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Everett Gorin, John Walter, and Henry Eyring

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The Optical Activity of Secondary Butyl Alcohol

EVERETT GORIN, JOHN WALTER AND HENRY EYRING

Frick Chemical Laboratory, Princeton, New Jersey

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A calculation of the optical activity of secondary butyl alcohol is presented based upon a one-electron model. The chromophoric electron is considered to be one of the nonbonding electrons on the oxygen atom. This electron is considered to be moving in a field of the other nuclei and electrons considered as charge distributions. The fields of the other electrons are obtained from the Slater type eigenfunctions for the various atoms. This amounts to a rough solution of the Hartree approximation for the chromophoric electron. The results obtained are somewhat larger or somewhat smaller than the experimental value depending on the exact orientation of the groups in their rotation about single bonds. The assignment of an absolute configuration in these calculations follows provided the exact orientation of the rotating groups is known. The orientations which we consider most likely lead to an assignment of the absolute configuration in agreement with that of Kuhn.

INTRODUCTION

IF the electric moment \mathbf{p} of a molecule is given by

$$\mathbf{p} = \alpha \mathbf{E}' - (\beta/c) \dot{\mathbf{H}}, \quad (1)$$

where α , \mathbf{E}' , $\dot{\mathbf{H}}$, and c , are the polarizability, effective electric field on the molecule, time derivative of the magnetic field, and the velocity of light, respectively, then the rotatory power of the medium is given by

$$\varphi = \frac{16\pi^3 N_1 \beta}{\lambda^2} \frac{n^2 + 2}{3}, \quad (2)$$

where N_1 , λ , and n are the number of molecules per cc, the wave-length, and the index of refraction, respectively. Using quantum mechanics, Rosenfeld¹ obtained the relationship

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

where ν , ν_{ba} , $(a|\mathbf{p}|b)$, $(b|\mathbf{m}|a)$, are the frequency of the light used, the frequency corresponding to the transitions between levels b and a , the matrix component for the electric moment and the matrix component for the magnetic moment for the transition from level a to b , respectively. Finally we have

$$\beta = \sum_a p_a \beta_a, \quad (4)$$

where p_a is the probability of a molecule lying in

¹ Rosenfeld, *Zeits. f. Physik* **52**, 161 (1928).

the state a . For most substances the number of molecules in any but the lowest electronic level may be neglected, but unless the molecule is rigid it is necessary to average over the various possible internal configurations. As written, both β_a and β are already averaged over all possible orientations with respect to the polarized beam passing through the material. Condon² has given a detailed derivation of these equations in his presentation of the theories of optical rotatory power. In any quantum mechanical treatment of optical activity it is convenient to start with (3). Kirkwood³ has based his interesting theory on this equation and the same is true of a treatment by Condon, Altar, and Eyring.⁴ These latter authors showed that a single electron moving in a field of suitable dissymmetry gives rise to optical activity. Previous theories of optical activity, aside from the first treatment by Drude, are based on coupled oscillators. Drude's model has been rejected by Born and Kuhn.⁵ Kuhn's proof⁶ that one electron cannot show optical activity on the basis of classical theory requires the further assumption that the electronic displacement be infinitesimal, as he has recently emphasized.⁷ For the finite displacements always involved in actual transitions, the carrying over of the quantum mechanical formula to the clas-

² Condon, *Rev. Mod. Phys.* **9**, 432 (1937).

³ Kirkwood, *J. Chem. Phys.* **5**, 479 (1937).

⁴ Condon, Altar, and Eyring, *J. Chem. Phys.* **5**, 753 (1937).

⁵ See: Lowry, *Optical Rotatory Power*, p. 372.

⁶ Kuhn, *Zeits. f. physik. Chemie* **B20**, 235 (1933).

⁷ Kuhn, *Naturwiss.* **19**, 289 (1938).

sical case by the use of the correspondence principle yields optical activity for one electron.³ The necessary condition for optical activity to result from a single electron in a properly dissymmetric field is thus that finite displacements be involved. Finite displacements always occur in actual molecules and are automatically considered in quantum mechanics, but were ordinarily not considered in classical theory.

The chief concern of Condon, Altar and Eyring⁴ was to demonstrate one-electron optical activity. A simple three-dimensional harmonic oscillator in a perturbing field was chosen because it permitted a comparatively simple calculation. The perturbation considered was that which arose by assigning such charges to the various atoms as would account for the known dipole moments associated with the bonds. The contributions of these atomic charges to the field in which the chromophoric electron moved was then expressed in the usual series expansion and only the leading terms retained. Although in certain cases the results obtained are of the order of magnitude of those found experimentally, this was not true in the case of secondary butyl alcohol where the calculated value was about one five-hundredths of that found experimentally.

A rigorous application of Eq. (3) requires a knowledge of the exact eigenfunctions for secondary butyl alcohol in its normal and excited states. Unfortunately these are not available at the present time and one is forced to use approximate models. Kuhn has extended Born's coupled oscillator treatment and has treated secondary butyl alcohol. Boys⁸ has proposed a model consisting of four isotropic polarizable groups situated at the vertices of an irregular tetrahedron. The rotation of the plane of polarization is assumed to arise from the way the scattered secondary wavelets from each group reinforce one another. Such a model can at most apply at very long wave-lengths since it does not take explicit account of the various electronic transitions involved, which dispersion data show are intimately connected with optical activity. Kirkwood⁵ has improved upon Boys' model by taking into account the anisotropy of the component groups and by employing a quantum mechanical treatment based upon Eq. (3). He

treats the OH groups, however, as isotropic, which our results show to be quite unjustifiable. Kirkwood's treatment has the merit of summing over the contributions of all transitions involved in the four groups surrounding the central carbon. However, Kuhn⁷ * concludes from a survey of the experimental rotatory dispersion data that in the case of secondary butyl alcohol the sign and magnitude of the rotation in the visible is controlled by the transitions nearest the visible which in this case are associated with the hydroxyl group. It thus seems feasible to center our attention on the transitions in the hydroxyl group. This is an important simplification of the problem and forms the basis for our subsequent treatment.

A ONE-ELECTRON MODEL

In actual atomic transitions, although the quantum number of only one electron is usually represented as changing, the orbits of the remaining electrons are modified to a certain extent. This may be thought of as due to a change in the screening constant of the electron which jumps and also of the other electrons.⁹ Optical transitions involving an electron outside a closed shell can be treated, however, as a one-electron transition to a good approximation.¹⁰

We have considered that the transitions in the OH group involve the nonbonding electrons on the oxygen atom. The configurations of the normal and excited states in the C—O—H part of the molecule can be represented as:

| | | | | |
|----------------|-----|---------------------|-------------------|-------------------|
| Normal State | | $(2t_z \cdot 2pz')$ | $(1s \cdot 2py')$ | $(2px \cdot 2px)$ |
| Excited States | I | $(2t_z \cdot 2pz')$ | $(1s \cdot 2py')$ | $(2py \cdot 2px)$ |
| | II | $(2t_z \cdot 2pz')$ | $(1s \cdot 2py')$ | $(2pz \cdot 2px)$ |
| | III | $(2t_z \cdot 2pz')$ | $(1s \cdot 2py')$ | $(3s \cdot 2px)$ |

The first, second, and third parentheses represent the electrons forming the C—O bond, the O—H bond, and the two nonbonding electrons on the oxygen, respectively. The z direction lies along the O—C bond. The y direction lies in the C—O—H plane and the x direction is perpendicular to this plane. Due to the distortion of the C—O—H valence angle from ninety degrees, the

* Levene and Rothen (*Gilman Organic Chemistry*, Vol. II, p. 1801) do not agree with this conclusion. In any case, if other electrons need be considered, their contributions can be simply added to the value already calculated.

⁹ Slater, *Phys. Rev.* **34**, 57 (1930).

¹⁰ McDougall, *Proc. Roy. Soc.* **A138**, 550 (1932).

⁸ Boys, *Proc. Roy. Soc. London* **A144**, 655, 675 (1934).

TABLE I.

| | 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 | -0.92 | -0.92 | 0.92 | -0.92 | 0.92 | 0.0 | 0.0 | 1.85 | 1.24 | 0.0 | 0.0 | 0.0 |
| <i>y</i> | 0 | 1.08 | 1.60 | 0.53 | -1.60 | -1.60 | -3.05 | -3.05 | -1.85 | 0.94 | 0.04 | 0.77 | 0.0 | -1.43 | -2.40 |
| <i>z</i> | 0 | 1.08 | 2.55 | 1.80 | 2.55 | 2.55 | 0.78 | 0.78 | -0.18 | -0.24 | 2.55 | 1.94 | 1.42 | 1.94 | 0.76 |

function $2pz'$ is nearly equal to $2pz$ but is a linear combination with $2py$. $2py'$ is the corresponding orthogonal linear combination.¹¹ $2t_i$ is the carbon tetrahedral bonding eigenfunction.

For the usually measured wave-lengths those transitions will be most important which require the least energy. The bonding electrons are more tightly held than the nonbonding electrons, as is shown by the fact that in H₂ it requires about two more volts to ionize an electron than in the hydrogen atom, and over a volt more to reach the first resonance potential than does the hydrogen atom. On the other hand, the nonbonding electrons of oxygen are a little more easily ionized than in the free atom as is shown by the fact that the ionization potential of water is at least a half volt less than in the oxygen atom.¹² The transition $^3P \rightarrow ^3S$ in the oxygen atom requires about 9.0 volts, while judging from the dispersion data on alcohols the optically active absorption band lies at about 7.5 volts above the normal state.¹³ The fact that the measured excited level is lower in the alcohols than in the oxygen atom indicates that a nonbonding electron is involved. This conclusion is somewhat different from that of Kuhn, who interprets the greater polarizability of the CH₃OH molecule in the C—O—H plane to mean that in his treatment the important transition of the three dimensional oscillator lies in the C—O—H plane.¹⁴ In our treatment the eigenfunction is initially nearly odd, and ends up by being nearly even, with respect to the C—O—H plane.

Our procedure consists in obtaining a rough solution to the Hartree equation for the nonbonding oxygen electron moving in the Hartree field of the rest of the molecule.

¹¹ We wish to thank Professor R. S. Mulliken for a very helpful discussion in connection with the assignment of possible transitions.

¹² Smyth, *Rev. Mod. Phys.* **3**, 347 (1931).

¹³ Lowry, *Optical Rotatory Power*, p. 265; Levene and Rothen, *J. Biol. Chem.* **116**, 209 (1936).

¹⁴ Kuhn, *Zeits. f. physik. Chemie* **B31**, 23-57 (1935).

$$\nabla^2\psi + \frac{h^2}{8\pi^2m} \left((E - V(r)) - \sum_i \sum_k \left[e^2 \int \frac{\varphi_{ik}^2}{r_{ik}} d\tau_k - \frac{ze^2}{r_i} \right] \right) \psi = 0. \quad (5)$$

$V(r)$ is the potential field for the oxygen atom and was assumed to be hydrogen-like for the various series electrons. The values of Z were 2 for the s and p series, and 1.5 for the d series. These values of Z were necessary if one is to obtain the right ionization and resonance potentials, and still neglect all changes in the remaining electrons. The first resonance potential was chosen to correspond to that in alcohol and the separation between the $3s$ and $3d$ levels, although unknown for alcohols, was taken from the value in atomic oxygen.

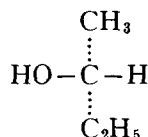
The last set of terms in Eq. (5) corresponds to the potential of the atomic kernels, while the next to the last set arises from the electrostatic potential of the electron clouds around each kernel. The index i refers to the kernels and the index k to the electrons. The eigenfunctions φ_{ik} were taken to be the ordinary atomic functions for the hydrogens and the functions for the carbon valence electrons were taken after Slater with the difference that the two $1s$ electrons were assumed to screen the nucleus perfectly. This slight modification somewhat simplified the calculations without materially affecting the results. The carbon atom in its 3S valence state is spherically symmetric so that the potential energy is simply a function of the distance r from the carbon kernel.

$$V_C = -\frac{4e^2}{a_0} e^{-2.95r_i/a_0} \left[\frac{1.070r_i^2}{a_0^2} + 2.175\frac{r_i}{a_0} + 2.213 + \frac{a_0}{r_i} \right].$$

The potential function of the hydrogen atom is likewise spherically symmetric.

$$V_H = -\frac{e^2}{a_0} e^{-2r_i/a_0} \left[1 + \frac{a_0}{r_i} \right].$$

r_i is the distance from the i th atom and a_0 is the Bohr radius. The exact configuration first investigated was that of Condon, Altar and Eyring.⁴ The coordinates are given in Table I since it was convenient to use a coordinate system in which the signs of the y and z coordinates were reversed and also to correct a misprint in the original table. We will refer to this as orientation I. (In general we propose to use the word orientation for an exact configuration in which the relative positions of all the atoms are specified and use the word configuration in the usual sense to specify merely the general positions of the groups with respect to the asymmetric carbon.) It corresponds to the following absolute configuration. Dotted lines indicate groups below the plane.



The carbon atoms are numbered in order along the chain with the O-H group on C₂. Hydrogen atoms 0, 1, 2 are on C₁, 3 is on C₂, 4, 5 are on C₃, 6, 7, 8 on C₄, while H₉ is the hydrogen of the hydroxyl group.

Orientation II corresponds to a small rotation of the hydroxyl hydrogen such that C₂, O, H₉, and H₃ become coplanar. Thus all the atoms have the same coordinates as in orientation I except H₉ which has the coordinates (-0.82, +0.47, -0.24). In addition the case of free rotation of the O-H group was considered.

The last two terms in Eq. (5), which we will indicate by the symbols H' and H'' , were treated by a perturbation method. H' refers to the perturbations due to the carbon and hydrogen atoms bound to the oxygen, while H'' refers to the perturbations due to the remaining atoms. The unperturbed normal state is given by the hydrogen-like eigenfunction

$$\psi_1 \equiv \psi_{2px} = \frac{1}{4(2\pi)^{\frac{1}{2}}} \left(\frac{2}{a_0} \right)^{\frac{3}{2}} \frac{2r}{a_0} \exp \left(-\frac{r}{a_0} \right) \left(\frac{x}{r} \right).$$

The unperturbed excited levels are given by the three hydrogen-like functions which are even with respect to reflection in the C-O-H plane

$$\psi_2 \equiv \psi_{3s} = \frac{1}{81(3\pi)^{\frac{1}{2}}} \left(\frac{2}{a_0} \right)^{\frac{3}{2}} \left(27 - \frac{36r}{a_0} + 8 \left(\frac{r}{a_0} \right)^2 \right) \times \exp \left(-\frac{2r}{3a_0} \right),$$

$$\psi_3 \equiv \psi_{3py} = \frac{2^{\frac{1}{2}}}{81\pi^{\frac{1}{2}}} \left(\frac{2}{a_0} \right)^{\frac{3}{2}} \left(\frac{12r}{a_0} - 4 \left(\frac{r}{a_0} \right)^2 \right) \times \exp \left(-\frac{2r}{3a_0} \right) \left(\frac{y}{r} \right),$$

$$\psi_4 \equiv \psi_{3pz} = \frac{2^{\frac{1}{2}}}{81\pi^{\frac{1}{2}}} \left(\frac{2}{a_0} \right)^{\frac{3}{2}} \left(\frac{12r}{a_0} - 4 \left(\frac{r}{a_0} \right)^2 \right) \times \exp \left(-\frac{2r}{3a_0} \right) \left(\frac{z}{r} \right).$$

The odd function ψ_{3px} was not considered since to include it would considerably complicate the calculation without giving an important contribution to the optical activity. The functions ψ_2 , ψ_3 , and ψ_4 all correspond to the same energy. The degeneracy is removed by the perturbations of the term in brackets. The usual proper linear combination is determined by solving the usual set of linear equations which lead to the secular determinant

$$\begin{vmatrix} H_{22} - W & H_{23} & H_{24} \\ H_{32} & H_{33} - W & H_{34} \\ H_{42} & H_{43} & H_{44} - W \end{vmatrix} = 0 \quad (6)$$

$$H_{ij} = \int \psi_i H' \psi_j d\tau.$$

We thus obtain three eigenfunctions

$$\psi_n' = c_{n2}\psi_2 + c_{n3}\psi_3 + c_{n4}\psi_4, \quad (7)$$

where n goes from 1 to 3. After removal of the degeneracy these functions are combined by the perturbation H' with the functions $\psi_5 \equiv \psi_{2py}$ and $\psi_6 \equiv \psi_{2pz}$. These wave functions are then

$$\psi_n'' = \psi_n' + c_{n5}\psi_5 + c_{n6}\psi_6,$$

$$\text{where } c_{n5} = \frac{\int \psi_n' H' \psi_5 d\tau}{E_n - E_5}, \quad c_{n6} = \frac{\int \psi_n' H' \psi_6 d\tau}{E_n - E_6}$$

and where $E_5 = E_6 = E_1$ is the energy of the normal state and E_n is the energy of the unperturbed eigenfunctions ψ_2, ψ_3 , or ψ_4 . The functions ψ_n'' are all even with respect to the C-O-H plane and consequently transitions to them would not be optically active. If however, we consider linear combinations of these functions with the odd functions $\psi_7 \equiv \psi_{3dxz}$ and $\psi_8 \equiv \psi_{3dxy}$, the resulting wave functions χ_1, χ_2 , and χ_3 lead to optically active transitions from the ground state.

$$\chi_n = c_{n2}\psi_2 + c_{n3}\psi_3 + c_{n4}\psi_4 + c_{n5}\psi_5 \\ + c_{n6}\psi_6 + c_{n7}\psi_7 + c_{n8}\psi_8,$$

where n goes from 1 to 3 and

$$c_{ni} = \frac{\int \psi_n' H'' \psi_i d\tau}{E_n - E_i},$$

where $i=7$ or 8 . The f, g , and higher functions are omitted since they do not contribute to the optical activity. The reason for omitting the higher d levels will be discussed later.

The perturbation H'' acting upon the eigenfunction for the normal state may be omitted to a good approximation. Considering only the perturbation H' we have for ψ_1'

$$\psi_1' = \psi_1 + a_9\psi_9,$$

where $\psi_9 \equiv \psi_{3pz}$ and

$$a_9 = \int \psi_1 H' \psi_9 d\tau / (E_1 - E_9).$$

The matrix components for magnetic and electric moments calculated with these wave functions are

$$(b|\mathbf{m}|a) \equiv (\chi_n|\mathbf{m}|\psi_1') = \frac{eh}{4\pi mci} [(c_{n6}\mathbf{j} - c_{n5}\mathbf{k}) \\ + (c_{n4}\mathbf{j} - c_{n3}\mathbf{k})], \quad (8)$$

$$(b|\mathbf{p}|a) \equiv (\chi_n|\mathbf{p}|\psi_1') = ea_0 \{ D \{ c_{n7}\mathbf{j} + c_{n8}\mathbf{k} \} \\ + Fa_9 \{ c_{n7}\mathbf{j} + c_{n8}\mathbf{k} \} + Cc_{n2}\mathbf{i} \}, \quad (9)$$

where $D = \int \psi_{3dxy} y \psi_{2pz} d\tau$; $F = \int \psi_{3dxy} y \psi_{3pz} d\tau$;
 $C = \int \psi_{3dxz} x \psi_{2pz} d\tau$.

The operators m and p are

$$\mathbf{m} = \frac{eh}{4\pi mci} \left\{ \left(y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right) \mathbf{i} + \left(z \frac{\partial}{\partial x} - x \frac{\partial}{\partial z} \right) \mathbf{j} \right. \\ \left. + \left(x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right) \mathbf{k} \right\} \\ \mathbf{p} = e(x\mathbf{i} + y\mathbf{j} + z\mathbf{k}).$$

Substituting Eqs. (8) and (9) in Eq. (3) we get for the rotatory parameter

$$\beta = \frac{e^2 a_0}{12\pi^2 m} \frac{1}{\nu_n^2 - \nu^2} \{ D(c_{n5}c_{n8} - c_{n6}c_{n7}) \\ + a_9(c_{n3}c_{n7} - c_{n4}c_{n8}) + Fa_9(c_{n5}c_{n8} - c_{n6}c_{n7}) \\ + Fa_9^2(c_{n3}c_{n8} - c_{n4}c_{n7}) \}, \quad (10) \\ \nu_n = \frac{E_2 - E_1 + W_n}{h},$$

where W_n is the n th root of the secular Eq. (6).

The justification for omitting d levels with principal quantum number greater than 3 is that the integral D corresponding to the electric moment for a transition from the state $2p$ to nd falls off very rapidly as n becomes greater than 3.

The evaluation of the matrix components involved the usual transformation to elliptic coordinates

$$u = (r_a + r_b)/R, \quad v = (r_a - r_b)/R,$$

$$r_a = \frac{R}{2}(u+v), \quad r_b = \frac{R}{2}(u-v), \quad z_a = \frac{R}{2}(1+uv),$$

$$d\tau = (R^3/8)(u^2 - v^2) du dv d\phi$$

with the limits of integration

$$-1 \leq v \leq 1, \quad 1 \leq u \leq \infty, \quad 0 \leq \phi \leq 2\pi.$$

The potentials of the hydrogen and carbon atoms become

$$V_H = -\frac{e^2}{a_0} \exp \left(-\frac{R(u-v)}{a_0} \right) \left(1 + \frac{2a_0}{R(u-v)} \right),$$

$$V_C = -\frac{4e^2}{a_0} \exp \left(-\frac{1.475R}{a_0}(u-v) \right) \\ \times \left\{ \frac{1.07}{4} \left(\frac{R}{a_0} \right)^2 (u-v)^2 + \frac{2.175}{2} \left(\frac{R}{a_0} \right) \right. \\ \left. + 2.213 + \frac{2a_0}{R(u-v)} \right\}$$

where R is the distance from the oxygen atom to the atom under consideration. c_{n7} may be written, for example, in terms of its component integrals as follows:

$$c_{n7} = \frac{\sum_i \sum_j \int (c_{n2}\psi_2 + c_{n3}\psi_3 + c_{n4}\psi_4) (V_{Hi} + V_{Cj}) \psi_7}{E_n - E_7} \quad (11)$$

where the indices i and j refer to the various hydrogen and carbon atoms, respectively. Take for example the integral $\int \psi_2 V_{Hi} \psi_7 d\tau$ (12) contributing to c_{n7} . We write the radial parts of ψ_2 and ψ_7 in elliptic coordinates

$$\begin{aligned}\psi_2 \equiv \psi_{3s} &= \frac{1}{81(3\pi)^{\frac{1}{2}}} \left(\frac{2}{a_0}\right)^{\frac{3}{2}} \left(27 - 18\left(\frac{R_i}{a}\right)(u+v)\right. \\ &\quad \left.+ 2\left(\frac{R_i}{a_0}\right)^2(u+v)^2\right) \exp\left(-\frac{R_i(u+v)}{3a_0}\right), \\ \psi_7 \equiv \psi_{3d_{xz}} &= \frac{(2)^{\frac{1}{2}}}{324\pi^{\frac{1}{2}}} \left(\frac{1.5}{a_0}\right)^{\frac{3}{2}} (1.5)^2 \left(\frac{R_i}{a_0}\right)^2 (u+v)^2 \\ &\quad \times \exp\left(-\frac{1.5}{6} \frac{R_i}{a_0}(u+v)\right) \frac{xz}{r^2}.\end{aligned}$$

The factor xz/r^2 in ψ_7 refers to the angular part in the original polar coordinates. It is now convenient to transform to a new set of coordinates such that the new z axis lies along the line joining the two atomic centers. The old coordinates in terms of the new are then given by

$$\begin{aligned}x &= \alpha_1 x' + \beta_1 y' + \gamma_1 z', \\ y &= \alpha_2 x' + \beta_2 y' + \gamma_2 z', \\ z &= \alpha_3 x' + \beta_3 y' + \gamma_3 z'.$$

γ_1, γ_2 , and γ_3 are the direction cosines of the new z axis in the old coordinate system and are equal to X_i/R_i , Y_i/R_i , and Z_i/R_i , respectively. X_i , Y_i , and Z_i are the coordinates of the i th atom in the initial coordinate system, since the oxygen atom is at the center of coordinates. Since the directions of the new x and y axes are immaterial, the α 's and β 's can be left arbitrary, and as we shall see do not enter into the final expression for the integral. By symmetry considerations only even powers of x' and y' contribute. Therefore the contributing terms in xz are

$$xz = \alpha_1 \alpha_3 x'^2 + \beta_1 \beta_3 y'^2 + \gamma_1 \gamma_3 z'^2.$$

Since the integral with x'^2 is the same as with y'^2 and since $\alpha_1 \alpha_3 + \beta_1 \beta_3 + \gamma_1 \gamma_3 = 0$, this can be simplified to $xz = \gamma_1 \gamma_3 (z'^2 - x'^2)$. The integral (12) can then be written in the form

$$I_{12} = \gamma_1 \gamma_3 \int F(u, v) \exp(-au - bv) (z'^2 - x'^2) du dv.$$

$F(u, v)$ is a polynomial in u and v and conse-

quently the integral can be easily evaluated in terms of the elementary integrals

$$\begin{aligned}A_m &= \int_1^\infty u^m \exp(-au) du, \\ B_n &= \int_{-1}^1 v^n \exp(-bv) dv.\end{aligned}$$

The values of the various integrals in electron volts contributing to c_{n7} and c_{n8} are given in Table II for various distances. The calculation of the coefficients c_{n7} and c_{n8} involve a knowledge of the coefficients c_{n2} , c_{n3} , and c_{n4} obtained from a solution of the secular Eq. (6). The matrix components H_{mn} in (6) are computed in the way described for I_{12} . Their values along with those of the three roots of the determinant in electron volts and the corresponding three sets of coefficients are given in Table III.

The coefficient a_3 in Eq. (10) turned out to be very small so that all but the first term in (9) could be neglected. The contributions to β_α due to transitions to the three levels χ_1 , χ_2 , and χ_3 , corresponding to W_1 , W_2 , and W_3 , are listed below:

$$\begin{aligned}\beta_{\alpha 1} &= 2.18 \times 10^{-35}, \\ \beta_{\alpha 2} &= -1.02 \times 10^{-35}, \\ \beta_{\alpha 3} &= -3.86 \times 10^{-35}.\end{aligned}$$

Summing over the levels we have

$$\sum \beta_\alpha = -2.70 \times 10^{-35},$$

to be compared with the experimental value $\beta = -1.4 \times 10^{-35}$ for laevo-secondary butyl alcohol. In calculating the rotatory parameter for a new configuration where the H atom is rotated through an angle θ it should be remembered that the coordinate system was so defined that the z axis was coincident with the C—O bond and the x axis normal to the C—O—H plane. Keeping this choice of coordinates such a rotation can be represented as a rotation around the z axis through an angle $-\theta$ of all except the three atoms C—O—H. The calculation remains the same except that we use a new set of γ 's in calculating the coefficients c_{n7} and c_{n8} defined by

$$\begin{aligned}\gamma_1' &= \gamma_1 \cos \theta + \gamma_2 \sin \theta, \\ \gamma_2' &= -\gamma_1 \sin \theta + \gamma_2 \cos \theta, \\ \gamma_3 &= \gamma_3.\end{aligned}$$

TABLE II.

| R | V=V _H 2.09 | V=V _H 2.40 | V=V _H 3.16 | V=V _C 2.43 |
|---|---|---|---|---|
| $\int \psi_2 V \psi_7$ | $-0.0935 \gamma_1 \gamma_3$ | $-0.1859 \gamma_1 \gamma_3$ | $-0.2278 \gamma_1 \gamma_3$ | $-0.8836 \gamma_1 \gamma_3$ |
| $\int \psi_3 V \psi_7$ | $.3219 \gamma_1 \gamma_2 \gamma_3$ | $.4122 \gamma_1 \gamma_2 \gamma_3$ | $.3759 \gamma_1 \gamma_2 \gamma_3$ | $1.931 \gamma_1 \gamma_2 \gamma_3$ |
| $\int \psi_4 V \psi_7$ | $.3564 \gamma_1 \gamma_3^2$ $+ .0115 \gamma_1 (1-3\gamma_3^2)$ | $.4452 \gamma_1 \gamma_3^2$ $+ .0110 \gamma_1 (1-3\gamma_3^2)$ | $.4053 \gamma_1 \gamma_3^2$ $+ .0098 \gamma_1 (1-3\gamma_3^2)$ | $2.083 \gamma_1 \gamma_3^2$ $+ .0507 \gamma_1 (1-3\gamma_3^2)$ |
| $\int \psi_2 V \psi_8$ | $-.0935 \gamma_1 \gamma_2$ | $-.1859 \gamma_1 \gamma_2$ | $-.2278 \gamma_1 \gamma_2$ | $-.8836 \gamma_1 \gamma_2$ |
| $\int \psi_3 V \psi_8$ | $.3564 \gamma_1 \gamma_2^2$ $+ .0115 \gamma_1 (1-3\gamma_2^2)$ | $.4452 \gamma_1 \gamma_2^2$ $+ .0110 \gamma_1 (1-3\gamma_2^2)$ | $.4053 \gamma_1 \gamma_2^2$ $+ .0098 \gamma_1 (1-3\gamma_2^2)$ | $2.083 \gamma_1 \gamma_2^2$ $+ .0507 \gamma_1 (1-3\gamma_2^2)$ |
| $\int \psi_4 V \psi_8 = \int \psi_3 V \psi_7$ | | | | |

The results for orientation II are then

$$\beta_{\alpha 1} = -0.934 \times 10^{-35},$$

$$\beta_{\alpha 2} = -0.248 \times 10^{-35}, \quad \sum \beta_{\alpha} = -9.67 \times 10^{-35},$$

$$\beta_{\alpha 3} = -8.493 \times 10^{-35}.$$

In the case of free rotation of the hydroxyl hydrogen about the C—O axis it is necessary to average the expression $c_{n5}c_{n8} - c_{n6}c_{n7}$ in Eq. (10), over the angle of rotation θ from 0 to 2π . (As before we neglect the remaining small terms containing a_9 .) The result is

$$\begin{aligned} \beta_{\alpha n} = & \sum_{ij} D_{ni} E_{nj} \gamma_{3i} (\pi/2) (\gamma_{1i} \gamma_{2i} \gamma_{2j}^2 \\ & - \gamma_{1i} \gamma_{2i} \gamma_{1j}^2 + \gamma_{1i}^2 \gamma_{1j} \gamma_{2j} - \gamma_{2i}^2 \gamma_{1j} \gamma_{2j}) \\ & + \pi (\gamma_{1i} \gamma_{2j} - \gamma_{2i} \gamma_{1j}) [(A_{ni} \gamma_{3i} \\ & + B_{ni} \gamma_{3i}^2 + C_{ni}) (G_{nj} + F_{nj} \gamma_{3nj})] \\ & - \pi E_{nj} \gamma_{3j} \{ (B_{ni}/4) [-\gamma_{1i}^2 \gamma_{1j} \gamma_{2i} \\ & + \gamma_{1i}^3 \gamma_{2j} - \gamma_{2i}^3 \gamma_{1j} + \gamma_{2i}^2 \gamma_{1i} \gamma_{1j}] \\ & + C_{ni} (\gamma_{1i} \gamma_{2j} - \gamma_{1j} \gamma_{2i}) \}, \end{aligned}$$

where the summation i and j extends over all the atoms except the three atoms C—O—H. The quantities A_j to E_j are derived from integrals similar to those in Table II and are defined below.

$$\begin{aligned} A_{ni} &= \frac{-c_{n2} \int \Psi_{3s} V_i \Psi_{3d} (Z_i^2 - X_i^2)}{2.95}, \\ B_{ni} &= \frac{-c_{n4} \int \Psi_{3p} V_i \Psi_{3d} (Z_i^3 - 3Z_i X_i^2)}{2.95}, \\ C_{ni} &= \frac{-c_{n4} \int \Psi_{3p} V_i \Psi_{3d} X_i^2}{2.95}, \end{aligned}$$

$$D_{ni} = \frac{-c_{n3} \int \Psi_{3p} V_i \Psi_{3d} (Z_i^3 - 3Z_i X_i^2)}{2.95},$$

$$E_{nj} = \frac{+c_{n3} \int \Psi_{3p} V_j \Psi_{2p} (Z_j^2 - X_j^2)}{7.54},$$

$$F_{nj} = \frac{+c_{n4} \int \Psi_{3p} V_j \Psi_{2p} (Z_j^2 - X_j^2)}{7.54},$$

$$G_{nj} = \frac{c_{n2} \int \Psi_{3s} V_j \Psi_{2p} Z_j}{7.54},$$

where V_i refers to the potential of the i th atom. Z_i and X_i refer to the coordinates defined such that the z axis lies along the line joining the atom i with the oxygen atom. The functions Ψ_{3s} , Ψ_{3p} , Ψ_{2p} and Ψ_{3d} are the functions $\Psi_{3d_{zz}}$, Ψ_{3p_y} , etc., with the factors xz , y , etc., omitted. The result is then $\beta_{\alpha} = +0.68 \times 10^{-35}$. If one should neglect the small parts of c_{n5} and c_{n6} which arise from the atoms outside of the C—O—H plane the result would be identically zero.

DISCUSSION OF RESULTS

It is clear from the above results that the magnitude as well as the sign of the rotation for a given absolute configuration depends upon the relative orientation of the groups about the single bonds. Thus to determine the absolute configuration we must know how to weight the various orientations. Further, since the above calculations took no account of the neighboring molecules the question arises as to whether the gaseous value so calculated corresponds to that of the liquid. In a series of ten compounds inves-

tigated by Guye and Amarel¹⁵ the value for the specific rotation always shows agreement in sign between liquid and vapor and agrees always within a factor of two in magnitude. One of these compounds, amyl alcohol, which is very similar to our case, changed from 5.1 in the liquid to 6.5 in the vapor. There are cases known, however, where the sign changes. Thus Kenyon¹⁶ found a value for $[\varphi]$ of 20.1 for β -hexyl stearate in alcohol as compared to -8.93 in carbon disulfide. The effect of solvents has been reviewed by Condon² and by Lowry in *Optical Rotatory Power*.

Since orientations I and II correspond to the maximum hydrogen bonding with the oxygen in the gas phase, our calculations lead to the assignment of our configuration in the figure to the laevo form. This happens to agree with Kuhn⁷ and to disagree with Boys⁸ and Kirkwood.³ Had we used the result calculated on the basis of free rotation of the hydroxyl the assignment would have agreed with Boys and Kirkwood. This would be equivalent to Kirkwood's assumption of axial symmetry of the O—H group. However the evidence is against the possibility of free rotation.^{17, 18}

We should expect that optically active molecules in the vapor phase should show very small temperature coefficients unless the various orientations were separated by small energy differences. If the minima of potential energy for the rotations about single bonds are deep and sharp then the temperature coefficient would be very small due to the very small number of freely rotating molecules at ordinary temperatures. The temperature coefficient in the liquid may be enhanced due to association. The value of the optical rotation should approach that of the vapor as the critical temperature is reached, aside from the small field effect due to the factor $(n^2 + 2)/3$.

ALTERNATIVE CALCULATIONS

Replacing the term in brackets in (5) by the potential energy due to dipole charges as assigned by Condon, Altar, and Eyring³ we obtain

¹⁵ Guye and Amarel, Arch. Sci. Phys. Nat. Geneva **33**, 409, 513 (1895).

¹⁶ Pickard and Kenyon, J. Chem. Soc. **105**, 830 (1914).

¹⁷ Schumann and Aston, J. Chem. Phys. **6**, 480 (1938).

¹⁸ Borden and Barker, J. Chem. Phys. **6**, 553 (1938).

$\beta_\alpha = +5.7 \times 10^{-37}$ for orientation I. In this calculation no expansion was made of the potential of the dipoles around the oxygen atom since it was found that the series rapidly diverged in this case. This result is much smaller and even of opposite sign.

A value of $\beta_\alpha = -1.2 \times 10^{-35}$ was obtained upon considering the same perturbations as previously in the C—O—H group but only the dipoles in the rest of the molecule. This is of the same order of magnitude as that obtained above. It should be pointed out that in the dipole calculation the carbon atoms being negative give contributions of opposite sign to those of the hydrogen atoms. In the electron cloud distribution calculation (i.e., the calculation first described) both carbon and hydrogen atoms contribute with the same sign. This is in agreement with the fact discussed by Kuhn that the sign of the rotation remains fixed if one replaces the largest group by one greater in mass than the next largest one. Mulliken¹⁹ has pointed out that the electron cloud distribution corresponding to homopolar bonds gives rise to an assignment of dipoles to the bonds. Smyth²⁰ quotes a calculation by Hirschfelder which shows that in the case of the C—H bond this calculation agrees with previous estimations. In the case of large dipoles or ions arising from polar eigenfunctions the corresponding charge distribution and potential can be calculated in the same way and the calculation of the rotatory power carried through as before. Our procedure is thus a general one, applicable to any molecule or crystal.

Our eigenfunction for the chromophoric electron in the normal state spreads out more than the function calculated by Hartree and Black²¹ for oxygen. This arises from the screening constants which were necessary in order to give the observed ionization and resonance potentials. Exact eigenfunctions for two states associated

TABLE III.

| | | | | | | | |
|----------|--------|----------|--------|----------|--------|----------|--------|
| H_{22} | -.6502 | W_1 | -.7629 | W_2 | -.5593 | W_3 | -.4177 |
| H_{23} | .1025 | | | | | | |
| H_{24} | .0489 | c_{12} | -.6923 | c_{22} | .6822 | c_{32} | .2359 |
| H_{34} | -.1155 | c_{13} | .5460 | c_{23} | .2835 | c_{33} | .7975 |
| H_{33} | -.5314 | c_{14} | .4718 | c_{24} | .6740 | c_{34} | -.5555 |
| H_{44} | -.5585 | | | | | | |

¹⁹ Mulliken, J. Chem. Phys. **3**, 573 (1935).

²⁰ Smyth, J. Phys. Chem. **41**, 214 (1937).

²¹ Hartree and Black, Proc. Roy. Soc. **A139**, 311 (1933).

with transitions would no doubt show changes in more than one electron. Treatments such as that of Zener and Slater take care of this by assigning different screening constants to electrons which do not change quantum numbers. Our treatment which attributes to a single electron the entire change in a transition should give better results for properties in which the operators can be broken into a sum of terms depending on single electrons such as optical activity than for operators such as the energy where such a decomposition into terms depending upon single electrons is not possible.

In considering the excited states the $2py$ and $2pz$ functions of the oxygen have been treated as though they were completely available to the excited chromophoric electron whereas these states are at least partly filled by the two valence electrons contributed by the adjacent C and H atoms. However, there are effects which at least partly compensate for this deficiency in our treatment. (1) The effect of these valence electrons on the chromophoric electron is at least partly taken care of by the assumed charge distribution. (2) If the screening constant of these bonding electrons were changed the $2pz$ and $2py$ functions would automatically become included in the upper state. (3) The removal of the $2px$ antibonding electron will modify the bonding electrons such that the $2pz$ and $2py$ states will be somewhat more empty.

Whether or not this term or the term calculated by Kirkwood is the more important will be one of the subjects of further investigation.

In the case of one electron transitions it is easy to assign a unique center about which to calculate the magnetic moment. However, for a multiple electron transition the calculated optical activity will depend upon the center chosen unless the functions used to represent the initial and final states are eigenfunctions of some Hamiltonian operator. With our present knowledge of one-electron eigenfunctions this is difficult to insure in practice. That this is true may be seen from the following.

The magnetic moment for the transition from the state a to the state b may depend upon the

center of coordinates chosen. If \mathbf{r}_k is the position vector in the first coordinate system and \mathbf{r}_i that in the new system, then

$$\mathbf{r}_i = \mathbf{r}_k - \mathbf{R}_{ik}, \quad (12)$$

where \mathbf{R}_{ik} is the vector joining the two centers. The magnetic moment for the transition about the new center is then

$$(b|\mathbf{m}|a) = \frac{e}{2mc}(\mathbf{r}_i \times \mathbf{P})_{ba} \\ = \frac{e}{2mc}\{(\mathbf{r}_k \times \mathbf{P})_{ba} - \mathbf{R}_{ik} \times \mathbf{P}_{ba}\}, \quad (13)$$

where the large \mathbf{P} is the electronic momentum. Using the relation

$$(\hbar/2\pi i)\dot{\mathbf{r}} = H\mathbf{r} - \mathbf{r}H, \quad (14)$$

one finds that

$$\mathbf{P}_{ba} = \frac{2\pi i m v_{ba}}{e}(b|\mathbf{p}|a), \quad (15)$$

provided that the functions b and a are eigenfunctions for some Hamiltonian operator H . The second term in (13) is therefore perpendicular to the electric moment vector $(b|\mathbf{p}|a)$, and on forming the dot product with $(b|\mathbf{p}|a)$ will give no contribution to the optical activity. However, this is contingent on relationship (15) which depends upon b and a being eigenfunctions for some Hamiltonian operator. If, for example, we consider the case where a is an eigenfunction for some Hamiltonian operator H and b is some linear combination of eigenfunctions of H , then in place of \mathbf{P}_{ba} in (13) we have a sum of terms connecting state a with a linear combination of eigenstates b . The orthogonality between this sum of terms and the corresponding sum of terms for the electric moment will now no longer hold and we will get a contribution which will depend upon where the center for calculating the magnetic moment is chosen. This illustrates, from the present point of view, one of the more serious difficulties in considering more than one electron transitions such as one would have if one used bond functions for the upper and lower states.