Substituting these expressions in (4) we have

$$\mathbf{E}_+ = \{e_+ E_0 e^{i\psi}\} = \frac{E_0}{\sqrt{2}} (i \cos \psi - j \sin \psi) \quad (5a)$$

$$\mathbf{E}_- = \{e_- E_0 e^{i\psi}\} = \frac{E_0}{\sqrt{2}} (i \cos \psi + j \sin \psi)$$

That these represent right and left cpl can be seen by putting $t = 0$ and observing that the vectors trace out right and left spirals in space on substituting $\psi = -nkz$.

In forming the magnetic polarization vectors for cpl, care must be taken that these have the proper phase relations with the electric vectors. This is accomplished with the rotation matrix \mathbf{R} defined above. $\mathbf{h}_+ = \mathbf{R}\mathbf{e}_+$ and $\mathbf{h}_- = \mathbf{R}\mathbf{e}_-$. The results are

$$\mathbf{H}_+ = \{h_+ H_0 e^{i\psi}\} \text{ with } h_+ = \frac{1}{\sqrt{2}} \begin{pmatrix} -i \\ 1 \end{pmatrix} \quad (5b)$$

$$\mathbf{H}_- = \{h_- H_0 e^{i\psi}\} \text{ with } h_- = \frac{1}{\sqrt{2}} \begin{pmatrix} i \\ 1 \end{pmatrix}$$

The results and notation for the polarization vectors are summarized in Table I.

The instantaneous intensity of the radiation is given by the Poynting vector $\mathbf{S} = (c/4\pi)\mathbf{E} \times \mathbf{H}$, where the real values of \mathbf{E} and \mathbf{H} must be used in forming the product. For linearly polarized light $\mathbf{v}_e \times \mathbf{v}_h = \mathbf{k}$ and the phase dependence is $\cos^2 \psi$. Averaging the latter over a cycle yields a factor of $1/2$. The mean scalar intensity is then

$$I = |\mathbf{S}| = \frac{cnE_0^2}{8\pi} = \frac{cH_0E_0}{8\pi} = c \frac{H_0^2}{n8\pi} \quad (6)$$

The three forms of the intensity expression on the right will lead to different refractive corrections for different modes of interaction.

Though (6) was derived for the linearly polarized case, it may be shown that it is valid for any polarization, provided \mathbf{v} is normalized such that $\mathbf{v}^* \cdot \mathbf{v} = 1$. Further, the above discussion assumed a single frequency for the radiation. Any real radiation is polychromatic, and the operative electric field, magnetic field, and the intensity must be obtained by a summation or integration over the frequency. Absorption and circular dichroism spectroscopy belong to the domain of linear optical effects where this is a valid procedure.

IV. Molecules in Periodic Fields

The electronic state of a molecule may be described by the formula $\Psi = \sum a_i \Psi_i$, where the $\Psi_i = \psi_i e^{-iE_i t/\hbar}$ are the time-dependent wave functions of the eigenstates with energy E_i . The probability that a molecule is in state i is $|a_i|^2 = a_i^* a_i$, which is a function of time in the presence of an external perturbation. Time-dependent perturbation theory states that the coefficients are governed by the differential equation

$$\frac{da_i}{dt} = \frac{1}{i\hbar} \sum a_j \mathcal{U}_{ij} \quad (7)$$

where

$$\mathcal{U}_{ij} = \int \Psi_i^* \mathcal{U} \Psi_j d\tau = \exp\left[\frac{i(E_i - E_j)t}{\hbar}\right] \int \psi_i^* \mathcal{U} \psi_j d\tau = \exp[i\omega_{ij} t] \int \psi_i^* \mathcal{U} \psi_j d\tau$$

Here ω_{ij} is the circular Bohr frequency $(E_i - E_j)/\hbar$ for the transition $j \rightarrow i$, and τ represents the coordinates (including the spin) of all the electrons and nuclei of the molecule and \mathcal{U} is the interaction Hamiltonian of the perturbing field and the molecule. In this paper the interaction Hamiltonian consists simply of the interaction of the electric (μ) and magnetic (m) moments of the molecule with \mathbf{E} and \mathbf{H} of the radiation field.

$$\mathcal{U} = -\boldsymbol{\mu} \cdot \mathbf{E} - \mathbf{m} \cdot \mathbf{H} \quad (8)$$

It is preferable to leave \mathcal{U} unspecified for the moment except for its time dependence which will be assumed to be periodic with circular frequency ω .

$$\mathcal{U} = \{V e^{i\omega t}\} = \frac{1}{2}[V e^{i\omega t} - V^* e^{-i\omega t}] \quad (9)$$

V is the time-independent part of \mathcal{U} and represents the amplitude of \mathcal{U} in its time variation. Only the time dependence is required for the integration of eq 7. In normal spectroscopy virtually all molecules are in the ground electronic state so that for a selected excited state m

$$\left(\frac{da_m}{dt} = \frac{1}{i\hbar} \mathcal{U}_{m0} = \frac{1}{2i\hbar} [\exp[i(\omega_{m0} + \omega)t] V_{m0} - \exp[i(\omega_{m0} - \omega)t] V_{m0}^*] \right)$$

where $V_{m0} = \int \psi_m^* V \psi_0 d\tau$. Following the usual course of time-dependent perturbation theory, the expression for da_m/dt is integrated with boundary conditions $a_0 = 1$ and $a_m = 0$ at $t = 0$. The first term in the above expression leads to a term with $(\omega_{m0} + \omega)$ in the denominator. This leads to negligible contributions unless $(\omega_{m0} + \omega) \cong 0$ in which case there is spontaneous emission to a lower energy state. Such states are precluded by our assumptions. With the deletion of the first term and with the given boundary conditions

$$a_m = -\frac{V_{m0}^* (\exp[i(\omega_{m0} - \omega)t] - 1)}{2\hbar (\omega_{m0} - \omega)}$$

The probability that a molecule has absorbed a photon to jump to state m is given by

$$a_m a_m^* = \frac{|V_{0m}|^2}{4\hbar^2} \left[\frac{\sin^2\left(\frac{\omega_{m0} - \omega}{2} t\right)}{\left(\frac{\omega_{m0} - \omega}{2}\right)^2} \right] \quad (10)$$

where the manipulations have followed the course: $(e^{ix} - 1)(e^{-ix} - 1) = 2(1 - \cos x) = 4 \sin^2(x/2)$. We note that $|V_{0m}|^2 = V_{m0}^* V_{m0} = V_{0m} V_{0m}^* = V_{0m} V_{m0}$, etc., because V is Hermitian. The time dependence of $|a_m|^2$ is contained in the factor in brackets. The detailed behavior of this function with time and frequency is discussed in texts on quantum mechanics (see especially Kauzmann¹¹ and Schiff¹³). For our purposes, its most interesting property is its relationship with the δ function. We introduce the abbreviation $\Delta = (\omega_{m0} - \omega)/2$ and rewrite the expression as follows

$$\frac{\sin^2(\Delta t)}{\Delta^2} = \pi t \left[\frac{\sin^2 \Delta t}{\pi t \Delta^2} \right] = \pi t \delta(\Delta) \quad (\text{for } t \rightarrow \infty) \quad (11)$$

The expression in brackets has all the properties of the delta function:¹⁴ at $\Delta = 0$ it is given by $t/\pi \rightarrow \infty$ as $t \rightarrow \infty$. For $\Delta \neq 0$, it is of the order of $1/t \rightarrow 0$ as $t \rightarrow \infty$. The factor of π was introduced to normalize the integration. This permits the writing of (10) as

$$|a_m|^2 = \frac{\pi}{4} \frac{|V_{0m}|^2}{\hbar^2} t \delta(\Delta)$$

and for the energy absorbed per molecule per second

$$w_m = \hbar \omega \frac{d|a_m|^2}{dt} = \frac{\pi \omega |V_{0m}|^2}{4\hbar} \delta(\Delta) = \frac{\pi \omega |V_{0m}|^2}{2\hbar} \delta(\omega_{m0} - \omega) \quad (12)$$

In the form at the right, Δ has been eliminated in favor of the circular frequency utilizing the formula $\delta(ax) = (1/a)\delta(x)$.

This is the standard formula for a periodic perturbation. The δ function guarantees conformity to the Bohr frequency condition $\omega = \omega_{m0}$. Its presence demands an eventual integration over frequency which will be supplied physically by the fact that neither the incoming radiation nor the energy states are infinitely sharp.¹⁵ It should also be remarked that the conditions assumed for the above derivation (the growth of a population of molecules in state m) does not accord with the conditions of normal spectroscopic measurements which are performed under conditions of a steady state. A more careful analysis shows that the rate of absorption predicted for steady-state conditions and for the boundary conditions given above are identical, provided the fraction of molecules in the excited state remains very small. This is usually the case.

V. Broad Electronic Bands of Molecules

The factors which dictate the shape of electronic absorption bands of molecules containing more than two atoms are extremely complex,¹⁶ particularly in solution. Transitions from the ground state must be summed over all vibrational levels with Boltzmann weighting factors. A molecule sufficiently large to be optically active has many atoms and, as a consequence, many low-energy degrees of freedom which are thermally excitable. The excited state is still more complicated. A typical band width of 2000 cm^{-1} may encompass thousands of different combinations of vibrational excitations. The spectrum of a moderately simple molecule in the vapor phase consists of a large number of lines that are not resolvable with an ordinary spectrophotometer. In solution, the solvent cage provides an external and varying force field which alters the electronic energy of both the ground and excited states. Further, rotational and translational degrees of freedom are quenched into librational motions by interaction with solvent molecules. The result is a highly degenerate continuum of energy levels, which may or may not show bumps arising from the varied excitation of large vibrational quanta.

It is desirable to bypass consideration of band shape in a general discussion of electronic absorption and circular dichroism. This can be done by introducing a weighting function $\rho(\omega_{m0})$ for the probability of a transition within the manifold of the electronic transition $0 \rightarrow m$ where ω_{m0} is considered as a variable within the limits of the electronic band. Thus instead of the expression $|V_{0m}|^2$ for the electronic transition at a single frequency, we substitute $\rho(\omega_{m0}) |V_{0m}|^2$ which describes the probability of the electronic transition taking place at the frequency ω_{m0} . It is clear that ρ has the shape of the absorption band. It may be regarded either as the subject for eventual theoretical consideration or as an empirical function which determines band shape. It will also be assumed to be normalized to unity so that

$$\int \rho(\omega_{m0}) d\omega_{m0} = 1 \quad (13)$$

This involves an approximation which is discussed in the Appendix. Each monochromatic transition at ω_{m0} given by eq 12 is weighted by the "transition density" $\rho(\omega_{m0})$ to give

$$w(\omega_{m0}) = \frac{\pi \omega |V_{0m}|^2 \rho(\omega_{m0})}{2\hbar} \delta(\omega_{m0} - \omega) \quad (14)$$

This equation applies for radiation at the frequency ω . If eq 14 is now integrated over ω_{m0} in keeping with the continuous nature of the absorption, we find

$$w(\omega) = \frac{\pi\omega |V_{m0}|^2 \rho_m(\omega)}{2\hbar} \quad (15)$$

where the δ function has permitted the substitution of ω , the frequency of the radiation, for ω_{m0} . The subscript on ρ keeps track of the fact that ρ is the shape factor for the $o \rightarrow m$ transition.

This extremely simple formula is the cornerstone of molecular spectroscopy. The nature of the perturbation V has not yet been specified except for its periodicity in time. Selection of V appropriate to the problem at hand leads to formulas for ordinary absorption, linear and circular dichroism, etc. Superposition of a constant magnetic field leads to the basic formulas for magnetic CD and nuclear and electronic spin spectroscopy. The equation has the form of the "golden rule" for the transition to the continuous states of free particles.¹³ The interpretation of $\rho(\omega)$ is different, however, since in the free particle case it represents a state density (including spatial degeneracy) whereas in (15) it is a transition density. For each $\rho(\omega)$ there is a large variety of initial states, final states, and selection rules at work. A formula for $\rho(\omega)$ is derived in the Appendix.

VI. Absorption Spectra and Linear Dichroism

It is easier to recognize the unique terms which are responsible for circular dichroism, if ordinary absorption is treated as a previous case. This will be done in this section.

The perturbation producing ordinary electronic spectra is the interaction of the electric field of the radiation with the electric moment of the molecule. In this case, $V = -\boldsymbol{\mu} \cdot \mathbf{E}_0$ where $\boldsymbol{\mu} = e\sum \mathbf{r}_i$, with e the electronic charge and \mathbf{r}_i the position vector of the i th electron of the molecule, and \mathbf{E}_0 is the amplitude vector of the electric field. The time dependence of \mathbf{E} has been removed by integration; the space dependence does not contribute to ordinary absorption, i.e., electric dipole absorption. Thus $\mathbf{E}_0 = \mathbf{v}_e E_0$ and $V_{om} = E_0 \mathbf{v}_e \cdot \boldsymbol{\mu}_{om}$. Substituting this relation into (15) we have

$$w(\omega) = \frac{\pi\omega |\mathbf{E}_0 \cdot \boldsymbol{\mu}_{om}|^2 \rho_m(\omega)}{2\hbar} = \frac{\pi\omega |\mathbf{v}_e \cdot \boldsymbol{\mu}_{om}|^2 \rho_m(\omega) E_0^2}{2\hbar} \quad (16a)$$

$$= \frac{4\pi^2\omega |\mathbf{v}_e \cdot \boldsymbol{\mu}_{om}|^2 \rho_m(\omega) I}{\hbar n c} \quad (16b)$$

where in (16b) E_0^2 has been eliminated in favor of the intensity by eq 6. w is proportional to the intensity as demanded by the Beer-Lambert law. Using this formula for w in eq 1

$$\epsilon = \frac{4\pi^2\omega \rho_m(\omega) N}{2303\hbar n c} |\mathbf{v}_e \cdot \boldsymbol{\mu}_{om}|^2 \quad (17)$$

If impinging light is linearly polarized in the x direction, the orientational part of (17) becomes $|\mathbf{v}_e \cdot \boldsymbol{\mu}_{om}|^2 = |(\mu_x)_{om}|^2$. For randomly oriented molecules, the average over all orientations gives

$$\langle |\mu_x|^2 \rangle = |\boldsymbol{\mu}|^2 / 3$$

and

$$\epsilon = \frac{4\pi^2\omega \rho_m(\omega) N}{3(2303)\hbar n c} D_{om} \quad (18)$$

In (18) μ_{om}^2 has been replaced by the dipole strength which is defined as $D_{om} = |\mu_{om}|^2$.

This equation applies equally to linearly polarized light in the y direction and to nonpolarized light, which can be regarded as the superposition of two independent beams

TABLE II. Formulas Relating Extinction Coefficients and Strengths of Transitions^a

Absorption	Circular dichroism
$\epsilon = \frac{4\pi^2\beta N \lambda \rho(\lambda) D_{om}}{3(2303)\hbar c}$	$\Delta\epsilon = \frac{16\pi^2\beta N \lambda \sigma(\lambda) R_{om}}{3(2303)\hbar c}$
$D_{om} = \frac{3(2303)\hbar c}{4\pi^2 N} \int \frac{\epsilon d\lambda}{(\beta^2/n)\lambda}$	$R_{om} = \frac{3(2303)\hbar c}{16\pi^2 N} \int \frac{\Delta\epsilon d\lambda}{\beta\lambda}$
In Numerical Form ^b	
$D_{om} = 9.18 \times 10^{-3} \int \frac{\epsilon d\lambda}{(\beta^2/n)\lambda} \text{ (debye}^2\text{)}$	$R_{om} = 0.248 \int \frac{\Delta\epsilon d\lambda}{\beta\lambda} \text{ (Debye-Bohr magnetons)}$

^a To convert to wave numbers, replace λ by $\bar{\nu}$. To convert to ellipticities, replace $\Delta\epsilon$ by $M_\theta/3300$, where $(4500 \ln 10)/\pi = 3300$,²⁰ $\beta = (n^2 + 2)/3$. ^b The unit for dipole strength is (debyes)² = 10^{-36} cgs unit. The unit for rotatory strengths is the (Debye-Bohr magnetons) = 0.9273×10^{-38} cgs unit. Very frequently β and β^2/n are equated to unity and λ is replaced by λ_{max} in the integral.

of light of half the intensity, polarized in the x and y directions.

If the molecular system is in a crystal, oriented film, electric or hydrodynamic field, etc., an assembly of molecules will produce linear dichroism. This is measured by comparing the extinction coefficient for two different polarization directions, x and y . Then, from (17)

$$\epsilon_x - \epsilon_y = \Delta\epsilon = \frac{4\pi^2\omega \rho_m(\omega) N}{2303\hbar n c} (\langle \mu_x^2 \rangle - \langle \mu_y^2 \rangle) = \frac{4\pi^2\omega \rho_m(\omega) N D_{om}}{2303\hbar n c} \langle \sin^2 \theta \rangle \langle \cos 2\phi \rangle \quad (19)$$

where θ is the angle the transition dipole makes with the direction of propagation of light, ϕ is the standard meridional angle relative to the x axis, and the averages are over the distribution function appropriate to the method of orientation.

The above formulas contain no correction for the local field on the chromophore in condensed media. It is common practice either to ignore the local field problem or to apply the Lorentz correction. The latter is easily introduced. According to the Lorentz theory, the field on the chromophore is given by $F = \beta E$ with $\beta = (n^2 + 2)/3$, rather than the macroscopic field itself. This introduces the factor $[(n^2 + 2)/3]^2 E_0^2$ into eq 16a instead of E_0^2 so that, instead of (18), we have

$$\epsilon_{om} = \frac{1}{n} \left(\frac{n^2 + 2}{3} \right)^2 \frac{4\pi^2\omega \rho_m(\omega) N}{3(2303)\hbar c} D_{om} \quad (20)$$

Finally, circular frequency is an inconvenient unit for experimental work where wavelength in nanometers or frequency in cm^{-1} ($\bar{\nu}$) is usually preferred. Conversion to these other units follows directly from the requirement that the shape function be normalized in its own units; that is, $\int \rho(\omega) d\omega = \int \rho(\bar{\nu}) d\bar{\nu} = \int \rho(\lambda) d\lambda = 1$, from which we deduce that $\omega \rho(\omega) = \bar{\nu} \rho(\bar{\nu}) = \lambda \rho(\lambda)$. Thus the change in spectral units introduces no changes in the constants of the absorption formula. The results are summarized in Table II.

VII. Circular Dichroism

To obtain a theory of circular dichroism, it is necessary to add the small magnetic interaction of radiation with electrons to the dominant electric interaction. Thus in eq 15, $V = -\boldsymbol{\mu} \cdot \mathbf{E} - \mathbf{m} \cdot \mathbf{H}$, where \mathbf{m} is the magnetic moment (operator) of the molecule given by

$$\mathbf{m} = \frac{e}{2mc} \sum (\mathbf{L}_i + 2\mathbf{S}_i) \quad (21)$$

where \mathbf{L}_i is the orbital angular momentum and \mathbf{S}_i the spin angular momentum of the i th electron. Spin magnetic moments usually make negligible contributions to circular dichroism and will be dropped from the discussion which follows. With known or assumed wave functions, magnetic transition moments are easy to calculate. What happens in the interaction of cpl with molecules can be made much more transparent if circularly polarized components of the transition moments are introduced. Thus in place of μ_x and μ_y , we utilize the electric moments

$$\mu_+ = \frac{\mu_x + i\mu_y}{\sqrt{2}} \quad \mu_- = \frac{\mu_x - i\mu_y}{\sqrt{2}}$$

so that

$$\mu_x = \frac{\mu_+ + \mu_-}{\sqrt{2}} \quad \mu_y = \frac{\mu_+ - \mu_-}{\sqrt{2}i}$$

and

$$\boldsymbol{\mu} = \mu_x \mathbf{i} + \mu_y \mathbf{j} + \mu_z \mathbf{k}$$

becomes

$$\boldsymbol{\mu} = \mu_- \mathbf{e}_+ + \mu_+ \mathbf{e}_- + \mu_z \mathbf{k}$$

where \mathbf{e}_+ and \mathbf{e}_- are the unit polarization vectors for the electric field of right and left circularly polarized light. The introduction of μ_+ and μ_- involves the decomposition of linear moments into circular components. This is a familiar device in the discussion of magnetic resonance interactions. The magnetic moment \mathbf{m} can be similarly decomposed, but in so doing it will be desirable to maintain the same kind of phase relationships between \mathbf{m} and $\boldsymbol{\mu}$ as exist between \mathbf{H} and \mathbf{E} . In accordance with Table I we define

$$m_+ = \frac{-im_x + m_y}{\sqrt{2}} \quad m_- = \frac{im_x + m_y}{\sqrt{2}}$$

$$m_x = \frac{-m_+ - m_-}{\sqrt{2}i} \quad m_y = \frac{m_+ + m_-}{\sqrt{2}}$$

In these terms the magnetic moment operator is

$$\mathbf{m} = m_- \mathbf{h}_+ + m_+ \mathbf{h}_- + m_z \mathbf{k}$$

In terms of the circularly polarized moments the interaction takes a very simple form. For right and left circularly polarized light we have respectively $\mathbf{E}_+ = \mathbf{e}_+ E_0$, $\mathbf{H}_+ = \mathbf{h}_+ H_0$, and $\mathbf{E}_- = \mathbf{e}_- E_0$, $\mathbf{H}_- = \mathbf{h}_- H_0$. Utilizing the relations $\mathbf{e}_+ \cdot \mathbf{e}_+ = \mathbf{h}_+ \cdot \mathbf{h}_+ = 0$ and $\mathbf{e}_+ \cdot \mathbf{e}_- = \mathbf{h}_+ \cdot \mathbf{h}_- = 1$, we find

$$(V_+)_{om} = -(\mu_+)_{om} E_0 - (m_+)_{om} H_0 \quad (22)$$

$$(V_-)_{om} = -(\mu_-)_{om} E_0 - (m_-)_{om} H_0$$

where V_+ and V_- refer respectively to the interaction with right and left cpl.

Evaluation of $|V_{om}|^2$ can be cumbersome because of the three possible sources of imaginary quantities contained in (22). These are the wave functions themselves, the complex expression for circular polarization, and the magnetic moment operator. The latter is a pure imaginary since, in a coordinate representation, \mathbf{L} in eq 21 is given by $\mathbf{L} = (\hbar/i) \sum_j \mathbf{r}_j \times \nabla_j$, where the summation is over electrons. The work proceeds more simply if we take the following steps: (1) Assume all wave functions are real. This is in accord with a theorem of Van Vleck¹⁷ which states that the wave functions of a molecule in a nondegenerate state are necessarily real in the absence of an external field. A complex phase factor may be introduced, but it is devoid of physical significance. (2) Temporarily define a real operator $\mathbf{g} = -i\mathbf{m}$. In terms of this operator

$$m_+ = \frac{g_x + ig_y}{\sqrt{2}}$$

$$m_- = \frac{-g_x + ig_y}{2}$$

Substituting in eq 22 and separating the equation into its real and imaginary parts

$$(V_{\pm})_{om} = -[(\mu_x)_{om} E_0 \pm (g_x)_{om} H_0] - i[(\pm(\mu_y)_{om} E_0 + (g_y)_{om} H_0)]$$

This is now in the form $V = a + ib$ with a and b real so that

$$|V|^2 = a^2 + b^2$$

$$(V_{\pm})_{om}^2 = \frac{[(\mu_x)_{om}^2 + (\mu_y)_{om}^2] E_0^2 + [(g_x)_{om}^2 + (g_y)_{om}^2] H_0^2}{2} \pm [(\mu_x)_{om} (g_x)_{om} + (\mu_y)_{om} (g_y)_{om}] E_0 H_0 \quad (23)$$

Averaging over all orientations of the molecules utilizing the relation $\langle a_x b_x \rangle = \langle a_y b_y \rangle = \langle a \cdot b \rangle / 3$, we have

$$(V_{\pm})_{om}^2 = \frac{(\boldsymbol{\mu})_{om}^2}{3} E_0^2 + \frac{(\mathbf{g})_{om}^2}{3} H_0^2 \pm \frac{2}{3} (\boldsymbol{\mu}_{om} \cdot \mathbf{g}_{om}) E_0 H_0$$

The field quantities can be eliminated by means of eq 6. We also introduce the quantities:

$$D_{om} = (\boldsymbol{\mu}_{om})^2 = \boldsymbol{\mu}_{om} \cdot \boldsymbol{\mu}_{mo} \quad \text{electric dipole strength} \quad (24a)$$

$$G_{om} = (\mathbf{g}_{om})^2 = \mathbf{m}_{om} \cdot \mathbf{m}_{mo} \quad \text{magnetic dipole strength} \quad (24b)$$

$$R_{om} = -\boldsymbol{\mu}_{om} \cdot \mathbf{g}_{om} = \text{Im}(\boldsymbol{\mu}_{om} \cdot \mathbf{m}_{mo}) \quad \text{rotatory strength} \quad (24c)$$

D_{om} , G_{om} , and R_{om} are molecular measures of electric dipole absorption, magnetic dipole absorption, and circular dichroism, respectively. In the second part of eq 24c, R_{om} has been converted to its customary form by substituting $-\mathbf{g}_{om} = +i\mathbf{m}_{om} = +i\mathbf{m}_{mo}^* = -i\mathbf{m}_{mo}$. But this equals $\text{Im}(\mathbf{m}_{mo})$ in the sense that if $z = x + iy$, $-iz = \text{Im}[z] = y$, when $x = 0$.

Making the substitutions from the three forms of eq 6 and the three terms of eq 23

$$(V_{\pm})_{om}^2 = \frac{8\pi I}{3c} \left[\frac{D_{om}}{n} + nG_{om} \mp 2R_{om} \right] \quad (25)$$

We may now utilize eq 15 and 1 to obtain expressions for the extinction. In so doing it is necessary to recall that the transition density function depends not only on the upper and lower states, but on the matrix elements connecting them. There are three combinations of matrix elements in (24) and each has its own transition density function. We will call these $\rho(\omega)$, $\tau(\omega)$, and $\sigma(\omega)$. Utilizing the equations mentioned above

$$\epsilon_{\pm} = \frac{4\pi^2 \omega N}{3(2303) \hbar c} \left[\frac{D_{om}}{n} \rho(\omega) + n\tau(\omega) G_{om} \mp 2\sigma(\omega) R_{om} \right] \quad (26a)$$

If we take into account the possibility that the local field, F , differs from E , i.e., $F = \beta E$, then this equation takes the form

$$\epsilon_{\pm} = \frac{4\pi^2 \omega N}{3(2303) \hbar c} \times \left[\frac{\beta^2}{n} D_{om} \rho(\omega) + n\tau(\omega) G_{om} \mp 2\beta\sigma(\omega) R_{om} \right] \quad (26b)$$

The three terms in (26) represent electric dipole absorption, magnetic dipole absorption, and circular di-

chroism. Magnetic dipole absorption has only been detected in a few simple molecules in the gaseous state. It is extremely weak since the ratio of magnetic intensity to electric intensity is of the order of the square of the ratio of the Bohr magneton to the debye unit, i.e., about 10^{-4} . The term in G_{om} will be dropped in subsequent formulas.

If the incident light is linearly polarized or unpolarized, the radiation may be treated as a mixture of $rcpl$ and $lcpl$ so that the CD term cancels. Thus

$$\epsilon = \frac{4\pi^2\lambda N}{3(2303)\hbar c} \frac{\beta^2}{n} D_{om}\rho_{om}(\lambda) \quad (27a)$$

where circular frequency has been replaced by wavelength. This permits the evaluation of D_{om} from experimental data. Recalling that

$$\int \rho_{om}(\lambda) d\lambda = 1$$

$$D_{om} = \frac{3(2303)\hbar c}{4\pi^2 N} \int \frac{n\epsilon}{\beta^2\lambda} d\lambda \quad (27b)$$

This can be replaced with a moderately good approximation by considering n , β , and ν constant over the width of the absorption; thus

$$D_{om} \cong \frac{3(2303)\hbar c}{4\pi^2 N\lambda_{max}} \frac{n}{\beta^2} \int \epsilon d\lambda \quad (27c)$$

where n and β are evaluated at $\lambda = \lambda_{max}$.

If circular dichroism is measured, $\epsilon_- - \epsilon_+$ is determined. From eq 25b this is

$$\Delta\epsilon = \epsilon_- - \epsilon_+ = \frac{16\pi^2\lambda N\beta\sigma_{om}(\lambda)R_{om}}{3(2303)\hbar c} \quad (28a)$$

Rearranging and integrating over the band

$$R_{om} = \frac{3(2303)\hbar c}{16\pi^2 N} \int \frac{\Delta\epsilon}{\beta\lambda} d\lambda \quad (28b)$$

or

$$R_{om} \cong \frac{3(2303)\hbar c}{16\pi^2 N\beta\lambda_{max}} \int \Delta\epsilon d\lambda \quad (28c)$$

with the same approximations as before. This provides the experimental method of evaluating rotatory strengths.

In discussing the shapes of circular dichroism bands, a parameter of considerable importance is the anisotropy factor g , which is the ratio of CD to ordinary absorption $g = \Delta\epsilon/\epsilon$. This is in general a function of frequency. From eq 26a and 27a it is given by

$$g = \frac{4n}{\beta} \frac{\sigma(\omega)}{\rho(\omega)} \frac{R_{om}}{D_{om}} \quad (29a)$$

g is seen to depend on the ratio of the shape factors for CD and absorption as well as a weak variation with n/β . Moscovitz¹⁸ has shown that in many strong bands the CD signal and the absorption signal have the same shape. In this case $\sigma(\nu)/\rho(\nu) = 1$ and

$$g = \frac{4n}{\beta} \frac{R_{om}}{D_{om}} \quad (29b)$$

The conditions for this approximation are discussed in the Appendix.

This formula is usually given as $g = 4R_{om}/D_{om}$, which is probably a good approximation. On the other hand, it is usually understood that the latter formula represents "ignoring the internal field correction." This is not the case. If the internal field is ignored, $\beta = 1$ and, for $\sigma/\rho = 1$, $g = 4n(R_{om}/D_{om})$. The refractive index, n , can differ appreciably from unity, especially in the ultraviolet part of the spectrum where CD is usually measured. The appearance of n in this equation has nothing to do with internal

field corrections but with the fact that the wavelength in the medium is shortened by a factor of $1/n$. In the energy balance this compression of the wave plus the electric polarization requires that $H = nE$. If the Lorentz formula is applicable $n/\beta = 3n/(n^2 + 2)$. This is close to unity for most realistic values for n . It is unity at $n = 1$, reaches a maximum of 1.06 at $n = \sqrt{2}$, goes through unity at $n = 2$, and attains a value of 0.91 at $n = 2.5$. We see then that the validity of the formula $g = 4R_{om}/D_{om}$ depends not on the absence of an internal field but in the cancellation of the intrinsic effect of refractive index by the internal field dependence. This cancellation is very effective for a Lorentz internal field, and one may at least assume this to be so for the more complex fields which arise in situations which are not cubic in symmetry as required for the Lorentz expression.

Frequently circular dichroism spectra are reported as molar ellipticities. This usage is related to an older technique of measuring CD by measuring the ellipticity of light produced by optically active substances. It is not difficult to show¹⁹ that the molar ellipticity is related to $\Delta\epsilon$ by the relation

$$M_\theta = \frac{4.5(2303)}{\pi} \Delta\epsilon \cong 3300\Delta\epsilon \quad (30)$$

Substituting from eq 28a

$$M_\theta = \frac{24\pi N\beta\lambda\sigma_{om}(\lambda)R_{om}}{\hbar c} \quad (31)$$

Both (27a) and (29) are useful since the former permits direct comparison of circular dichroism with absorption spectra and the latter with optical rotation.

In eq 19, we had a relation for the absorption of linearly polarized light of an oriented system. It may appear that a similar possibility of development for oriented CD is contained in eq 23. This is not so. In an oriented system, quadrupole terms which we have neglected contribute to circular dichroism. Their contribution vanishes when the system is optically isotropic. Thus the derivation given in this paper is valid for circular dichroism only if uniform spatial averaging is employed. Theories which include quadrupole terms for oriented systems have been developed by a number of writers.^{8,9,20-22}

VIII. Optical Rotatory Dispersion

As mentioned in the introduction, the theory of optical rotation is usually derived directly from Maxwellian susceptibility theory or as a coherent scattering process. Here we adopt the approach of considering optical rotation as a dispersive property determined by the form of the absorptive property, CD, rather than the converse. Going either way the correlation is rigorously dictated by the Kronig-Kramers transform relations between the dispersive and absorptive properties of material media.^{19,23} If the wavelength is chosen as the independent variable, the form of the Kronig-Kramers transform which is appropriate for the transformation of the circular dichroism spectrum into the optical rotation spectrum is given by¹⁹

$$M_\alpha = \frac{2}{\pi} \int_0^\infty \frac{tM_\theta(t)dt}{\lambda^2 - t^2} \quad (32)$$

where M_α is the molar rotation. The symbol \int means the principal value is to be taken:

$$\int_0^\infty \frac{f(t)dt}{\lambda^2 - t^2} = \lim_{\delta \rightarrow 0} \left[\int_0^{\lambda-\delta} \frac{f(t)dt}{\lambda^2 - t^2} + \int_{\lambda+\delta}^\infty \frac{f(t)dt}{\lambda^2 - t^2} \right]$$

Referring back to eq 28a, it is seen that the form of the rotatory dispersion is governed by the form of the shape

function $\sigma(\lambda)$. In the absence of a general theoretical form for the shape of circular dichroism bands, we shall utilize the three most commonly considered empirical forms: infinitely sharp lines, Lorentzian or forced oscillator response, and Gaussian bands.

A. Line Spectra

If the spectrum may be considered as a series of lines of negligible breadth, $\sigma(\lambda)$ may be represented as a sum of δ functions $\sigma(\lambda) = \sum \sigma_m = \sum_m \delta(\lambda - \lambda_m)$, where the λ_m are the wavelengths of the lines. Substituting eq 31 into eq 32 and utilizing the properties of the δ function, we obtain Rosenfeld's equation

$$M_\alpha = \frac{\beta 48N}{\hbar c} \sum \frac{\lambda_m^2 R_{0m}}{\lambda^2 - \lambda_m^2} \quad (33)$$

Note that the rotation is undefined at $\lambda = \lambda_m$ because in this case the δ function is located at the singularity of the integral. Equation 33 may be also expressed

$$M_\alpha = \sum \frac{A_i \lambda_i^2}{\lambda^2 - \lambda_i^2} \quad (34)$$

with $A_i = 48\beta N/\hbar c$. In this form it is called the Drude equation since it was first derived by Drude on the basis of a helical oscillator without damping. It has been shown by Moscovitz¹⁹ and Kuhn and Braun³ that the above expression holds with high accuracy for broad bands provided that the separation between the wavelength of measurement and the band center is sufficiently greater than the band width.

B. Lorentzian Bands

It is possible to develop classical forced oscillator theories of optical activity with typical damping terms. This approach was first developed by Natanson²⁴ and was later elaborated upon considerably by Kuhn²⁵ with his coupled oscillator model. As would be anticipated, the result is a Lorentzian dependence on wavelength or frequency, so that the shape factor takes the form

$$\sigma(\lambda) = \frac{\text{constant}}{(\lambda^2 - \lambda_m^2)^2 + \Gamma_m^2 \lambda^2} \quad (35)$$

where λ_m is the wavelength of maximum CD and Γ_m is the damping parameter. Since σ is normalized, we must have $\int \sigma_m(\lambda) d\lambda = 1$, which gives for the constant the approximate value $2\lambda_m^2 \Gamma_m / \pi$. Thus

$$\sigma(\lambda) = \frac{2\lambda_m^2 \Gamma_m}{\pi [(\lambda^2 - \lambda_m^2)^2 + \Gamma_m^2 \lambda^2]} \quad (36)$$

and from eq 31

$$M_{\theta,m} = \frac{48N\beta\lambda_m^2 \Gamma_m \lambda R_{0m}}{\hbar c [(\lambda^2 - \lambda_m^2)^2 + \Gamma_m^2 \lambda^2]} \quad (37)$$

In performing the integration it has been assumed that $\lambda \cong \lambda_m$ except in the term $(\lambda^2 - \lambda_m^2)^2$. The exact expression for the constant gives a more complicated formula.

It is customary to simplify the Lorentzian band by making the same approximation in the shape function itself. Putting $\lambda \cong \lambda_m$, we find

$$\sigma_m(\lambda) = \frac{\gamma_m}{\pi [(\lambda - \lambda_m)^2 + \gamma_m^2]} \quad (38)$$

where $\gamma = \Gamma/2$ is the half-width of the band. Utilizing this form for $\sigma(\lambda)$ in eq 31

$$M_{\theta,m} = \frac{24N\beta\lambda_m \gamma_m R_{0m}}{\hbar c [(\lambda - \lambda_m)^2 + \gamma_m^2]} \quad (39)$$

The Kronig-Kramers transform can now be used to obtain the appropriate expression for Lorentzian optical rotation. Defining $x = (\lambda - \lambda_m)/\gamma_m$, eq 39 can be put into the form $\text{const}[1/(x^2 + 1)]$. One of the simplest transforms is

$$\frac{1}{x^2 + 1} \leftrightarrow \frac{x}{x^2 + 1}$$

This gives for the molar rotation

$$M_{\alpha,m} = \frac{24N\beta\lambda_m(\lambda - \lambda_m)R_{0m}}{\hbar c [(\lambda - \lambda_m)^2 + \gamma_m^2]} \quad (40)$$

Equations 37 and 38 give a good representation of the shape of the circular dichroism and optical rotation within the absorbing region of a Lorentzian band but are less satisfactory outside the band. In particular when $(\lambda - \lambda_m) \gg \gamma_m$, eq 38 gives a term in $1/(\lambda - \lambda_m)$ rather than a Drude term. To obtain the correct form for dispersion far from the absorbing region, eq 35 must be used. In this case

$$M_{\alpha,m} = \frac{48N\beta\lambda_m^2(\lambda^2 - \lambda_m^2)R_{0m}}{\hbar c [(\lambda^2 - \lambda_m^2)^2 + \Gamma_m^2 \lambda^2]} \quad (41)$$

This has essentially the same shape as (40) within the band but reduces to a Rosenfeld-Drude equation when $(\lambda^2 - \lambda_m^2) \gg \lambda_m^2$ (eq 33 and 34). Since (41) and (37) represent the in-phase and out-of-phase response of a forced oscillator, they are obtained simultaneously in the solution of the problem so that it is not necessary to perform the Kronig-Kramers transform. A pair of equations of the form of (37) and (41) were first proposed by Natanson²⁴ on the basis of an outmoded classical model.

In any event, the Lorentzian shape has had less importance in the interpretation of electronic CD spectra than in other branches of spectroscopy. The width of an electronic band of a molecule complicated enough to show circular dichroism arises from the wide range of energies of the initial and excited states and not from the intrinsic width of absorption. As a result, a Lorentzian which is broad enough to represent the shape of the band close to the maximum tails off much too slowly to represent band shape far from the center.

C. Gaussian Bands

This case has been developed by Moscovitz¹⁹ and Kuhn³ and has found the most extensive application in the interpretation of CD band shapes. In this case the shape factor has the normalized form

$$\sigma_m(\lambda) = \frac{1}{\Delta_m \sqrt{\pi}} \exp \left[-\left(\frac{\lambda - \lambda_m}{\Delta_m} \right)^2 \right] \quad (42)$$

where Δ_m is the exponential half-width. Again utilizing eq 31

$$M_\theta = \frac{24\sqrt{\pi} N\beta\lambda_m R_{0m}}{\hbar c \Delta_m} \exp \left[-\left(\frac{\lambda - \lambda_m}{\Delta_m} \right)^2 \right] \quad (43)$$

The Kronig-Kramers transform^{3,19} is

$$M_{\theta,m} = \frac{48\beta N\lambda_m R_{0m}}{\hbar c \Delta_m} \left[\exp[-x^2] \int_0^x \exp(x^2) dx + \frac{\Delta_m}{2(\lambda + \lambda_m)} \right] \quad (44)$$

where $x = (\lambda - \lambda_m)/\Delta_m$. Moscovitz has shown that this equation goes over to Rosenfeld's equation when $x > 4$. The integral in (44) is known as a Dawson integral and is tabulated in a number of places (see especially ref

TABLE III. Optical Activity for Three Band Shapes^a

	$M_{\theta,m}$	M_{α}	R_{om}
Lines	$\frac{48\beta NR_{om}\lambda_m}{\hbar c} \delta(\lambda - \lambda_m)$	$\frac{48\beta N}{\hbar c} \sum_m \frac{\lambda_m^2 R_{om}}{\lambda^2 - \lambda_m^2}$	
Lorentzian (eq 39 and 40)	$\frac{24\beta NR_{om}}{\hbar c} \frac{\gamma_m \lambda_m}{(\lambda - \lambda_m)^2 + \gamma_m^2}$	$\frac{24\beta NR_{om}}{\hbar c} \frac{\lambda - \lambda_m}{(\lambda - \lambda_m)^2 + \gamma_m^2}$	$\frac{\hbar c}{24N} \frac{\gamma_m M_{\theta,m}^0}{\lambda_m \beta}$
Lorentzian (eq 37 and 41)	$\frac{48\beta NR_{om}}{\hbar c} \frac{\Gamma_m \lambda \lambda_m^2}{(\lambda^2 - \lambda_m^2)^2 + \Gamma_m^2 \lambda^2}$	$\frac{48\beta N}{\hbar c} \frac{\sum \lambda_m^2 (\lambda^2 - \lambda_m^2) R_{om}}{[(\lambda^2 - \lambda_m^2)^2 + \Gamma_m^2 \lambda^2]}$	$\left(\frac{\hbar c}{48N}\right) \frac{\Gamma_m M_{\theta,m}^0}{\lambda_m \beta}$
Gaussian	$\frac{24\sqrt{\pi}\beta NR_{om}\lambda_m}{\hbar c \Delta_m} \exp\left[-\left(\frac{\lambda - \lambda_m}{\Delta_m}\right)^2\right]$	$\frac{48\beta N \lambda_m R_{om}}{\hbar c \Delta_m} F(\lambda, \lambda_m, \Delta_m)$	$\left(\frac{\hbar c}{24\sqrt{\pi}N}\right) \frac{\Delta_m M_{\theta,m}^0}{\lambda_m \beta}$

^a $M_{\theta,m}^0 = 3300\Delta\epsilon_{\max}$ is the maximum in molar ellipticity. $F(\lambda, \lambda_m, \Delta_m) = \left\{ \exp[-x^2] \int_0^x \exp[t^2] dt + [\Delta_m/2(\lambda + \lambda_m)] \right\}$ with $x = (\lambda - \lambda_m)/\Delta_m$. The frequently occurring constant $(48N/\hbar c) = 9.145 \times 10^{41}$. If one wishes to go directly from molar ellipticities or rotations to rotatory strengths in Debye-Bohr magnetons, this constant is to be replaced by 8.480×10^3 , the reciprocal of which is 1.179×10^{-4} . Other symbols are defined in the text and in Table II.

27). Carver, Shechter, and Blout²⁸ have devised a rapidly converging procedure for evaluating the integral which is utilized in most contemporary curve fitting programs for evaluating and resolving circular dichroism curves.

Chemical absorption bands are frequently represented as a sum of Gaussian-shaped bands. Unless this representation has physical significance in the realm of spectroscopic assignments, i.e., each term represents a distinct transition with a Gaussian shape, the rotatory strengths associated with each Gaussian lose their significance and only the sum of the absorption envelope has significance. With CD bands obviously separated into vibronic components, the rotatory strength associated with a given electronic transition can be partitioned into vibronic components.

Table III summarizes the results of this section.

IX. Discussion

In general the theory of optical activity may be divided into three parts: (1) the relationship between experimental observations of circular dichroism and optical rotation and the quantum mechanical quantity-rotatory strength; (2) the development of mechanisms for the rotatory strength in terms of the electronic structure of the molecule under consideration (here the one-electron mechanism of Condon, Altar, and Eyring,²⁹ the coupling mechanism of Kirkwood,³⁰ and the exciton mechanism of Moffitt³¹ come prominently to mind); and (3) the relationship between the rotatory strength and the three-dimensional structure of the molecule. This paper has been concerned entirely with the first problem. In particular, the formulas developed apply to single conformations. If a molecule possesses conformational freedom, the formulas must be averaged over conformation to provide a representation of experimental results.

The method of this paper consists in utilizing semiclassical perturbation theory retaining only electrical and magnetic dipole interactions with radiation. Band shape questions are handled by means of a golden-rule formulation with transition density functions. Optical rotation is approached as the transform of circular dichroism. The familiarity of the mathematical apparatus makes this approach especially simple. Moreover, the relationship of CD with absorption as well as its distinctive features are brought out with considerable clarity. Questions concerning the internal field correction and its relationship with absorption mechanism (eq 26b) are automatically answered. Finally, the problem of bandshape and its variation with mechanism is obtrusively present in the deriva-

tion so that the assumptions made in a number of currently used formulas can be clearly stated.

X. Appendix

The transition densities ρ and σ are extremely complicated functions for solvated, polyatomic molecules, but it is possible to obtain formal expressions for them. We expand the notation so that the ground and excited states are designated by $o\alpha$ and $m\beta$, respectively. o and m are labels for the electronic state as defined for an isolated molecule in its lowest state of nuclear motion, and α and β are descriptive labels for the entire set of nuclear coordinates and their states of motion. These include not only the internal vibrations and librations of the absorbing molecules but also the solvent cage. An energy is associated with each label α and β , but the situation is highly degenerate in that for a given energy there will be a large number of combinations of internal vibrations, librations, and solvent perturbations which are possible. The probability that a transition $o\alpha \rightarrow m\beta$ takes place is governed by eq 15 with $|V_{om}|^2$ replaced by $|V_{o\alpha,m\beta}|^2$. On the other hand, spectroscopic observations combine all transitions of the same Bohr frequency so that the transition density for a given frequency must be summed over all initial and final states separated by the same frequency. The probability of the initial state α is governed by

$$\rho_{\alpha} = e^{-E_{\alpha}/kT} / \sum_{\alpha} e^{-E_{\alpha}/kT} \quad (A1)$$

Grouping transition probabilities with regard to frequencies instead of states, the probability of a transition at energy ω_{m0} will be proportional to

$$\sum_{\alpha} \rho_{\alpha} \sum'_{\beta} |V_{o\alpha,m\beta}|^2 \quad (A2)$$

where the prime on the second sum indicates that only those states β are included for which $E_{\beta} - E_{\alpha} = \hbar\omega_{m0}$. In the text the probability of this transition was represented by $\rho(\omega_{m0}) |V_{om}|^2$ which is a definition of $\rho(\omega_{m0})$. Thus

$$\rho(\omega_{m0}) = \sum_{\alpha} \rho_{\alpha} \sum'_{\beta} |V_{o\alpha,m\beta}|^2 / |V_{om}|^2 \quad (A3)$$

If $\rho(\omega_{m0})$ is defined also as being normalized over the band $o \rightarrow m$, then $|V_{om}|^2$ is simply proportional to the integrated absorption intensity. One would like $|V_{om}|^2$ to be the transition probability for an isolated molecule in its lowest state of nuclear motion since this is frequently calculable from molecular quantum mechanics. This is not necessarily so, though it is often a good approxima-

tion. Only the product $\rho(\omega_{m_0})|V_{m_0}|^2$ is defined so that, if $|V_{m_0}|^2$ refers to the electronic states of the isolated molecule, $\rho(\omega_{m_0})$ is not necessarily normalized since changes in intensity produced by solvent interactions or vibrations must be reflected in its behavior. On the other hand, if $\rho(\omega_{m_0})$ is defined as normalized as in the text, then $|V_{m_0}|^2$ in general must contain the effects of solvent and vibrations.

It turns out that the crux of the matter is whether or not the Born-Oppenheimer approximation can be applied. If it can, the wave functions for α and $m\beta$ can be written in the form

$$\begin{aligned} |o\alpha\rangle &= |o\rangle|\alpha\rangle \\ |m\beta\rangle &= |m\rangle|\beta\rangle \end{aligned} \quad (\text{A4})$$

The electronic wave functions are of the form $\psi_m(q, Q)$ and the nuclear wave functions are $\chi_\beta(Q)$, where the q are electronic coordinates and the Q are nuclear coordinates including solvent nuclei as parameters.

Looking first at the dipole strength, we need to evaluate $|\mu_{o\alpha, m\beta}|^2$. In the Born-Oppenheimer approximation we have

$$\mu_{o\alpha, m\beta} = \langle \alpha | \langle o | \mu | m \rangle | \beta \rangle \quad (\text{A5})$$

If the electric transition moment is large, it is not greatly affected by nuclear motions so that $\psi(q, Q)$ may be replaced by $\psi(q, 0)$ where the nuclei are placed in their equilibrium positions. Then (A5) may be factored and we have $|\mu_{o\alpha, m\beta}|^2 = \mu_{om}^2 \langle \alpha | \beta \rangle^2$ where the $\langle \alpha | \beta \rangle$ are Frank-Condon nuclear overlap integrals.¹⁶ As is well known, these partition the intensity of electronic bands among the vibronic levels of the excited state. Substituting in (A3), we have

$$\rho(\omega_{m_0}) = \frac{\sum_{\alpha} \rho_{\alpha} \sum_{\beta} \mu_{om}^2 \langle \alpha | \beta \rangle^2}{\mu_{om}^2} = \sum_{\alpha} \rho_{\alpha} \sum_{\beta} \langle \alpha | \beta \rangle \quad (\text{A6})$$

Thus $\rho(\omega_{m_0})$ contains the combined effect of temperature (in ρ_{α}) and the Frank-Condon principle (in $\langle \alpha | \beta \rangle$). Integrating over the whole band is equivalent to eliminating the stricture on the summation over β since the sum is then over all frequencies

$$\int \rho(\omega_{m_0}) d\omega_{m_0} = \sum_{\alpha} \sum_{\beta} \rho_{\alpha} \langle \alpha | \beta \rangle^2$$

If $|\alpha\rangle$ and $|\beta\rangle$ are members of complete orthonormal sets, it can be shown that $\sum_{\beta} \langle \alpha | \beta \rangle^2 = 1$.³² Since $\sum_{\alpha} \rho_{\alpha} = 1$ by definition, $\rho(\omega_{m_0})$ is normalized to unity. The conditions required are the applicability of the Born-Oppenheimer principle and the assumption that the transition is sufficiently strongly allowed that small nuclear displacements do not appreciably affect the transition so that the Q can be equated to their equilibrium values in the electronic integrals.

Applying the same analysis for the rotatory strength, we find

$$\sigma(\omega_{m_0}) = \frac{\sum_{\alpha} \rho_{\alpha} \sum_{\beta} (\mu_{o\alpha, m\beta})(m_{m\beta, o\alpha})}{\mu_{om} \cdot m_{mo}} \quad (\text{A7})$$

The symbol lm is not necessary since the factors of i cancel.

Assuming the Born-Oppenheimer approximation and equilibrium nuclear coordinates in electronic integrals

$$\sigma(\omega_{m_0}) = \sum_{\alpha} \rho_{\alpha} \sum_{\beta} \langle \alpha | \beta \rangle^2 \quad (\text{A8})$$

This is the same formula as for $\rho(\omega_{m_0})$ so that, under these circumstances, circular dichroism and absorption have the same shape and eq 29b is applicable for the anisotropy factor of the band.⁶

There are a number of instances in which one or the other of the two approximations do not apply. Circular dichroism is frequently observed in exciton systems for which the Born-Oppenheimer approximation is not applicable.³³ It often arises with weak absorption bands which are essentially electric-dipole forbidden, but magnetic-dipole allowed. In these circumstances, it is not permissible to use equilibrium nuclear coordinates in evaluating μ_{om} . It is, however, usually possible to equate the areas under absorption and CD curves with the dipole strengths and rotatory strengths of electronic transitions, but the shapes of the curves for absorption and CD can differ markedly. In particular, contributions to D and R can arise in mutually exclusive vibrational progressions.^{6,34}

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