in increased enolization. This may be explained by steric interaction between the alkoxy protons and those of the acetyl methyl group in the keto tautomer. This interaction forces the carbonyls into a position in which the electrostatic repulsion between carbonyls is larger and consequently results in a shift in the position of equilibrium toward the enol tautomer.

General Characteristics of Magneto-optical Rotation Spectra

BY VICTOR E. SHASHOUA

The magneto-optical rotation (m.o.r.) spectra of a number of optically inactive substances were obtained through a study of magnetically induced optical rotations (Faraday effect) as a function of wave length in the ultraviolet and visible regions of the spectrum. Several different types of characteristic spectra were observed at the absorption regions of molecules, and these have been tentatively classified into five spectral types. The instrumentation and technique of measurement using magnetic field strengths of 10,000 gauss are described. Typical m.o.r. spectra of organic molecules, such as acetone, phenazine, acridine, furan, and inorganic molecules, such as cobaltous salts, potassium ferricyanide, nickel sulfate, etc., are illustrated. The results, to date, indicate that m.o.r. spectroscopy might extend the scope of the optical rotatory dispersion method to a wide variety of optically inactive molecules.

Introduction

One of the most useful methods developed in recent years for the study of the stereochemistry of simple and macromolecules is the optical rotatory dispersion (o.r.d.) technique.[1] In this method, the optical rotation of plane polarized light is studied as a function of wave length to give an o.r.d. spectrum. The method, however, is limited to naturally optically active molecules and cannot be applied to the vast majority of compounds which are optically inactive.

In a previous communication from these laboratories[2] magneto-optical rotation (m.o.r.) spectroscopy was described as a possible means of extending the optical rotatory dispersion method to all molecules, irrespective of whether they possess natural activity; m.o.r. spectroscopy is based on Faraday's[3] discovery, in 1846, that any molecule will rotate the plane of polarized light when a magnetic field is applied parallel to the light beam. Verdet[4] studied the Faraday effect and showed that, at a fixed wave length, the optical rotation θ was related to the magnetic field strength H, and the path length of the sample L, by the equation

$$\theta = VHL$$

where V is a constant known as the Verdet constant.

In a review of the literature on the Faraday effect, Partington[5] points out that aside from sporadic attempts to measure the rotation at different wave lengths, most of the work of the past 120 years was confined to measurements at the sodium D-line wave length. Perkin,[5] in numerous papers, correlated stereochemical features of molecules with magnetic rotations measured at the sodium D-line wave length. Becquerel[6] described some of the first dispersion measurements. Cotton and Scherer[7] were the first to carry out dispersion measure-

ments on cobaltous chloride in the absorption region of the molecules. These results have been confirmed in more recent investigations.[8,9]

In addition, magneto-optical rotation studies in the vicinity of the absorption bands are discussed by Roberts and Stone for cerous sulfate[10] and titanium tetrachloride.[11] Garner, Nutt, and Labbauf[12] described a study of various hydrocarbons. More recently, Eberhardt[13] investigated the magnetic rotation spectra of certain diatomic molecules and gaseous organic molecules, such as formaldehyde. It is of interest to note that the Faraday effect is quite a general phenomenon and has been observed in the microwave region,[14] infrared region,[15] X-ray region,[16] as well as in the visible and ultraviolet regions of the electromagnetic spectrum. The literature, however, contains no systematic studies of optical rotations as a function of wave length in the absorption regions of molecules.

This paper describes the results of an experimental investigation of m.o.r. spectroscopy, in the ultraviolet and visible regions of the spectrum, to determine the general characteristics of m.o.r. spectra in the absorption regions of molecules. Through a rigorous study of the experimental problems in measurement, a number of instrumental errors was found in our initial results.[2] These difficulties were eliminated in a new apparatus specially constructed for this work. The major objective of this study was to determine whether magneto-optical rotation spectra exhibit anomalous dispersion features at the absorption band regions of molecules and, if so, to correlate spectral features with molecular structure.

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Experimental

Apparatus.—Magneto-optical rotatory spectroscopy requires a recording spectropolarimeter and a means for applying a uniform field through the sample parallel to the optic axis of the instrument. Figure 1 shows a diagram of the apparatus used. The light source is a 150-watt xenon arc, and wave length isolation is obtained by use of a double monochromator.[17] The quartz
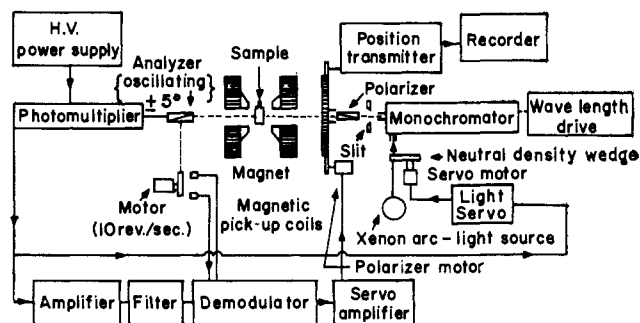

Fig. 1.—Block diagram of m.o.r. spectropolarimeter.

polarizer and analyzer are rochon prisms. The light passes through a $^3/_8$-in. axial hole in the 12-in. diameter pole pieces of the magnet.[18] The magnetic field is precisely controlled to provide field strengths up to 18,000 gauss. The sample is placed between the magnet pole pieces, and the rotation of the plane of polarized light is detected with an analyzer–photomultiplier system.

The analyzer is normally set with its polarizing axis at 90° to the axis of the polarizer (i.e., at null). A variable light intensity output is then obtained by oscillation of the analyzer axis to ±5° on either side of the null position at 10 c.p.s. The electronic system of the m.o.r. spectropolarimeter is designed to compare the light intensity at the extremes of this oscillation, i.e., at +5° and −5°, and to operate a servo motor which rotates the polarizer to a position providing equal light intensities.

The output of the m.o.r. spectropolarimeter is a plot of the angular position of polarizer prism vs. wave length; m.o.r. spectra are generally precise to 0.01°. A determination of the magnitude of experimental error gave the value of ±0.003° for the mean standard deviation in the measured rotation angles.

A servo-controlled, metallized quartz neutral-density wedge is used to adjust the light intensity so that the signal from the photomultiplier is always within the dynamic range of the amplifier. With a fixed slit setting, this permits all spectra to be obtained at a constant and reproducible spectral band width (3.5 mμ per mm. at most of the visible and part of the ultraviolet region). The sample cell was maintained at a constant temperature within 0.1°.

Materials.—The compounds used in this investigation were all commercially available. Inorganic solids were reagent grade chemicals and used without further purification. The organic solids, such as acridine and phenazine, were purified by sublimation *in vacuo*. The organic liquids and solvents were distilled before use and stored under dry nitrogen to avoid water pickup. With the exception of aqueous systems, all the solutions, preparations, and transfers to sample cells were carried out in a drybox under nitrogen.

Method of Measurement.—In the magnetic field, every substance will rotate the plane of polarized light so that it is necessary to measure independently the rotations for the solvent (R_0) with the sample cell, for the solution (R_s) with the sample cell, and for the empty sample cell (K). From these data, the rotations of the solute are calculated as

$$\theta_s = R_s - K$$
$$\theta_0 = R_0 - K \qquad (1)$$

where θ_s, θ_0, and K are the measured rotations due to solution, solvent, and sample cell.

To correct for solvent molecules displaced by solute when a solution is measured, the rotation of the solute α is then given by

$$\alpha = \theta_s - [(\rho_s - C)/\rho_0]\theta_0 \qquad (2)$$

(17) Cary Model 14 monochromator, Applied Physics Corp., Monrovia, Calif.

(18) Varian Magnet V4012A, Varian Associates, Palo Alto, Calif.

where C is the concentration (g./cc.) of the solute, and ρ_s and ρ_0 are the densities of the solution and pure solvent.

From the values of α in eq. 2, the values for specific magnetic rotation $[\alpha]_{sp}$ are calculated as

$$[\alpha]_{sp} = \alpha/lC \qquad (3)$$

where l is the path length of the sample in decimeters.

For substances where the molecular weight (M) is known and comparison of magnetic rotation with structure is desired, the values of $[\alpha]_M$ may be calculated as

$$[\alpha]_M = [\alpha]_{sp}M/100 \qquad (4)$$

The values of α, $[\alpha]_{sp}$, and $[\alpha]_M$, will, of course, depend on temperature, wave length, and magnetic field strength. A magnetic field strength of 10,000 gauss was chosen as a reference standard. All $[\alpha]_{sp}$ and $[\alpha]_M$ values reported in this paper have been normalized to 10,000 gauss. Thus, eq. 3 and 4 should be multiplied by the factor $10,000/H$ where H is the magnetic field strength (gauss). Under the experimental conditions used in this work, the light beam was passed through the polarizer toward the analyzer along the north–south direction of the magnetic field. Measurements of a clockwise rotation of the plane of polarized light for observations opposite to the direction of travel of the light beam were designated as positive. This is in the same sense as the Faraday rotation for a pure solvent outside its absorption region.

Errors in Measurement.—A major source of experimental error arises from the quality of monochromatic light used in a measurement. It is important in spectropolarimetry to note the stray light level passed by the monochromator.[19] For example, in single prism monochromators, a stray light level of 0.1 to 1% can give rise to reproducible errors in the measured optical rotations of at least 10% to over 100% when the sample under investigation has an absorbance (optical density) of 2. In the instrument used in this work the stray light error was reduced to a minimum by the use of a double monochromator.[17] Such a monochromator has a stray light level in the monochromatic light output of about 1×10^{-5} to 1×10^{-6} which reduces the experimental error due to stray light down to less than 0.1% at an optical density of 2. This was experimentally confirmed by the use of a mercury line source for m.o.r. measurements at selected wave lengths.

As further illustration of the magnitude of this effect, it is of interest to compare the new data on azobenzene with our preliminary measurements[2] obtained in a single prism monochromator instrument. Even though the precaution of using a solution of low optical density had been taken in the earlier work (i.e., optical density 0.6 for a 0.01% solution), an m.o.r. spectrum with erroneous anomalous dispersion features was obtained for the 440 mμ absorption band which actually gives a plain dispersion curve (see Discussion section on type V spectra).

A number of other precautions were taken to ensure the validity of the experimental results. These include: (1) the use of a nuclear magnetic resonance probe to set repeatedly the magnetic field to the same level within 0.5 gauss, (2) the control of the slit width of the monochromator to maintain a band pass equal to about one-tenth of the half-width of the absorption band under investigation, and (3) the control of the sample temperature to within 0.1°.

Figure 2 shows a plot of the results for cobaltous acetate in water at the absorption region of the compound. The results of two separate determinations on two separate solutions 1 month apart are illustrated. The good agreement in the results demonstrates the type of reliability that can be obtained with the instrument.

Experimental Variables.—Before discussing specific results, it is useful to consider the effects of such variables as magnetic field strength, path length of the sample, and concentration on the experimental results.

The linear dependence of magnetic rotation on field strength is quite well known[4,5] for measurements outside the absorption band region of molecules. However, no results have been reported for measurements within the absorption region of substances, where some molecules exhibit varying amounts of positive and negative magnetic rotations while others show no anomalous dispersion. Figure 3 illustrates the results for furan and cobal-

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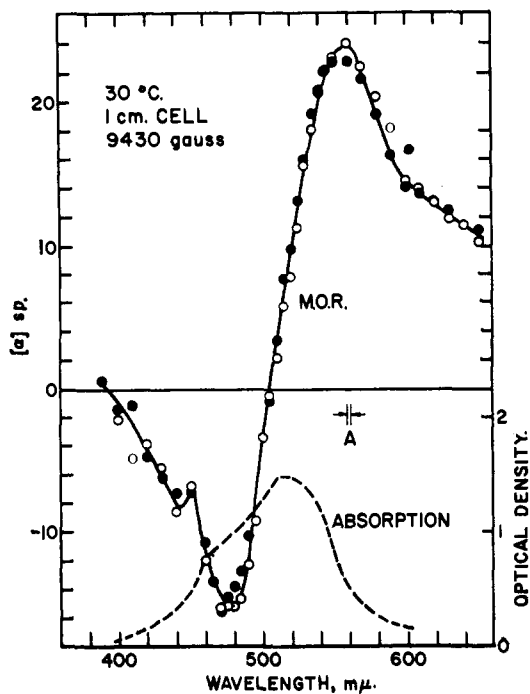
Fig. 2.—Reproducibility of results. M.o.r. spectra of cobaltous acetate in water; A, monochromator band pass.

tous acetate at several wave lengths. The linear dependence of rotation on magnetic field strength is clearly evident. It is interesting to note that a linear relationship with field strength is maintained even in the negative rotation region of the m.o.r. spectrum of cobaltous acetate.

Similar experiments at the absorption region of the spectrum demonstrated that the magnetic rotation varied linearly with the path length, within experimental error, for cell lengths from 0.5 up to 10 mm. This is consistent with a reliable choice of experimental conditions of measurement such as a narrow monochromator band pass, a uniform magnetic field in the sample chamber, and negligible stray light effects.

The variations of magnetic rotations with concentration have previously been studied for both binary[20] and ternary[21] mixtures of hydrocarbons at spectral regions outside the absorption bands. These investigations showed the magnetic rotation to be an additive property when no association occurred and the change in solution density on mixing was small. The present investigation includes no systematic study of this variable for molecules at wave lengths outside their absorption regions. However, in one series of experiments, aqueous solutions of cobaltous acetate at three different concentrations were studied at the absorption region of the molecule. Figure 4 shows the plots of $[\alpha]_{sp}$ vs. wave length for concentrations of 5, 10, and 20%. Such a plot should give identical curves for the three concentration values studied if a linear dependence on concentration is maintained. The general sigmoid shape of the m.o.r. curve is present in each case, but the secondary positive peak at 620 and the secondary negative peak at 430 mμ are no longer present at the highest concentration, possibly due to some molecular associations. These results, in addition to other observations throughout this paper, indicate a linear dependence of magnetic rotation on concentration provided that no intermolecular or intramolecular effects take place. Associations of molecules, hydration shells, and possibly long-range forces between molecules could influence the results. Magneto-optical rotation spectroscopy may play a useful role in detailed studies of these effects.

Results and Discussion

The general characteristics of m.o.r. spectra in the ultraviolet and visible regions of the spectrum were determined through a systematic study of various classes of organic and inorganic compounds. The

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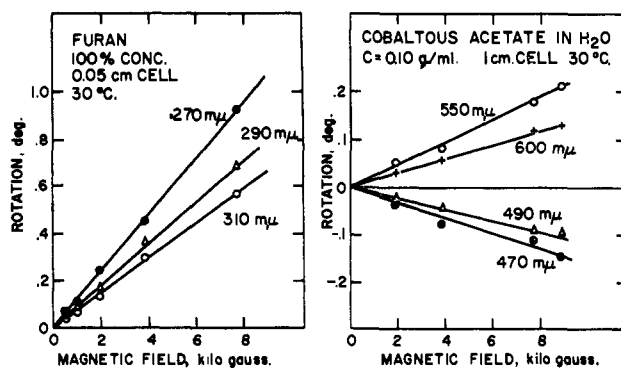(21) T. Tadayon, A. H. Nissan, and F. H. Garner, Anal. Chem., 21, 1532 (1949).

Fig. 3.—Influence of magnetic field strength on m.o.r. spectra.
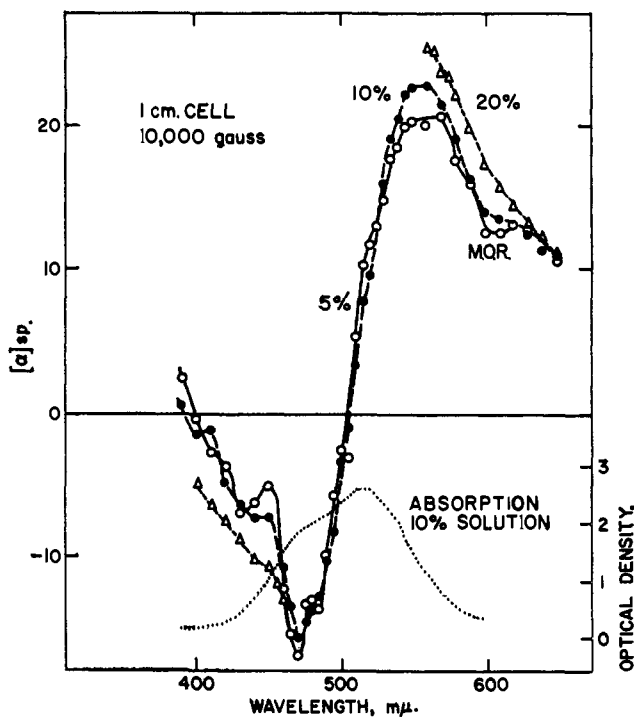

Fig. 4.—Influence of concentration on m.o.r. spectra. Results for cobaltous acetate in water. 30°.

magnitudes of the specific magnetic rotations were found to be in the same range (10 to 20,000) as the optical rotatory dispersion results obtained for naturally optically active substances in the absence of a magnetic field. By analogy to optical rotatory dispersion studies, the most significant regions of the m.o.r. spectra of molecules were expected to be at wave lengths corresponding to absorption bands. Accordingly, the experiments were directed toward investigating the features of an m.o.r. spectrum at the absorption band wave lengths. The results obtained to date indicate that the main features of m.o.r. spectra can be classified into five general types (see Table I).

Type I Spectra.—Figure 5 shows the features of a type I m.o.r. spectrum together with the corresponding position of the absorption band. Here the magneto-optical rotation follows a sigmoid curve with a variation from a positive maximum at long wave lengths through zero to a negative minimum at short wave lengths. The inflection point of the curve coincides with the peak wave length of the absorption band of the compound. Figure 6 shows a typical m.o.r. spectrum of this class and a conventional absorption spectrum for a 12% solution of cobaltous sulfate in water. The

TABLE I

SUMMARY OF M.O.R. SPECTRAL DATA

No.	Compound	Solvent	M.o.r. spectrum type	$[\alpha]_{sp}$ max. range[a]
1	Cobaltous acetate	Water	I	−15 to +15
2	Cobaltous chloride	Water	I	
3	Cobaltous sulfate	Water	I	−10 to +15
4	Cobaltous nitrate	Water	I	−13 to +13
5	Ferric chloride	Ethanol	II	−2700 to +1000
6	Potassium ferricyanide	Water	II and I	−4000 to +2000
7	Iron phthalocyanin	N-Methylpyrrolidene	II and III	−8000 to +2000
8	Phenazine	Chloroform	III	−2000
9	Acetone	Isooctane	III	−150
10	Fluorene	Chloroform	III	0 to −15,000
11	Carbazole	Dioxane	III	−300 to +100
12	Ethylene trithiocarbonate	Chloroform	III	−125
13	Acridine	Chloroform	III and IV	−13000 to +17000
14	Acetophenone	Isooctane	IV	+200
15	Benzophenone	Isooctane	III and IV	+150
16	Furan	None	VA	+18 to +22
17	Azobenzene (440 mμ band)	Chloroform	VA	−100 to 200
18	Nickelous sulfate	Water	VA	400 to 830
19	Manganous nitrate	Water	VB	−100 to −400

[a] The range of $[\alpha]_{sp}$ is reported only for the absorption band region.

sigmoid-shaped curve with some fine structure is clearly evident in the m.o.r. spectrum. The peak of the absorption band appears to coincide with the in-
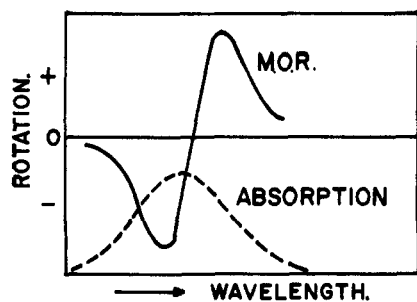

Fig. 5.—Characteristic curve for a type I m.o.r. spectrum.

flection point region of the m.o.r. spectrum. Molecules which exhibit a type I m.o.r. spectrum are cobaltous chloride, cobaltous acetate (Fig. 2), cobaltous sulfate (Fig. 6), and cobaltous nitrate (Fig. 7). It is interesting
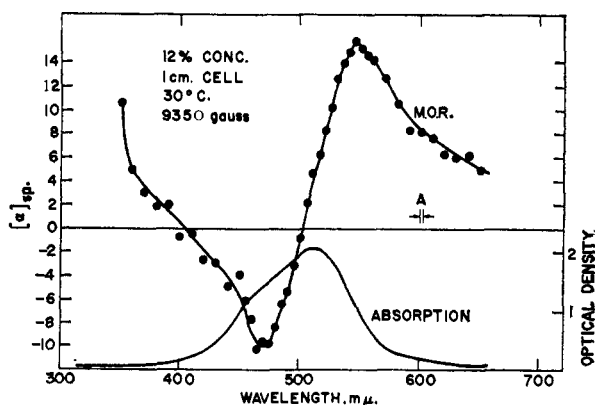

Fig. 6.—M.o.r. spectrum of cobaltous sulfate in water; A, monochromator band pass.

to note that all the compounds studied to date, which gave a type I m.o.r. spectrum, contained a paramagnetic positive ion. Also, the magnitude of the specific magnetic rotation was relatively small, varying from a maximum of about +15 to a minimum of −15 (degrees cm.^{2}/g. per 10,000 gauss).

Type II Spectra.—The shape of a type II m.o.r. spectrum is the inverse of type I. Here the rotation on the long wave length side of the absorption band is
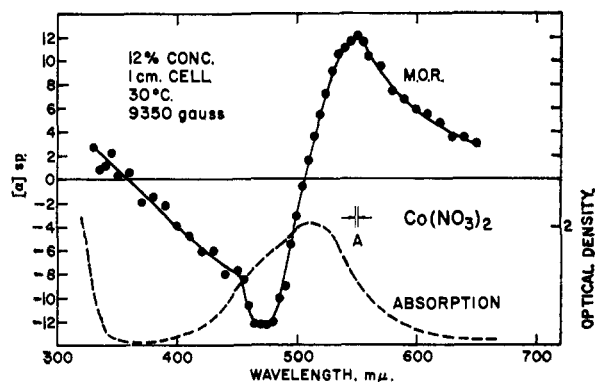

Fig. 7.—M.o.r spectrum of cobaltous nitrate in water; A, monochromator band pass.

negative, while on the short wave length side it is positive, as shown in Fig. 8. Examples of molecules exhibiting type II m.o.r. spectra are potassium ferricyanide, ferric chloride, and iron phthalocyanine. Figure 9
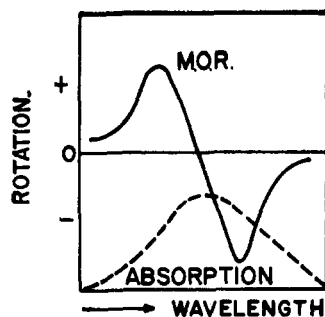

Fig. 8.—Characteristic curve for a type II m.o.r. spectrum.

illustrates the m.o.r. data and the corresponding absorption spectrum for a solution of 0.08% ferric chloride (FeCl$_3$·6H$_2$O) in ethanol, measured in a 1-cm. cell at 30°. The characteristic shape of a type II m.o.r. spectrum is clearly evident. In addition, there appears to be a negative displacement of the curve, possibly due to the influence of the rotations from shorter wave
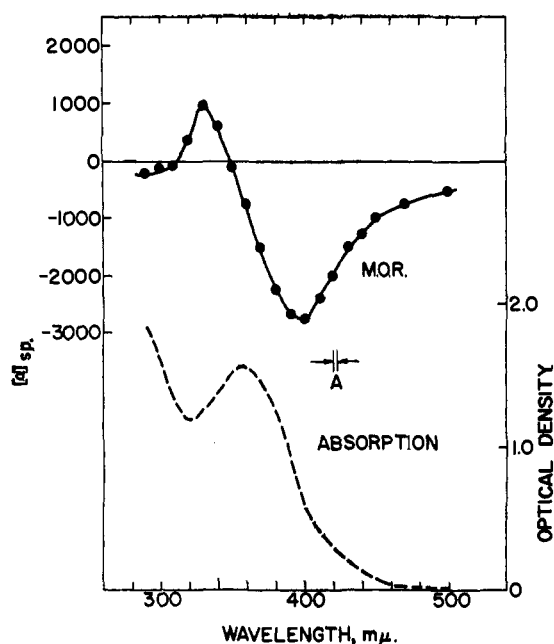
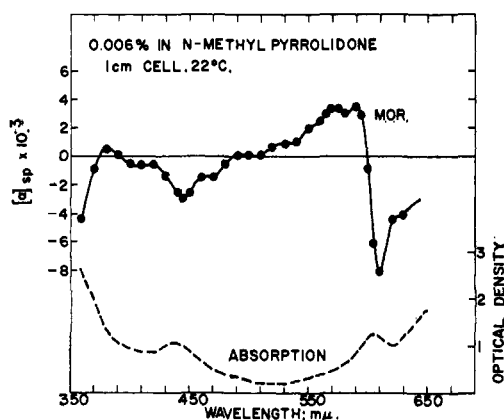Fig. 9.—M.o.r. spectrum of ferric chloride in ethanol; A, monochromator band pass.

Fig. 10.—M.o.r. spectrum of iron phthalocyanine in N-methyl-pyrrolidone.

length bands. Similar results were obtained for a freshly prepared solution of iron phthalocyanine in N-methylpyrrolidone (Fig. 10) and for the 420 mμ band of potassium ferricyanide (Fig. 16). The magnitudes of the specific magnetic rotations for the type II spectra varied from 1000 to 8000 at 10,000 gauss field.

Type III Spectra.—In this class, the m.o.r. spectrum exhibits a negative rotation peak coincident with the wave length of maximum absorption of the compound (Fig. 11). Most of the molecules studied to date which had type III spectra were organic compounds. Figure 12 shows a plot of the magnetic rotation data for an 0.5% solution of phenazine in chloroform.[22] At this concentration, phenazine absorbs light too strongly to permit rotation measurements at wave lengths corresponding to the absorption band peak, but results obtained in both wings of the absorption band, where the optical density was 2 or less, suggest high negative rotations at the wave length region of the absorption band. Other examples of type III m.o.r. spectra were observed for acetone (Fig. 13), and for parts of the

(22) The m.o.r. spectrum of phenazine previously published[2] contained instrumental errors resulting from stray light. The corrected data for phenazine are shown in this paper.
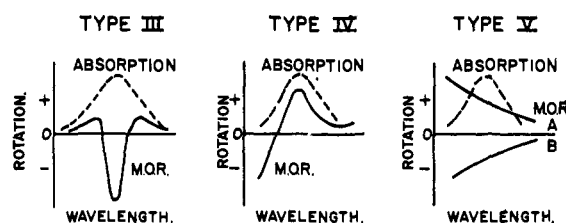

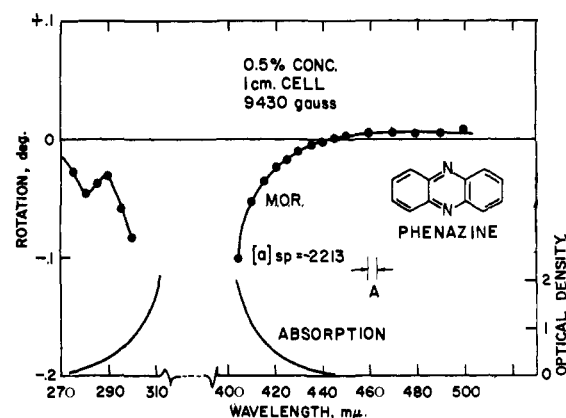Fig. 11.—Characteristic curves for types III, IV, and V m.o.r. spectrum.

Fig. 12.—M.o.r. spectrum of phenazine in chloroform; A, monochromator band pass.
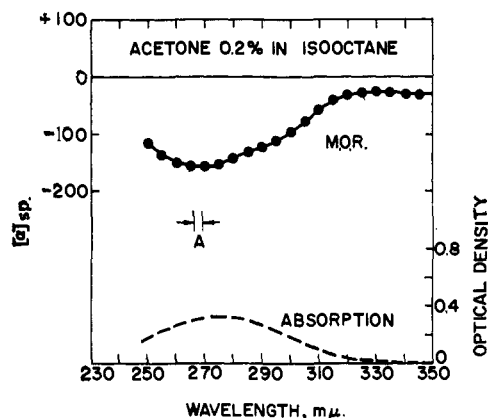

Fig. 13.—M.o.r. spectrum of acetone in isooctane; A, monochromator band pass.

spectra of carbazole, fluorene, ethylene trithiocarbonate, and acridine.

The observed specific magnetic rotations for molecules with a type III spectrum cover a relatively wide range, from 100 to about 20,000, suggesting that the rotational strengths for specific functional groups in molecules must be of variable magnitude and also depend on the over-all configuration. Thus, the following average $[\alpha]_{sp}$ values were obtained for absorption bands due to the long wave length transitions of the compounds: —200 in carbazole, over —2000 in phenazine, about —10,000 in acridine, and about —15,000 for fluorene. More experimental evidence of this type will be obtained to evaluate the relationship of the type and symmetry properties of a given transition to the magnitude of the magneto-optical rotation. These factors, with additional examples, will be discussed in another paper.

Type IV Spectra.—A type IV m.o.r. spectrum, as shown in Fig. 11, exhibits a maximum positive rotation coinciding with the wave length peak of the absorption
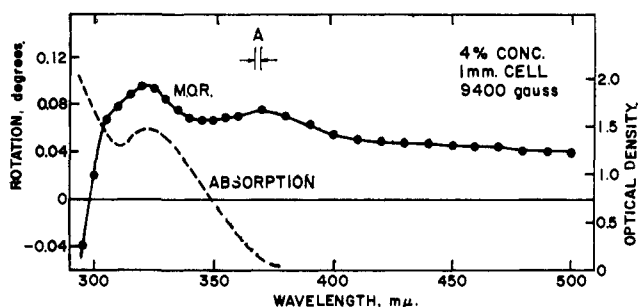
Fig. 14.—M.o.r. spectrum of acetophenone in isooctane; A, monochromator band pass.
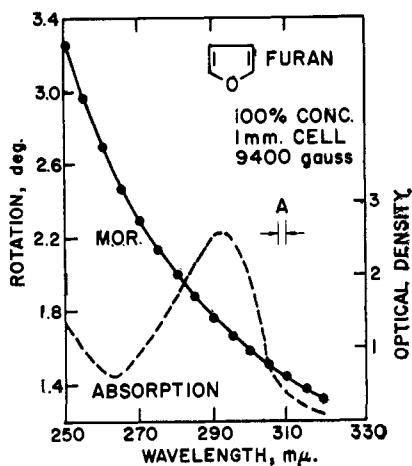

Fig. 15.—M.o.r. spectrum of furan; A, monochromator band pass.

Fig. 16.—M.o.r. spectrum of potassium ferricyanide; A, mono chromator band pass.

bands of molecules. The spectra of benzophenone, acetophenone, and possibly certain features of the acridine spectrum are examples of type IV. The spectrum of acetophenone (Fig. 14) is especially interesting in that it has two positive peaks, one at the absorption band maximum and one outside the absorption band region which may correspond to the wave length position of a singlet–triplet transition[2] of the compound. Eberhardt[13] has also observed anomalous magnetic rotations for certain gaseous molecules at wave lengths corresponding to the position of singlet–triplet transitions outside the absorption band regions.

Type V Spectra.—One of the surprising results of this investigation was that certain molecules exhibited no anomalous dispersion of the magnetic rotation at the wave length region of the absorption bands. The m.o.r. spectrum appears to ignore completely the presence of the absorption band of the compound (Fig. 11). Furan is a typical case. Figure 15 shows the results for the pure liquid. The same results were obtained for a number of experiments using different temperatures and solvents, such as chloroform and isooctane, to eliminate any possible solvent interaction effects. Other compounds exhibiting type V spectra include the 440 mμ absorption band of azobenzene and some inorganic molecules with paramagnetic cations, such as nickel sulfate and manganous nitrate. The case of manganous nitrate is somewhat unique in that the magnetic rotation is negative throughout the visible region, so that one may consider the type V m.o.r. spectra to consist of two cases: VA with positive rotations and VB with negative plain dispersion curves. These observations were supplemented by other measurements
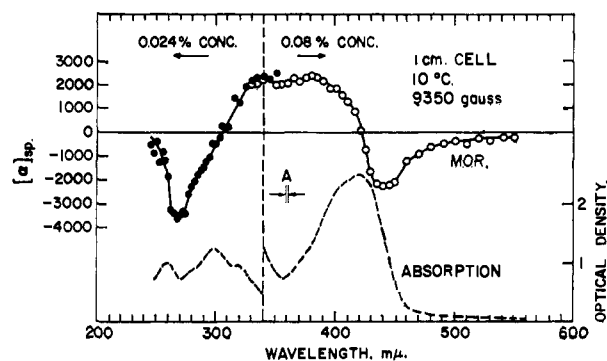
to determine any possible influence of the magnetic field strength and temperature, but there were no significant changes in the shape of the spectrum.

Some General Remarks.—The five types of the observed m.o.r. spectra are a convenient means of describing the results. At present, there appears to be no specific relationship between a given spectral type and a particular class of molecules; in fact, some compounds exhibit two or more types of spectra. For example, acridine and carbazole show both type III and IV curves. One outstanding example is potassium ferricyanide which has absorption bands at 420 and at 300 mμ. Figure 16 shows the composite m.o.r. spectrum obtained for measurements at two concentrations chosen so that separate measurements could be made at each of the absorption bands of the compound. At the long wave length absorption region, a type II m.o.r. spectrum is obtained, while at the short wave length absorption region, a type I m.o.r. spectrum is observed. These observations indicate that the m.o.r. spectrum type is characteristic of a specific electronic transition in a molecule rather than the molecule as a whole.

The experimental results of this paper suggest a number of comparisons between m.o.r. spectroscopy and natural optical activity. For example, we can consider the possibility that there may be some structure for the excited state of a molecule analogous to the asymmetric center of natural optical activity. Types III and IV would be comparable to the L- and D-configurations. Moreover, the fact that some absorption bands are not "magnetically active" (i.e., no anomalous dispersion of magnetic rotation) indicates the possibility that cancellation of "magnetic activity" may occur. This feature may be compared to the loss of optical rotation properties for "*meso*" configurations of naturally optically active molecules. While such considerations are interesting, a useful interpretation of spectra can only come from a theoretical understanding of the fundamentals of m.o.r. spectroscopy.

Many theories have been proposed in the published literature for the Faraday effect.[5] Most recently, Hameka[23] and, independently, Groenewege[24] have derived a new quantum mechanical theory for magnetic rotation spectra. Our experimental data will be used to test certain features of these theoretical approaches.

Conclusions.—The results described in this paper demonstrate that anomalous dispersions are obtained

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(24) M. P. Groenewege, *Mol. Phys.*, **5**, 540 (1962).

in magneto-optical rotation spectra at the absorption band regions of molecules. Moreover, the shapes of the dispersion curves are defined by five types rather than the two characteristic Cotton effects[25] of natural optical activity measurements. In addition, the type of m.o.r. spectrum obtained is characteristic of particular transition rather than the molecule as a whole. The experimental observations studied so far indicate that m.o.r.

spectroscopy may prove useful for studying molecular structure and configuration.

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A Method of Diatomics in Molecules. III. H₂X and X₂H (X = H, F, Cl, Br, and I)[1]

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Diatomics in molecules theory[2] is applied to the elementary reactions $H_2 + X = H + HX$ and $X_2 + H = X + HX$, where $X = H, F, Cl, Br$, or I, for linear configurations only. The combined three-atom systems are represented by a resonance of the two canonical structures A–B C and A B–C. The energy matrix elements can be expressed in terms of overlap matrix elements (for the polyatomic structures) and experimental ground and excited state energies of the diatomic and monatomic fragments. Hulburt–Hirschfelder potential curves are employed for diatomic ground states, approximate potentials are developed and used for diatomic excited states, and accurate curves are also used for H_2. Classical activation energies, which are in good agreement with accepted experimental values, bond energies, and optimum bond lengths are calculated. Uncertainties introduced by the use of approximate diatomic potential energy curves in diatomics in molecules theory are discussed.

In a previous paper,[2] a new approximate theory was developed for calculating the energy of a polyatomic molecule (for any fixed positions of the nuclei) in terms of empirical ground and excited state energies of all possible diatomic and monatomic fragments which comprise the polyatomic as well as all overlap integrals between valence-bond wave functions postulated to describe it. The theory contains two fundamental assumptions: (1) the electronic structure of a polyatomic molecule *can* be represented adequately by a reasonably limited set of canonical valence-bond structures; and (2) the ground and excited state eigenfunctions of all possible diatomic and monatomic fragments can be represented adequately by valence-bond wave functions built from appropriate subsets of the same atomic orbital basis set as employed in the total polyatomic description. No approximations of integrals and no adjustable parameters are necessary in the theory, although it has been noted that neglect of overlap integrals between atomic orbitals has little effect on the final energies.

Results of applications to H_2O, H_3, and H_3^+ are encouraging[2,3]; calculated molecular energies differ from experiment by only 1–2, 5, and possibly 6–10 kcal., respectively. In this paper, diatomics in molecules theory is applied to the systems H_2X and HX_2, where $X = F, Cl, Br$, or I. For these cases, one of the main stumbling blocks in applying the theory is met squarely, namely, that accurate potential energy curves for both ground and excited diatomic states are necessary ingredients. Since these are not available for HX and X_2, approximate curves are developed, and the theory also is reapplied to H_3, for which accurate calculations have already been made.[3]

(1) Supported in part by a grant from the National Science Foundation.
(2) F. O. Ellison, *J. Am. Chem. Soc.*, **85**, 3540 (1963), to be referred to as paper I.
(3) F. O. Ellison, N. T. Huff, and J. C. Patel, *ibid.*, **85**, 3544 (1963), to be referred to as paper II.

Previous semiempirical calculations on these systems as well as others include, for example, early applications of the London–Eyring–Polanyi method by Eyring[4] and Hirschfelder,[5] the modification thereof by Sato,[6] and a recent new procedure by Johnston and Parr.[7]

Theory

The reactions

$$H_2 + H \rightleftharpoons H + H_2 \tag{1}$$

$$H_2 + X \rightleftharpoons H + HX \tag{2}$$

$$X_2 + H \rightleftharpoons X + XH \tag{3}$$
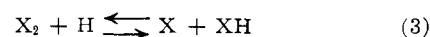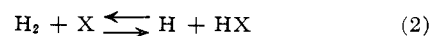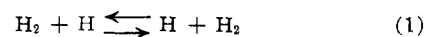
where $X = F, Cl, Br$, or I, may all be written as AB + C = A + BC. Linear configurations of the combined three-atom system ABC should be representable in the first approximation by resonance of two canonical structures A–B C and A B–C.

$$\Psi = a_1\Psi_1 + a_2\Psi_2 \tag{4}$$

$$\Psi_1 = |a\bar{b}c| - |\bar{a}bc| \tag{5}$$

$$\Psi_2 = |a\bar{b}c| - |ab\bar{c}|$$

If atom B is H, for example, then b represents a 1s orbital on that center; a bar over the orbital denotes β-spin, no bar means α-spin. If, on the other hand, atom B is Br, then b represents a 4p orbital on that center, and it is understood that the nonbonding $1s^2$-$2s^22p^63s^23p^64s^23d^{10}4p^4$ electron orbitals should also be written into the determinantal wave functions. In order to determine the optimum coefficients a_n for which the expectation value of the molecular energy

(4) H. Eyring, *ibid.*, **53**, 2537 (1931).
(5) J. O. Hirschfelder, *J. Chem. Phys.*, **9**, 645 (1941).
(6) S. Sato, *ibid.*, **23**, 592, 2465 (1955).
(7) H. S. Johnston and C. Parr, *J. Am. Chem. Soc.*, **85**, 2544 (1963).