

asserted that the additional terms were important even for infinite helical polymers. Examination of the work of the authors listed above has revealed two errors in Mason's work. These are as follows.

(a) Mason utilizes only the exciton wave functions of Moffitt's original work,<sup>16</sup> terming these wave functions the "symmetric" and "antisymmetric coupling modes." MFK showed, however, that these wave functions are inadequate in first order for calculations of rotatory power.

(b) Mason's calculations for the rotatory power of coupled dipoles (eq. 4-7 in ref. 19), although correct in themselves, lead to mistaken conclusions that some terms cancel one another. For the symmetric coupling mode, the rotational strength  $R^s_{m,m+n}$  of two dipoles at loci  $m$  and  $m+n$  in a right-handed helix is

$$R^s_{m,m+n} = 4dq_vq_t \sin^2(\alpha_n/2) - nZ(q_r^2 - q_t^2) \sin(\alpha_n) \quad (\text{IV})$$

Here  $d$  is the helix radius,  $q_r$ ,  $q_t$ , and  $q_v$  are the radial, tangential, and vertical components of the electric dipole transition moment,  $Z$  is the pitch of the helix, and  $\alpha_n = 2\pi n/P$ , where  $P$  is the number of dipoles per turn of the helix. In contrast to Mason's conclusion, both the first and second terms in (IV) are even functions of  $n$ , so that summations of the form ( $R^s_{m,m+n} + R^s_{m,m-n}$ ) do not lead to cancellations of terms.

It may be noted that a summation of paired terms of the form ( $R^s_{m,m+n} + R^s_{m,m-n}$ ) occurs in the article of MFK in going from their eq. 20 to their eq. 21. Their vector analysis, which is correct, also shows that a cancellation of terms does not occur.

## Magnetic Circular Dichroism and Magnetic Optical Rotatory Dispersion

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*The relative merits of magnetic circular dichroism and magnetic optical rotatory dispersion are discussed and some examples of dichroism spectra are presented. These spectra appear to be of two classes which are designated as (1) Zeeman splitting and (2) perturbation. Possible applications of magnetic circular dichroism are considered briefly.*

A recent paper of Shashoua<sup>1</sup> describes some measurements of the optical rotatory dispersion of samples in a magnetic field (MORD), *i.e.*, the dispersion of the Faraday effect. These dispersion measurements were made through absorption bands most of which exhibited a magnetic Cotton effect; *i.e.*, there was a characteristic anomaly similar to that observed in the absorption bands of naturally optically active molecules. Associated with this anomaly is a "magnetic circular dichroism" (MCD), and the object of this paper is to report some measurements of MCD and comment on their relationships to the work of Shashoua.

The experiments were made using a commercial Jouan circular dichrometer which is capable of measuring differences in the absorbance of right- and left-handed light of about  $10^{-4}$ . The sample was mounted between iron pole pieces attached to a permanent magnet and with a gap of approximately 2 mm.; the average field was 8.1 kgauss (as determined by Faraday rotation measurements on water at 436 m $\mu$ ). For all measurements reported, the samples used were 1 mm. thick.

Basically there appear to be two general types of MCD spectra. These are the spectra obtained (1) by a longitudinal Zeeman splitting and (2) by a magnetic perturbation giving a small difference in the absorption

of right- and left-handed light. Splittings can be recognized by characteristic positive and negative peaks (located approximately under the steepest portions of the absorption band) with a cross-over point at the same wave length as the center of the ordinary absorption band. By analogy with the convention adopted for optical rotatory dispersion (ORD) for naturally active compounds,<sup>2</sup> the splitting will be called positive if the molecular extinction coefficient of left-handed light is greater than that of right-handed light ( $\epsilon_L > \epsilon_R$ ) for the peak with the longer wave length. It can easily be shown that positive splitting will lead to a characteristic three-peaked MORD curve with positive, negative, and positive peaks on going from longer to short wave lengths. This type of MORD curve is called type III by Shashoua. A negative splitting will give a similar curve, but will be reflected through the wave length axis. MCD spectra with a "perturbation origin" consist of a single peak centered at approximately the same wave length as the ordinary band. If  $\epsilon_L > \epsilon_R$ , the associated MORD curve has the appearance of the ordinary positive anomalous dispersion curve; *i.e.*, on going from long to shorter wave length, the curve is first positive and then negative. This is referred to as type I by Shashoua, and the corresponding negative dispersion is called type II.

It can easily be shown that splittings are most readily detected in absorption bands with very narrow band widths. For this reason, and because compounds with varying degrees of paramagnetism could be studied, the MCD spectra of several rare earths were measured. As an example, Figure 1 shows the splittings obtained with

(1) V. E. Shashoua, *J. Am. Chem. Soc.*, **86**, 2109 (1964).

(2) C. Djerassi, "Optical Rotatory Dispersion," McGraw-Hill Book Co., Inc., New York, N. Y., 1960.

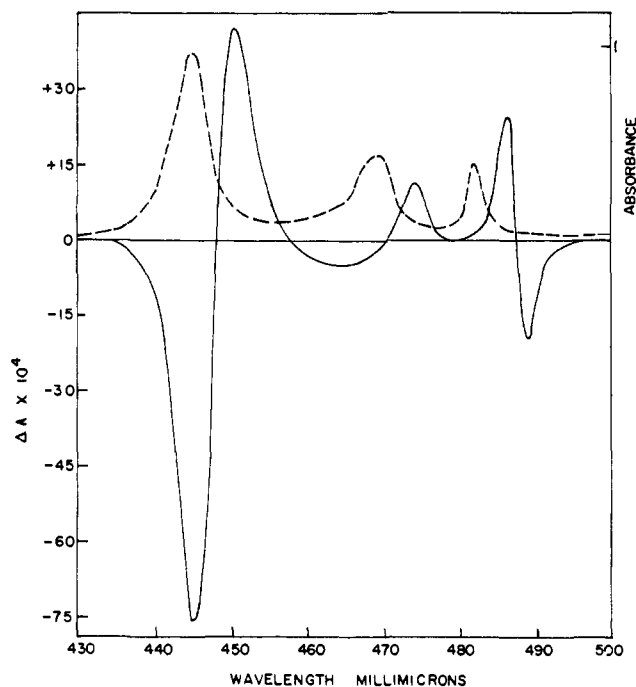


Figure 1. Magnetic circular dichroism spectrum in an 8.1-kgauss field and ordinary absorption spectrum (dashed curve) of a 1-mm. thick aqueous solution of praseodymium chloride. Maximum absorbance was 0.968 at 445  $m\mu$  and the band pass was approximately 0.5  $m\mu$ . The circular dichroism peak near 446  $m\mu$  corresponds to a 50-mm. pen displacement, and the noise level was approximately 1 mm. ( $\Delta A = 1.5 \times 10^{-4}$ ). Assuming the dispersion of the Jouan monochromator is similar to that of a Beckman DU, the band pass at 445  $m\mu$  is approximately 4  $m\mu$ .

an aqueous solution of praseodymium chloride (Lindsay Division, American Potash Co.). The ordinary absorption spectrum of this compound has three absorption bands, at 482, 468, and 445  $m\mu$ , and these are split into one negative and two positive MCD bands, respectively. If it is assumed that the ordinary absorption bands are Gaussian and that the longitudinal Zeeman splitting gives only two bands, then it can easily be shown that the magnitude of the splitting  $\delta$  (in Å.) is given by

$$\delta = \pm \frac{\Delta}{0.428} \frac{\Delta\epsilon}{\epsilon} \quad (1)$$

where  $\Delta$  is the half-band width,  $\Delta\epsilon = \epsilon_L - \epsilon_R$ , and  $\epsilon$  is the molecular extinction coefficient. From this equation, the calculated Zeeman splittings are 0.2, 0.1, and 0.5 Å. for the 482-, 468-, and 445- $m\mu$  peaks. These values are similar to those obtained by the direct measurement of the Zeeman splittings in a field of this magnitude (8.1 kgauss). Because of their extremely narrow absorption bands, the MCD peak heights for the rare earths are very sensitive to the slit width used in a simple low dispersion quartz monochromator of the type employed on the Jouan dichrometer. For example, the peak height at 446  $m\mu$  is almost reduced to half its value if the slit width is changed from 0.24 (used for the measurement shown in Figure 1) to 0.38 mm. If only for this reason, the magnitudes of the splittings calculated above can only be qualitatively correct. Other compounds giving measurable longitudinal Zeeman splittings are aqueous solutions of holmium and samarium chlorides, cytochrome *c*, and ferric chloride

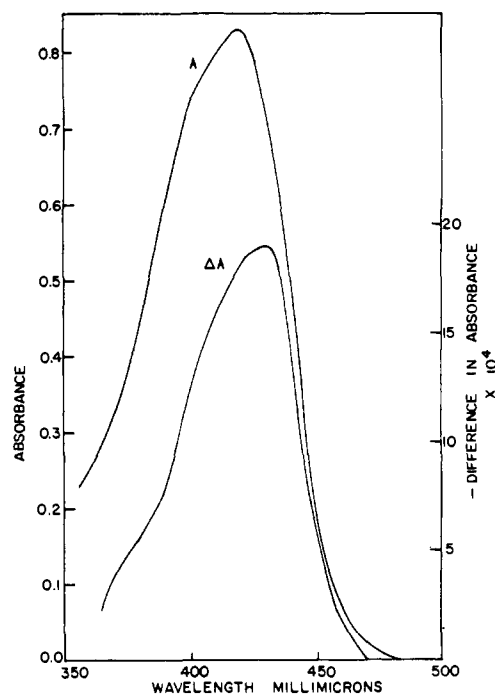


Figure 2. Magnetic circular dichroism spectrum in an 8.1-kgauss field and ordinary absorption spectrum of a 1-mm. thick sample of  $8.1 \times 10^{-3} M$  potassium ferricyanide; the peak near 430  $m\mu$  corresponds to a 12-mm. pen displacement.

in concentrated hydrochloric acid. As shown by eq. 1, it is only with compounds having very narrow band widths that splittings can be readily observed. Thus in compounds with typical half-band widths of 20  $m\mu$  a 0.1-Å. splitting will only give a signal of approximately  $10^{-4}$  in a solution having an absorbance of 2.

Some examples of compounds giving easily measurable MCD spectra of a perturbation origin are aqueous cobaltous chloride, cobaltous acetate, potassium ferricyanide, and cobaltous chloride in amyl alcohol. (Solutions of the latter were cooled to liquid nitrogen temperatures to obtain an estimate of the temperature dependence of the MCD. There was very little change in the MCD, but the solutions, which are dark blue at room temperature, became pink. Therefore, it was not possible to draw conclusions about the temperature dependence of the MCD of the original band without more detailed studies.)

Data for potassium ferricyanide are shown in Figure 2 with for comparison, its ordinary absorption spectrum. These data also are conveniently expressed as a  $\Delta\epsilon$  for a 10,000-gauss field. For the band shown in Figure 2,  $\Delta\epsilon_{430} = -0.26$ . There are also bands in the ultraviolet near 300  $m\mu$  ( $\Delta\epsilon_{300} = +0.4$ ) and a smaller negative one near 260  $m\mu$ .

In addition to the compounds mentioned thus far, a number of others have been studied which give either no observable MCD spectrum or else ones which are barely measurable. These would correspond to Shashoua's class V. (Such a class does not appear to be of any fundamental importance since whether or not a compound falls into it will depend on instrumental factors.)

There appear to be several virtues in measuring MCD spectra rather than MORD curves. First, the resulting data are simpler in appearance and therefore easier

to interpret. As a first approximation for every peak observed with MCD spectra, *two* will be observed in the corresponding MORD curve. Second, in solutions, a rather sizable solvent rotation (commonly larger than the rotation of the solute being studied) must be subtracted from the measured solution rotation when measuring magnetic optical rotations. With MCD spectra one uses a transparent solvent just as for ordinary spectral measurements in solution. (This advantage of MCD is particularly striking when studying glasses, as the authors realized when measuring MCD spectra and MORD curves of a Corning CS-138 rare earth filter.) On the other hand, one drawback to the MCD measurements may be a somewhat less favorable signal to noise ratio. One can show theoretically that a circular dichrometer capable of measuring differences of  $10^{-4}$  between the absorption of right- and left-handed light should be able to do as well as a polarimeter sensitive to  $10^{-3}^\circ$ . But judging from our experience thus far, it is not possible to measure a useful MCD spectrum for some compounds for which MORD curves are now published; *e.g.*, acetone.<sup>1</sup>

The most useful application of MCD spectra (and MORD curves) will probably be to a classification of spectral transitions. For example, the transitions of Figure 1 look superficially similar in an ordinary ab-

sorption spectrum but qualitatively different in the MCD spectrum. At present, there do not seem to be any simple relationships between the symmetry of a molecule and the presence or absence of MCD in a particular band such as exists for naturally active molecules. (Actually the usual statement about nonsuperimposable mirror image molecules exhibiting optical activity does not say that any *particular* band will exhibit circular dichroism. It simply states that there *is* at least one absorption band exhibiting dichroism.) To the best of the authors' knowledge, all known substances exhibit a Faraday effect, and therefore all substances must have at least one band exhibiting magnetic circular dichroism. Thus it would appear that there either are no symmetry requirements or they are very weak ones. A relationship might also be expected between the paramagnetism of a sample and its magnetic circular dichroism. It is true that all of the compounds studied thus far which give appreciable MCD spectra are paramagnetic, but most paramagnetic compounds did not give any measurable dichroism. Furthermore, Shashoua reports<sup>1</sup> MORD anomalies for a number of diamagnetic compounds.

*Acknowledgment.* The authors wish to thank Mr. Robert Meglen for technical assistance and the United States Public Health Service for financial support.

## Preparation and Characterization of New Fluoroxy Compounds<sup>1,2</sup>

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*Contribution No. 304 from the Central Research Laboratories, Minnesota Mining and Manufacturing Company, St. Paul 19, Minnesota. Received September 2, 1964*

*The preparation and characterization of the following fluoroxy-containing compounds are presented: CF<sub>3</sub>-CF<sub>2</sub>OF, CF<sub>3</sub>CF<sub>2</sub>CF<sub>2</sub>OF, (CF<sub>3</sub>)<sub>2</sub>CFOF, (CF<sub>3</sub>)<sub>3</sub>COF, O<sub>2</sub>N-CF<sub>2</sub>CF<sub>2</sub>OF, ClCF<sub>2</sub>CF<sub>2</sub>OF, Cl<sub>2</sub>CFCF<sub>2</sub>OF, and Cl<sub>3</sub>CCF<sub>2</sub>OF. These materials are obtained by direct fluorination of appropriate carbon-oxygen compounds under mild conditions. Fluorine nuclear magnetic resonance was found to be particularly useful in establishing their identity. Other data presented include infrared spectra, elemental analyses, molecular weights, and oxidizing power. Certain reactions are described, including those with reducing agents. These compounds are thermally stable at room temperature for extended periods of time. Mechanisms of reactions involving reduction, as well as chain decomposition, are discussed.*

(1) In accordance with the recommendations of the ACS Committee on Nomenclature of Highly Fluorinated Molecules, we have named these materials as fluoroxy derivatives.

(2) (a) Presented at the 148th National Meeting of the American Chemical Society, Chicago, Ill., Aug. 30-Sept. 4, 1964. (b) This research was supported by the Advanced Research Projects Agency under Contract NOrd 18688 and was monitored by the Bureau of Naval Weapons.

### Introduction

The only substances known which contain carbon and the OF group are CF<sub>3</sub>OF and the unstable acyl-OF compounds, CF<sub>3</sub>C(O)OF and C<sub>2</sub>F<sub>5</sub>C(O)OF.<sup>3</sup> The compound CF<sub>3</sub>OF was first prepared by Cady and Kellogg<sup>4</sup> by the AgF<sub>2</sub>-catalyzed fluorination of methanol, carbon monoxide, or carbonyl fluoride at 160-180°. In the 16 years following the disclosure of CF<sub>3</sub>OF, several attempts to prepare higher fluoroxyperfluoroalkanes were reported. Toward this goal, the fluorination<sup>5,6-8</sup> of a variety of substances, including ethanol, *t*-butyl alcohol, acetic acid, acetone, and cyclohexanone, was investigated, as well as the reaction<sup>7</sup> of O<sub>2</sub>F<sub>2</sub> with certain olefins. No higher fluoroxyperfluoroalkanes were thus obtained.

(3) G. H. Cady and K. B. Kellogg, *J. Am. Chem. Soc.*, **75**, 2501 (1953); A. Menefee and G. H. Cady, *ibid.*, **76**, 2020 (1954).

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(5) G. H. Cady and K. B. Kellogg, U. S. Patent 2,689,254 (1954).

(6) J. W. Dale, Abstracts of the First International Fluorine Symposium, Birmingham, England, July 14-17, 1959, p. 29.

(7) R. T. Holzmann and M. S. Cohen, *Inorg. Chem.*, **1**, 972 (1962).

(8) G. H. Cady, *Proc. Chem. Soc.*, 133 (1960).