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E. U. Condon, William Altar, and Henry Eyring

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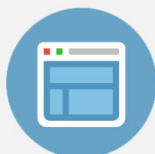
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One-Electron Rotatory Power*

E. U. CONDON, WILLIAM ALTAR AND HENRY EYRING
Princeton University, Princeton, New Jersey

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It is shown that a single electron moving in a field of suitable dissymmetry can give rise to optical rotatory power in a medium containing molecules of this type. This effect is called *one-electron rotatory power* and is in striking contrast to the models developed by Born, Oseen, Gray and others in which a dynamic coupling between several electronic oscillators is responsible for the rotatory power. The detailed calculations are carried out for the potential function,

$$V = \frac{1}{2}(k_1x^2 + k_2y^2 + k_3z^2) + Axyz,$$

which shows rotatory power both quantum mechanically and classically. Next it is shown how fields of this type may be adapted to an approximate description of the field in which the chromophoric electrons of a molecule move, the constants k_1 , k_2 , k_3 and A being largely determined by the average charge on the different atoms of the molecule as found from additivity of dipole moments due to the bonds in the molecule. As illustrations of the theory absolute calculations are made for the contribution of the nitrite group to the rotatory power of methyl phenyl carbinol nitrite which agrees satisfactorily with experimental data, for the phenyl group contribution of the same

molecule and for the hydroxyl group contribution in secondary butyl alcohol. In the latter two instances the theoretical values are much too small but as there is a great deal of freedom in the choice of the configuration because of free rotation these results merely indicate need for more detailed calculations. The general quantum-mechanical theory of circular dichroism is developed and a quantum-mechanical derivation of Natanson's rule is given. The quantum-mechanical definition of Kuhn's "anisotropy factor" is given and an alternative measure of the contribution of an absorption band to rotatory power called the *rotatory strength* is defined and discussed. It is shown that spin magnetic moments may generally be neglected in calculation of rotatory power owing to the weakness of spin-orbit interaction. Interpretation of experiments of Schwab, Rost and Rudolph on the catalytic dehydration of butyl alcohol on active quartz is discussed and kinetic arguments advanced to show how the relative configuration of quartz and butyl alcohol may be inferred from such data. The relation of one-electron rotatory power to known dipole moment and solvent effects on rotatory power is briefly discussed.

I. INTRODUCTION

THE property of some liquids to rotate the plane of polarization of linearly polarized light traversing them has played a great role in the development of stereochemistry. In spite of the fact that an enormous amount of work has been devoted to the subject it cannot be said that the theory of the molecular actions responsible for this behavior is in a very satis-

factory state. In this paper we shall attempt to carry the quantum-mechanical treatment of the subject further in terms of a simple model which exhibits the main features of the phenomenon.

By way of review let it be recalled that the rotation is produced as an indirect effect of circular double refraction, that is, because of the medium's having slightly different indices of refraction for right and left circularly polarized light. The rotation is called positive if the plane is turned in a clockwise direction as viewed by an observer into whose eyes the light enters and

* A preliminary account of the main results of this paper was presented at the Denver Meeting of the American Physical Society, June 26, 1937.

the classical analysis due to Fresnel¹ shows that φ , the rotation per unit length of path, is given by

$$\varphi = (\pi/\lambda)(n_l - n_r) \quad (1)$$

in which λ is the vacuum wave-length and n_l , n_r are the refractive indices for left and right circularly polarized light, respectively. On the electromagnetic theory of light circular double refraction can be described phenomenologically by assuming that the medium is characterized by a parameter g defined by the equation

$$\begin{aligned} \mathbf{D} &= \epsilon \mathbf{E} - g \dot{\mathbf{H}}, \\ \mathbf{B} &= H + g \dot{\mathbf{E}}, \end{aligned} \quad (2)$$

in which \mathbf{D} and \mathbf{B} are the electric and magnetic inductions and \mathbf{E} and \mathbf{H} the field strengths, ϵ the effective dielectric constant for the frequencies involved, so that ϵ equals the square of the mean refractive index. Then a solution of Maxwell's equations by standard methods gives for the rotatory power

$$\varphi = (2\pi/\lambda)^2 cg. \quad (3)$$

The parameter g is the macroscopic representative of a corresponding microscopic parameter representing the response of individual molecules to the applied fields of the light wave. Let \mathbf{p}_1 be the induced electric moment of the molecule due to the fields of the light wave and \mathbf{m}_1 the corresponding induced magnetic moment. Then we assume that these are of the form

$$\begin{aligned} \mathbf{p}_1 &= \alpha \mathbf{E}' - (\beta/c) \dot{\mathbf{H}}, \\ \mathbf{m}_1 &= +(\beta/c) \dot{\mathbf{E}}, \end{aligned} \quad (4)$$

where α is the quantity commonly called the polarizability of the molecule, β is a new parameter that is responsible for the optical activity, and \mathbf{E}' is the effective field acting on a molecule. Accepting the Lorentz' result that

$$\mathbf{E}' = \mathbf{E} + 4\pi \mathbf{P}/3, \quad (5)$$

where $\mathbf{P} = N_1 \mathbf{p}_1$ is the electric moment in unit volume, N_1 being the number of molecules in unit volume, then the standard definitions $\mathbf{D} = \mathbf{E} + 4\pi \mathbf{P}$ and $\mathbf{B} = \mathbf{H} + 4\pi \mathbf{M}$ lead to the following connections between α and ϵ , and β and g , respectively,

$$\frac{4\pi N_1 \alpha}{3} = \frac{\epsilon - 1}{\epsilon + 2}; \quad \frac{4\pi N_1 (\beta/c)}{3} = \frac{g}{\epsilon + 2}. \quad (6)$$

¹ Fresnel, Ann. chim. phys. 28, 147 (1825).

The first of these is the familiar result from the ordinary theory of dispersion, the second is its analog for the theory of optical activity. Using the well-known result $n^2 = \epsilon$ where n is the mean index of refraction, a combination of (6) and (3) permits the expression of the rotatory power φ in terms of the molecular parameter β and other defined properties of the medium,

$$\varphi = (16\pi^3/\lambda^2) N_1 \beta \cdot \frac{1}{3}(n^2 + 2). \quad (7)$$

With this equation the task is completed of expressing the observed rotation per unit length φ in terms of the molecular parameter β , the number of active molecules in unit volume N_1 , the vacuum wave-length λ and the mean index of refraction, n . In this way the theory of optical activity is referred back to a molecular theory of β .

Instead of dealing with the rotatory power itself it is often convenient to deal with the molecular rotatory power which is defined as $\varphi M/\rho$ where M is the molecular weight and ρ is the density. Denoting the molecular rotatory power with Φ one has

$$\Phi = (16\pi^3/\lambda^2) N \beta (n^2 + 2)/3, \quad (8)$$

where N is Avogadro's number. Either (7) or (8) may be used to compute value of β from experimental data on the rotatory power. Unfortunately values of the refractive index are often not given in the literature so the factor $(n^2 + 2)/3$ has to be estimated.

The appropriate extension of the quantum-mechanical theory of dispersion needed to give the theory of the parameter β has been given by Rosenfeld.² Suppose the quantum states of the molecule are labeled by a, b, \dots where a single letter stands for the totality of quantum numbers needed to specify the state. Then the matrix components of the electric moment of the molecule are denoted by $(a|\mathbf{p}|b)$ and those of magnetic moment by $(a|\mathbf{m}|b)$ where

$$\mathbf{p} = e \sum_i \mathbf{r}_i; \quad \mathbf{m} = \frac{e}{2mc} \sum_i (\mathbf{r}_i \times \mathbf{p}_i + 2\mathbf{S}_i), \quad (9)$$

the sum being extended over all the electrons in the molecule, \mathbf{r}_i being position, \mathbf{p}_i momentum

² Rosenfeld, Zeits. f. Physik 52, 161 (1928); see also Condon, "Theories of Optical Rotatory Power," Rev. Mod. Phys. (in press).

and \mathbf{S}_i spin angular momentum of the i th electron. The necessary generalization of the ordinary dispersion theory is obtained by taking into account to the first order the finite ratio of molecular diameter to wave-length of light. The end result of Rosenfeld's calculations is that

$$\beta_a/c = \frac{1}{3\pi h} \sum_b \frac{\text{Im}\{(a|\mathbf{p}|b) \cdot (b|\mathbf{m}|a)\}}{\nu_{ba}^2 - \nu^2}, \quad (10)$$

where the expression has been simplified to take account of the fact that the molecules are oriented at random. In this expression ν is the light frequency and ν_{ba} is the frequency associated with a transition from state a to state b . The symbol $\text{Im}\{ \}$ means "imaginary part of" in the sense

$$\text{Im}\{u + iv\} = v \quad (11)$$

if u and v are real. The subscript a on β means that the formula gives the appropriate value of β for molecules in the state a . If in the actual material the molecules are distributed over various initial states such that $N_1(a)$ is the number of molecules in unit volume in the state a then the effective value of β for use in (4) is the weighted average

$$\beta = (1/N_1) \sum_a N_1(a) \beta_a. \quad (12)$$

Equation (10) for (β_a/c) is entirely analogous to the more familiar equation for the ordinary polarizability, α_a ,

$$\alpha_a = \frac{2}{3h} \sum_b \frac{\nu_{ba} |(a|\mathbf{p}|b)|^2}{\nu_{ba}^2 - \nu^2}. \quad (13)$$

The work of Rosenfeld thus refers the parameter β and hence the optical activity back to the matrix components of electric and magnetic moment as contained in (10). It appears that in all the years since Rosenfeld's paper no attempts have been made to discuss the quantum-mechanical formula (10) in relation to an actual molecular model. Instead there has been a tendency to revert to the original coupled oscillator model of Born,³ Oseen⁴ and Gray⁵ in what attempts have been made recently⁶⁻⁸ to

discuss the theory of optical activity. The opinion prevalent in the literature⁹ seems to be that the only models which need be considered to explain optical activity are those involving coupled oscillators. The model originally proposed by Drude⁹ involved only one oscillating particle, and its rejection by Born and Kuhn⁹ has done much to strengthen the common belief, that single oscillators are neither adequate nor important in providing a mechanism. In the following we propose to show that electric fields known to be present in molecules actually endow single dispersion electrons with optical activity of the magnitude observed. Consequently we feel that more is to be gained by attempting to discuss the actual application of (10) to molecular models. That is what is done in this paper.*

2. A SIMPLE MODEL FOR OPTICAL ACTIVITY

A characteristic feature of the modern theory of atomic and molecular spectra is the use of what may be called the Hartree approximation, in which each electron in the system moves in an average field due to the average action on it of all the other atoms and the nuclei. The detailed coupling of the electrons may then be taken into account in higher approximations. It seems, therefore, that the best approach to optical activity is gained by studying some simple potential field, in which a single electron moves, of such a character as to give activity. Such a calculation will be made in this section and later sections will be devoted to the correlation of the simple model with the structure of actual molecules.

The force field, $V(x, y, z)$, must be such that it has no planes of symmetry and no center of symmetry. This is true because if there were such an element of symmetry then the states could be classified as even or odd with regard to this symmetry element, and \mathbf{p} and \mathbf{m} would have selection rules of opposite kind with regard to

⁶ Kuhn, *Zeits. f. physik. Chemie* **B4**, 14 (1929); *Trans. Faraday Soc.* **26**, 293 (1930).

⁷ Born, *Proc. Roy. Soc.* **A150**, 84 (1935).

⁸ Oke, *Proc. Roy. Soc.* **A153**, 339 (1935).

⁹ See: Lowry, *Optical Rotatory Power*, p. 372 f. Kuhn has actually demonstrated that Drude's result was obtained by unjustifiably neglecting certain terms.

* *Added in proof:* These remarks, of course, do not apply to the recent important paper of Kirkwood, *J. Chem. Phys.* **5**, 479 (1937) who has taken steps toward the use of (10) in definite molecular models.

³ Born, *Physik. Zeits.* **16**, 251, 437 (1915); *Ann. d. Physik* **55**, 177 (1917).

⁴ Oseen, *Ann. d. Physik* **48**, 1 (1915).

⁵ Gray, *Phys. Rev.* **7**, 472 (1916).

this character so there would be no states a and b for which $(a|\mathbf{p}|b)$ and $(b|\mathbf{m}|a)$ were both different from zero.

A simple field satisfying this requirement is given by

$$V(x_1x_2x_3) = (1/2)(k_1x_1^2 + k_2x_2^2 + k_3x_3^2) + Ax_1x_2x_3, \quad (14)$$

where the Cartesian coordinates of the particle are x_1, x_2, x_3 . The motion of a particle of mass μ in such a field may be treated by the standard form of perturbation theory, treating the $Ax_1x_2x_3$ term as a perturbation.

In the zeroth approximation the energy levels are given by

$$W(n_1, n_2, n_3) = (n_1 + \frac{1}{2})h\nu_1 + (n_2 + \frac{1}{2})h\nu_2 + (n_3 + \frac{1}{2})h\nu_3 \quad (15)$$

and the zero-order wave functions are

$$\psi(n_1, n_2, n_3) = \varphi_{n_1}(x_1/a_1)\varphi_{n_2}(x_2/a_2)\varphi_{n_3}(x_3/a_3), \quad (16)$$

in which

$$2\pi\nu_i = (k_i/\mu)^{1/2}, \quad (2\pi a_i)^2 = h/\mu\nu_i; \quad (17)$$

and the φ functions are the normalized orthogonal system involving the Hermitian polynomials

$$\varphi_n(\xi) = (2^n n! \pi^{-1/2})^{-1} H_n(\xi) e^{-\xi^2/2}. \quad (18)$$

The calculation of the matrix components of the perturbation energy $Ax_1x_2x_3$ with respect to the wave functions (16) is very readily made since the perturbation energy and the wave functions each factor into simple functions of an individual coordinate. Since the recursion formula for the functions (18) can be written

$$\xi\varphi_n(\xi) = [(n+1)/2]^{1/2}\varphi_{n+1}(\xi) + (n/2)^{1/2}\varphi_{n-1}(\xi), \quad (19)$$

the nonvanishing matrix components of ξ are in a one-dimensional scheme

$$(n|\xi|n') = [(n)/2]^{1/2} \quad \text{where } n' = n \pm 1 \quad (20)$$

and (n) means the larger of n or n' . Hence the nonvanishing matrix components of the perturbation energy are given by

$$(n_1n_2n_3|Ax_1x_2x_3|n'_1n'_2n'_3) = Aa_1a_2a_3 8^{-1/2} [(n_1)(n_2)(n_3)]^{1/2} \quad (21)$$

where $n'_1 = n_1 \pm 1$, $n'_2 = n_2 \pm 1$ and $n'_3 = n_3 \pm 1$ and (n_i) means the larger of n_i and n'_i . It will be convenient to introduce an abbreviation

$$\lambda = Aa_1a_2a_3/8^{1/2}h. \quad (22)$$

Then by the standard perturbation theory we see that to the first order the energy levels remain the same as (15) since the diagonal elements of the perturbation vanish. The first-order perturbed wave function is

$$\Psi(n_1n_2n_3) = \psi(n_1n_2n_3) - \sum_{n'_i} \frac{\psi(n'_1n'_2n'_3)(n'_1n'_2n'_3|Ax_1x_2x_3|n_1n_2n_3)}{W(n'_1n'_2n'_3) - W(n_1n_2n_3)}, \quad (23)$$

where the summation contains at most eight terms because of the simplicity of (21).

Now for the optical activity one needs the matrix components of \mathbf{r} and \mathbf{L} , the orbital angular momentum calculated with respect to the perturbed wave functions (23). Denoting these with square brackets and matrix components with respect to unperturbed functions with round brackets one has, to the first approximation for any quantity F ,

$$[n_1n_2n_3|F|n'_1n'_2n'_3] = (n_1n_2n_3|F|n'_1n'_2n'_3) - \lambda \{ \bar{\psi}_1(n_1n_2n_3) F \psi(n'_1n'_2n'_3) + \bar{\psi}(n_1n_2n_3) F \psi_1(n'_1n'_2n'_3) \}, \quad (24)$$

in which $\lambda\psi_1(n_1n_2n_3)$ is written for the second term on the right side of (23) and where $\bar{\psi}_1 F \psi$ means that the expression is to be integrated over the configuration space.

The matrix components of \mathbf{r} with regard to the unperturbed functions follow at once from (20) the result being

$$(n_1n_2n_3|\mathbf{r}|n'_1n'_2n'_3) = 2^{-1/2} \{ \mathbf{i}(n_1)^{1/2}\delta(n_2, n'_2)\delta(n_3, n'_3)a_1 + \mathbf{j}(n_2)^{1/2}\delta(n_1, n'_1)\delta(n_3, n'_3)a_2 + \mathbf{k}(n_3)^{1/2}\delta(n_1, n'_1)\delta(n_2, n'_2)a_3 \}. \quad (25)$$

Here \mathbf{i} , \mathbf{j} and \mathbf{k} are the usual unit vectors and $\delta(x, y) = 0$ for $y \neq x$ and 1 for $y = x$. Hence to get nonvanishing matrix components two of the n 's must be unchanged and the third must be given by $n'_i = n_i \pm 1$.

The matrix components of \mathbf{L} with regard to the unperturbed functions may be obtained as follows: from the theory of the Hermite polynomials in one dimension one has for the momentum operator p ,

$$p\varphi_n = -\frac{i\hbar}{a} \left[\frac{1}{2}(n+1) \right]^{\frac{1}{2}} \varphi_{n+1} - \frac{i\hbar}{a} \left[\frac{1}{2}n \right]^{\frac{1}{2}} \varphi_{n-1}. \quad (26)$$

From the definition of orbital angular momentum \mathbf{L} ,

$$L_1 = x_2 p_3 - x_3 p_2,$$

so using (19) and (26)

$$L_1 \psi(n_1 n_2 n_3) = -\frac{i\hbar a_2 a_3}{2} \sum [\pm a_3^{-2} \mp a_2^{-2}] [(n_2)(n_3)]^{\frac{1}{2}} \psi(n_1, n_2 \pm 1, n_3 \pm 1), \quad (27)$$

in which the \sum extends over the four possible signs for $n_2 \pm 1$ and $n_3 \pm 1$ taken independently and where the sign choice on $\pm a_i^{-2}$ is the same as that on $n_i \pm 1$. As before (n_2) means the larger of n_2 or $n_2 \pm 1$. The expressions for $L_2 \psi(n_1 n_2 n_3)$ and $L_3 \psi(n_1 n_2 n_3)$ may be written down by cyclic permutation of the indices 1, 2, 3. In other words the nonvanishing unperturbed matrix components of \mathbf{L} are therefore

$$\begin{aligned} (n_1, n_2 \pm 1, n_3 \pm 1 | L_1 | n_1 n_2 n_3) &= \frac{i\hbar a_2 a_3}{2} \left(\pm \frac{1}{a_3^2} - \pm \frac{1}{a_2^2} \right) [(n_2)(n_3)]^{\frac{1}{2}}, \\ (n_1 \pm 1, n_2, n_3 \pm 1 | L_2 | n_1 n_2 n_3) &= \frac{i\hbar a_3 a_1}{2} \left(\pm \frac{1}{a_1^2} - \pm \frac{1}{a_3^2} \right) [(n_3)(n_1)]^{\frac{1}{2}}, \\ (n_1 \pm 1, n_2 \pm 1, n_3 | L_3 | n_1 n_2 n_3) &= \frac{i\hbar a_1 a_2}{2} \left(\pm \frac{1}{a_1^2} - \pm \frac{1}{a_2^2} \right) [(n_1)(n_2)]^{\frac{1}{2}}. \end{aligned} \quad (28)$$

From (28) and (25) it is obvious why an ordinary anisotropic harmonic oscillator is not optically active, for the nonvanishing matrix components in (25) require that two n 's be unchanged whereas in (28) only one n is unchanged; hence there are no pairs of levels $(n_1 n_2 n_3)$ and $(n_1' n_2' n_3')$ for which both the \mathbf{r} and the \mathbf{L} matrix components have a nonvanishing value.

The optical activity is produced by the perturbing effect of the $Ax_1 x_2 x_3$ term by means of the terms proportional to λ in (24). For the sake of clarity and in view of the applications to be made, it will be sufficient to work out in detail the special case of activity due to molecules in the lowest state (000). Consideration of (23) combined with (21) shows that the perturbed wave function for (000) involves only (000) and (111) wave functions,

$$\Psi(000) = \psi(000) - \frac{\lambda}{\nu_1 + \nu_2 + \nu_3} \psi(111).$$

Hence by (25) the only states for which $[000 | \mathbf{r} | n_1 n_2 n_3]$ has a nonvanishing zero-order value are (100), (010) and (001). These are the ordinary one-quantum jumps of the anisotropic oscillator. For these transitions \mathbf{L} has a vanishing zero-order matrix component but a nonvanishing first-order component owing to the fact that by (23) and (21), $\Psi(100)$ contains $\psi(001)$. More explicitly

$$\Psi(100) = \psi(100) - \frac{\lambda 2^{\frac{1}{2}}}{\nu_1 + \nu_2 + \nu_3} \psi(211) + \frac{\lambda}{-\nu_1 + \nu_2 + \nu_3} \psi(011)$$

so using (24) and (28)

$$[100|\mathbf{L}|000] = -\frac{i\lambda\hbar(a_2^2 - a_3^2)}{2a_2a_3} \left[\frac{2\nu_1}{(\nu_2 + \nu_3)^2 - \nu_1^2} \right] i, \quad (29)$$

and by cyclic substitution the formulas for $[010|\mathbf{L}|000]$ and $[001|\mathbf{L}|000]$ can be written down. Hence the three absorption lines $(000 \rightarrow 100)$ $(000 \rightarrow 010)$ and $(000 \rightarrow 001)$ give rise to optical activity in the first order, the appropriate strengths as occurring in (10) being given by

$$[000|\mathbf{r}|100] \cdot [100|\mathbf{L}|000] = -i \frac{Ah^2}{128\pi^5\mu^2} \left(\frac{1}{\nu_2} - \frac{1}{\nu_3} \right) \frac{1}{(\nu_2 + \nu_3)^2 - \nu_1^2}; \quad (30)$$

the other two of similar type being obtainable by cyclic substitution. As the right-hand side of (30) is pure imaginary, the imaginary part needed for (10) is just equal to the right-hand side of (30) with the i omitted.

These three lines therefore give rise to optical activity of the first order in virtue of zero-order matrix components of \mathbf{r} combined with the first-order contributions to the matrix components of \mathbf{L} . Similarly there are three more lines which will give first-order optical activity in virtue of the first-order change in the matrix components of \mathbf{r} combined with the zero-order matrix components of \mathbf{L} . These two sets of lines will exhaust the possibilities for optical activity of the ground state to the first order in the asymmetry coefficient A .

There will be an interesting contrast in type of the two sets of lines. For the set given by (30) the ordinary optical absorption will be strong since $[a|\mathbf{r}|b]$ has a nonvanishing zero-order value. But for the other type, whose optical activity is of the same order of magnitude, the ordinary optical absorption will be weak. Thus the model gives a division of the critical frequencies into two types—both of comparable contribution to the rotatory power but one strong in absorption, the other weak. This corresponds to a general experimental fact as recognized by Kuhn and interpreted by him in terms of the crossed oscillator model.

The states for which $[n_1n_2n_3|\mathbf{L}|000]$ has a nonvanishing zero-order value are, by (28), (110), (101) and (011). For these we need to calculate the first-order matrix components of \mathbf{r} by a combination of (24), (23) and (25). The result is

$$[000|\mathbf{r}|011] = 2^{\frac{1}{2}}\lambda a_1 \frac{\nu_1}{(\nu_2 + \nu_3)^2 - \nu_1^2} i, \quad (31)$$

the other two being obtained by cyclic substitution. Hence for this line the contribution to the optical activity is given by

$$[000|\mathbf{r}|011] \cdot [011|\mathbf{L}|000] = +i \frac{Ah^2}{128\pi^5\mu^2} \left(\frac{1}{\nu_2} - \frac{1}{\nu_3} \right) \frac{1}{(\nu_2 + \nu_3)^2 - \nu_1^2}, \quad (32)$$

the other two being obtained by cyclic substitution. It is interesting to note that (32) is exactly equal and opposite to (30). Hence the sum of the rotatory strengths associated with the jumps $(000) \rightarrow (100)$ and $(000) \rightarrow (011)$ is zero, verifying the general sum rule for the numerators in the rotatory dispersion formula.

The general sum rule is that the sum of the numerators in (10) is zero. This may be proved very simply. One has for this sum

$$\text{Im} \left\{ \sum_b (a|\mathbf{p}|b) \cdot (b|\mathbf{m}|a) \right\} = \text{Im} \{ (a|\mathbf{p} \cdot \mathbf{m}|a) \}$$

by the matrix law of multiplication. The quantity on the right vanishes since $(a|\mathbf{p} \cdot \mathbf{m}|a)$ is a diagonal matrix element of a real observable and hence is real.

In view of the fact that $\mathbf{p} = e\mathbf{r}$ and $\mathbf{m} = (e/2\mu c)\mathbf{L}$ for a single charged particle one can write down

the complete formula for the parameter β by combining (10), (30) and (32). The result is

$$\beta_{000} = \frac{A\hbar e^2}{12(2\pi)^5\mu^3} \left\{ \left(\frac{1}{\nu_2} - \frac{1}{\nu_3} \right) \frac{1}{(\nu_2 + \nu_3)^2 - \nu_1^2} \left[-\frac{1}{\nu_1^2 - \nu^2} + \frac{1}{(\nu_2 + \nu_3)^2 - \nu^2} \right] + \left(\frac{1}{\nu_3} - \frac{1}{\nu_1} \right) \frac{1}{(\nu_3 + \nu_1)^2 - \nu_2^2} \right. \\ \left. \times \left[-\frac{1}{\nu_2^2 - \nu^2} + \frac{1}{(\nu_3 + \nu_1)^2 - \nu^2} \right] + \left(\frac{1}{\nu_1} - \frac{1}{\nu_2} \right) \frac{1}{(\nu_1 + \nu_2)^2 - \nu_3^2} \left[-\frac{1}{\nu_3^2 - \nu^2} + \frac{1}{(\nu_1 + \nu_2)^2 - \nu^2} \right] \right\}. \quad (33)$$

It will be noticed that if any two of the frequencies ν_1, ν_2, ν_3 are equal the whole expression vanishes. This is in accord with the symmetry properties, for if, say, ν_2 and ν_3 are equal this implies k_2 and k_3 are equal so the harmonic oscillator potential has the x_1 axis as an axis of symmetry and therefore any plane through this axis is a plane of symmetry for the harmonic oscillator potential. Now $x_1 x_2 x_3$ has the plane $x_2 = x_3$ as a plane of symmetry so if $\nu_2 = \nu_3$ the plane $x_2 = x_3$ is a plane of symmetry of the model so the optical activity should vanish.

By combining (33) with (7) or (8) one has an explicit formula for the rotatory power of a molecule which contains electrons moving in a field of the type postulated in (14).

3. OPTICAL ACTIVITY OF THE MODEL IN HIGHER QUANTUM STATES. CLASSICAL MECHANICS AS A LIMITING CASE

The extension of the preceding calculation to states with three arbitrary quantum numbers $(n_1 n_2 n_3)$ instead of (000) is of considerable interest not only because it applies to media with part of their molecules in excited states but also because the generalized formula taking the place of (33) leads for high quantum numbers asymptotically, in the sense of the correspondence principle, to an expression for the rotatory power of the classical model. We shall see that in going to this limit the system retains a finite rotatory power, and a simple expression in terms of the amplitudes will be given.

The procedure is of course closely analogous to the derivation previously given for the ground state. Again we start from Eqs. (10), (23), (25) and (28). When applied to our model, Eq. (23) gives:

$$\Psi(n_1 n_2 n_3) = \psi(n_1 n_2 n_3) - \lambda \sum \psi(n_1 \pm 1, n_2 \pm 1, n_3 \pm 1) \frac{[(n_1)(n_2)(n_3)]^{\frac{1}{2}}}{\pm \nu_1 \pm \nu_2 \pm \nu_3}, \quad (34)$$

where the summation is over all possible sign combinations and where equal signs are taken for the change of quantum number in any of the three axes, n_i , and the corresponding ν_i in the denominator. Consequently one obtains

$$[n_1 n_2 n_3 | \mathbf{r} | n'_1 n'_2 n'_3] \cdot [n'_1 n'_2 n'_3 | \mathbf{L} | n_1 n_2 n_3] = \\ -\lambda \sum \frac{[(n_1)(n_2)(n_3)]^{\frac{1}{2}}}{\pm \nu_1 \pm \nu_2 \pm \nu_3} \{ (n_1 n_2 n_3 | \mathbf{r} | n'_1 n'_2 n'_3) (n'_1 n'_2 n'_3 | \mathbf{L} | n_1 \pm 1, n_2 \pm 1, n_3 \pm 1) \\ + (n_1 \pm 1, n_2 \pm 1, n_3 \pm 1 | \mathbf{r} | n'_1 n'_2 n'_3) (n'_1 n'_2 n'_3 | \mathbf{L} | n_1 n_2 n_3) \} + \\ -\lambda \sum \frac{[(n'_1)(n'_2)(n'_3)]^{\frac{1}{2}}}{\pm \nu_1 \pm \nu_2 \pm \nu_3} \{ (n_1 n_2 n_3 | \mathbf{r} | n'_1 n'_2 n'_3) (n'_1 \pm 1, n'_2 \pm 1, n'_3 \pm 1 | \mathbf{L} | n_1 n_2 n_3) \\ + (n_1 n_2 n_3 | \mathbf{r} | n'_1 \pm 1, n'_2 \pm 1, n'_3 \pm 1) (n'_1 n'_2 n'_3 | \mathbf{L} | n_1 n_2 n_3) \}. \quad (35)$$

The zero-order term $(n | \mathbf{r} | n') \cdot (n' | \mathbf{L} | n)$ is absent in (35) because the selection rules of \mathbf{r} and \mathbf{L} mutually exclude each other in the unperturbed case which has three planes of symmetry. The following transitions are found to contribute to $(n | x | n') (n' | L_x | n)$:

| | | | |
|-----|--|-----|--|
| (a) | $(n_1 n_2 n_3) \rightarrow (n_1 + 1, n_2, n_3),$ | (d) | $\rightarrow (n_1, n_2 - 1, n_3 + 1),$ |
| (b) | $\rightarrow (n_1 - 1, n_2, n_3),$ | (e) | $\rightarrow (n_1, n_2 + 1, n_3 - 1),$ |
| (c) | $\rightarrow (n_1, n_2 + 1, n_3 + 1),$ | (f) | $\rightarrow (n_1, n_2 - 1, n_3 - 1).$ |

If we denote these six transitions for brevity by letters *a* to *f* in the order listed, it is easily seen that *a* and *b*, *c* and *f*, *d* and *e* have equal and opposite transition frequencies, namely $\pm\nu_1$, $\pm(\nu_2+\nu_3)$ and $\pm(\nu_2-\nu_3)$ respectively. Since transition frequencies $\nu_{nn'}$ enter into (10) for β , in the second power, each pair of transitions will jointly give rise to one dispersion term of the general type that was previously obtained in Eq. (30). Actually it is found that only the first and third term in (35) will contribute by virtue of a transition *a* or *b*, and similarly only the second and the fourth term of (35) contribute in transitions *c*, *d*, *e*, *f*. There are, in all, 32 terms to be considered for the matrix product $(n|x|n')(n'|L|n)$ and 64 more terms are obtained by cyclic substitution to give contributions toward the *y* and the *z* matrix components. A simple though lengthy calculation leads after much simplification and canceling to the final formula for β :

$$\begin{aligned} \beta_{n_1 n_2 n_3} = & \frac{A\hbar e^2}{12(2\pi)^5 \mu^3} \left\{ \left(\frac{1}{\nu_2} - \frac{1}{\nu_3} \right) \frac{(n_2 + n_3 + 1)}{(\nu_2 + \nu_3)^2 - \nu_1^2} \left[-\frac{1}{\nu_1^2 - \nu^2} + \frac{1}{(\nu_2 + \nu_3)^2 - \nu^2} \right] \right. \\ & + \left(\frac{1}{\nu_2} + \frac{1}{\nu_3} \right) \frac{(n_2 - n_3)}{(\nu_2 - \nu_3)^2 - \nu_1^2} \left[-\frac{1}{\nu_1^2 - \nu^2} + \frac{1}{(\nu_2 - \nu_3)^2 - \nu^2} \right] \\ & + \left(\frac{1}{\nu_3} - \frac{1}{\nu_1} \right) \frac{(n_3 + n_1 + 1)}{(\nu_3 + \nu_1)^2 - \nu_2^2} \left[-\frac{1}{\nu_2^2 - \nu^2} + \frac{1}{(\nu_3 + \nu_1)^2 - \nu^2} \right] \\ & + \left(\frac{1}{\nu_3} + \frac{1}{\nu_1} \right) \frac{(n_3 - n_1)}{(\nu_3 - \nu_1)^2 - \nu_2^2} \left[-\frac{1}{\nu_2^2 - \nu^2} + \frac{1}{(\nu_3 - \nu_1)^2 - \nu^2} \right] \\ & + \left(\frac{1}{\nu_1} - \frac{1}{\nu_2} \right) \frac{(n_1 + n_2 + 1)}{(\nu_1 + \nu_2)^2 - \nu_3^2} \left[-\frac{1}{\nu_3^2 - \nu^2} + \frac{1}{(\nu_1 + \nu_2)^2 - \nu^2} \right] \\ & \left. + \left(\frac{1}{\nu_1} + \frac{1}{\nu_2} \right) \frac{(n_1 - n_2)}{(\nu_1 - \nu_2)^2 - \nu_3^2} \left[-\frac{1}{\nu_3^2 - \nu^2} + \frac{1}{(\nu_1 - \nu_2)^2 - \nu^2} \right] \right\}. \quad (36) \end{aligned}$$

This clearly contains the previous result, (33), as a special case, but also exhibits some new features. First of all we have now three resonance frequencies for the rotatory dispersion, instead of the two previously obtained. Of these, ν_1 , represents a frequency which is also strongly pronounced in absorption, but there are now two weak absorption bands $(\nu_2 + \nu_3)$ and $(\nu_2 - \nu_3)$ which may exhibit strong rotatory power. Again the sum rule is obviously fulfilled as the numerator going with the strong absorption frequency is equal and opposite to the sum of the other two. Eq. (36) may also be written in a slightly modified form:

$$\begin{aligned} \beta_{n_1 n_2 n_3} = & -\frac{A\hbar e^2}{12(2\pi)^5 \mu^3} \sum_{\text{cycl.}} \left\{ \left(\frac{1}{\nu_k} - \frac{1}{\nu_l} \right) \frac{(n_k + n_l + 1)}{[(\nu_k + \nu_l)^2 - \nu^2][\nu_i^2 - \nu^2]} \right. \\ & \left. + \left(\frac{1}{\nu_k} + \frac{1}{\nu_l} \right) \frac{(n_k - n_l)}{[(\nu_k - \nu_l)^2 - \nu^2][\nu_i^2 - \nu^2]} \right\}. \quad (36a) \end{aligned}$$

Here $\sum_{\text{cycl.}}$ means sum over $(kli) = (2, 3, 1)$, $(3, 1, 2)$ and $(1, 2, 3)$.

In order to derive a limiting expression for β in terms of the amplitudes $A_1 A_2 A_3$ of the particle's motion in the three axial directions we express the quantum numbers in terms of the amplitudes by means of the energy relation valid for a harmonic oscillator:

$$\begin{aligned} n_1 \hbar \nu_1 &= (1/2) k_1 A_1^2 = 2\pi^2 \nu_1^2 A_1^2 \mu, \\ \hbar \nu_1 &= 2\pi^2 \mu A_1 \nu_1^2, \end{aligned} \quad (37)$$

and two similar equations for the other two quantum numbers. Substituting from (37) into (36) we have at once

$$\beta(A_1A_2A_3) = \frac{e^2A}{384\pi^4\mu^2} \left\{ \left(\frac{1}{\nu_2} - \frac{1}{\nu_3} \right) \frac{\nu_2A_2^2 + \nu_3A_3^2}{(\nu_2 + \nu_3)^2 - \nu_1^2} \left[-\frac{1}{\nu_1^2 - \nu^2} + \frac{1}{(\nu_2 + \nu_3)^2 - \nu^2} \right] \right. \\ \left. + \left(\frac{1}{\nu_2} + \frac{1}{\nu_3} \right) \frac{\nu_2A_2^2 - \nu_3A_3^2}{(\nu_2 - \nu_3)^2 - \nu_1^2} \left[-\frac{1}{\nu_1^2 - \nu^2} + \frac{1}{(\nu_2 - \nu_3)^2 - \nu^2} \right] \right. \\ \left. + \text{four more lines obtained from these by cyclic permutation of the indices} \right\}. \quad (38)$$

This result does not contain h or other quantum-mechanical concepts and represents in the limit, according to the correspondence principle, the response of our model if it were a system obeying classical mechanics.

4. QUALITATIVE PROPERTIES OF THE FIELD

Before discussing the application of the results of Section 2 to actual molecules it is worth while to form a mental picture of the kind of potential field represented by (14). This is best done by considering the shape of the equipotential surfaces. Suppose for definiteness that $k_1 > k_2 > k_3$ and at first that $A = 0$. Then the equipotential surfaces will be ellipsoids whose principal axes are the coordinate axes and whose axes increase in the order $x_1 < x_2 < x_3$. The sections of any such ellipsoid by a plane $x_3 = \text{constant}$ will then be ellipses all of whose principal axes are parallel to the x_1 and x_2 axes. Now suppose that the $Ax_1x_2x_3$ term is present, say with $A > 0$. Then the equation of the intersection of an equipotential with the plane $x_3 = Z$ is

$$\frac{k_1}{2}x_1^2 + \frac{k_2}{2}x_2^2 + AZx_1x_2 = (V - \frac{1}{2}k_3Z^2).$$

This is the equation of an ellipse whose axes have been twisted relative to parallelism with the x_1 and x_2 axes in the counter-clockwise sense as viewed from the positive x_3 axis, the angle of twist being θ where

$$\tan 2\theta = \frac{AZ}{\frac{1}{2}(k_1 - k_2)}. \quad (39)$$

The angle of twist therefore increases with increasing Z , in other words the equipotential surface is a kind of twisted ellipsoid something like what one might get if an ordinary ellipsoid of three unequal axes were subjected to a torsional stress twisting it around the x_3 axis in

the sense of a right-handed screw. The angle through which an axis is twisted can never exceed 45° .

Similarly the sections of the equipotentials by the planes $x_1 = X$ are also ellipses which are skewed around in the same screw sense for the angle of twist is given by (39) with the cyclic substitutions $Z \rightarrow X$, $k_1 \rightarrow k_2$, $k_2 \rightarrow k_3$ and the sense remains the same because we have assumed $k_2 > k_3$. The sections of the equipotentials by the planes $x_2 = Y$ are also a set of ellipses, but they are skewed around in the opposite sense for the form of (39) applicable to this case involves $(k_3 - k_1)$ in the denominator which is negative in the case we are discussing.

It should be clear that no matter what are the relative magnitudes of k_1 , k_2 and k_3 the situation will always be the same in that the sections of the equipotential surface by planes parallel to any of the coordinate planes will be sets of ellipses, two of which screw around in the same sense while the third has the opposite screw sense.

Comparing these qualitative properties of the field with the formula (33) for β_{000} we see that if $A > 0$ and $k_1 > k_2 > k_3$ then the ν_1 and ν_3 absorption lines contribute positive quantities to β while the ν_2 line contributes a negative quantity. There is, therefore, an absolute correlation of the screw sense in the potential field and the sign of the contribution to β . The rule is: *the contribution to the rotation of the absorption line ν_i is dextro-rotatory if the screw sense of the equipotential surfaces with regard to the x_i axis is positive*. This rule affords a basis for discussion

of the age-old problem of absolute configuration in optically active molecules.

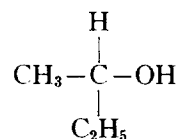
The rule is exactly what one would expect from a simple consideration of the relation of the field to formula (4). The absorption line ν_3 corresponds to the excitation of a vibratory motion that is essentially parallel to the x_3 axis. Owing to the spread of the wave function in the x_1 and x_2 directions the motion is not confined entirely to motion precisely along the x_3 axis. Owing to the screw twist in the field there is a corresponding screw twist in the wave functions so the electron tends to screw around in a somewhat helical way, following the places where the potential energy is least. Suppose now the motion is in phase with the electric vector, then the velocity will be in phase with \vec{E} and so owing to the particle's following a somewhat helical path there will be a circular current around the x_3 axis, in phase with which will produce the effective induced magnetic moment \mathbf{m}_1 , directed along the x_3 axis and so vectorially proportional to the \vec{E} which produced it.

The induction of an electric moment vectorially proportional to \vec{H} but of opposite sign as in (4) may also be easily visualized. Suppose that \vec{H} is parallel to the x_3 axis. Then it corresponds to a rate of change of flux through the x_1x_2 plane which therefore is accompanied by induced electromotive forces tending to make the electron move around in the x_1x_2 plane in the clockwise, or negative sense, owing to Lenz's law for induced currents. Owing to the helical constraints, when the electron does this it is caused to move toward the $-x_3$ direction and thus to produce an electric moment in the direction $-\vec{H}$ as given by (4). (The foregoing statements are made for a positive electron—for a negative electron the results are the same because change in sign not only reverses the direction of the forced motion but also reverses the sense of the moments resulting from the forced motion, corresponding to the occurrence of e^2 in (33).)

5. ADAPTATION OF THE MODEL TO ACTUAL MOLECULES

The simplest kind of optically active molecule conceivable is that in which four different single atoms are attached to a central carbon atom.

Such compounds have never been prepared, at least not in active form. The next simplest type is that in which the four attachments to a central carbon atom may be organic radicals, as in the case of secondary butyl alcohol,



Such a molecule will be characterized by a very complicated electronic absorption spectrum, lying entirely in the ultraviolet in the case of colorless liquids. The absorption spectrum is complicated not only because of the large number of electronic transitions possible but also because of the complexity of structure arising from the great variety of vibrational and rotational jumps which can be associated with a given electronic jump. In the face of such a complex situation some simplifying assumptions must be made.

Study of polyatomic absorption in the ultraviolet has shown that it is possible in most cases to associate a given set of bands with an electron transition occurring in a fairly definite part of the molecule. The group of atoms or radical in which the transition occurs is then said to be the chromophoric group or the chromophore for that system of bands.

The optical activity associated with a given electronic jump in the molecule arises essentially from the cooperation of two factors: (1) the electronic jump occurs in the molecule in a fairly well-localized place in some definite group in the molecule, (2) the electron which makes a transition is moving in a force field principally due to the immediate atoms to which it belongs, but secondarily due to the fields set up by the effective charge distributions of the other atoms in the molecules. It is the contribution of the neighboring atoms to the force field in which the chromophoric electron moves which is responsible for the optical activity.

This action of neighboring groups on the chromophoric group has generally been called *vicinal action* in a general way. In what follows we give a more precise picture of the nature of vicinal action.

Of course any electron in the molecule is the

chromophoric electron for those transitions in which its state changes. But the important electron transitions will be those lying in the near ultraviolet which will mean that those electrons contained in groups that absorb in the near ultraviolet, or in the visible when present, will dominate the situation. This statement is much nearer the truth here than in the case of ordinary refraction for here the contributions to β of different bands in the deep ultraviolet are of different sign and so tend to cancel whereas in ordinary refraction they are all of the same sign so the cumulative effect of many of them may be considerable.

Suppose, for example, that the chromophoric electron in the near ultraviolet is a bonding electron between C and the OH in secondary butyl alcohol. Then in the absence of the other groups, or if the three other groups were all alike, the effective field in which that electron would move has the C—O direction as an axis of symmetry and would be more extended along the bond direction than transverse to it. The equipotential surfaces would be shaped like rather prolate ellipsoids of revolution. The actual space dependence of the potential energy would, of course, go asymptotically to a constant value like the Coulomb law for large distances.

Now the behavior of the field at large distances does not matter much if we confine ourselves to the two lowest states for in these the wave functions are essentially confined to a small region near the potential minimum. Therefore for discussion of the two lowest states it will be fairly accurate to represent the effective field due to the C and O atoms by a harmonic oscillator potential, having the C—O line as an axis of revolution. Choosing the C—O direction as the Z axis the potential will then be approximately

$$V_0 = \frac{1}{2}k_1(x_1^2 + x_2^2) + \frac{1}{2}k_3z^2, \quad (40)$$

where the origin of coordinates will be somewhere between the carbon and oxygen nuclei at a place that can only be made definite on the basis of more exact information about the actual molecular orbitals in this bond.

Next we have to consider the way in which (40) is affected by the vicinal action of the neighboring groups. As a preliminary, consider

the potential

$$U = [(X_1 - x_1)^2 + (X_2 - x_2)^2 + (X_3 - x_3)^2]^{-\frac{1}{2}} \quad (41)$$

at the position (x_1, x_2, x_3) due to unit charge located at $X_1X_2X_3$. If $x_1x_2x_3$ are all small compared to $X_1X_2X_3$ as will be the case if $x_1x_2x_3$ are the coordinates of the chromophoric electron and $X_1X_2X_3$ are those of the distant vicinal group, then the potential can be developed as

$$U = \frac{1}{R} - x_i \frac{\partial}{\partial X_i} \left(\frac{1}{R} \right) + \frac{1}{2} x_i x_j \frac{\partial^2}{\partial X_i \partial X_j} \left(\frac{1}{R} \right) - \frac{1}{6} x_i x_j x_k \frac{\partial^3}{\partial X_i \partial X_j \partial X_k} \left(\frac{1}{R} \right), \quad (42)$$

in which summations over repeated indices are implied and $R = [X_1^2 + X_2^2 + X_3^2]^{\frac{1}{2}}$. The constant term is of no interest, since the zero of energy has to be arbitrarily fixed anyway. The linear terms represent a certain general average field acting on the electron which will produce a slight displacement of the equilibrium position.

The important terms in (41) for application of the results of Section 2 are the quadratic and the cubic. The total action of the charge distribution in the vicinal groups will be obtained by summing (37) over the charges in the vicinal groups. The quadratic and cubic terms coming from the summed expression may be written

$$\frac{1}{2}a_{ij}x_i x_j + \frac{1}{6}b_{ijk}x_i x_j x_k. \quad (43)$$

These have to be added to (40) to get our approximation to the full field in which the chromophoric electron moves. The terms in (43) are supposed to be small compared with those in (41).

Considering first the effect of adding the quadratic part of (43) to (40) we see that the resulting harmonic potential will in general be one in which the principal axes are tilted with respect to the original coordinate axes and in which the axis of symmetry has, in general, been removed. The tilting of one principal axis (x_3) away from the bond axis will in general be negligibly small if the original field V_0 is sufficiently anisotropic, i.e., if the cross terms a_{13} and a_{23} (which cause the tilting) are small compared with $|k_1 - k_3|$ in (40). Neglecting this slight tilting amounts to neglecting completely the a_{13} , and a_{23} terms. The terms involving a_{11} , a_{12} and a_{22} however are important for it is

these which determine the previously indeterminate principal axes by removing the symmetry of (40) about the x_3 axis.

After adding the important quadratic part of (40) the dependence of the potential on x_1x_2 becomes

$$\frac{1}{2}(k_1 + a_{11})x_1^2 + a_{12}x_1x_2 + \frac{1}{2}(k_1 + a_{22})x_2^2.$$

A rotation of the axes through an angle γ is described by

$$\begin{aligned} x_1 &= x_1' \cos \gamma - x_2' \sin \gamma \\ x_2 &= x_1' \sin \gamma + x_2' \cos \gamma \end{aligned} \quad (44)$$

and the potential energy in terms of the x_1' and x_2' is

$$\begin{aligned} &\frac{1}{2}(k_1 + a_{11} \cos^2 \gamma + 2a_{12} \sin \gamma \cos \gamma \\ &\quad + a_{22} \sin^2 \gamma)x_1'^2, \\ &+ \frac{1}{2}(k_1 + a_{11} \sin^2 \gamma - 2a_{12} \sin \gamma \cos \gamma \\ &\quad + a_{22} \cos^2 \gamma)x_2'^2, \end{aligned} \quad (45)$$

provided that γ has been chosen to make the coefficient of $x_1'x_2'$ vanish. The value of γ which does this is given by

$$\tan 2\gamma = \frac{2a_{12}}{a_{11} - a_{22}}. \quad (46)$$

Hence the important effect of the quadratic terms due to the vicinal groups is the removal of the axis of symmetry of the effective field of the chromophoric electron.

If now one transforms the cubic terms of (43) to the coordinate system (x_1', x_2', x_3) defined by (44) and (46) then the particular term which involves the product of the coordinates $x_1'x_2'x_3$ is the important one and is the term to be identified with the $Ax_1x_2x_3$ term of Section 2.

At first sight it might seem that all of the cubic terms in the potential would contribute to the optical activity and it is true that they do in higher approximations. But in the first approximation of the perturbation theory as used in Section 2 the contribution due to each cubic term would be linear in the coefficient of that term so the first approximation cannot take account of the joint action of several such terms. On the other hand, of the various kinds of cubic terms $Ax_1x_2x_3$ is the only one which removes all the planes of symmetry possessed by the

harmonic oscillator potential, and therefore it is the only one which produces optical activity in the first approximation. For instance the potential x_1^3 leaves the x_1x_2 and x_1x_3 planes as planes of symmetry. A combined action of $(x_1^3 + x_2^3 + x_3^3)$ in the cubic potential would remove all the symmetry planes in the field but its contribution to the rotatory power would not appear in the first approximation as it depends on the joint presence of three cubic terms.

To summarize: we suppose the effective field in which the chromophoric electron would have moved if the vicinal action were neglected to be given by (40). As this is simply a formal representation to produce wave functions of approximately the correct spatial extent, one has to pick k_1 and k_3 in this to correspond to the frequencies of the lowest electronic jumps for the electron, the k 's being related to the ν 's by (17).

In general the bonding electron in this approximation will be a Σ electron and the first excited state corresponding to motion along the figure axis will also be a Σ state for the electron so k_3 is the oscillator force constant which gives the frequency through (17) of the lowest $\Sigma \rightarrow \Sigma$ electronic transition. Similarly the excited states corresponding to excitation of transverse motion will be Π states so k_1 will be chosen to make ν_1 the frequency of the lowest $\Sigma \rightarrow \Pi$ electron transition in that chromophore.

The next step consists in analyzing the probable charge distribution of the vicinal groups. If one had exact knowledge of the molecular orbitals this would be given at once by the density of the orbitals of the rest of the molecule. In the absence of such knowledge one has to try to piece together the main essentials by use of the results of dipole moment studies. These assign measured dipole moments to various bonds in the molecule which may be represented by net charges on the two atoms at opposite ends of a bond chosen so the product of net charge by bond distances is equal to bond dipole moment. This will be discussed later in connection with a specific example.

Finally with a known charge distribution, say charges e_s located at points X_{1s}, X_{2s}, X_{3s} , one has to calculate the quadratic terms in the potential energy due to the charges of the vicinal group as in (41) and (42). This will determine the way

in which the axis of symmetry of the chromophoric field is removed through (44) and (46). Finally with axes chosen along the principal axes of the quadratic part of the chromophoric field of all the cubic potential terms one has to calculate only $Ax_1x_2x_3$. In this way we see that k_1 and k_3 are principally determined by the local field to which the chromophore electron belongs, while $k_1 - k_2$ and A are determined by the fields of the vicinal groups.

The discussion may be made more precise by writing the explicit formulas for the important quantities. Calculating the derivations in (42) one finds for the potential energy of an electron of charge e in the vicinal field of charges $e_1 \dots e_s \dots$

$$a_{11} = e \sum_s e_s (3X_{1s}^2 - R_s^2) \frac{1}{R_s^3}, \quad (48)$$

$$a_{12} = e \sum_s e_s \frac{3X_{1s}X_{2s}}{R_s^5}, \quad (49)$$

and a corresponding formula for a_{22} , obtained by substituting 2 for 1 in (48). Then the transformation to principal axes is given by (45) and (46). Finally the coefficient of the cubic term in the potential energy $Ax_1'x_2'x_3$ is given by

$$A = + (5/2) e \sum_s e_s \frac{X_{1s}'X_{2s}'X_{3s}'}{R_s^7}, \quad (50)$$

in which X_{1s}' and X_{2s}' are coordinates of vicinal charges referred to the principal axis coordinate system defined by (44) and (46).

6. APPLICATION TO METHYL PHENYL CARBINOL NITRITE

We next proceed to test our thesis that coulombic force action from vicinal groups is responsible for the term $Ax_1x_2x_3$ in the potential function (14). To do this we compute the rotatory power of the nitrite band and the phenyl band in methyl phenyl carbinol nitrite.¹⁰ In molecules containing the nitrite group $-O-N=O$ the existence of an absorption band well removed from the neighborhood of other bands, and in the experimentally accessible region

around 3650Å, provides a convenient means for such a study because here one can identify with reasonable assurance what part of the rotatory power measured at any given wave-length is contributed by that particular band. The nitrite contribution appears surprisingly rich in structural detail, superimposed on the much stronger and slowly varying contribution from the phenyl band. The assignment to phenyl follows from a comparison with methyl cyclohexyl carbinol nitrite, and with methyl *n*-hexyl carbinol nitrite. In both of these cases where the phenyl has been replaced by other substituents we find that the contribution allegedly coming from the phenyl band is suppressed as one would expect from this assignment.

In what follows we adopt with minor modifications the general outline given in Section 5. In one essential point, however, we allow our conception of the nitrite band to differ from an assumption made in that section. We regard the chromophoric electron which is instrumental in the nitrite absorption at 3650Å as being isotropically bound to its equilibrium position; isotropically, that is, except for the perturbation effect which the electric dipole field from the other three groups exert upon it. In view of the presence of big charges in the nitrite group itself this assumption can hardly be more than an approximation. At the same time it is dictated by the very uncertain way in which these charges are distributed with respect to the rest of the molecule. Since the distribution varies with the free rotation of the ONO group around the single C-O bond the actual orientation of the "unperturbed" polarization ellipsoid is extremely elusive. If, then, we simply consider the unperturbed problem as threefold degenerate it is quite clear that in the perturbed case the orientation of all three principal axes will be sensitive to the perturbing field, and not merely two as was assumed in the last section. The remark should be added that, since the rotatory power of our model is proportional to the three differences between ν_1 , ν_2 and ν_3 , one must expect the resulting β to be small of higher order in the case where the frequencies are different from each other merely as a consequence of the perturbing field than if they had been different in the unperturbed oscillator.

¹⁰ Kuhn and Biller, Zeits. f. physik. Chemie **B29**, 1 (1935).

In Section 5 it was explained that the numerical problem is essentially a determination of the asymmetry coefficient A of (50), when the potential has been referred to three axes $x_1'x_2'x_3'$ in which the quadratic terms of V reduce to a sum of squares. An isotropic oscillator which will absorb at 3650Å, the absorption wave-length of the nitrite band, has three equal force constants $k_1=k_2=k_3=24,000$, in absolute units. Thus, to second-order terms the potential can be represented by

$$U_2 = \sum_{ik} a_{ik} x_i x_k = 12,000(x_1^2 + x_2^2 + x_3^2) + \sum x_i x_k \sum_s \frac{ee_s}{2R_s^5} (3X_{is}X_{ks} - \delta_{ik}R_s^2),$$

where δ_{ik} is 1 or 0 depending on whether i and k are equal or not. This follows from (38) and (49). The second term of the above equation can be obtained from a list of coordinates of the individual vicinal charges e_s if these charges are referred to a right-handed coordinate system with the supposed chromophoric electron at the origin. We have tentatively chosen this position to coincide with the oxygen nearest to the asymmetric carbon atom. A list of coordinates and charges is given in Table I. The vicinal charges have been located at the position of the atoms so as to be compatible with the known bond moments and interatomic distances. The dipole moments used were: +0.35 for the CH bonds, -0.85 for the C-O, +0.30 for O-N, -2.15 for N=O. The last two moments were determined so as to give a resultant dipole moment of -1.90 for the nitrite group. All moments are

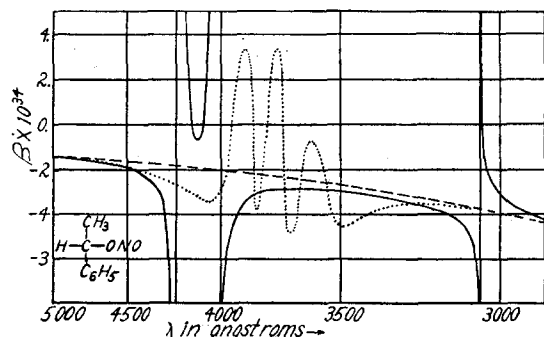


FIG. 1. Dotted curve, experimental $[M]$ values (Fig. 1a of Kuhn and Biller, Zeits. f. physik. Chemie B29, 1 (1935)) translated into B values. Broken line, estimated contribution of bands in far ultraviolet. Full lines, calculated.

TABLE I.

| ATOM: | H _a | H ₁ | H ₂ | H ₃ | C ₁ | C ₂ | O ₁ |
|---------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|
| CHARGE: | 0.28 | 0.28 | 0.28 | 0.28 | -0.28 | -0.84 | 0.00 |
| X_1 | 0.93 | -0.93 | 0.93 | 0.00 | 0.00 | 0.00 | 0.00 |
| X_2 | -.53 | 1.67 | 1.67 | 2.16 | 0.00 | 0.00 | 0.00 |
| X_3 | -1.80 | -2.54 | -2.54 | -1.03 | -1.43 | -1.92 | 0.00 |

given in Debye units. Zero bond moment has been assumed for the phenyl group.

Principal axes of U_2 as is well known are most conveniently determined by solving the homogeneous set of three linear equations

$$\begin{aligned}(a_{11}-k)u + a_{12}v + a_{13}w &= 0, \\ a_{21}u + (a_{22}-k)v + a_{23}w &= 0, \\ a_{31}u + a_{32}v + (a_{33}-k)w &= 0,\end{aligned}$$

where k must be determined so that this set has a solution different from zero. In other words k must be a solution of the secular equation $|a_{ik} - \delta_{ik}k| = 0$. For each of the three roots k_1', k_2', k_3' there exists one solution of the linear set which can be so normalized as to represent the direction cosines $\alpha_{i1}, \alpha_{i2}, \alpha_{i3}$ ($i=1, 2, 3$), of the three principal axes. These α_{ik} represent the matrix of the linear orthogonal transformation which provides us with the coordinates X_1', X_2', X_3' of the vicinal charges in the new coordinate system. Using (50) one thus determines the numerical value of A for the nitrite absorption band in methyl phenyl carbinol nitrite to be

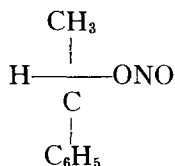
$$A = 1.46 \cdot 10^{10}.$$

The new wave-lengths into which the threefold degenerate band at 3650 is split are the following: $\lambda 4215$, $\lambda 4026$ and $\lambda 3054$. With the numerical values of A and ν_1, ν_2, ν_3 given one is in a position to apply (33) to calculate β as a function of the frequency of the incident light, and to compare it with the experimental dispersion curve as reported by Kuhn.¹¹ Fig. 1 gives the experimental values together with a theoretical curve which was obtained by adding the calculated contribution from the nitrite band to the part presumably coming from the phenyl band which can be fairly well estimated from the empirical curve by smooth interpolation (dotted curve). The

¹¹ W. Kuhn and H. Biller, Zeits. f. physik. Chemie B29, p. 1 (1935). See especially Fig. 1.

agreement between theory and experiment is satisfactory particularly in the long wave range of the diagram. As a matter of fact one should keep in mind that our oscillator model was primarily designed to represent the low energy quantum states approximately. But actual transitions which involve higher energies than $h\nu$ of the harmonic oscillator are probably not well represented by matrices derived from oscillator eigenfunctions, and the calculated energy differences are larger than the transition energies in the actual physical system.

An interesting consequence of the computation just given is that it implies an *absolute configuration* for the compound discussed. The absolute configuration for the methyl phenyl carbinol nitrite which we used in the above computation of A is



Our computation shows that this should be identified with the laevorotatory isomer. When chemists relate this compound to other *d*- or *l*-compounds their absolute configuration will automatically follow.

If one tries to compute the phenyl contribution using the assumption that the phenyl chromophor is bound isotropically to its equilibrium position, with force constants giving the absorption band of phenyl at 2600Å, one obtains a value $A = 0.83 \cdot 10^{10}$, that is considerably smaller than was obtained for the contribution of the nitrite band. This calculation takes into account the perturbing effect of all the other three charges, including the nitrite group as the latter no doubt is the controlling factor in the production of an asymmetric field at the center of the phenyl group. The configuration most likely to occur on statistical grounds, and at the same time the one most effective in producing the desired effect is that configuration in which the nitrite group lies in the plane through the two bonds $\text{C}_1\text{—O}$ and $\text{C}_1\text{—phenyl}$ with the double-bonded oxygen in a position closest to the center of the phenyl group. In view of the large dipole moments of the nitrite group and the high polarizability of the phenyl group this configura-

tion (or a very similar one) must be quite stable compared with others. The result of the calculation is instructive in the following detail. It is found that only about two percent of the total value calculated for A is caused by the highly charged oxygen nearest to the phenyl; the reason being that its charge determines the principal axes of the perturbed polarization ellipsoid to such an extent that, lying almost exactly in one of the new coordinate planes it contributes practically nothing to the sum $\sum e_s R_s^{-7} X_{1s}' X_{2s}' X_{3s}'$. On the other hand, our assumption that the phenyl chromophor is isotropically bound is far more objectionable according to all that is known about the electronic structure of the benzene ring, than was the analogous assumption in the case of the nitrite chromophor. As the phenyl electron is actually much more stiffly bound in the direction at right angles to the ring than in the other two directions, it will offer a certain amount of resistance to tilting of its principal axes, with the result that the oxygen will lie well away from all three coordinate planes and thus will contribute generously to the asymmetry factor A . In this connection it is interesting to see in a simple way how much a given charge e_s at a given distance R_s can at best contribute to A . Since the optimal position for e_s is to make equal angles with all three principal axes of U_2 , it is easily seen from (50) that with

$$\begin{aligned} X_1' = X_2' = X_3' &= R/(3)^{\frac{1}{2}}, \\ A_{\max} &= (5/2) \frac{ee_s}{R^4(27)^{\frac{1}{2}}} = \frac{229.5e_s}{R^4} 10^{10}, \\ e_s &\text{ in } 10^{-10} \text{ e.s.u., } R \text{ in Å.} \end{aligned}$$

Since the double-bonded nitrite oxygen represents a charge of $-1.76 \cdot 10^{-10}$ e.s.u. at a distance $R = 2.05\text{Å}$, we find that its contribution to A might under favorable circumstances reach a value as big as 23×10^{10} . Rapidly diminishing optimal contributions are obtained for the other charges as their distance from the phenyl grows bigger ($A_{\max} = 4.9 \times 10^{10}$ for N, and $= 1.13 \cdot 10^{10}$ for O_1). On the whole one sees from this over-all estimate that a potential reservoir of rotatory power is available in our model of this compound which is easily sufficient to account for the observed big rotations associated with the phenyl group.

7. QUANTUM MECHANICS OF CIRCULAR DICHROISM

Closely associated with optical activity is the phenomenon of circular dichroism which is observed experimentally as the Cotton effect.¹² The quantum-mechanical formulation of this effect is a fairly obvious extension of the ordinary theory of absorption transition probabilities but, as it appears not to have been worked out explicitly before, it is perhaps useful to work it out here.

The effect in question is that the absorption coefficients for right and left circularly polarized waves are different for the absorption bands which contribute to the optical activity. It may be worked out either by the original theory¹³ in which the fields of the light wave are regarded as causing transitions, or by the quantized field method due to Dirac.¹⁴ We shall use the former method as this involves somewhat simpler equations. The end result is the same by both methods, of course.

Suppose then the light wave is represented by a vector potential

$$\mathbf{A} = \frac{1}{2} [\mathbf{A} \exp [iE(t - \mathbf{k} \cdot \mathbf{r}/c)/\hbar] + \bar{\mathbf{A}} \exp [-iE(t - \mathbf{k} \cdot \mathbf{r}/c)/\hbar]], \quad (51)$$

in which $E = h\nu$ and ν is the frequency of the light. The interaction energy of the light wave and the charges in the molecule is represented by

$$H = - (e/mc) \sum_i \mathbf{A}_i \cdot \mathbf{p}_i - (e/mc) \sum_i \mathbf{S}_i \cdot (\text{curl } \mathbf{A})_i, \quad (52)$$

the sum being over the various electrons in the molecule. The second term represents the direct interaction of the spin magnetic moment with the magnetic vector of the light wave.

Let the molecule be initially in quantum state a and the light wave begin to act at $t=0$. Then for $t>0$ we can write

$$\Psi = \psi(a) \exp [-iW_a t/\hbar] + \psi_1(a) \quad (53)$$

and the dynamical equation of quantum mechan-

ics for $\psi_1(a)$ is

$$\left(H_0 - i\hbar \frac{\partial}{\partial t} \right) \psi_1(a) = -H\psi(a) \exp (-iW_a t/\hbar), \quad (54)$$

where H_0 is the Hamiltonian of the unperturbed molecule. This has to be solved with the initial condition, $\psi_1(a)=0$ for $t=0$. The solution is found in the usual way. Expand the right side of (54) in a series of unperturbed wave functions.

$$\begin{aligned} -H\psi(a) \exp (-iW_a t/\hbar) &= (1/2) \sum_b \psi(b) \\ &\times \exp (-iW_a t/\hbar) [(b|H+|a) \exp i(W_{ba}+E)t/\hbar \\ &\quad + (b|H-|a) \exp i(W_{ba}-E)t/\hbar] \end{aligned} \quad (55)$$

and assume for $\psi_1(a)$ a similar expansion. The coefficients are then determined to satisfy (54) and the initial condition. The result is

$$\begin{aligned} \psi_1(a) &= (1/2) \sum_b \psi(b) \exp (-iW_a t/\hbar) \\ &\times \left[\frac{(b|H+|a)(\exp [i(W_{ba}+E)t/\hbar] - 1)}{W_{ba}+E} \right. \\ &\quad \left. + \frac{(b|H-|a)(\exp [i(W_{ba}-E)t/\hbar] - 1)}{(W_{ba}-E)} \right]. \end{aligned} \quad (56)$$

Here $W_{ba} = W_b - W_a$ and the coefficients in (55) are given explicitly by

$$\begin{aligned} (b|H \pm |a) &= \int \bar{\psi}(b) (\sum_i (e/mc) \mathbf{p}_i \\ &\quad \times \exp (\pm i\mathbf{k} \cdot \mathbf{r}_i E/\hbar c) \psi(a) \cdot \mathbf{A} \\ &\quad \mp \frac{iE}{\hbar c} \int \bar{\psi}(b) (\sum_i (e/mc) \mathbf{S}_i) \psi(a) \cdot (\mathbf{k} \times \mathbf{A}), \end{aligned} \quad (57)$$

in which $\bar{\mathbf{A}}$ is to be written for \mathbf{A} when the lower sign is used, the retardation of the wave has been neglected in the smaller spin term of the third line, and \int means the usual integration over the entire configuration space involved in calculating matrix components.

In (56) if $W_{ba} > 0$ as is the case in absorption only the term in $(b|H-|a)$ is important owing to the resonance denominator. Assuming E almost equal to W_{ba} so $W_{ba}-E = \Delta$, a small quantity one may write

¹² Cotton, *Ann. chim. phys.* **8**, 347 (1896).

¹³ Schrödinger, *Ann. d. Physik* **81**, 109 (1926); Slater, *Proc. Nat. Acad.* **13**, 7 (1927); Pauling and Wilson, *Quantum Mechanics*, p. 302.

¹⁴ Dirac, *Proc. Roy. Soc.* **A112**, 661 (1926); **A114**, 243 (1927); or *Quantum Mechanics*, second edition, Chap. XI.

$$\psi_1(a) = (1/2)\psi(b) \exp[-iW_b t/\hbar] \\ \times \frac{(b|H-|a) \sin \Delta t/2\hbar}{\Delta} \cdot 2i \exp(i\Delta t/2\hbar).$$

The probability that the molecule is in state b at time t is given by the absolute square of the coefficient of $\psi(b)$ in $\psi_1(a)$. The transition probability therefore is

$$P(a \rightarrow b) = |(b|H-|a)|^2 \frac{\sin^2 \Delta t/2\hbar}{(\Delta t/2\hbar)^2} \cdot \left(\frac{t}{2\hbar}\right)^2. \quad (58)$$

This is exactly the same as in the usual theory where the retardation of the light wave is neglected. Hence there is no need to repeat the standard treatment of (58) here. The next step is to consider $(b|H-|a)$ more closely. By expanding the exponential function in (57) and saving only the first two terms this can be written

$$(b|H-|a) = (i/\hbar c)W_{ba}(b|\mathbf{p}|a) \cdot \bar{\mathbf{A}} - \frac{EW_{ba}}{2\hbar^2 c^2} \mathbf{k} \\ \cdot (b|\mathbf{N}|a) \cdot \bar{\mathbf{A}} + (iE/\hbar c)(b|\mathbf{m}|a) \cdot (\mathbf{k} \times \bar{\mathbf{A}}), \quad (59)$$

in which \mathbf{p} and \mathbf{m} are electric and magnetic dipole moments as in section 1 and \mathbf{N} is the electric quadrupole moment. The quadrupole moment term may be neglected for present purposes as it contributes nothing to circular dichroism. Neglecting the quadrupole moment term we see from (59) that the reduction of (58) will proceed exactly as in the usual theory except that $(b|\mathbf{p}|a) \cdot \bar{\mathbf{A}}$ will be replaced by

$$(b|\mathbf{p}|a) \cdot \bar{\mathbf{A}} + (E/W_{ba})(b|\mathbf{m}|a) \cdot (\mathbf{k} \times \bar{\mathbf{A}}). \quad (60)$$

As the square of the magnitude of $(b|H-|a)$ appears in (58) this means that in place of $|(b|\mathbf{p}|a) \cdot \bar{\mathbf{A}}|^2$ in the usual discussion we have here

$$|(b|\mathbf{p}|a) \cdot \bar{\mathbf{A}}|^2 + 2(E/W_{ba})R \\ \times \{\mathbf{A} \cdot (a|\mathbf{p}|b)(b|\mathbf{m}|a) \cdot (\mathbf{k} \times \bar{\mathbf{A}})\}. \quad (61)$$

We have now to consider the average of this over all orientations of the molecules. For brevity write $\mathbf{P} = (a|\mathbf{p}|b)$ and $\mathbf{M} = (b|\mathbf{m}|a)$ in the following calculations. The first term is

$$|\mathbf{P} \cdot \mathbf{A}|^2 = |(\mathbf{P}_1 + i\mathbf{P}_2) \cdot (\mathbf{A}_1 + i\mathbf{A}_2)|^2 \\ = (\mathbf{P}_1 \cdot \mathbf{A}_1)^2 + (\mathbf{P}_1 \cdot \mathbf{A}_2)^2 + (\mathbf{P}_2 \cdot \mathbf{A}_1)^2 \\ + (\mathbf{P}_2 \cdot \mathbf{A}_2)^2 + (\mathbf{P}_1 \cdot \mathbf{A}_1 \mathbf{P}_2 \cdot \mathbf{A}_2 + \mathbf{P}_2 \cdot \mathbf{A}_1 \mathbf{P}_1 \cdot \mathbf{A}_2). \quad (62)$$

The average of $(\mathbf{P}_1 \cdot \mathbf{A}_1)^2$ over all orientations of \mathbf{P}_1 is $(1/3)P_1^2 A_1^2$ and similarly for the other three terms of this form. For the last two terms in (62) we use the identity

$$\mathbf{P}_1 \cdot \mathbf{A}_1 \mathbf{P}_2 \cdot \mathbf{A}_2 + \mathbf{P}_2 \cdot \mathbf{A}_1 \mathbf{P}_1 \cdot \mathbf{A}_2 = (\mathbf{P}_1 \times \mathbf{P}_2) \cdot (\mathbf{A}_1 \times \mathbf{A}_2).$$

Averaging over all directions for \mathbf{P}_1 and \mathbf{P}_2 with a fixed angle between them amounts to averaging over all directions of $(\mathbf{P}_1 \times \mathbf{P}_2)$ so the term on the right vanishes. Hence on averaging the last two terms of (62) cancel so the first term of (61) can be written

$$(1/3)|(b|\mathbf{p}|a)|^2 |\mathbf{A}|^2.$$

The second term of (61) can be averaged as follows: the dyad \mathbf{PM} multiplied into $(\mathbf{k} \times \bar{\mathbf{A}})$ gives a vector along \mathbf{P} which when averaged over all values of \mathbf{P} making the fixed angle with \mathbf{M} gives a vector along \mathbf{M} of amount $\mathbf{P} \cdot \mathbf{M}_0 \mathbf{M} \cdot (\mathbf{k} \times \bar{\mathbf{A}})$ where \mathbf{M}_0 is a unit vector in the direction of \mathbf{M} . When this is averaged over all values of \mathbf{M} which make a fixed angle with $(\mathbf{k} \times \bar{\mathbf{A}})$ the result is a vector along $(\mathbf{k} \times \bar{\mathbf{A}})$ of magnitude $\mathbf{P} \cdot \mathbf{M} \cos^2 \theta$ where θ is the angle between \mathbf{M} and $(\mathbf{k} \times \bar{\mathbf{A}})$. Averaging over all values of θ one has $\text{Avg} [\cos^2 \theta] = \frac{1}{3}$ so the average of $\mathbf{PM} \cdot (\mathbf{k} \times \bar{\mathbf{A}})$ is a vector of magnitude $\frac{1}{3} \mathbf{P} \cdot \mathbf{M} \mathbf{k} \times \bar{\mathbf{A}}$ hence the average obtained is

$$\text{Avg} \{\mathbf{A} \cdot \mathbf{PM} \cdot (\mathbf{k} \times \bar{\mathbf{A}})\} = (1/3) \mathbf{P} \cdot \mathbf{MA} \cdot (\mathbf{k} \times \bar{\mathbf{A}}).$$

Now writing $\mathbf{A} = \mathbf{A}_1 + i\mathbf{A}_2$ one has

$$\mathbf{A} \cdot (\mathbf{k} \times \bar{\mathbf{A}}) = i[A_2 \cdot (\mathbf{k} \times \mathbf{A}_1) - A_1 \cdot (\mathbf{k} \times \mathbf{A}_2)],$$

so this factor is pure imaginary and therefore on taking the real part as needed for the second term of (61) only the imaginary part of $\mathbf{P} \cdot \mathbf{M}$ will come in. In particular if the wave traveling in the \mathbf{k} direction is circularly polarized then

$$\mathbf{A} = (1/\sqrt{2})A(i \pm j), \quad (63)$$

where A is a real amplitude and where the upper sign represents right, the lower left circularly polarized light. For this one has

$$\mathbf{A} = (\mathbf{k} \times \bar{\mathbf{A}}) = \pm iA^2.$$

Hence finally the averaged form of (61) can be written

$$(1/3)A^2[(b|\mathbf{p}|a)|^2 \mp 2(E/W_{ba})\text{Im}\{(a|\mathbf{p}|b) \cdot (b|\mathbf{m}|a)\}], \quad (64)$$

where the upper sign applies for right, the lower for left circularly polarized light.

Hence the mean absorption transition probability ϵ will be the same as when retardation is neglected. But the difference between the two kinds will be in the following ratio to the mean

$$\frac{\epsilon_l - \epsilon_r}{\epsilon} = 4 \cdot \frac{\nu}{\nu_{ba}} \cdot \frac{\text{Im}\{(a|\mathbf{p}|b) \cdot (b|\mathbf{m}|a)\}}{|(b|\mathbf{p}|a)|^2}, \quad (65)$$

in which ϵ_l and ϵ_r are written for the absorption transition probability for right and left circularly polarized light respectively.

These calculations provide the quantum-mechanical proof of Natanson's rule¹⁵ previously obtained by classical methods. The rule is: if an absorption band absorbs left-circularly polarized light more strongly than right, then it contributes dextro-rotation to the medium for frequencies lower than that of the absorption band.

The results follow by comparing (65) with a combination of (7) and (10) resulting from elimination of β .

8. ROTATORY STRENGTH AND ANISOTROPY FACTOR

In numerical discussions of the rotatory dispersion formula it is convenient to have a handy measure of the contribution of a given band to the rotatory power. For the absorption line $a \rightarrow b$ this is measured by

$$R(b, a) = \text{Im}\{(a|\mathbf{p}|b) \cdot (b|\mathbf{m}|a)\} \quad (66)$$

where we shall call $R(b, a)$ the rotational strength of the line $a \rightarrow b$. It has the same dimensions as the ordinary line strength,¹⁶ $(a|\mathbf{p}|b)^2$. It will be convenient to measure $R(b, a)$ in atomic units, that is, to measure \mathbf{p} in units of ea where a is the radius of the first Bohr orbit, and \mathbf{m} in Bohr magnetons. Both of these units are rather large for the quantities to be measured so we shall expect $R \ll 1$ in general.

Conventionally φ is given in degrees/decimeter and what is conventionally called the

molecular rotatory power M is

$$[M] = (\varphi/\rho)M/100, \quad (67)$$

where φ is in degrees per decimeter, ρ is in gram/cm³ and M is the molecular weight. Hence the connection between $[M]$ and Φ is

$$[M] = (18/\pi)\Phi \quad (68)$$

so, combining (8) and (10) one has

$$\frac{[M]}{(1/3)(n^2+2)} = 24N(\hbar/\mu c)^2 \sum_b \frac{R_{ba}\nu^2}{\nu_{ba}^2 - \nu^2}. \quad (69)$$

Here R_{ba} is expressed in atomic units. The coefficient in (69) has the numerical value

$$24N(\hbar/\mu c)^2 = 21,700. \quad (70)$$

It is easy to calculate the value of the rotatory strength of an absorption band from the dispersion data as usually given by using (69) and (70). As an example consider Hunter's data¹⁷ on *d*-sec-octyl alcohol. This extends from $\lambda 6708$ to $\lambda 3650$ and is represented by

$$[M] = \frac{4.08}{\lambda^2 - 0.0283},$$

where λ is in microns. Hunter has measured the refractive index n and from his data we find that $(1/3)(n^2+2)$ is 1.34 at $\lambda 6438$ and 1.36 at $\lambda 3650$ so this factor is essentially equal to 1.35 throughout the range. One has therefore

$$\frac{[M]}{(1/3)(n^2+2)} = \frac{3.02}{\lambda^2 - 0.0283} = \frac{106.9\sigma^2}{35.4 - \sigma^2},$$

where σ is the wave number in reciprocal microns. Hence comparing with (69) one has that the main absorption band is at $\lambda 1680$ and the strength of this is

$$R_{ba} = 106.9/21,700 = 4.92 \times 10^{-3}.$$

In this way it is easy to calculate the rotatory strengths of the absorption lines when a rotatory dispersion formula is given.

Kuhn¹⁸ has introduced another way of describing the rotatory strength of an absorption band by means of what he calls the anisotropy factor. Although the definitions he gives are in terms

¹⁵ Natanson, J. de phys. **8**, 321 (1909).

¹⁶ Condon and Shortley, *The Theory of Atomic Spectra* (Cambridge, 1935), p. 98.

¹⁷ Hunter, J. Chem. Soc. **123**, 1671 (1923).

¹⁸ Kuhn, Trans. Faraday Soc. **26**, 300 (1930).

of his coupled oscillator model it is readily seen that they amount to the following: the oscillator strength of the absorption line ν_{ba} is defined as the dimensionless number

$$f(b, a) = (8\pi^2\mu/3e^2h)\nu_{ba}|(a|\mathbf{p}|b)|^2. \quad (71)$$

Then Kuhn defines the anisotropy factor $g(b, a)$ for this line as

$$g(b, a) = \text{Im}\{(a|\mathbf{p}|b) \cdot (b|\mathbf{m}|a)\} / |(a|\mathbf{p}|b)|^2. \quad (72)$$

The relation of Kuhn's anisotropy factor to our rotatory strength is then

$$f(b, a)g(b, a) = (2\pi/3)(a/\lambda_{ba})R(b, a), \quad (73)$$

in which $R(b, a)$ is expressed in atomic units, a is the radius of the first Bohr orbit and λ_{ba} is the wave-length of the absorption line $a \rightarrow b$. Thus the product fg is generally smaller by a factor of one to three thousand than the rotatory strength $R(b, a)$.

9. THE CONTRIBUTION OF SPINS TO OPTICAL ROTATION

If a molecule contains an even number, $2n$, of valence electrons they can be paired in $(2n)!/n!2^n$ ways to give this number of distinguishable singlet bond eigenfunctions corresponding to each particular electronic configuration. To the very good approximation that the various operators for spin commute with the energy operator (i.e., neglecting magnetic interactions which are responsible in atoms for the fine structure) we can write down a bond function

$$B_i = \frac{1}{((2n)!)^{\frac{1}{2}}} \sum \pm P[\varphi_i(x_1 y_1 z_1 \cdots z_n) \cdot \prod_{\text{all bond pairs}} (\alpha_i \beta_j - \alpha_j \beta_i)]$$

for each one of the $(2n)!/n!2^n$ ways of choosing the n bonds. Here φ_i is a function of space coordinates only and

$$\prod_{\text{all bond pairs}} (\alpha_i \beta_j - \alpha_j \beta_i) \equiv g_i$$

of spins alone. The antisymmetrizing operator $\Sigma \pm P$ indicates summation over all permutations of the electrons in the product $\varphi_i g_i$ taking the positive sign for even and the minus sign for odd permutations. This antisymmetric B_i satisfies

the Pauli principle. Of these singlet bond functions only $(2n)!/n!(n+1)!$ are linearly independent. Now the lowest energy state of molecules having an even number of electrons is always a singlet so that the expression for optical activity will involve the term

$$\text{Im} \sum_{n'} (n|\mathbf{r}|n') \cdot (n'|\mathbf{L} + 2\mathbf{S}|n),$$

where n indicates the singlet bond function B_n which therefore satisfies the equation

$$\mathbf{S}^2 B_n = 0 B_n = \tilde{S}_x S_x B_n + \tilde{S}_y S_y B_n + \tilde{S}_z S_z B_n.$$

Since each term after the last equality is zero or positive, each must be zero, so that $2(iS_x + jS_y + kS_z)B_n = 0$. Thus spin will not contribute to the optical activity of unexcited molecules containing an even number of electrons. Since it is never possible to obtain excited molecules in sufficient amounts to contribute to optical activity, even if the spin were effective, the spin from such molecules never need be considered.

Next consider the case where there are $2n-1$ electrons, n still being an integer. Actual examples are provided by free radicals. States of lowest energy as before correspond to maximum electron pairing. Corresponding to each of the B_i functions for $2n$ electrons we now have a bond function

$$B'_i = (1/[(n-1)!]^{\frac{1}{2}}) \sum \pm P[\varphi'_i(x_1 \cdots z_{n-1}) \cdot \alpha_k \prod_{\substack{\text{over} \\ n-1 \\ \text{bond pairs}}} (\alpha_i \beta_j - \alpha_j \beta_i)]$$

which contains one unpaired electron and therefore satisfies the equation $S_z B'_i = (h/4\pi) B'_i$. Still another set B'' which satisfy the equation $S_z B'' = -(h/4\pi) B''$ is obtained by replacing α_k by β_k in each B'_i . Again consider the quantity $\text{Im}\{\Sigma(n|\mathbf{r}|n') \cdot (n'|\mathbf{L} + 2\mathbf{S}|n)\}$. Now

$$\begin{aligned} 2\mathbf{S} B'_n &= 2(iS_x + jS_y + kS_z) B'_n \\ &= (1/[(n-1)!]^{\frac{1}{2}}) \sum \pm P[\varphi'_n(x_1 \cdots z_{n-1}) \cdot 2(i\beta_k + j(i\beta_k) + k\alpha_k) \prod_{\substack{\text{over} \\ n-1 \\ \text{bond pairs}}} (\alpha_i \beta_j - \alpha_j \beta_i)]. \end{aligned}$$

Thus if both B'_n and

$$B_n \text{ are real } (n'|\mathbf{L} + 2\mathbf{S}|n) \equiv \sum_{\text{spin space}} B'_n 2\mathbf{S} B'_n d\tau$$

contains an imaginary term only if in B_n' and $B_{n'}'$ the odd electron is assigned to an α state in one eigenfunction and a β state in the other; but in this case $(n|\mathbf{r}|n')$ is zero because of this difference in spin of the odd electron in the initial and final states.

The only way then that

$$\text{Im}\{\Sigma(n|\mathbf{r}|n') \cdot (n'|2\mathbf{S}|n)\}$$

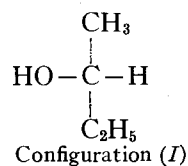
can be different from zero (for real eigenfunctions) would be for $\text{Im}(n|\mathbf{r}|n')$ to be different from zero for the transition but this is impossible. However, suppose B_n' or $B_{n'}'$ contains an imaginary part. Since the operator H is real both the real and imaginary parts of any complex B_i' is separately an eigenfunction of H as one sees immediately by equating both the real and imaginary part of the corresponding Schrödinger equation to zero. There is therefore no loss in generality in assuming all B 's to be either purely real or purely imaginary functions. Suppose now one of the B 's is imaginary then the preceding argument about $\text{Im}\{(n|\mathbf{r}|n') \cdot (n'|2\mathbf{S}|n)\}$ being zero can be taken over completely since the only effect is to multiply the result for real eigenfunctions by -1 . Similarly if both eigenfunctions are imaginary the only effect is to multiply them by $+1$. Thus we have shown that to the approximation in which magnetic terms in the energy can be neglected the spins do not contribute to optical activity.

It follows from the above formulations and from the fact that \mathbf{r} and \mathbf{L} are each the sums of terms involving only one electron that exactly the same value is obtained for the optical activity when the φ 's are used to calculate the matrices for \mathbf{r} and \mathbf{L} as when the antisymmetric B 's are used. This is an important simplification. It is useful to make one further simplification which is justified by the observation that most transitions are satisfactorily described as single rather than multiple electron jumps. Thus we write $\varphi(x_1 \cdots z_n) = \psi_1(x_1 y_1 z_1) \psi_2(x_2 \cdots z_n)$ where $\psi_2(x_2 \cdots z_n)$ is unchanged in the transition and so can be integrated out before calculating the matrix components for \mathbf{r} and \mathbf{L} . It is this approximation which forms the basis of our present treatment.

10. THE ABSOLUTE CONFIGURATION OF SECONDARY BUTYL ALCOHOL

The procedure which we have applied to methyl phenyl carbinol nitrite leads to a definite statement for the absolute configuration of any molecule where the charge distribution about the chromophoric electron is known. Where the total rotatory power can be analyzed into the contribution from the different chromophoric electrons the theory provides a way of checking the assigned structure since a single assignment of charge distribution must give correctly the optical activity of all the different chromophoric electrons of the molecules. Such crucial tests will help to establish the range of validity of the present theory.

At least three determinations of the absolute configuration of butyl alcohol have been published. We indicate the configuration of butyl alcohol by the structural formula



where the full lines indicate that H and OH lie in the plane of the paper and the dotted lines joining CH_3 and C_2H_5 to C indicate these groups lie below the plane of the paper. Boys'¹⁹ rule applied to this configuration leads to the dextro-rotatory assignment. Kuhn²⁰ on the other hand using the theory of coupled oscillators comes to the conclusion that this isomer is laevo-rotatory. Finally Kirkwood,²¹ concludes this isomer is dextro-rotatory in agreement with Boys.

While we shall use our theory to calculate the absolute configuration of secondary butyl alcohol it is of interest to consider another method of obtaining this same information. Schwab, Rost and Rudolph²² report that dextro-rotatory quartz partially covered with copper or nickel provides a catalyst which dehydrates laevo-rotatory secondary butyl alcohol faster than the dextro-

¹⁹ Boys, Proc. Roy. Soc. **A144**, 655 (1934).

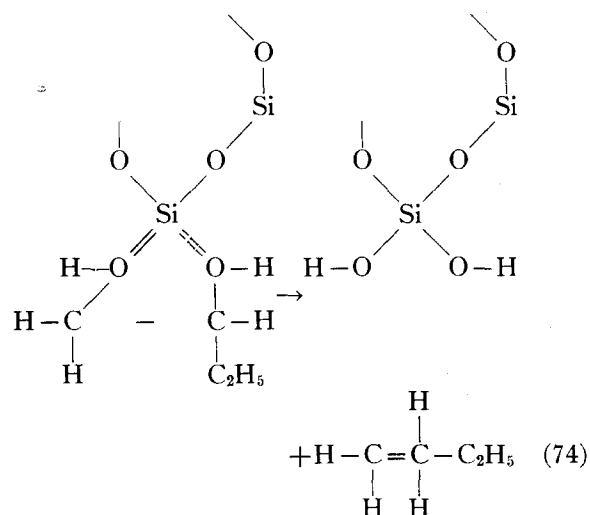
²⁰ Kuhn, Zeits. f. physik. Chemie **B31**, 18 (1935).

²¹ Kirkwood, J. Chem. Phys. **5**, 479 (1937).

²² Schwab, Rost and Rudolph, Kolloid Zeits. **63**, 157 (1934).

rotatory form. Now quartz is known to crystallize in the form of spirals in which silicon and oxygen atoms alternate. Each spiral is connected with neighboring spirals since each silicon is bound to 4 oxygens and each oxygen to two silicons. Now there are right- and left-hand quartz spirals and they rotate plane polarized light in opposite directions. If some means can be devised to determine the absolute configuration of quartz, then as we shall see, a proper interpretation of experiments such as those of Schwab, Rost and Rudolph will fix the absolute configuration of secondary butyl alcohol.

First suppose that when water is removed from secondary butyl alcohol²³ the reaction may be represented as follows:



Suppose further that the butyl alcohol reacting belongs to configuration (*I*). Then as viewed normal to a plane passing simultaneously through the reacting H and OH and through the two carbon atoms to which these atoms are attached the molecule has the properties of a left-hand screw, since the ethyl group occupies more space than the hydrogen attached to the same carbon atom. If as we now explicitly assume there is an increased activation energy due to the steric hindrance of nonreacting groups then such a left-hand screw alcohol should react faster with right-hand quartz since screws of unlike sense fit along side of each other better

²³ Schwab, Rost and Rudolph imply that the butylene formed from the dehydration of secondary butyl alcohol has the double bond in the 1,2 position but do not say they have investigated this point.

than like screws. Such a consideration relates the configuration of the alcohol to that of the quartz. Two different methods for arriving at the absolute configuration of macroscopic hemihedral crystals such as quartz can be suggested. (1) As Pasteur demonstrated long ago it is frequently possible to pick out the two kinds of optically active crystals by the fact that different faces are developed on the two kind of crystals. The identification is then completed if crystal faces can be related to the structure of the crystal. Thus this problem resolves itself into an investigation of the factors responsible for the growth of crystal faces and avoids optical theory entirely in establishing absolute configuration. Such a method could of course be applied to any optically active crystal such as the tartrates thus avoiding uncertainties in deducing relative configurations. We now consider the second method.

(2) Optical theory can be applied directly to the crystal to deduce its absolute configuration. We leave to a future time the application of the present theory to quartz and accept provisionally Hylleraas²⁴ application of the Born coupled oscillator theory in which he finds that right spiraling β -quartz is dextro-rotatory. Assuming this same relation holds for the slightly different low temperature α -quartz we are led by using our other considerations to the decidedly provisional result that laevo-rotatory butyl alcohol has configuration (*I*). This would be in agreement with Kuhn. While this result must be regarded as purely tentative it seems of very considerable interest to develop further both theoretically and experimentally this approach to absolute configuration because of the light it throws on surface reactions and optically active synthesis.

We now examine in more detail some of the steps in the preceding argument. Suppose that the dehydration of configuration (*I*) actually results in the formation of a double bond between the second and third carbon atoms instead of 1-2 butylene as we first supposed. Examination of the model shows that this can occur by the OH giving off with either of the two hydrogens on the third carbon atom. In the mechanism we will call (1) the four carbon atoms will lie in a plane so that such a molecule

²⁴ Hylleraas, Zeits. f. Physik **44**, 871 (1927).

would react equally well with either right or left quartz. Thus whatever part of the reaction goes this way cannot be responsible for the observed differential rate and is therefore not interesting for optical activity. It is very likely that steric repulsions between the hydrogens on the end carbon atoms are responsible for reducing the importance of this mechanism. The product of such a mechanism would be 2-3 *cis* butylene.

By mechanism (2) 2-3 *trans* butylene will be the product and configuration (*I*) can be seen, by examining a model to behave like a right screw so that by our former assumption, of fastest reaction between unlike screws, it should go fastest on left spiraling quartz. Thus if 2-3 *trans* butylene (and not 1-2 butylene) is the chief decomposition product in the Schwab, Rost and Rudolph experiment then keeping our tentative assignment of the absolute configuration of quartz we would conclude that configuration (*I*) is the dextro form.

The preceding discussion then suggests that experiments designed to answer the following questions will be particularly valuable.

(1) Is the product of dehydration of secondary butyl alcohol 1-2 or 2-3 butylene and, if the latter, is it *cis* or *trans*?

(2) What is the function of the metal in the dehydration?

(3) Is the rate of dehydration of the secondary alcohol slowed down by replacing nonreacting radicals in the molecule by larger substituents?

From the point of view of the catalytic theory it is particularly significant that the spiral character of quartz in bulk still persists in the surface layer.

We have made a provisional calculation of the rotatory power of butyl alcohol considering only the contribution from the hydroxyl as chromophoric group. The configuration adopted is that of (*I*), the carbon atoms are numbered in order along the chain with the OH group on C₂.

Hydrogen atoms 0 and 1 are on C₁, 3 is on C₂, 4 and 5 are on C₃ and 6, 7, 8 on C₄ while H₉ is the hydrogen of the hydroxyl group. The assumed coordinates of the atoms are given in Table II. Here the coordinates are given in angstrom units. The charges assumed for the atoms are (in 10⁻¹⁰ e.s.u.): given in the last line of the table. This set of charges and coordinates determines the principal axes of the quadratic potential terms in accordance with the following linear transformation

$$\begin{aligned}u &= -0.9797x + 0.510y + 0.1939z, \\v &= +0.0015x - 0.9691y + 0.2465z, \\w &= +0.1999x + 0.2398y + 0.9498z,\end{aligned}$$

in terms of which it is found that the dissymmetry coefficient has the value, $A = 2.8153 \cdot 10^{10}$. If the unperturbed force constant is chosen so that the longest wave-length absorption band is at 1620Å (this is the critical frequency in the empirical one-term dispersion formula) the three calculated frequencies associated with the three axes become,

$$\begin{aligned}\nu_u &= 2.3873 \cdot 10^{15}, & \nu_v &= 1.8518 \cdot 10^{15}, \\& & \nu_w &= 2.2568 \cdot 10^{15}.\end{aligned}$$

These lead to a theoretical value of the parameter β which is

$$\beta = 3.644 \cdot 10^{-38}$$

as the contribution of the hydroxyl group to rotatory power at the NaD line wave-length. The experimental value of β calculated from the observed rotatory power by means of (6) is $\beta = 1.40 \cdot 10^{-35}$. This value of course includes the contribution from all electrons and is the average effect allowing for all configurations assumed under conditions of more or less free rotation about the bond axes. The large discrepancy may of course mean that the one-electron model is of secondary importance in this case. On the other hand other possible configurations and assumptions concerning the unperturbed state would give a much more favorable result. Thus a

TABLE II.

| | O | H ₁ | H ₂ | H ₃ | H ₄ | H ₅ | H ₆ | H ₇ | H ₈ | H ₉ | H ₀ | C ₁ | C ₂ | C ₃ | C ₄ |
|----------|-------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|
| <i>x</i> | 0 | +1.85 | +0.96 | +1.85 | -0.92 | +0.92 | -0.92 | +0.92 | 0 | 0 | -0.92 | +1.24 | 0 | 0 | 0 |
| <i>y</i> | 0 | -1.08 | -1.60 | -0.04 | +1.60 | +1.60 | +3.05 | +3.05 | +1.85 | -0.94 | -0.53 | -0.77 | 0 | +1.43 | +2.40 |
| <i>z</i> | 0 | -1.08 | -2.55 | -2.55 | -2.55 | -2.55 | -0.78 | -0.78 | +0.18 | +0.24 | -1.80 | -1.94 | -1.42 | -1.94 | -0.76 |
| <i>e</i> | -2.16 | | | | | | | | | | | -0.84 | +0.32 | -0.56 | -0.84 |

all hydrogens +0.28

moderate change in the difference between ν_u and ν_w would introduce a power of ten and a more favorable relation of the principal axes would help very much. We shall consider these possibilities more fully at a later time.

11. OTHER CONSEQUENCES OF THE THEORY

The known dipoles of various bonds lead us to locate charges on the atoms from which we can calculate the contribution to the potential coming from these coulomb forces. Other contributions toward rotatory power will arise from the coupling of the chromophoric electron with other electrons in the molecule. It is this latter effect which in the past has been considered to the complete exclusion of other mechanisms. Wherever charges are present both mechanisms undoubtedly contribute to the total effect.

Empirically it has been known²⁵ for some time that there is a relationship between total dipole moment and optical activity. Furthermore Rule²⁶ has attempted to relate optical activity to the constituent moments particularly with respect to their size and propinquity to the optically active carbon atom. From the theory presented here we are compelled to postulate the existence of such relationships in a definite quantitative way. Particularly large effects are to be expected wherever the chromophoric electron is closely and asymmetrically surrounded by ions such as are found in ionic crystals (quartz, cobalt-oxalate crystals, etc.) Another effect the quantitative treatment of which falls naturally within the scope of this approach is the large change caused by polar and polarizable solvents on rotatory power. This effect interpreted in accord with the present formulation makes it possible to apply optical activity in a quantitative way to the study of liquid structure. As Wolf and Volkmann,²⁷ Beckmann and Cohen²⁸ and others

have pointed out it is due to the electric forces originating from solvent dipoles surrounding the active molecules. We now readily understand that such forces will change the potential in which the chromophoric electron is moving without having to postulate, as Beckmann and Cohen do, an actual distortion of the molecular frame.

A polar solvent tends to form a compound with highly charged parts of the optically active molecule; in so doing it partially neutralizes these charges thereby reducing the rotatory power. Thus the general effect of polar solvents should be to lower optical activity except in special cases where enhancement results from neutralization of charges which were themselves previously acting to lower the optical activity. These expectations are born out by experiment.²⁹

Comparatively small changes in charge distribution may in fact lead to large changes or even reversal of sign of the asymmetry coefficient A . Thus when the shape of the molecule is not rigidly fixed the over-all rotatory power of the compound will show great sensitivity to all factors which modify the statistical weight of particular configurations. The classical example for this is furnished by tartaric acid and its salts and esters where free rotation about single bonds is restricted by steric effects and compound formation. This results in the well-known temperature and concentration anomaly.

Our thesis that any dispersion electron is made optically active whenever it is brought into a dissymmetric field provides a clear explanation of "induced optical activity" in the sense discussed by Lowry in cases where the dispersion electron is not directly attached to an asymmetric center. The carbonyl group in sugars is a striking example of this possibility. In such a case as this the asymmetric influence cannot be transmitted by way of bonds so that the conclusion seems inescapable that the effect is a coulombic one transmitted through space.

²⁵ Betti, *Trans. Faraday Soc.* **26**, 227 (1930).

²⁶ See Lowry, *Optical Rotatory Power*, pp. 326 *et seq.*

²⁷ *Zeits. f. physik. Chemie* **B3**, 139 (1929).

²⁸ Beckmann and Cohen, *J. Chem. Phys.* **4**, 784 (1936).

²⁹ Lowry, *Optical Rotatory Power* (Longmans Green 1936), p. 350.