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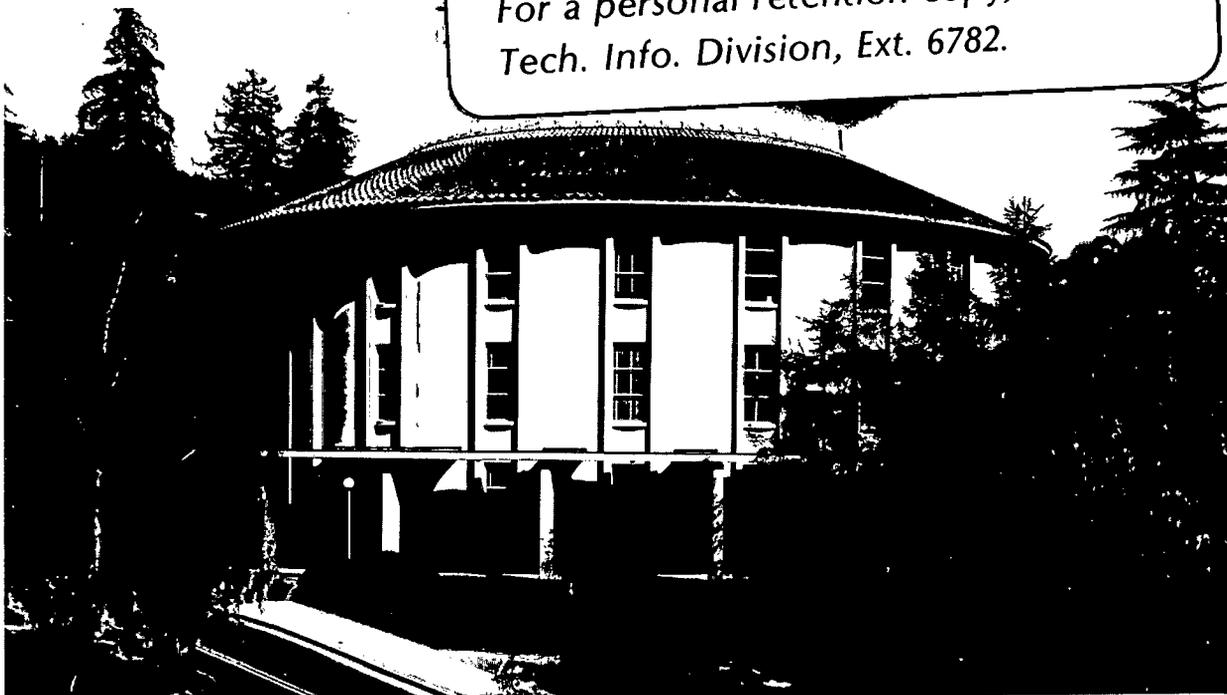
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SCATTERING OF CIRCULARLY POLARIZED RADIATION

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The differential refraction and absorption of circularly polarized light was applied by Henry Eyring and co-workers to study configuration and conformation of small molecules. The differential scattering as a function of angle of circularly polarized light can provide structural information about large scattering systems. We present the general equations relating circular differential scattering to the eigenfunctions of a scatterer which is of arbitrary size relative to the wavelength of light. An equivalent experiment is to measure the ellipticity of the scattered light when linearly polarized light is incident.

Introduction

The interaction of circularly polarized light with matter has been a field of intense interest to a small group of scientists for many years. Originally the practical experiment was measurement of the rotation of linearly polarized light; this is equivalent to determination of circular birefringence (the difference in refractive index for left and right circularly polarized light). More recently, measurement of circular dichroism (the difference in extinction coefficient for left and right circularly polarized light) has also become practical.

Henry Eyring was a charter member of the group of physical chemists in the United States interested in these chiral phenomena. In 1937 three theoretical papers appeared which provided the foundation for further work in this country. Condon, Altar and Eyring¹ derived the optical rotation caused by one electron in a perturbed harmonic oscillator potential.

$$V = (1/2) k_1 x^2 + (1/2) k_2 y^2 + (1/2) k_3 z^2 + Axyz \quad (1)$$

$$k_1 \neq k_2 \neq k_3$$

This was important because, as classical theories used coupled oscillators, a one-electron mechanism was a novel model. Kirkwood² provided a quantum mechanical derivation for the optical rotation of a molecule in terms of electronic interactions between polarizable groups in the molecule. His model was essentially a quantum mechanical version of the classical coupled oscillator model. Condon³ wrote a thorough review of the subject which showed (following Rosenfeld⁴) how the optical rotation was related to the eigenfunctions of an electronic system. The significant parameter is the rotational strength for each transition from ground state, o, to excited state, a.

$$R_{oa} = \text{Im} [\langle o | \underline{\mu} | a \rangle \cdot \langle a | \underline{m} | o \rangle] \quad (2)$$

The absorption is dependent on the more familiar dipole strength.

$$D_{oa} = \text{Re} [\langle o | \underline{\mu} | a \rangle \cdot \langle a | \underline{\mu} | o \rangle] \quad (3)$$

Here $\underline{\mu}$ is the electric dipole operator and \underline{m} is the magnetic dipole operator. These equations were derived for the wavelength of light large compared to the size of the electronic system characterized by o and a , and for an unoriented system. Therefore, for all molecules in the X-ray region and for very large molecules in the visible region, more appropriate equations must be considered. If no assumptions are made about the size of the system relative to the wavelength of light, the expression which gives the circular dichroism and optical rotation is⁵⁻⁷

$$R_{oa}(\underline{k}_o) = -\hat{k}_o \cdot [\text{Im} \langle o | \underline{T}(\underline{k}_o) | a \rangle \times \langle a | \underline{T}^*(\underline{k}_o) | o \rangle] \quad (4)$$

$$\underline{T}(\underline{k}_o) = \sum_j e^{i\underline{k}_o \cdot \underline{r}_j} \underline{p}_j$$

where \underline{r} , \underline{p} are the position and linear momentum operators, and \underline{k}_o is the wave vector, $(2\pi/\lambda)$ times the unit vector \hat{k}_o along the direction of propagation of the light. The rotational strength, $R_{oa}(\hat{k}_o)$, is given for an oriented system of arbitrary size relative to the wavelength of light, therefore it depends explicitly on the wave vector, (\underline{k}_o) , of the light, and on the cross product of the matrix elements.

The original Eq. (2) of Rosenfeld, Condon, Eyring and Kirkwood is correct for nearly all molecules in the visible region, because although a macromolecule may be larger than the wavelength of light, it can be treated as a collection of interacting small subunits. However, for the shorter wavelengths becoming available from synchrotron radiation, Eq. (4) will be needed.

The corresponding expression for the absorption of unpolarized light is

$$D_{oa}(\underline{k}_o) = (1 - \hat{k}_o \hat{k}_o) : \langle o | \underline{T}(\underline{k}_o) | a \rangle \langle a | \underline{T}^*(\underline{k}_o) | o \rangle \quad (5)$$

For polarized light with polarization unit vector, $\hat{\epsilon}_o$, the dipole strength will depend both on the wavevector, \underline{k}_o , and polarization vector, $\hat{\epsilon}_o$. The dipole strength is obtained by replacing $(1 - \hat{k}_o \hat{k}_o)$ with $(\hat{\epsilon}_o \hat{\epsilon}_o^*)$. In Eqs. (4,5) we are considering the general case of an oriented system of arbitrary size relative to the wavelength of light. They reduce to Eqs. (2,3) for randomly oriented systems which are small compared to the wavelength of light.

Differential Scattering of Circularly Polarized Radiation

Nearly all the experimental and theoretical publications on the interaction of circularly polarized light with matter have dealt with the transmitted beam. However, it is obvious that the scattered radiation is just as important. Barron and Buckingham⁸ derived expressions for circular differential Rayleigh and Raman scattering. That is, they assumed that the wavelength of light was large compared to the size of the molecules, and they calculated the difference in scattered intensities when left and right circularly polarized light is incident on randomly oriented molecules. As the molecules are small relative to the wavelength, the angular dependence of the Rayleigh scattering is not relevant. For Raman scattering the angular dependence is also not relevant, because the scattering is incoherent. Studies of Raman optical activity (and the related vibrational circular dichroism) are providing useful new information about stereochemistry and chirality.⁹

When the scattering system is large relative to the incident wavelength, the results of Barron and Buckingham cannot be applied. The circular dichroism or optical rotation of an array of small, non-interacting units can

be treated by neglecting the wavelength (Eq. 2), but the circular differential scattering cannot. Therefore, either for crystals and macromolecules in the visible range, or for crystals and all molecules at shorter wavelengths, a scattering equivalent of Eq. (4) is needed. Harris and McClain⁹ have given very general equations for scattering of light by polymers; we will explicitly consider circular differential scattering here.

The angular dependence of the scattering cross-section (cm^2) for incident light of polarization $\hat{\epsilon}_0$ when the polarization of the scattered light is $\hat{\epsilon}$ ($\hat{\epsilon}_0$ and $\hat{\epsilon}$ are unit vectors) is¹¹

$$\sigma(\theta, \phi) = \frac{1}{(4\pi)^2 c^4} \left| \hat{\epsilon}^* \cdot \underline{\pi} \cdot \hat{\epsilon}_0 \right|^2 \quad (6)$$

$$\underline{\pi} = \frac{e^2}{m} \langle o | \sum_j e^{-i(\underline{k}-\underline{k}_0) \cdot \underline{r}_j} | o \rangle \underline{1}$$

$$- \frac{e^2}{m^2} \sum_a \left[\frac{\langle o | \underline{T}^*(\underline{k}) | a \rangle \langle a | \underline{T}(\underline{k}_0) | o \rangle}{h(\nu_{oa} - \nu)} + \frac{\langle a | \underline{T}^*(\underline{k}) | o \rangle \langle o | \underline{T}(\underline{k}_0) | a \rangle}{h(\nu_{oa} + \nu)} \right]$$

$$\underline{T}(\underline{k}_0) = \sum_j e^{i\underline{k}_0 \cdot \underline{r}_j} \underline{p}_j$$

$$\underline{T}(\underline{k}) = \sum_j e^{i\underline{k} \cdot \underline{r}_j} \underline{p}_j$$

Here e and m are the electronic charge and mass; $\underline{1}$ is the unit tensor; ν is the frequency of the incident and scattered radiation and ν_{oa} is the frequency corresponding to the transition from o to a . The angles θ and ϕ are the usual polar and azimuthal angles of a spherical coordinate system. The sum over j is over the electrons; the sum over a is over states. The equation is written for elastic scattering by electrons only; extension to inelastic scattering is straightforward.

The first term in π represents the Thompson scattering of light by electrons, which is dominant at very short wavelengths (the X-ray region); the other terms characterize contributions from the transitions to all intermediate states. If left and right circularly polarized light is incident on a system, the circular differential scattering cross-section as a function of angle is

$$\sigma_L - \sigma_R = \frac{-i}{(4\pi)^2 c^4} [\hat{\epsilon}^* \cdot (\underline{\pi} \times \underline{\pi}^\dagger) \cdot \hat{\epsilon}] \cdot \hat{k}_0 \quad (7a)$$

The scattering cross-section depends on the polarization of the scattered light, which is specified by $\hat{\epsilon}$; $\underline{\pi}^\dagger$ is the Hermitean conjugate of $\underline{\pi}$. An equivalent way of writing Eq. (7a) is

$$\sigma_L - \sigma_R = \frac{1}{(4\pi)^2 c^4} [\eta_{\alpha ij} \pi_{\beta i} \pi_{j\gamma}^* \hat{k}_{o\alpha} \hat{\epsilon}_\beta^* \hat{\epsilon}_\gamma] \quad (7b)$$

where $\eta_{\alpha ij}$ is the completely antisymmetric unit tensor of rank three (the components of $\underline{1} \times \underline{1}$). Eq. (6) for the scattering cross-section can also be written as

$$\begin{aligned} \sigma_L + \sigma_R &= \frac{1}{(4\pi)^2 c^4} [\hat{\epsilon}^* \cdot \underline{\pi} \cdot (\underline{1} - \hat{k}_0 \hat{k}_0) \cdot \underline{\pi}^\dagger \cdot \hat{\epsilon}] \quad (8) \\ &= \frac{1}{(4\pi)^2 c^4} [\pi_{\beta\alpha} \pi_{\delta\gamma}^\dagger (\delta_{\alpha\delta} - \hat{k}_{o\alpha} \hat{k}_{o\delta})] \hat{\epsilon}_\beta^* \hat{\epsilon}_\gamma \end{aligned}$$

for incident left and right circularly polarized light (or incident unpolarized light). The circular intensity differential scattering (CIDS) is defined as the difference in scattered intensities when left and right circularly polarized light is incident, divided by the sum.

$$CIDS = \frac{I_L - I_R}{I_L + I_R} = \frac{\sigma_L - \sigma_R}{\sigma_L + \sigma_R} \quad (9)$$

$$\text{CIDS} = -i \left[\frac{[\hat{\underline{\epsilon}}^* \cdot (\underline{\pi} \times \underline{\pi}^\dagger) \cdot \hat{\underline{\epsilon}}] \cdot \hat{\underline{k}}_0}{\hat{\underline{\epsilon}}^* \cdot \underline{\pi} \cdot (\underline{1} - \hat{\underline{k}}_0 \hat{\underline{k}}_0) \cdot \underline{\pi}^\dagger \cdot \hat{\underline{\epsilon}}} \right] \quad (10)$$

The presence of the cross product in Eq. (7) and Eq. (10) is what distinguishes the differential scattering from the normal scattering; it is analogous to the cross product in Eq. (4) for the circular dichroism. An alternative method to obtain $\underline{\pi} \times \underline{\pi}^\dagger$ is to shine linearly polarized light on the sample and to measure the state of ellipticity of the scattered light. The ellipticity is the ratio of the minor axis of the ellipse to the major axis.

$$\text{ellipticity} = -i \left[\frac{\hat{\underline{k}} \cdot [\hat{\underline{\epsilon}}_0 \cdot (\underline{\pi} \times \underline{\pi}^\dagger) \cdot \hat{\underline{\epsilon}}_0^*]}{\hat{\underline{\epsilon}}_0^* \cdot \underline{\pi}^\dagger \cdot (\underline{1} - \hat{\underline{k}} \hat{\underline{k}}) \cdot \underline{\pi} \cdot \hat{\underline{\epsilon}}_0} \right] \quad (11)$$

Because of the $\underline{\pi} \times \underline{\pi}^\dagger$ cross product, the circular intensity differential scattering (or the ellipticity of the scattered light) is zero for wavelengths of light very short compared to the size of the scattering system ($\nu \gg \nu_{0a}$), or the wavelength of light very large compared to the size of the scattering system ($|\underline{k}| = |\underline{k}_0| \cong 0$).

If the scattering system can be considered to be a collection of independent subunits, then $\underline{\pi}$ can be written as

$$\underline{\pi} = \sum_j \text{units} e^{-i(\underline{k} - \underline{k}_0) \cdot \underline{R}_j} \underline{\pi}_j \quad (12)$$

\underline{R}_j is the vector which specifies the position of the subunit relative to a common origin and $\underline{\pi}_j$ is the scattering contribution of the subunit (See Eq. 6). That is, each $\underline{\pi}_j$ depends only on the electrons and states of subunit j . For subunits which are small compared to the wavelength, $\underline{\pi}_j$ takes the more familiar form

$$\pi_j = \frac{e^2}{m} \langle o|o \rangle \underline{1} - \frac{2e^2}{m^2} \sum_a \left[\frac{\langle o|p^*|a \rangle \langle a|p|o \rangle}{h(\nu_{oa}^2 - \nu^2)} \right] \nu_{oa} \quad (13)$$

Here p is implicitly a sum over all electrons in subunit i and the sum over a refers only to states in subunit j ; π_j is thus proportional to the polarizability of the subunit. If the subunits are not independent, but are weakly coupled without electron exchange between units, a perturbation method can be used to include dipole coupling between subunits; this modifies the form of Eq. (12).

For independent, or weakly coupled subunits, a classical approach is appropriate and easy.¹² The scattering of each subunit is proportional to a polarizability tensor, α_i (analogous to π_j in Eq. 13). The polarizability is complex and is a function of wavelength; the real part characterizes the dispersion; the imaginary part characterizes the absorption. The circular differential scattering cross-section (analogous to Eq. 7) is

$$\sigma_L - \sigma_R = i \frac{\pi^2}{\lambda^4} \sum_i \sum_j \alpha_i \alpha_j^* e^{i(\underline{k} - \underline{k}_0) \cdot (\underline{R}_j - \underline{R}_i)} (\hat{\underline{\epsilon}} \cdot \hat{\underline{\epsilon}}_i) (\hat{\underline{\epsilon}}^* \cdot \hat{\underline{\epsilon}}_j) (\underline{e}_j \times \underline{e}_i) \cdot \hat{\underline{k}}_0 \quad (14)$$

The principal axes of the polarizability tensors are $\underline{e}_i, \underline{e}_j$ (with principal values α_i, α_j). The scattering cross-section (analogous to Eq. 8) is

$$\begin{aligned} \sigma_L + \sigma_R = & \frac{\pi^2}{\lambda^4} \sum_i \sum_j \alpha_i \alpha_j^* e^{i(\underline{k} - \underline{k}_0) \cdot (\underline{R}_j - \underline{R}_i)} (\hat{\underline{\epsilon}} \cdot \hat{\underline{\epsilon}}_i) (\hat{\underline{\epsilon}}^* \cdot \hat{\underline{\epsilon}}_j) \\ & \times [\underline{e}_i \cdot \underline{e}_j - (\underline{e}_i \cdot \hat{\underline{k}}_0)(\underline{e}_j \cdot \hat{\underline{k}}_0)] \quad (15) \end{aligned}$$

In the limit of very short wavelengths the polarizability tensors become isotropic and proportional to the electron density.

Discussion

Differential scattering of circularly polarized light (wavelength 442 nm) has been used to investigate the structures of DNA in viruses and sperm in solution.^{13,14} Studies of oriented systems, such as films and crystals with short wavelengths, have not been reported. However, there are advantages to using incident circularly polarized radiation, if the experimental difficulties can be solved. Circular differential scattering retains information concerning the chiral properties of the scattering object even when the sample is partially or completely disordered. This property can be especially useful for large biological structures. For example, spherical viruses can be crystallized and studied by conventional X-ray diffraction techniques to give the structure of the protein coat molecules which surround the viral nucleic acid.^{15,16} However, the nucleic acid in the crystalline array is too disordered to give a useful diffraction pattern. Circular differential scattering could be used to answer questions concerning the packing of the nucleic acid inside the virus head: Is the nucleic acid randomly tangled like a ball of string or is it supercoiled? What is the pitch and radius of any helical structure? Circular differential scattering (or the equivalent measurement of the ellipticity of the scattered light) can reveal the chirality of the scattering system (left- or right-handed) without the requirement for anomalous diffraction. To have a non-zero value for $\sigma_L - \sigma_R$ the polarizability tensors must be anisotropic, but they need not be complex. The sign of $\sigma_L - \sigma_R$ then characterizes the chirality. Circular differential scattering in the short wavelength region can then be viewed as a potential complement to the familiar Patterson techniques.

More generally we can see that changes in polarization are more sensitive to structural details of the scatterer than are changes in intensity alone.

This added sensitivity is especially useful when the wavelength of the incident light is large compared to the scatterer. In particular, the circular scattering differential, $\sigma_L - \sigma_R$, carries information about the chiral organization of the scatterer even in the Rayleigh scattering limit, when the diffraction pattern is smooth.

Use of linearly polarized light in the X-ray region has recently become practical and worthwhile.¹⁵ We hope that circularly polarized light, which has been so important in the visible and ultraviolet wavelength region, will now also become increasingly important in the soft X-ray region and vacuum ultraviolet region. Measurement of scattering of circularly polarized incident light (or measurement of the circular polarization of the scattered light when linearly polarized light is incident) may be most useful for complex biological structures with dimensions of hundreds of angstroms.

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