

FAR INFRARED CIRCULAR DICHROISM AND MOLECULAR DYNAMICS.

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ABSTRACT

It is argued that circular dichroism in the far infra red power absorption coefficient is determined by a combination of rotational and translational molecular diffusion. Dichroism in the far infra red provides information on the way the molecular dynamics respond to left and right circularly polarised probe radiation from an interferometer or laser, and reveals subtle details of the statistical cross correlations between molecular rotation and translation. The sample may be structurally chiral, or structurally achiral in the presence of a magnetic field.

INTRODUCTION

Circular dichroism is usually the name given to differential absorption of right and left circularly polarised electromagnetic radiation by a medium, one which is circularly birefringent (1-5) and optically active. The phenomenon occurs in principle over the whole of the electromagnetic frequency range, but in practice its observation has been confined largely to the ultra-violet and visible, with recent developments (6-8) by Nafie and co-workers, using interferometry, down to about  $300\text{ cm}^{-1}$  in the mid infra red (vibrational circular dichroism). The intensity of the probe radiation falls rapidly as the far infrared region is approached, making the use of specialised equipment essential.

The fundamental equations are given in section (1), which shows that the effective angle of rotation, circular birefringence, and dichroism in the power absorption coefficient are fundamentally interrelated, and depend on the dipole orientation and rotational velocity time correlation functions of the molecular dynamics of the optically active sample, for example, an ensemble of chiral molecules. In section (2) some experimental conditions and details are suggested, based on recent advances (9-12) in experimental measurement of infrared dichroism, and on the rotatory power of available isotropic molecular liquid ensembles. Section (3) discusses the role of molecular dynamics computer simulation in the data interpretation.

## 1. FUNDAMENTAL CONSIDERATIONS

An ensemble of structurally chiral molecules is circularly birefringent and rotates the plane of polarised electromagnetic radiation with an angle of rotation  $\theta$ . The plane polarised radiation is assumed to propagate in the Z axis of the laboratory frame (X, Y, Z) and is a combination of left and right circularly polarised components whose velocities of propagation through the chiral ensemble are different. In general the sample absorbs, so that the plane wave in the ensemble becomes left or right elliptically polarised as the case may be. Defining  $\underline{i}$  as a unit vector in X and  $\underline{j}$  as a unit vector in Y the electric field components of the electromagnetic plane wave in the absorbing ensemble are

$$\underline{E}_L = E_0 (\underline{i} - i\underline{j}) e^{i\phi_L} ; \underline{E}_R = E_0 (\underline{i} + i\underline{j}) e^{i\phi_R} \quad (1)$$

Utilising these in the Maxwell equation provides the following standard expression ( 2 ) for circular birefringence

$$\langle n_{LZ}' - n_{RZ}' \rangle = -2\mu_0 c^2 N \langle d_{2XX}'' \rangle + \dots$$

This is the difference between the ensemble averaged real parts of the refractive index measured respectively in left and right circularly polarised far infra red radiation. The quantity  $\mu_0$  is the magnetic permeability in vacuo,  $N$  the number of molecules per metre cubed of sample,  $c$  the velocity of light, and  $\langle d_{2xx}'' \rangle$  the ensemble average over the imaginary part of the Rosenfeld tensor (2), an odd parity tensor which exists only in chiral ensembles. There are also terms in (2) depending on the electric dipole / electric quadrupole tensor, as in standard theory (2). The equivalent dichroism in the power absorption coefficient is

$$\langle A_{LZ} - A_{RZ} \rangle = 4\omega\mu_0 N \langle d_{2xx}' \rangle + \dots \quad (3)$$

and the angle of rotation is

$$\langle \theta \rangle = -l\mu_0 N \omega \langle d_{2xx}'' \rangle + \dots \quad (4)$$

where  $l$  is the sample thickness in metres and  $\omega$  the angular frequency. The chances of observing the rotation angle (with the use of a second wire grid polariser situated between the sample and detector) are governed by eqn. (4). The most intense far infra red radiation available is from a tunable submillimeter laser (13). The sample thickness  $l$  is typically about 0.1 cm, and in the far infra red the ratio  $(\omega/c)^2$  is  $(2\pi\bar{\nu})^2 = 10^4$ , where  $\bar{\nu}$  is the wavenumber. The ratio of dielectric loss to power absorption in the far infra red is typically of the order  $10^{-3}$ , so that the angle of rotation is determined typically by a small difference of quantities each of the order unity. The ability to observe  $\langle \theta \rangle$  comes down to maximising this small difference, i.e. to the necessity of using a sample that in the visible range is known to be able to rotate plane polarised radiation by several thousand degrees per metre. A rotation strength such as this is possessed by single crystals of helical macromolecules, for example. To observe far infra red optical activity in the liquid state it is clear that the chances are maximised with the liquid

or liquid crystal sample known to have the greatest literature optical rotation strength in the visible.

### The Faraday Effect in the Far Infra-red

The Faraday effect can be measured through the rotation of plane polarised electromagnetic radiation by a dielectric treated with a magnetic field co-linear with the propagation vector of the radiation. Recent work has shown (14 - 20) that it is accompanied by the much weaker magneto and spin chiral dichroic effects. The dielectric may be an ensemble of structurally achiral molecules, and is made circularly birefringent with the magnetic field. Once the circular birefringence has been established the fundamental classical field equations in section (1) govern the frequency dependence of the angle of rotation as the probe electromagnetic radiation is simultaneously absorbed.

In this case the largest rotations are probably observable with liquid crystals, in which birefringence is observable ( 21 ) even at radio frequencies with weak applied magnetic fields. A series of such rotation measurements, taken with different frequencies of a tunable submillimetre laser, will reveal the frequency dependence of the Faraday optical rotation in the far infra red, which is dependent on the molecular dynamics of the sample as described by the equation

$$\langle \theta \rangle_{\uparrow\uparrow} - \langle \theta \rangle_{\uparrow\downarrow} = 4\mu_0 c^2 N B_{SZ} \langle d_{1x/y/z}'' \rangle + \dots \quad (5)$$

where  $B_{SZ}$  is magnetic flux density, and  $\langle d_{1x/y/z}'' \rangle$  a totally antisymmetric components of the tensor that mediates the effect of  $B_S$  on  $d_1$ , the complex molecular polarisability. There are also terms in (5) dependent ( 2 ) on the molecular electric dipole / quadrupole tensor.

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Eqs. (2) to (5) show that far infra red dichroism, circular refraction and angle of rotation are all dependent on the molecular dynamics of the structurally chiral ensemble. The frequency dependent angle of rotation, for example, is given by the ratios of dielectric loss to power absorption in the far infra red for the right and left circularly polarised measuring electromagnetic plane wave. In this section we seek an explanation in terms of fundamental molecular dynamics for far infra red dichroism of this kind.

We consider firstly the case of right circularly polarised radiation absorbed by an ensemble of (R) molecular enantiomers. The dielectric complex permittivity at far infra red frequencies and below is related (22) to the Fourier transform of the molecular dipole correlation function

$$C_1(t) = \langle \underline{\mu}(t) \cdot \underline{\mu}(0) \rangle \quad (6)$$

and therefore to the molecular dynamics. Similarly, the far infra red power absorption coefficient is related through Fourier transformation to the rotational velocity correlation function

$$C_2(t) = \langle \underline{\dot{\mu}}(t) \cdot \underline{\dot{\mu}}(0) \rangle \quad (7)$$

Consider next the interaction of left circularly polarised radiation with the same ensemble. We observe a DIFFERENT frequency dependent complex permittivity and far infra red power absorption, and the explanation for this must be found somewhere in the nature of the ensemble dynamics of chiral molecules. (In ensembles of achiral molecules there is no dichroism and no optical activity, and the far infra red power absorption measured with left and right circularly polarised probe radiation is identical.)

What is the difference between the ensemble dynamics in the far infra red of chiral and achiral molecules?

The answer is known from recent molecular dynamics computer simulations (23 - 26) which show that the statistical

relation between centre of mass velocity ( $\underline{v}$ ) and angular velocity ( $\underline{\Omega}$ ) changes sign between diffusing chiral enantiomers. This occurs, however, in the frame (x, y, z) defined by the principal molecular moments of inertia, and not directly in the laboratory frame (X, Y, Z), where such correlations are allowed by symmetry (27 - 30), but have not been observed by computer simulation, and appear to be very small or zero (31). Group theoretical statistical mechanics (27 - 30) shows that in the lowest symmetry  $C_1$  chiral point group all nine elements of the cross correlation function (c.c.f.)

$$C_3(t) = \langle v_i(t) \underline{\Omega}_j(0) \rangle_{(x,y,z)} \quad (8)$$

exist for an ensemble of (R) enantiomers and all switch sign in the (S) enantiomer, vanishing in the racemic mixture. Furthermore, such behaviour is confined exclusively to this and related key "switching" c.c.f.'s, or time derivatives such as the c.c.f. in frame (x, y, z) between the net force and net torque of the same molecule.

The frequency dependent far infra red power absorption coefficients of an ensemble of (R) enantiomers and an ensemble of (S) enantiomers appear different in circularly polarised radiation (right or left), but are identical when measured with unpolarised radiation. The switching c.c.f. reveals its presence only indirectly, therefore, under the right observational conditions through the molecular "antennae", the permanent dipole moment and its time derivative.

We conclude that the c.c.f.  $\langle v_i(t) \underline{\Omega}_j(0) \rangle$ , with nine components in general, is responsible for this and is the dynamical manifestation of structural chirality, resulting in far infra red circular dichroism. Conversely the latter may be used to provide an experimental measure of the effect of the c.c.f., to measure its effect quantitatively in terms of 1) the power absorption coefficient; 2) the dielectric loss; 3) the angle of rotation.

This conclusion is reinforced from eqn. (3), which shows that far infra red dichroism in the power absorption coefficient

is directly proportional to an appropriate ensemble average of a scalar component of the Rosenfeld tensor, whose quantum mechanical origins ( 1, 2 ) make it a product of the molecular electric and magnetic dipole matrix elements. This product has the same symmetry as the cross correlation function between molecular rotation and translation. Furthermore the magnetic dipole is classically proportional to a molecular angular momentum, so that we expect to see a cross correlation of the type  $\langle \underline{\mu}_i(t) \underline{\Omega}_j(0) \rangle$  whose elements switch from one enantiomer to the opposite in the laboratory frame. Far infra red dichroism provides specific information on this type of switching correlation function, which can be built up by computer simulation. Finally it is known from computer simulation (32, 33) that the electric dipole  $\underline{\mu}$  is correlated directly in the laboratory frame to linear velocity through a non-vanishing  $\langle \underline{\mu}_i(t) \underline{v}_j(0) \rangle$  leading again to the expectation that  $\underline{v}$  is correlated to  $\underline{\Omega}$  in opposite ways for opposite enantiomers. This is a fundamental and general result for all structurally chiral ensembles.

### 3. EXPERIMENTAL DETAILS.

We have argued that far infra red dichroism, if observable experimentally under optimised conditions, is an elegant method of isolating the effect of the switching c.c.f.'s which are solely responsible for the effect. In this section we suggest methods of optimising the experimental conditions using submillimetre laser and interferometric spectroscopy).

#### a) Use of Tunable Submillimetre Lasers.

Tunable lasers are now available which produce many spot frequencies ( 13 ) throughout the far infra red range. One of the strongest lines is near  $80 \text{ cm}^{-1}$ , and this should be chosen initially and stabilised. The output from the laser is plane polarised with an accurately machined vertical wire grid polariser and passed through a sample cell containing the maximum possible thickness of a liquid or liquid crystal with a visible optical rotation strength of thousands of degrees per metre. The

rotation of the plane of the output radiation is measured with a second wire grid polariser which is rotated until the signal at the detector is maximised. The rotation of the second wire grid polariser with respect to the first gives the angle  $\langle \theta \rangle$ .

The experiment is repeated a) as a function of sample thickness; b) of measuring frequency. The procedure is repeated for the racemic mixture to provide a baseline and to eliminate spurious effects. The rotation angle should be a linear function of the sample thickness in the enantiomer, and should vanish in the racemic mixture. Measurements at different laser frequencies provide the frequency dependence of the optical activity.

#### b) Interferometry

The above method using a laser provides information at spot frequencies only, and should be supplemented with broad band far infra red Michelson interferometry ( 22 ). However, this method must utilise circularly polarised radiation directly, i.e. must separate the right and left circularly polarised components of plane polarised far infra red radiation. The elegant work of Nafie and co-workers ( 6 - 8 ) has provided data to  $300 \text{ cm}^{-1}$  using Nicolet 7199 interferometer with a piezo-optic modulator to switch the probe broad band radiation from right to left circularly polarised at 60 kHz ( 6 - 8 ). Vibrational circular dichroism has by now provided information on chiral complexes, cyclic macromolecules, and simple chiral molecular structures, utilising a germanium ( 34 ) modulator which is transparent in far infra red, and optimising beam divider material, source (high pressure mercury), and detector (helium cooled Rollin), the instrument designed by Nafie et al. can probably reach the far infra red, thus opening up an area rich in information ( 22 ). Another source of information is dispersive far infra red interferometry ( 35 ), where the sample is held in one arm of interferometer, and which gives the frequency dependent



## DISCUSSION

Far infra red dichroism elegantly isolates the influence of laboratory and moving frame switching c.c.f.'s on the "antenna" correlation functions whose Fourier transforms are the far infra red power absorption and dielectric complex permittivity. These are the molecular rotational velocity ( 22 ) and dipole correlation functions respectively. The switching c.c.f.'s are the only source of difference between the far infra red power absorption of an enantiomer measured with left and right circularly polarised radiation.

Vibrational absorptions in the infra red and Raman are accompanied by rotational detail, which in the liquid state becomes broadened and fused into shoulders around the vibrational peak frequency which contain information about the liquid state molecular dynamics. The antenna in this case is the infra red transition dipole moment and its time correlation function in frame (X, Y, Z). In general the spectrum is the result of molecular dynamics involving statistical cross correlation between vibration, rotation and translation. If any of these cross correlations switch sign between enantiomers there will be an effect on the shoulders of the already observable ( 6 - 12 ) vibrational circular dichroism which is frequency dependent. The "baseline" spectrum, where these cross correlation cancel, is again that of the racemic mixture. We conclude that vibrational circular dichroism also provides information on "hidden" cross correlation functions of a chiral liquid, information which can be computer simulated and animated. In general there are many vibrational proper modes which can be used for this type of study for a particular chiral liquid. The higher the frequency, the greater the dichroism.

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