OCTOBER 15, 1937 PHYSICAL REVIEW VOLUME 52

Magnetic Rotation Spectra of Diatomic Molecules†

THOMAS CARROLL*
Sloane Physics Laboratory, Yale University, New Haven, Connecticut

(Received July 6, 1937)

The general theory of the Faraday effect associated with a single molecular absorption line is presented. The effect of the perturbation of the transition probabilities by the field in producing asymmetrical rotation is discussed, and calculated for alkali band systems and for I_2. The observations on asymmetrical rotation in I_2 agree with the predictions. The longitudinal Zeeman patterns and the changes in these patterns produced by the field are related to the vector model by use of the criterion that transitions which involve little change in the direction of J, the rotational axis, are the most probable ones. It is shown that all known facts about the $^1\Sigma\leftarrow{}^1\Sigma$ magnetic rotation systems of Na_2 and K_2 can be explained by assuming the upper state to be perturbed by an unknown $^3\Pi_0$ state. The constants have been calculated for this predicted perturbing state in Na_2.

THE magnetic rotation spectrum of a gas is the spectrum of the light transmitted through crossed polarizing prisms when the magnetized gas is placed between the prisms so that the light travels along the magnetizing field. The observation by Righi in 1898 that I_2, Br_2 and NO_2 produced such spectra provided the first evidence that a magnetic field could affect band lines.[1] Wood, from 1906 to 1909 cataloged extensively lines of the magnetic rotation spectrum of Na_2 in the region of the red and blue-green band systems, and as well measured the sign of the rotation outside six iodine absorption lines covered by the broadened mercury green line.[2] After the advent of the modern theory of band spectra, Loomis[3–5] observed that magnetic rotation lines appeared just outside the heads of the absorption bands of $^1\Pi\leftarrow{}^1\Sigma$ band systems of the alkali molecules. He and his students used the magnetic rotation spectra of such band systems with conspicuous success to obtain extended vibrational analyses and thus to estimate accurately the heats of dissociation. After the rotational analysis of the Na_2 red bands made it clear that these bands are of the $^1\Sigma\leftarrow{}^1\Sigma$ type, the problem arose of explaining the strong magnetic rotation spectrum of Na_2 in the red. $^1\Sigma\leftarrow{}^1\Sigma$ lines should show no Zeeman effect, nor Faraday effect, since $^1\Sigma$ states are insensitive to a magnetic field. Fredrickson and Stannard[6] succeeded in assigning quantum numbers to the magnetic rotation lines of the Na_2 red system in a very plausible way, which suggested strongly that perturbation of a few of the levels of the upper $^1\Sigma$ state was responsible for the appearance of the magnetic rotation spectrum. It is the purpose of this paper to corroborate this hypothesis as to the nature of this long puzzling magnetic rotation spectrum of the $^1\Sigma\leftarrow{}^1\Sigma$ system of Na_2. In particular, it will be shown that the sign of the rotation as well as its asymmetry is in agreement with modern theory. The magnetic rotation spectrum of the analogous infrared system of K_2 has been investigated, and its general characteristics fit nicely with the same explanation used for Na_2. In the theoretical discussion particular attention is given to the difference between the Faraday effect connected with a molecular spectral line, and that connected with an atomic line. Emphasis is placed on the quantum mechanical refinement of Faraday effect theory.

1. EXPERIMENTAL DETAILS

For the magnetic field a solenoid was used, as had been done by Loomis and Fredrickson. The

---

† Part of a dissertation presented to the Faculty of the Graduate School of Yale University in candidacy for the degree of Doctor of Philosophy.

* Now at College of New Rochelle.

[1] A. Righi, Comptes rendus **127**, 216 (1898); **128**, 45 (1898).

[2] R. W. Wood and F. E. Hackett, Astrophys. J. **30**, 399 (1909).

[3] F. W. Loomis and R. E. Nussbaum, Phys. Rev. **40**, 380 (1932).

[4] F. W. Loomis and M. J. Arvin, Phys. Rev. **46**, 286 (1934).

[5] P. Kusch, Phys. Rev. **49**, 218 (1936).

[6] W. R. Fredrickson and Carl R. Stannard, Phys. Rev. **44**, 632 (1933).

solenoid has two layers of flat copper ribbon (0.5″×0.056″) wound on edge, with the plane of the ribbon perpendicular to the axis of the solenoid. There is a space of $\frac{1}{4}''$ between the layers for cooling water, and a water jacket surrounds the two layers. Thin dipped enamel provides sufficient insulation between turns. The completed solenoid is $2\frac{1}{2}$ feet long, with a useful working space 2 inches in diameter. Laminar type windings of flat copper ribbon use the winding space most efficiently, and at the same time allow for effective cooling. Heat developed in the coil never has to pass through more than one layer of insulation before it reaches the cooling water, which makes contact with both edges of every turn. The completed solenoid weighs about 75 pounds.

The maximum current obtainable, 125 amperes, was run through the two layers in series. The resistance under these conditions is about 0.3 ohm, and $\int Hdl$ along the axis of the solenoid is $1.2(10)^5$ gauss cm. The field at the center of the solenoid is therefore about 2000 gauss.

The continuous light source, condensing lens, polarizing prism, absorption tube inside the solenoid, analyzing prism and focusing lens were mounted in the order named directly in line with the slit of the grating spectrograph. A 100 cp Pointolite lamp was used for continuous source, because this highly concentrated source could be collimated rather well into a parallel beam before passage down the long absorption tube. Steel absorption tubes 4 feet long and 1 inch in diameter were used for the alkali metals. It was found that the steel did not appreciably shield the inside of the tube from the magnetic field of the solenoid. Electrical heating was provided for the two and one-half feet of the absorption tube actually inside the solenoid. The ends of the tube were cooled and the windows waxed on. A few lumps of the metal were placed at the middle, and distillation to the cool ends was hindered by the presence of about 5 mm of nitrogen or helium.

The proper vapor density for obtaining the magnetic rotation spectra was always determined in advance by finding the temperature of the absorption tube which gave strong, but well defined, discrete absorption lines. In general, for frequencies well outside the Zeeman pattern of a line, the magnitude of the rotation due to the line is proportional to the number of molecules per unit volume, the path length, and the field strength. In a molecular band system, however, too high a vapor density develops so many overlapping bands that absorption becomes practically complete and no magnetically rotated light can be observed. The temperatures used for Li_2, Na_2, and K_2 were approximately 850°, 460°, and 350°C, respectively. All spectrograms were made with a 21-foot grating in a stigmatic mounting, which gave a dispersion of 4.9A per mm in the first order around 8000A. The exposure times necessary for photographing magnetic rotation spectra ranged from one hour for the rotation in the Na_2 red bands, to 36 hours for the infrared K_2 system, using Eastman *Q* plates.

Some information about the sign of the rotation in the red Na_2 system and the infrared K_2 spectrum was obtained by the familiar quartz wedge scheme. A pair of 25° wedges was used, placed directly in front of the slit. For these spectrograms the crossed analyzing prism was placed between the slit and the mirror of the stigmatic mounting.

2. General Theory of the Faraday Effect Associated with a Single Spectral Line

Light propagated along the field through a magnetized medium experiences longitudinal magnetic double refraction. There are two and only two types of electromagnetic waves which progress along the field without change of form, but with different velocities. If the medium is isotropic except for the field, these two types are circularly polarized waves which rotate in the sense of a right- (+) or left-handed (−) screw advancing along the field direction. Light of any polarization entering such a medium can be considered decomposed uniquely into the sum of two circular waves with opposite polarizations. The character of the polarization at any point in the medium is most easily obtained by considering the difference in phase of the two circular polarizations occasioned by the difference of their velocities of propagation to the point. This difference of indices of refraction of the two circular polarizations is determined by the longitudinal Zeeman pattern of the absorption lines. Those components absorbing right- or

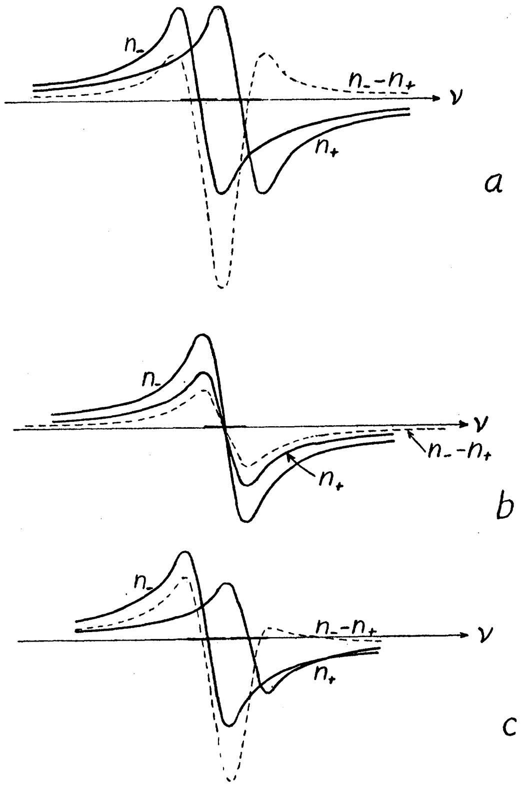

FIG. 1. Dispersion curves and Faraday rotations for light propagated along the magnetic field through a gas with a single sbsorption line. The half-widths of the components in absorption are indicated by the thickened portions of the frequency axis. (a) Lorentz doublet on classical theory. (b) Hypothetical line for which the intensities of the components are perturbed by the field, but for which there is no change in their frequencies. (c) Lorentz doublet with components both shifted in frequency and perturbed in intensity by the field.

left-handed polarizations affect the indices of refraction for right- or left-handed polarizations respectively, and to the same relative degree that they affect the absorption. Let plane polarized light, equivalent to two equal waves of opposite circular polarizations, be incident normally on a slab of magnetized medium. The longitudinal double refraction of the magnetized substance causes these disturbances to be propagated with unequal velocities. If the absorption coefficient for both waves is the same, their resultant at a distance l inside the medium will again be plane polarized, but with its plane of polarization turned through an angle θ given by

$$\theta=(\pi l/\lambda_{\mathrm{vac}})(n_--n_+), \tag{1}$$

where $n\pm$ = index of refraction of right- (+) or left- (−) handed polarized light.

If the absorption coefficients for the two circular waves are unequal, the originally plane polarized light will become elliptically polarized at any point in the medium. The angle θ represents in this case the angle through which the major axis of the ellipse has been turned. The dotted line in Fig. 1a has a height proportional to (n_--n_+). This line shows the variation of θ connected with one absorption line showing a normal Lorentz doublet in longitudinal observation, with both components of the doublet of equal intensity. The rotation is symmetrical about the no-field position of the absorption line, approximately (exactly, if ν^2 is plotted along the horizontal axis instead of ν). Fig. 1b illustrates the case of a hypothetical line whose two magnetic components are not split apart by the magnetic field, but only changed in intensity. In this case, θ varies antisymmetrically about the absorption line. Fig. 1c illustrates the case where the field both splits apart the magnetic components of the line and changes the intensities at the same time. In this case the magnitude of θ is largest outside the low or high frequency side of the line according as the high or low frequency circular component is weakened by the field.

The rotation connected with absorption lines with more complex Zeeman patterns can be determined when the splittings and intensities of the components in the field are known. With no field, the sum of the intensities of the components affecting right circular light is exactly equal to the sum of the components affecting left circular light. This sum rule is just the mathematical statement of the fact that an unmagnetized gas does not alter the state of polarization of a light wave, provided that the direction of propagation of the light wave does not destroy the isotropy of the gas, producing optical activity. When a magnetic field is applied there are two distinct ways in which the sum of the intensities of the right- and left-handed components may become unequal. (1) If the ground state is magnetic, the different magnetic components of the ground level will have altered Boltzmann factors, which produce a difference in their populations. This will cause a difference in intensities of right- and left-handed components of the line roughly proportional to $(\Delta\nu)_n/kT((\Delta\nu)_n=$normal Zeeman splitting). This is the so-called "paramagnetic rotation," important mainly at low temperatures. This type of rotation is asymmetric about an absorption line. Since no known band magnetic rotation spectrum is due to paramagnetic molecules, we shall discuss only the asymmetrical rotation arising from the second cause. (2) The perturbation of the transition probabilities by the magnetic field may cause the sum of the intensities of the right-handed to be different from the sum of the intensities of the left-handed components of a line, the difference being proportional to the field strength. (Throughout the paper we calculate only the Zeeman splittings and intensity changes which are linear in H. In all cases we assume that the Zeeman splitting of the absorption line and the change in intensity of the Zeeman components are due to the magnetic sensitivity of the upper level of the absorption line.)

The Zeeman splitting of the upper state energy levels, proportional to H, is caused by the diagonal matrix elements of the perturbing potential $-\mu_z H$, while the difference in intensities is produced by nondiagonal matrix elements of μ_z. ($\mu_z=$electronic magnetic moment along z, the field direction.) In atoms μ_z is a diagonal matrix, in the J, M representation; hence the Zeeman pattern of an atomic absorption line is symmetrical about the no-field line both as to position and intensities, and the resulting variation of θ is symmetrical about the line as in Fig. 1a. (This statement is not true if there is a tendency toward the Paschen-Back effect, but no Faraday rotations have ever been observed near atomic lines at field strengths high enough for the Paschen-Back effect to become important.) Physically, this means only that the motion of the atom in the upper state is one of pure precession, in which the J vector remains constant in magnitude but precesses with uniform speed about the field direction, making a constant angle with it.

In molecules, on the other hand, μ_z is not a diagonal matrix in the quantum number J. While the total angular momentum of the molecule along z is fixed, $\mathbf{J}$ itself varies both in magnitude and direction. In other words the axis of rotation of the molecule wobbles as it precesses about the field. The magnetic field exerts a torque on the molecule which tends to line up with the field the magnetic moment μ_J, which is directed oppositely to J in all regular states. The resulting nutational motion of the $\mathbf{J}$ vector is a compromise between this tendency and the gyroscopic action which tends to produce pure precession. The nutational or "lining up" action of the field on the molecule produces changes in the energy levels proportional to H^2, and the higher even powers of H only, and such higher order effects we are neglecting. Nevertheless, the transition probabilities of any transition of the molecule to or from such a "nutating" state will be changed by an amount proportional to H (and higher odd powers of H). The ψ functions for a molecule in such a nutating state, correct to the first order of H, will be

$$\psi(n, J, M)=\psi^0(n, J, M)+\frac{(-H\mu_z(n, J, M; n', J+1, M))}{E_J-E_{J+1}}\psi^0(n', J+1, M)+\frac{(-H\mu_z(n, J, M; n', J-1, M))}{E_J-E_{J-1}}\psi^0(n', J-1, M). \tag{2}$$

The total angular momentum of the molecule is no longer constant either in magnitude or direction, since the correct ψ function is a linear combination of ψ functions belonging to several J values. One may describe the fact that J is no longer rigorously a good quantum number by saying that the field causes radiationless transitions in which $\Delta J=\pm 1$, with appreciable probability. The nutating ψ function of Eq. (2) will have new nondiagonal matrix components of the electric moment, so that the transition probabilities to or from the nutating state (2) will be affected by the field linearly in H.

3. Rigid Molecules

We shall show in this section how both the sign and the asymmetry of the rotation due to a single magnetically sensitive absorption line of a rigid molecule can be predicted qualitatively and calculated. The Verdet constant (rotation per unit path length per unit field strength) connected with a single magnetically sensitive absorption line is composed of two parts,

$$V \equiv V_A + V_B.$$

V_A varies symmetrically with frequency about the absorption line (outside the Zeeman pattern, the frequency dependence is ($V_A \propto \nu^2/(\nu_{jk}{}^2 - \nu^2)^2$). This is the rotation which one gets on a classical theory where only the Zeeman splitting of the lines is considered, and not the change in intensity which may be produced by the field (Fig. 1a). V_B varies antisymmetrically about the absorption line. (Well outside the half-width of the line this variation with frequency is $V_B \propto \nu^2/(\nu^2 - \nu_{jk}{}^2)$.) This part of the rotation comes from calculating the difference produced by the field between the sum of the intensities of the components which scatter right-handed light and the sum of intensities of the components which scatter left-handed light. This term is calculable only by quantum mechanics, and is the essential quantum mechanical refinement in Faraday effect theory.

Making the rigid molecule assumption that the motion of the electrons about the internuclear axis is unaffected by the rotation of the molecule as a whole, only matrix elements of μ_z in (1) need be considered which are diagonal in the electronic quantum numbers n. Ω, the component of the electronic angular momentum along the internuclear axis, can be considered rigorously a good quantum number.

Explicit calculations for V_A due to a single line of a $^1\Pi \leftarrow {}^1\Sigma$ system (Li_2, Na_2, K_2 visible absorption bands) have been given by Serber.[7] The explicit formulae for the V_B terms produced by the individual lines of the $^1\Pi \leftarrow {}^1\Sigma$ systems are given in Appendix I. These V_B terms produced by the perturbation of the transition probabilities by the field are proportional essentially to the ratio of the Larmor frequency to the frequency of rotation of the molecule about **J**, which is given by the difference in energy between two adjacent rotational levels, $2BJ = h^2/4\pi^2 I$. The greater the moment of inertia I of the molecule, or the higher the magnetic field, the more nearly will the precessional frequency of J become comparable to the frequency of rotation of the molecule about J, and the more important the nutation terms become.

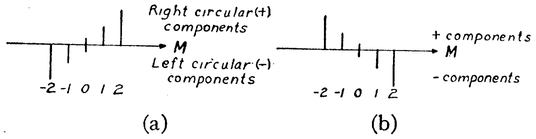

FIG. 2. (a) Longitudinal Zeeman pattern for an R branch line with $J=2$ in its upper state. The vertical lengths of the components are proportional to the intensities. (b) Longitudinal Zeeman pattern for a P branch line with $J=2$ in its upper state.

The sign of the rotation outside a line depends on the relative strengths and positions of the components of the longitudinal Zeeman pattern. Serber has shown that outside an R line of a $^1\Pi \leftarrow {}^1\Sigma$ transition, the rotation should be positive, while outside a P line, the rotation should be negative, considering only the V_A terms. Fig. 2a is the longitudinal Zeeman pattern for an R branch line with $J=2$ in its upper state. The vertical lengths of the components are proportional to the intensities. The upper half gives the pattern for right circular (+) light, the lower half for left circular (−) light. Assuming that the upper (magnetic) state is regular, that is, that the positive M levels lie highest in energy, and neglecting the perturbation of the intensities by the field, the diagram represents the longitudinal Zeeman pattern with ν increasing toward the right. Using the diagrams of Fig. 1, the rotation outside the line will be positive. Fig. 2b gives the corresponding pattern for a P branch line with $J=2$ in its upper state. In this case the rotation outside the line will be negative. The physical reason for the difference in the two patterns can be ascertained qualitatively from the following vector diagrams. (Fig. 3a, 3b.) When a molecule absorbs a + quantum ($M' = M'' + 1$), the **J** vector is turned more nearly parallel to the field (z direction). When the line is an R branch line ($J' = J'' + 1$), the amount of the turning is greater when M' is negative than when it is positive. Hence one should expect the components with negative M' to be weaker than those with positive M'. The molecule more frequently absorbs quanta in transitions which require little change in the orientation of the **J** vector, the axis of rotation. Stated wave mechanically, the ψ functions for states whose axes of rotation have nearly the same orientation in space overlap

---

[7] R. Serber, Phys. Rev. **41**, 489 (1932).

better to produce nonvanishing elements of the electric moment. Fig. 3 illustrates this. The relative probability or improbability of the various transitions indicated by arrows is judged by the amount of change in the orientation of the **J** vector which they entail. All the transitions are absorptive, in which the arrows point to the final, higher energy state. (Thus the dotted arrows apply to absorption transitions in which the ground state is magnetic.) The essential point which such diagrams illustrate is that when J and M change in the same algebraic sense during a transition, little change in the orientation of the molecule is entailed when M is positive and the transition is probable. When, however, M is negative, Fig. 3b, the change of M and J in opposite senses (algebraically) entails the least change in direction of **J**, and hence is the more probable case. Similar diagrams for Q branch transitions illustrate why the components with $M=0$ are strongest.

From Appendix 1 it can be seen that for an R branch line $V_B=k^2\nu^2/(\nu^2-\nu_{jk}^2)$, where k^2 is a positive number independent of ν. For a P branch line $V_B=-k^2\nu^2/(\nu^2-\nu_{jk}^2)$. This results from the fact that the presence of the field augments the + components of an R branch line, and diminishes the − components. The field has just the reverse effect on the components of a P branch line. This change in the intensities is greatest for the components with $M=0$. The torque on the molecule exerted by the field is $\boldsymbol{\mu}_j\times\mathbf{H}$, where μ_j is the average electronic magnetic moment along **J**. The nutation effect is largest therefore when **J** is perpendicular to **H**. ($M=0$.)

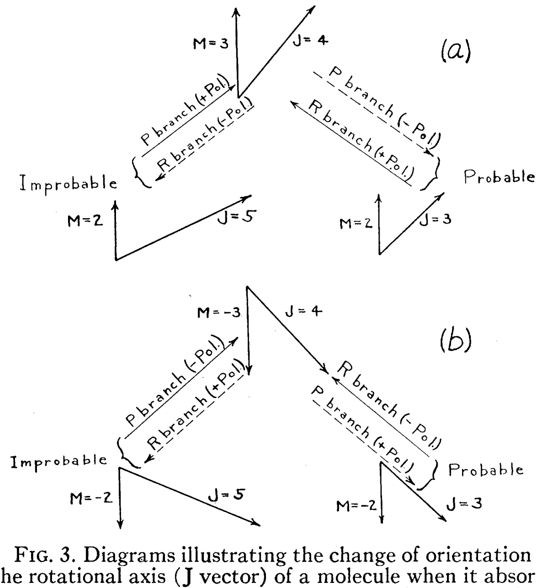

FIG. 3. Diagrams illustrating the change of orientation of the rotational axis (J vector) of a molecule when it absorbs circular quanta. The most probable transitions are those which can be accomplished with least change in the orientation of J. (a) Positive M; (b) negative M.

In Fig. 4 the upper diagram symbolizes the nutating upper state level with $M=0$. The two lightly drawn vectors represent the orientation of the rotational axis of the molecule as it nutates in the field. The projection of these vectors on the field direction is not zero, but the angular momenta connected with their precession just balances their projections along z, so that the total angular momentum about z is zero during all phases of the nutatory motion. (M remains a good quantum number, even with nutation; μ_z is a matrix diagonal in M.) The two light vectors when rotated about z generate cones which are the libration limits for the rotational axis in its nutatory motion. The top diagram of Fig. 4 assumes a regular state, that is that μ_j is opposite to **J** ($\mu_j=$ the average electronic moment along **J** on which the field exerts its torque). In this case, just as with classical tops, the angular momentum about the rotational axis increases to $J=4$ as μ_j is pulled toward alignment with the field, and decreases to $J=2$ when the nutation swings μ_j toward the antiparallel position.

Again in Fig. 4 all the transitions indicated by the arrows are to be considered absorptive transitions, that is, the arrows always point toward the state of highest energy. Probability of transition is improved by the field if the nutation makes the transition possible with less change in the direction of **J** than was necessary without the field. For the two transitions illustrated at the right of the diagram, the intensity is increased by the field, because the field itself tends part of the time to turn the rotational axis toward the direction of the J vector of the ground level. For the transitions indicated by the arrows at the left of Fig. 4, during the time when the field tends to make the rotational axes of the two states more aligned, the J values differ by 2, and radiation can only produce a unit change in the magnitude of J in any dipole transition. Hence nutation diminishes this transition probability.

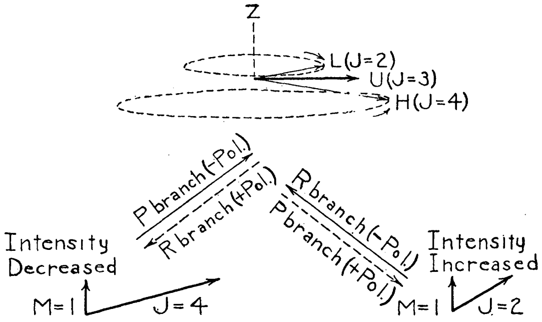

FIG. 4. Diagrams illustrating the effect of nutation on the transition probabilities.

It may seem at first sight curious that such quasi-classical vector diagrams give qualitatively the same effects on V_B and V_A as are calculated quantitatively with matrix elements. To be sure, when J and M for a state are known, we cannot say anything about the azimuth of J with the field, and we have only a probability distribution for the angle θ which J makes with the field. However, the vector of length $[J(J+1)]^{\frac{1}{2}}$ and projection M on H does have the most probable value of θ, or the direction of the maximum of the probability distribution in θ. The criterion that the orientation of J shall not change much in probable transitions is just another way of stating that the state functions of two levels connected by a probable transition must overlap well.

No detailed observation of the nature of the rotation due to a single band line of a ${}^1\Pi \leftarrow {}^1\Sigma$ system has been made. Considered together, the V_A and V_B terms predict, for R branch lines, strong positive rotation for frequencies just greater than that of the line, and weaker positive rotation for frequencies just less than that of the line. This makes another reason why only strong lines just to the violet of R band heads appear in Loomis' work.

The alteration of the transition probabilities in the presence of the field can be interpreted in terms of an energy level diagram (Fig. 5). Without the field, the anomalous dispersion curve for light of + polarization associated with the absorption line $U \leftarrow G$ is associated with scattering processes in which the molecule absorbs a quantum to enter the state U and then re-emits it spontaneously in returning to G. Suppose that the state U has a magnetic moment and that the rotational frequency is comparable to the Larmor frequency. Then the molecule will nutate in a magnetic field and the state U will share properties with the adjacent rotational states H and L, because there exist nondiagonal elements of the magnetic moment between these states and the state U. If now the transition $L \leftarrow G$ takes place, there is a finite chance that the magnetic field will cause a "radiationless transition" to the state U, from whence the molecule may emit a coherent quantum in returning to the state G. Thus the field affects the anomalous dispersion curve of + light in the vicinity of the line $U \leftarrow G$. Whether the change in intensity of the anomalous dispersion curve about the line $U \leftarrow G$ is an increase or decrease can be determined from the diagram of Fig. 4, as has already been explained.

4. ASYMMETRICAL ROTATION NEAR IODINE LINES

That magnetized I_2 vapor between crossed Nicols caused light to be transmitted through them in the region of the visible band system was discovered by Righi.[1] High dispersion and resolving power study of the spectrum was carried out later by Wood and Ribaud.[8, 9]

Modern theory ascribes the visible bands to an intersystem transition ${}^3\Pi_{0u}{}^+ \leftarrow {}^1\Sigma_g{}^+$, to the case *a* approximation, or $0_u{}^+ \leftarrow {}^1\Sigma_g{}^+$ if the large spin-orbit interaction is taken into account. At first sight this description of the electronic nature of the states involved in the visible bands seems to preclude the existence of the magnetic rotation spectrum, for the molecule does not have a magnetic moment along J, to the rigid molecule approximation. To be sure the upper ${}^3\Pi_0$ state has a magnetic moment of one Bohr magneton along the internuclear axis as a result of the magnetic anomaly of the spin. Because $\Omega = 0$ the magnetic moment remains perpendicular to J as the molecule rotates, and contributes nothing to the magnetic moment along J.

Serber has shown that the molecule in the upper state will acquire a magnetic moment along J when rotational distortion is taken into account.[7] This is due to nonuniform precession about the internuclear axis of the component of

---

[8] R. W. Wood and G. Ribaud, Phil. Mag. **27**, 1009 (1914).

[9] R. W. Wood and G. Ribaud, J. de phys. **4**, 378 (1914).

spin angular momentum perpendicular to this axis. Stated another way, the magnetic moment along J is produced by rotational distortion of the $^3\Pi$ spin multiplet. As we should expect, the faster the rotation, the larger the magnetic moment produced by rotational distortion. This explains why the magnetic rotation lines in I_2 appear to correspond to absorption lines of high J, and to be weak or absent near band heads or band origins. This hypothesis of spin uncoupling explains nicely the unusual sign of the rotation outside P and R lines. The wide $^3\Pi$ spin multiplet which contains the upper state for the visible bands is inverted, that is, states of largest Ω lie lowest in energy. This inversion of the spin multiplet causes magnetic energy sublevels with negative M to have the highest energy. Fig. 2 represents the polarization pattern for I_2 lines when frequency is assumed to increase toward the left in the direction of negative M. Formula (1) and the anomalous dispersion curves of Fig. 1 show that outside R branch lines the rotation should be negative, while outside P branch lines it should be positive.

Wood and Ribaud examined at high dispersion and resolving power the nature of the rotation outside six I_2 absorption lines covered by the broadened mercury green line.[8, 9] Loomis[10] found that five of these lines which show positive rotation were P lines, and the one which showed negative rotation on each side was an R line. Serber's hypothesis of spin uncoupling in an inverted $^3\Pi$ state explains this.

Wood and Ribaud published a qualitative sketch showing the nature of the rotation outside the six lines they observed.[8] They noted that the rotation seemed much stronger on one side of a line than on the other, in many cases as observed visually. Their qualitative sketch shows that outside the strongest P line observed (line 4 in Wood's numbering scheme), the positive rotation is strongest on the low frequency side of the line, while outside the strong R line observed, the negative rotation is strongest on the violet side of the line (line 3 on the published sketch).

Inasmuch as these are the only band lines outside which the detailed character of the rotation has ever been observed, it seemed of interest to see whether these asymmetries observed by Wood could be verified by extending Serber's calculation to take account of the perturbation of the intensities. The results of the calculation are given in Appendix 2. The calculations are not so readily visualized as those for rigid molecules, since we are now concerned with the effect of the simultaneous distortion of the electronic structure of the molecule in its upper state both by rotation of the molecule and by the field. The magnetic moment along J worked up by the rotation of the molecule is exceedingly small (of the order of 0.003 Bohr magneton when $J=100$).

In estimating the magnetic moment worked up by rotational distortion, Serber considered the nondiagonal rotational distortion matrix elements between $^3\Pi_0$ and $^3\Pi_1$ states. If the nondiagonal matrix elements of the magnetic moment between the same two states are considered, a V_B term also results for each line. The explicit formulae are in Appendix 2. The important thing about the formulae is the similarity in sign for the V_B terms for P and R branch lines. ($V_B=k\nu^2/(\nu_{jk}^2-\nu^2)$ for both branches, where k is a positive constant.) These V_B terms, when considered together with the V_A part of the rotation give just the type of asymmetry discernible near two lines in Wood's published sketch, which has been described above. Quantitative comparison of the V_B terms with the V_A terms calculated by Serber is impossible, for reasons given in the appendix, but qualitatively the V_B term does seem to explain the observed asymmetry, which was not expected by Wood in 1915, because all atomic lines give symmetrical rotations. Wood supposed the asymmetry to be

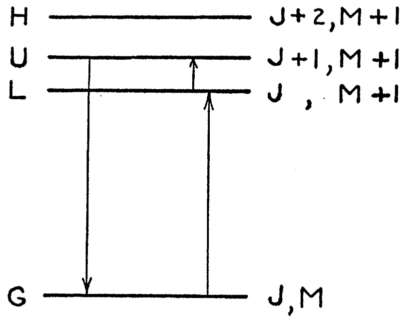

FIG. 5. Energy level diagram, illustrating the mechanism of the alteration of the intensities of the Zeeman components by the field.

---

[10] F. W. Loomis, Phys. Rev. 29, 123 (1927).

due to the influence of neighboring lines, but the very discreteness of the I_2 magnetic rotation spectrum makes this not very plausible.

5. Magnetic Rotation of the Sodium Red Bands

Strong magnetic rotation spectra are produced in the absorption band systems of Na_2 and K_2, which are due to transitions from the ground $^1\Sigma$ state to the first excited $^1\Sigma$ state of each molecule. The analogous absorption system of Li_2 gives no magnetic rotation spectrum. The Na_2 bands in question extend from the D lines to around 8800A; the K_2 bands have been observed from the K_2 resonance lines at 7600A to 10,500A. Ever since the analysis of these absorption bands in the light of modern quantum theory showed that the electronic states involved are $^1\Sigma$ states, the existence of a magnetic rotation spectrum produced by these bands has been a puzzle. To the rigid molecule approximation, molecules in $^1\Sigma$ states do not have on the average a magnetic moment in any direction. Hence there should be no Zeeman splitting of such states in a magnetic field, or no Zeeman or Faraday effects for band lines involving transitions to or from them. There are three difficulties with ascribing the effect to rotational distortion. First, all high J lines should be affected and cursory inspection of the spectra shows that this is not so. Secondly, Van Vleck's theory of rotational distortion shows that the magnetic moment along J produced by rotational distortion of the upper $^1\Sigma$ state is proportional to the ratio of the rotational frequency about J to the frequency of precession of the perpendicular component of electronic angular momentum about the internuclear axis. This is equal to the ratio of the energy difference between adjacent rotational levels of the $^1\Sigma$ state to the energy difference between the $^1\Sigma$ and the $^1\Pi$ state above it. This ratio is small in all these molecules, even for high J values, in agreement with the fact that the Λ doubling in the $^1\Pi$ states is exceedingly small. The third difficulty is the absence of the spectrum in Li_2. In connection with this work, a further search for magnetic rotation was made in the Li_2 red bands, but none was observed.

The absence of the spectrum in Li_2 makes it seem plausible that spin orbit interaction may be the cause of the unexpected magnetic rotation in Na_2 and K_2, for spin orbit interaction increases roughly as the cube of the nuclear charge. The separation of the Li, Na and K atomic resonance lines, which are proportional to the spin orbit interaction energies of the valence electrons are respectively 0.3, 17.2, and 57.5 cm^{-1}.

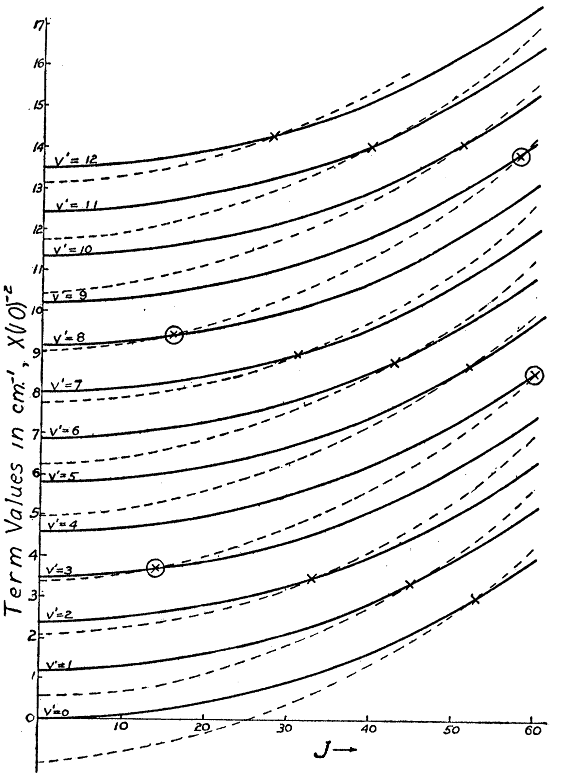

Fig. 6. Solid curves: energy levels of the upper state of the Na_2 red bands. ($^1\Sigma_u^+$). Broken curves: predicted energy levels of a $^3\Pi_{0u}^+$ state.

Fredrickson[6] succeeded in finding an assignment of quantum numbers for the lines of the red Na_2 magnetic rotation spectrum.[7] He discovered that most of the magnetic rotation lines involved a certain few of the upper state levels. He suggested on this basis the hypothesis that the spectrum was due to the perturbation of the upper $^1\Sigma$ state by some unknown magnetically sensitive state. The solid parabolic curves in Fig. 6 give the energies of the rotational states of the $^1\Sigma$ state as a function of J. (Since the B_v term in the rotation energy expression varies only slightly with v, the parabolas are almost parallel.) The energy levels found by Fredrickson to give magnetic rotation lines are marked by crosses.

Each of these levels will acquire a magnetic moment if it is perturbed by a level of a $^3\Pi$ state which does possess a magnetic moment. A perturbation between two levels may be described as a repulsion of the levels accompanied by a sharing of their properties. The magnetic moment which the perturbed $^1\Sigma$ level gets in this way will cause a Zeeman splitting for the level in a magnetic field, and hence magnetic rotation for transitions to this level. It is a fundamental rule in perturbation theory that the perturbation between two levels is appreciable only if the levels have the same J value and nearly the same energy. Therefore it should be possible to represent the levels of the $^3\Pi$ perturbing state on the diagram of Fig. 6 by a set of approximately parallel and equidistant parabolas which intersect the solid line parabolas very near the points indicated by crosses. It has been found that the set of perturbing state levels represented by the dashed curves in Fig. 6 do have their intersection point with the solid line parabolas very nearly at the crosses. The scale of the figure is too small to show the deviations. The positions of the dotted curves were arrived at in the following manner. (Unprimed letters refer to the constants of the $^3\Pi$ state.) It was observed that the large energy difference between perturbed rotational level $J'=14$, $v'=3$, and the next higher perturbed level $J'=60$, $v'=4$ can best be explained by the assumption that they are both perturbed by rotational levels belonging to a single vibrational level of the perturbing $^3\Pi$ state. In other words, a single dashed line parabola in Fig. 6 must pass through the points marked by circled crosses in levels $v'=3$ and $v'=4$. This requirement fixes the B value of the $^3\Pi$ state. Likewise the J values and term values of the perturbed levels in vibrational states $v'=8$ and $v'=9$ indicated by circled crosses, were used to fix the B value of another set of rotational levels of the $^3\Pi$ state. In both cases the B value turned out to be 0.140 cm^{-1}. The slight dependence of B on v was therefore neglected. Thus, from the known positions of the four circled crosses, we can determine the B constant for the $^3\Pi$ state and as well the positions of two of its vibrational levels, which will be determined by the points on the energy axis intersected by the two dotted parabolas through the circled crosses. We assume that these dotted parabolas refer to the levels $v=3$ and $v=7$ of the $^3\Pi$ state, and assume $x_e\omega_e$, which affects the calculations only slightly, to be 0.42 cm^{-1}, which is certainly of the right order of magnitude. Then we may calculate ω_e, knowing the energy difference between the $v=3$ and $v=7$ vibrational levels of the $^3\Pi$ state. It turns out to be 145 cm^{-1}.

With these approximate values of B and ω_e we may predict the positions of the rotational levels belonging to other vibrational levels of the $^3\Pi$ state to be those indicated by the other dotted parabolic curves in the figure. These dotted parabolas should intersect the solid parabolas at or near the circled crosses, in order that the required perturbations should occur at these places. Calculations show that they do, as is indicated on Fig. 6, where the scale is too small to make the deviations observable. Of course the v numbering of the vibrational levels of the perturbing state is arbitrary, and may have to be raised, with slight attendant change of ω_e. The constants of the $^3\Pi$ perturbing state so arrived at ($B=0.140$ cm^{-1}, $\omega_e=145$ cm^{-1}) agree with expectations, for they are intermediate between those of the ground state and those of the upper $^1\Sigma$ state of the red bands, as Mulliken has predicted for Li_2, and as is observed for H_2.[11]

6. Sign of the Rotations in the Sodium Red Bands

That the nature of the perturbing state must be $^3\Pi_{0u}{}^+$ can be deduced from the energy curves which Mulliken shows at the top of page 16 of reference 11, giving all the electronic states which can be formed out of one normal ^2S atom and one ^2P excited atom. The more complete label of the upper state of the red bands is $^1\Sigma_u{}^+$. Application of the perturbation theory rules that only levels with the same J and the same g or u and $+$ or $-$ symmetry can interact, excludes all but the $^1\Pi_u$ and $^3\Pi_u$ states from consideration as possible perturbers. The $^1\Pi$ state (upper state of the blue green bands) is known to lie too far above the $^1\Sigma$ state to cause any perturbations.

Singlet and triplet states may interact only by virtue of spin orbit interaction. Van Vleck has shown that the spin orbit interaction is diagonal in Ω. That is, only states with the same Ω may

---

[11] R. S. Mulliken, Rev. Mod. Phys. 4, 16 (1932).

interact via spin orbit interaction. This consideration leaves us no other choice but to ascribe the perturbation to the $^3\Pi_{0u}{}^+$ component of the $^3\Pi_u$ state. (Thus we were justified in neglecting the sextuplicity of the $^3\Pi$ state in our previous calculation of its probable constants.)

To the rigid molecule approximation the $^3\Pi_0$ state does not have a magnetic moment along J for the $^1\Sigma$ state to borrow in the perturbation. The $^3\Pi_0$ state may fairly easily acquire magnetic moment along J due to rotational distortion. The separation of the $^3\Pi_0$ and $^3\Pi_1$ levels may be calculated from the separation of the sodium D lines and Mulliken's table on page 35 of reference 11 to be just 5.7 cm^{-1}. Therefore, the $^3\Pi_0$ state will acquire a sizable magnetic moment due to rotational distortion, which increases with J. This increase with J of the magnetic moment in the $^3\Pi_0$ perturbing state may explain the variation of the intensities of Fredrickson's doublets, which can be noted on the top strip of Plate 1A of reference 7. Clearly the higher the J' value of a doublet, the more intense it is, taking due cognizance of the falling plate sensitivity toward the right. We should expect this, ceteris paribus, if the perturbing $^3\Pi_0$ levels of high J possessed the larger magnetic moments.

The $^3\Pi$ multiplet in Na_2 is a regular, not an inverted, spin multiplet. From this fact it follows that a rotationally distorted $^3\Pi_0$ level in a magnetic field will have its highest energy for positive M values. We suppose that this rotationally distorted $^3\Pi_0$ level engages in a spin orbit perturbation with a close lying $^1\Sigma$ level in the presence of a magnetic field. The spin orbit perturbation can be considered simply a repulsion between like M levels which is greater the closer the levels are together. Clearly this repulsion of like M levels will push apart the degenerate sublevels of the $^1\Sigma$ state in such a way that positive M values have the highest energy. Reference to Eq. (1) and the polarization patterns of Fig. 1 will show that the rotation should be positive outside R branch perturbed lines, and negative outside P branch lines.

These signs as predicted were just the reverse from those listed by Fredrickson, which were taken from the early work of Wood and Hackett.[2] Inspection of a quartz wedge spectrogram of the region below 7000A, where all of Wood and Hackett's observations on the sign of the rotation were made, showed that the signs in this paper should be just reversed. There can be no doubt about the signs on this plate because the positive rotation outside the D lines was visible on the plate along with the molecular lines. The signs in Wood and Hackett's paper are correct if it be assumed that by the term "positive rotation" they mean rotation produced outside lines due to positive electron oscillators, which on 1908 theory should be in the negative sense about the field.

Observationally then, the rotation outside R branch perturbed lines is positive, and that outside P branch perturbed lines is negative. This is precisely the behavior required by the theory of the perturbed lines presented above. The negative rotation outside these P branch lines was in 1908 taken as a possible indication that they were produced by positive electron oscillators. It is amusing to note that rather refined perturbation theory considerations are needed to show that these negatively rotated lines are after all just P branch lines due to conventional negative electrons.

It was noted long ago by Wood that magnetic rotation in these sodium bands seems always to occur on one side or the other of the absorption lines, and very rarely is equally strong on both sides. This behavior is just what we might expect on the hypothesis that they are due to perturbations, if we take into account changes in the transition probabilities of the various Zeeman components of the perturbed line, attendant on the perturbation process. Those magnetic sublevels of the $^1\Sigma$ level which are perturbed most by a nearby $^3\Pi$ level will have weakened transition probabilities with the ground state. This follows from the fact that a perturbation between two levels involves a sharing of properties between them. The normalization condition for the mixed wave function of a perturbed level shows that the more $^3\Pi$-like the perturbed level becomes, the less $^1\Sigma$ likeness it can exhibit. Transitions from the singlet ground state to a perturbed level occur only to the extent that the wave function of the perturbed level is $^1\Sigma$ like. Thus transitions to positive or negative M values of the $^1\Sigma$ perturbed level are likely to be inhibited most by the perturbation, depending on whether the $^3\Pi$ perturbing level is below or above the $^1\Sigma$ level it perturbs. Referring to the polarization patterns of Fig. 2, we can see that the sum of the intensities of the + and − circularly polarized components may not be equal any longer for the perturbed line in the presence of the field. This leads as before to asymmetrical rotation about the perturbed line. In fact if the difference in intensity of the + and − circular components is very marked, the rotation may conceivably be of opposite sign on the two sides of the line.

7. MAGNETIC ROTATION SPECTRUM OF THE INFRARED POTASSIUM BAND SYSTEM

The magnetic rotation spectrum of this band system was photographed in the region from 8100A to 10,000A. The lines in general are sharper than the iron comparison lines. The exposure times varied from 12 to 36 hours. An attempt to assign quantum numbers to the lines was unsuccessful, apparently because it was not possible to reduce the temperature of the vapor sufficiently to show only the $v''=0$ progression. This maneuver enabled Fredrickson to solve the Na_2 spectrum. The lower ω_e value for the ground state of K_2 makes it relatively harder to do this. In the heavier molecule, the rotational levels lie closer together, and at the same time the spin orbit interaction responsible for the perturbation is larger. Fredrickson likewise observed toward the red end of the Na_2 spectrum that the lines occurred in groups whose center of gravity could be arranged into doublets. This means that in Fig. 6 we should have marked a cluster of crosses at adjacent rotational levels of the lowest three vibrational states, because a number of adjacent rotational levels of these vibrational states show magnetic rotation lines as evidence of their being perturbed. In K_2 it appears that there are large groups of perturbed levels in each vibrational level, which give rise to so many magnetic rotation lines that the assignment of quantum numbers is well-nigh impossible.

Toward the red end of the spectrum the magnetic rotation lines form clearly defined groups of around 40 lines each, the centers of gravity of these groups being about 84 cm^{-1} apart. This spacing is almost certainly indicative of ground state progressions.

Out of all of the magnetic rotation lines measured, some certain empirical regularity was found at the extreme red end of the spectrum. Most of the lines in several of the groups near 9600A could be arranged into constant spaced series, with spacings of from 2 cm^{-1} to 5 cm^{-1}. Each series contained from fifteen to twenty-five lines, and each group had about 5 or 6 series in it. These series almost certainly represent small segments of P and R branches whose upper state levels have received magnetic moment by being perturbed. We do not think that the upper levels of these short series could acquire their magnetic moments by rotational distortion, for rotational distortion affects all high J levels and should be observable for more than 25 levels if it produces big enough magnetic moments to cause magnetic rotation for any lines at all. Using a plausible predicted B constant for the upper state rotational levels, one finds that the most closely spaced series correspond to J values around 65, while the widest spaced series corresponds to J values around 150. The series appear to have constant spacing, of course, because the parabolas of the Fortrat diagram cannot be distinguished from straight lines at such high J values over such a short piece of a branch, containing only 25 lines.

Quartz wedge spectrograms supply the strongest evidence that the K_2 infrared magnetic rotation spectrum is produced by perturbations, just as is the analogous Na_2 magnetic rotation spectrum. The similarity between the wedge spectrograms of K_2 and those published by Wood for the similar sodium system[8] is very striking. The similarity extends even to the one-sidedness of the magnetic rotation at most absorption lines, as was first noted by Wood for sodium. Close examination of the wedge spectrograms reveals that the needles of light jut down into the central dark band on one side or the other of an absorption line. The point to be emphasized is the unusual character of such wedge spectra. The $^1\Pi \leftarrow {}^1\Sigma$ absorption systems of the alkalis give a magnetic rotatory effect because they have a perfectly normal rigid molecule Zeeman effect in the upper $^1\Pi$ state. The Zeeman and Faraday effects for the lines of a band are inversely proportional to J. All one obtains on a magnetic rotation spectrum of the bands is a single strong line outside the R head of each band. The single strong magnetic rotation line just outside the head of each band is due to the contributions to the rotation at this frequency from the numerous low J lines piled up at the head of the band. We took wedge spectrograms of these bands in order to try to verify that the rotation outside the heads (formed in the R branch) was positive. It was found that the rotations were too small to be detected by the quartz wedge method. Precisely the same magnetic field, path length, and optimum vapor conditions were used for these bands as were used to produce the strong indications of rotation (and dichroism) near certain of the infrared lines. No needles of light outside the heads of bands could be observed to penetrate into the central dark fringe. The conclusion seems inescapable that the type of wedge spectrograms which is found only in the Na_2 and K_2 $^1\Sigma\leftarrow{}^1\Sigma$ absorption systems shows pathologically large rotations for band spectra. On the perturbation hypothesis, this unusually large effect is explained as has been outlined above, not only by the large magnetic moment which the perturbed level may possess, but also by the difference between the intensities of the right- and left-handed circularly polarized components of the perturbed level under the action of the magnetic field.

CONCLUSIONS

This study of diatomic magnetic rotation spectra was undertaken as a preliminary step with a view toward applying magnetic rotation spectra as a tool in the analysis of complicated polyatomic spectra, as had been suggested by Wood and Diecke,[12] and Loomis and Kusch.[13] These hopes appear not so very promising now. For one thing perturbations occur more frequently in polyatomic molecules than in diatomic ones. As in the Na_2 and K_2 systems just discussed, the magnetic rotation spectrum would just show the perturbations, the more complicated features of the spectrum, rather than its simplicities. The only case where any simplification might reasonably be expected would be the case of rigid linear molecules, which could give magnetic rotation lines at the heads of bands, similar to Loomis' spectra of alkali $^1\Pi\leftarrow{}^1\Sigma$ systems. If the magnetic rotation lines of a spectrum do not correspond to absorption heads, it is probable that the analysis of the magnetic rotation lines will be more difficult than the analysis of the absorption spectrum. The magnetic rotation spectrum seems most adapted as a sensitive means of detecting the presence of small magnetic moments in molecular levels, smaller than could be detected by other means (cf. the smallness of the magnetic moments responsible for the I_2 magnetic rotation spectrum. Section 4). The improvement in our understanding of the finer details of the Faraday effect in molecules which has been achieved by introducing quantum mechanical refinements, suggests the possibility that similar refinement of the transverse or Cotton-Mouton effect will lead to a better understanding of the details of that phenomenon, in particular its temperature dependence. Also it would seem interesting both to calculate theoretically and to look experimentally for the onset of saturation terms in the Faraday effect, particularly for heavy molecules with large moments of inertia where the first-order effect of nutation is appreciable, and the terms in the higher odd. powers of H should become appreciable.

In conclusion I wish to thank Professor W. W. Watson, who suggested this problem, for his valuable discussions and encouragement throughout the course of the work. I wish also to express my appreciation for the opportunity of having studied the theory of these problems under Professors L. Page and H. Margenau.

APPENDIX 1

Substituting in Serber's formula (10) matrix elements given for instance by Kronig in reference 14 one obtains

$$V_B(R\text{ branch})=\frac{4\pi|e|\nu^2P^2}{3hmc^2}\frac{B^0e^{-W_j/kT}}{\nu^0(1,\,J+1;\,1J)(\nu^2-\nu(1,\,J+1;\,0J))}\frac{J(J+2)}{J+1},$$

---

[12] R. W. Wood and G. H. Diecke, Nature **128**, 535 (1931).

[13] P. Kusch and F. W. Loomis, Phys. Rev. **49**, 879 (A) (1936).

[14] R. deL. Kronig, Zeits. f. Physik **45**, 458 (1927).

$$V_B(P\text{ branch})=\frac{4\pi|e|\nu^2P^2}{3hmc^2}\,\frac{B^0e^{-Wj/kT}}{\nu^0(1,\,J;\,1J-1)(\nu^2-\nu(1,\,J-1;\,0J)^2)}\,\frac{-(J-1)(J+1)}{J},$$

$$V_B(Q\text{ branch})=\frac{4\pi|e|\nu^2P^2}{3hmc^2}\,\frac{B^0e^{-Wj/kT}}{2B'_{v'}(\nu^2-\nu(1J,\,0J)^2)}\,\frac{-(2J+1)}{J^2(J+1)^2}.$$

We have used the rotational energy formula $h\nu(J)=Bv'J(J+1)$ in order to simplify expression for the Q branch. The notation is the same as Serber's. J is the rotational quantum number of the ground level. If one makes the assumption that ν is well outside the triplet of lines emanating from a given ground level J, all the V_B and V_A terms for these lines add together to give a rotation proportional only to the number of molecules per unit volume with that J value, and otherwise independent of J. This checks with Serber's application of Niessen's rule to rigid molecules.[7]

APPENDIX 2

Calculation of the asymmetrical notation outside iodine lines

Substituting matrix elements obtained from reference 14 into the third term of formula 8 of Serber's paper, one obtains

$$V_B(R\text{ branch})=\frac{\pi|e|Nv,\,J}{3hmc^2}\left[\frac{\nu^2}{\nu(^3\Pi_0,\,v',\,J+1;\,^1\Sigma,\,v,\,J)^2-\nu^2}\right]\left[\frac{J+1}{2J+1}\right]\left[\frac{\{Px'(^1\Sigma,\,^3\Pi_1)Sy'(^3\Pi_1,\,^3\Pi_0)Pz'(^3\Pi_0,\,^1\Sigma)}{\nu(^3\Pi_0,\,^3\Pi_1)}\right],$$

$$V_B(P\text{ branch})=\frac{\pi|e|Nv,\,J}{3hmc^2}\left[\frac{\nu^2}{\nu^2(^3\Pi_0,\,v',\,J-1;\,^1\Sigma,\,v,\,J)-\nu^2}\right]\left[\frac{J}{2J+1}\right]\left[\frac{\{Px'(^1\Sigma,\,^3\Pi_1)Sy'(^3\Pi_1,\,^3\Pi_0)Pz'(^3\Pi_0,\,^1\Sigma)\}}{\nu(^3\Pi_0,\,^3\Pi_1)}\right],$$

where $Nv,\,J$ = number of molecules per unit volume with vibrational quantum number v and rotational quantum number J of the ground electronic state ($^1\Sigma$),

$\nu(n,\,n')=(En-En')/h$, where En is the energy of the state with quantum numbers symbolized by the index n,

$x',\,y',\,z'$ = coordinates referred to axes fixed in the molecule, with z' axis running through the nuclei,

$Pz'(n,\,n'),\,Px'(n,\,n')$ = matrix elements of the components of the electric moment of the molecule, with no magnetic field,

$Sy'(n,\,n')$ = matrix element of the component of spin angular momentum perpendicular to the internuclear axis with no magnetic field.

The above V_B terms, together with V_A calculated by Serber, estimate the effect on the rotation of rotational distortion and the magnetic field. First-order perturbation of the intensities of transition by rotational distortion are considered negligible, because the terms would have the square of the large precessional frequency $\nu(^3\Pi_0,\,^3\Pi_1)$ in their denominators ($\sim$3800 cm^{-1}).

The formulae for V are not supposed to be quantitatively accurate. For one thing, in the calculations the diagonality with respect to v' was assumed of the various elements of the electric and magnetic moments between the $^3\Pi_0$ and $^3\Pi_1$ states. This is not at all legitimate, because the spin orbit interaction in I_2 is so large that the energy curves for these two components of the $^3\Pi$ spin multiplet are very different, and hence possess different sets of vibrational eigenfunctions. (Cf. the energy curves drawn in reference 15.)

As to the factors in the preceding expressions, the first brackets show the dependency on frequency. The second brackets give the variation with J. The numerator of the third factor, in curly brackets, is positive. Likewise the denominator is positive, because the $^3\Pi$ state is inverted. It is the curly bracket expression in the final factor which makes quantitative comparison of the relative magnitudes of V_B and V_A impossible. This factor makes V_B depend on a geometric mean of the intensities of the intersystem bands, $^3\Pi_1\leftarrow{}^1\Sigma$, and $^3\Pi_0\leftarrow{}^1\Sigma$. These transitions are observed only because of the strong spin orbit interaction, which renders the spin not rigorously a good quantum number. Van Vleck, in reference 15, tells why the intensities of two such intersystem transitions may be radically different. V_A, on the other hand, depends only on the intensities of the $^3\Pi_0\leftarrow{}^1\Sigma$ bands.

The important thing about the above formulae is the sign of the V_B term, which is the same for P and R branches. Taken in conjunction with V_A as calculated by Serber, these formulae produce the asymmetry of rotation outside P and R lines which was found by Wood and Ribaud and has already been discussed in Section 4.

---

[15] J. H. Van Vleck, Phys. Rev. **40**, 544 (1932).