

## OPTICAL ORIENTATION OF ATOMS AND ITS APPLICATIONS

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## INTRODUCTION

THE phenomenon of optical orientation of atoms or ions which have magnetic moments in their ground states can occur when they absorb light and subsequently emit it. The scattering of a circularly-polarized light quantum of the resonance frequency by an individual atom can result in transfer of the angular momentum of the photon to the atom, which leads to a change of the component of the magnetic moment of the atom along the direction of propagation of the light, i.e., to orientation of the atom. In other words, irradiation of an ensemble of atoms with light of the resonance frequency leads to a change of the populations of the energy sublevels of the ground state of the atoms. This process has received the name optical pumping (*pompage optique*).<sup>1</sup>

The phenomenon can be observed both with the Zeeman sublevels of atoms that are in an external magnetic field, and also in the absence of such a field. Under certain conditions the stationary distribution of the populations of the sublevels that arises under continuous illumination can be quite different from the distribution for thermal equilibrium.

As the result of the process of optical pumping one can get either a distribution of the populations of the sublevels such that the total magnetic moment of the system of atoms is zero (alignment) or a distribution such that the magnetic moment is different from zero (orientation).

Any change of the populations of hyperfine, Zeeman, or Stark sublevels, produced optically or by means of radio-frequency transitions, can be observed by the change of the intensity and polarization of the light scattered by the atoms. The combination of radio-

frequency resonance and optical pumping of atoms is a special kind of extension of the method of double resonance, with one of the frequencies used lying in the optical range.

Attention was first called to the possibility of optical orientation of atoms by Brossel and Kastler,<sup>2</sup> who proposed for its observation the method of radio-optical double resonance. This phenomenon was soon after observed with molecular beams of mercury and sodium.<sup>3</sup> The main features of the phenomenon and possible fields for its application were expounded in a general paper by Kastler.<sup>1</sup>

The first attempt to produce optical orientation of the atoms of saturated mercury vapor (at 0° C) in a light-absorption cell was unsuccessful.<sup>4</sup> This paper, however, gave an analysis of the causes of the negative result which soon after made it possible to perform a successful experiment on the orientation of sodium vapor in the ground state,<sup>5</sup> and later on the orientation of mercury vapor.<sup>6</sup>

Thus it was shown that optical orientation can be produced not only in beams, but also in vapors at low pressure. Thus a new way was found for studying the structures of energy levels not only in the ground state, but also in excited states. This was the start of numerous investigations, which led, on one hand, to the development of the method of optical orientation and of its detection, and on the other, to the development of the theory of the phenomena that accompany the process of optical pumping.

The set of phenomena occurring in the optical pumping of atoms makes up a new chapter of radio spectroscopy, which is closely related to optical spectroscopy.

The study of the phenomena that accompany the optical pumping of atoms in vapors and gases led to the

discovery of many-quantum transitions between sublevels, to the elucidation of the part played by the phenomenon of diffusion of radiation, which had not previously received much study, and to an understanding of the mechanism by which a buffer gas affects the degree of orientation of the atoms.

The method of radio-optical double resonance has been a convenient one for determining lifetimes of atoms in excited states and values of the magnetic dipole and electric quadrupole moments of nuclei, and is indispensable in the study of the Zeeman and Stark effects and also in the investigation of the shapes of narrow and closely spaced lines that are optically irresolvable. This method has been used to measure with great accuracy the hyperfine interaction constants of the isotopes of various elements. It has been found that orientation of atoms in optical pumping can be produced not only directly, but also through spin-exchange collisions of nuclei, atoms, and electrons.

The small width of the lines that correspond to hyperfine transitions opens up new possibilities for precise stabilization of frequencies and the development of exact time standards. The experimentally observed possibility of modulating the intensity of a light beam with the Larmor precession frequency has important future applications in radio engineering. Quite recently highly sensitive magnetometers have been developed in which use is made of the effect of optical pumping in rubidium vapor and in helium.

Studies have been begun on the possibility of optical orientation of atoms in solids at low temperatures. The first successful results have been obtained on the orientation of  $\text{Cr}^{+++}$  ions in  $\text{Al}_2\text{O}_3$  and  $\text{Eu}^{++}$  ions in  $\text{CaF}_2$  and  $\text{SrCl}_2$ .

## I. THE OPTICAL ORIENTATION OF ATOMS

### 1. Optical Pumping

Let us consider a gaseous ensemble of atoms whose energy spectrum in the ground state contains only two sublevels A and B. We shall denote by C the set of sublevels of the nearest optically excited state (Fig. 1). With such a very simple "equivalent" level system we can realize the process of optical pumping.

The fractional excess  $V$  of the population of the lower sublevel A of the ground state over that of the upper sublevel B can be found for thermal equilibrium from the Boltzmann relation:

$$V^T \equiv \frac{N_A^0 - N_B^0}{N_A^0 + N_B^0} = \text{th} \frac{E_B - E_A}{2kT^0}, \quad (1)^*$$

where  $T^0$  is the absolute temperature of the ensemble of atoms and  $N_A + N_B = N$  is the total number of atoms per unit volume.

We agree to give the name of pumping to any change of the thermal-equilibrium populations of the sublevels that is brought about by an outside cause.

\* $\text{th} = \tanh$ .

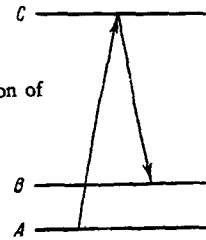


FIG. 1. Energy-level scheme for explanation of the process of optical pumping.

The distribution of the atoms between sublevels A and B can be changed in many ways, for example by bombardment with electrons of suitable energy, by the action of an electromagnetic field of the resonance frequency, and so on.

The phenomenon of optical pumping can occur when the ensemble of atoms is illuminated with light of the resonance frequency  $\nu_{AC} = (E_C - E_A)/h$ . In this case atoms which absorb light go from the state A to the excited state C, from which they fall down after a time  $\tau \sim 10^{-8}$  sec to the sublevels A and B of the ground state. Thus as a result of the resonance fluorescence there is pumping of atoms from sublevel A to sublevel B of the ground state through the system of sublevels of the excited state C. For such systems the process of optical pumping is always associated with a change of orientation of the angular momenta of the atoms. Pumping of atoms between Zeeman sublevels is accompanied by a change of the magnetization of the gas. Depending on the character of the polarization of the light and the sign of the gyromagnetic ratio  $\gamma_a$  of the atoms, orientation of the magnetic moments can occur either along the applied field or opposite to it.

### 2. The Orientation Parameters

We can describe the change with time of the populations  $N_A$  and  $N_B$  of the sublevels A and B by the system of equations

$$\left. \begin{aligned} -\frac{dN_A}{dt} &= (P_{AB} + W_{AB})N_A - (P_{BA} + W_{BA})N_B, \\ -\frac{dN_B}{dt} &= (P_{BA} + W_{BA})N_B - (P_{AB} + W_{AB})N_A, \end{aligned} \right\} \quad (2)$$

where  $P_{AB}$  and  $P_{BA}$  are the resultant probabilities for transitions from A to B and from B to A through the level C, and  $W_{AB}$  and  $W_{BA}$  are the probabilities of relaxation transitions between these sublevels.

It is convenient to characterize the degree of orientation of the atoms by the ratio

$$V = \frac{N_A - N_B}{N_A + N_B}, \quad (3)$$

whose change with time, according to the equations (2), is given by the equation

$$\frac{dV}{dt} + \frac{1}{\tau}(V - V^P) + \frac{1}{T_1}(V - V^T) = 0, \quad (4)$$

where

$$V^P = \frac{P_{BA} - P_{AB}}{P_{BA} + P_{AB}}, \quad V^T = \frac{W_{BA} - W_{AB}}{W_{BA} + W_{AB}}, \quad (5)$$

and

$$\frac{1}{\tau} = P_{BA} + P_{AB}, \quad \frac{1}{T_1} = W_{BA} + W_{AB}. \quad (6)$$

We can put Eq. (4) in the form

$$\frac{dV}{dt} + \frac{1}{T^*}(V - V^*) = 0, \quad (7)$$

where

$$\frac{1}{T^*} = \frac{1}{\tau} + \frac{1}{T_1}, \quad V^* = \frac{T_1 V^P + \tau V^T}{T_1 + \tau}. \quad (8)$$

The approach of the ensemble of atoms to the stationary state during the process of optical pumping is described by the solution of Eq. (7); for the initial condition  $V(0) = V^T$  this solution is

$$V(t) = V^*(1 - e^{-\frac{t}{T^*}}) + V^T e^{-\frac{t}{T^*}}. \quad (9)$$

As the result of illumination with light of constant intensity  $J(1/\tau = \alpha J)$  for a time  $t \gg T^*$ , the ensemble of atoms will reach the limiting degree of orientation  $V^*$ .

For the case considered above, in which the ensemble of atoms is illuminated with light of the resonance frequency  $\nu_{AC}$ , we have  $P_{BA} = 0$  and  $V^P = -1$ . For a rarefied gas the thermal relaxation time  $T_1$  is much larger than the optical relaxation time  $\tau$ , and  $V^T \ll 1$ ; therefore, according to Eq. (8), the limiting value of the orientation parameter

$$V^* = -1 + \frac{\tau}{T_1} \quad (10)$$

can reach a value close to  $-1$ .

Thus by the process of optical pumping one can not only equalize the populations of the sublevels of the ground state (saturation), but also maintain a stationary distribution of the atoms in which a large majority of the atoms are in state B.

When the number  $\rho$  of sublevels in the ground state is larger than two, the changes of the populations  $N_k$  with the time are described by the system of equations

$$-\frac{dN_k}{dt} = \sum_{s=1}^{\rho} (P_{ks} + W_{ks}) N_k - \sum_{s=1}^{\rho} (P_{sk} + W_{sk}) N_s, \quad (11)$$

which is a direct generalization of Eq. (2). Here  $P_{kS}$  is the probability of a resonance transition from the  $k$ -th sublevel of the ground state to the  $s$ -th sublevel of this same state through some optically excited intermediate level. The probability of the transition between these same sublevels under the action of relaxation process is denoted by  $W_{kS}$ . The terms with  $k = s$  in the right member of Eq. (11) can be omitted, since they do not affect the change of the population of the  $k$ -th sublevel.

If the energy  $kT^0$  of the thermal motion is much larger than the distance  $E_i - E_k$  between the sublevels, we can neglect the small difference between the equilibrium populations of the sublevels. In this case the probabilities for the relaxation transitions are equal,

$W_{kS} = W$ . Then

$$\sum_{s=1}^{\rho} W_{ks} = \rho W = \frac{1}{T_1}, \quad \sum_{s=1}^{\rho} W_{sk} N_s = \frac{N}{\rho T_1}, \quad (12)$$

where  $N = \sum_s N_s$  is the number of atoms per unit volume.

If we introduce the notations

$$P'_k = \sum'_s P_{ks}, \quad \mathcal{P}_k = P'_k + \frac{1}{T_1}, \quad (13)$$

where the prime on the summation sign means that the term with  $k = s$  is omitted, the equations (11) take the form:

$$\frac{dN_k}{dt} = -\mathcal{P}_k N_k + \sum'_s P_{sk} N_s + \frac{N}{\rho T_1}. \quad (14)$$

In the absence of the orienting radiation  $P_{sk} = 0$  and

$$\frac{dN_k}{dt} = -\frac{1}{T_1} \left( N_k - \frac{N}{\rho} \right), \quad (15)$$

from which it follows that  $T_1$  has the meaning of a longitudinal ("spin-lattice") relaxation time. The stationary value of the orientation parameter for two neighboring levels

$$V_{ik}^* = \frac{N_i - N_k}{N} \quad (16)$$

can be found by setting  $dN_k/dt = 0$ . We then get

$$N_k = \frac{\sum'_s P_{sk} N_s + \frac{N}{\rho T_1}}{\mathcal{P}_k}.$$

Thus we have

$$V_{ik}^* = \frac{\frac{1}{\mathcal{P}_i} - \frac{1}{\mathcal{P}_k}}{\sum_s \frac{1}{\mathcal{P}_s}}. \quad (17)$$

For the case of two levels the expression (17) goes over into Eq. (8) on the assumption  $V^T = 0$ .

### 3. Optical Orientation of Atoms. Alignment

Optical orientation of atoms was first produced in atoms of sodium vapor.<sup>5</sup> As a typical example of alkali-metal atoms, sodium vapor has repeatedly been the object of studies of various aspects of the phenomenon of the optical orientation of atoms.<sup>7,8,9</sup>

Part of the energy spectrum of an alkali-metal atom with nuclear spin  $I = 3/2$  ( $\text{Na}^{23}$ ,  $\text{Rb}^{87}$ ) in a weak magnetic field is shown in Fig. 2. In the case of  $\text{Na}^{23}$  the transition  $3P_{1/2} \rightarrow 3S_{1/2}$  corresponds to the emission of the yellow  $D_1$  line. The second line of the yellow doublet is the transition  $3P_{3/2} \rightarrow 3S_{1/2}$ . The atom emits circularly polarized light ( $\sigma^\pm$ ) if the change of the magnetic quantum number in the transition is  $\Delta m_F = \pm 1$ , and linearly polarized light ( $\pi$ ) if  $\Delta m_F = 0$ .

Let us examine the phenomena that will occur when a gas ensemble of sodium atoms is illuminated with

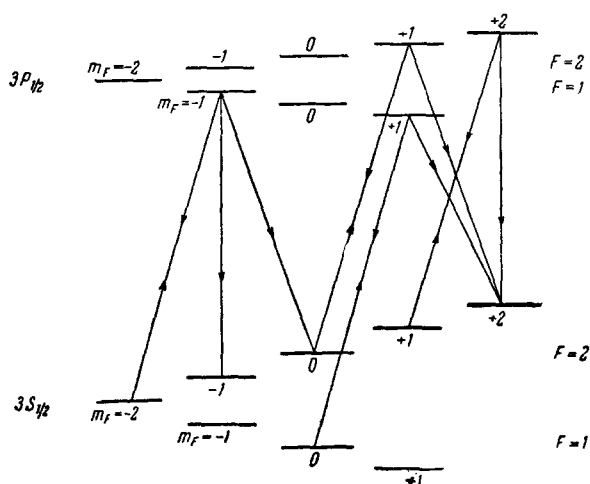


FIG. 2. The energy spectrum near the ground state for sodium in a weak external magnetic field. The arrows indicate certain allowed optical transitions for illumination with polarized light of the resonance frequency.

circularly polarized light ( $\sigma^+$ ) of the  $D_1$  line of sodium. The direction of propagation of the light is the direction of the constant magnetic field  $H_0$  (Fig. 3).

The absorption of the  $D_1$  line leads to transitions which satisfy the selection rules  $\Delta l = 1$ ,  $\Delta m_F = \pm 1$ . The probabilities are different for the absorption of light by electrons that are in different sublevels of the ground state. In particular, atoms in the state  $(F, m_F) = (2, 2)$  will not absorb the light at all, since there is no sublevel of  $3P_{1/2}$  to which a transition from  $(2, 2)$  would satisfy the selection rule  $\Delta m_F = 1$ . The number of atoms in this state can decrease only on account of relaxation processes.

The transition of excited atoms to the ground state is accompanied by the emission of both linearly and circularly polarized photons, corresponding to the selection rules  $\Delta m_F = 0, \pm 1$ . Thus the resonance-scattered radiation is depolarized, and the angular momentum that the incident  $\sigma^+$  radiation had remains partly in the system of atoms. As a result of the illumination with  $\sigma^+$  light, part of the atoms are in the

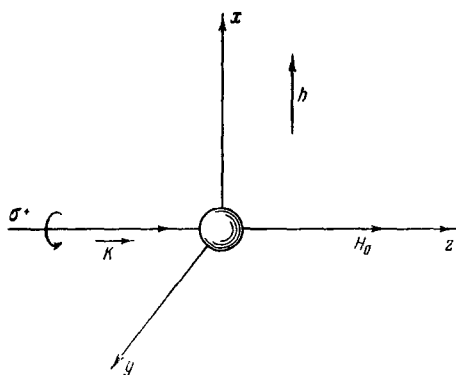


FIG. 3. Relations of the directions of the constant magnetic field  $H_0$  and the radio frequency magnetic field, and the direction  $K$  of propagation of the orienting light beam.

state  $(2, 2)$ , from which, as we have seen, they cannot be removed by the radiation. Thus atoms will gradually accumulate in the sublevel  $(2, 2)$  of the ground state until equilibrium is established between the processes of pumping and relaxation. If there were no relaxation there would be complete orientation of the atoms ( $V = -1$ ).

If the direction of the circular polarization is reversed (to  $\sigma^-$ ), it is not hard to see that there will be pumping of atoms into the state  $(2, -2)$ , in which the angular momentum of the atoms is directed opposite to the field. There is a corresponding change of the direction of magnetization of the gas.

It is now not hard to understand what happens when the gas ensemble is illuminated with unpolarized light of the  $D_1$  line. The intensities of the  $\sigma^+$  and  $\sigma^-$  components of the  $D_1$  line are the same, and we can represent the  $\pi$  component in the form of two oppositely polarized circular components. Therefore when sodium vapor is illuminated with natural light of the  $D_1$  line the atoms will be pumped into the states  $(2, 2)$  and  $(2, -2)$ , so that there will be equalization of the populations of these sublevels and the magnetization of the gas will be equal to zero. This phenomenon has been given the name of optical alignment.

The calculation of the resonance fluorescence probabilities  $P_{KS}$  has been carried out in reference 10, which expounds the general theory of the phenomenon. In reference 7 expressions for the  $P_{KS}$  are obtained which take into account the overlapping of the levels of the excited state which can occur on account of collisions that disturb the orientation. For  $\text{Na}^{23}$  the probabilities have been found for transitions between the sublevels of the ground state under the action of circularly polarized ( $\sigma^+$ ) light of the  $D_1$  and  $D_2$  lines.

The table of values of  $\mathcal{P}_{KS} = P_{KS} + W_{KS}$  can be regarded as the matrix of an operator  $\hat{\mathcal{P}}$  which acts on a vector whose components  $N_K$  are the initial populations of the sublevels of the ground state. The components of the resulting vector are the stationary populations of the levels after each of the atoms has scattered just one photon. The components of the initial vector are determined by the state of thermal equilibrium. By applying the operator  $\hat{\mathcal{P}}$   $n$  times one can find the stationary populations after  $n$  processes of absorption and subsequent emission of light. A theoretical calculation which does not take relaxation processes into account<sup>7</sup> shows that the degree of orientation increases with increase of the number of successive acts of scattering.

In experiments on the optical pumping of atoms one usually uses as the illuminating light not the single  $D_1$  line of sodium or a single line of the corresponding doublet of another alkali metal, but both lines  $D_1$  and  $D_2$  ( $\lambda = 5890 \text{ \AA}$ ). In this case only a limited degree of orientation can be attained even in the absence of relaxation. In the example considered above the atoms that are in the state  $(2, 2)$  absorb the light of the line

$D_2$  and go into the state  $3P_{3/2}$ . In the case of both D lines the degree of orientation that can be attained will be larger if the difference of the intensities of the  $D_1$  and  $D_2$  lines is larger:

$$Q = \frac{J(D_1) - J(D_2)}{J(D_2)}. \quad (18)$$

Bell and Bloom<sup>8</sup> have found solutions of the system of equations (11), using the relative probabilities of transitions under the action of the  $D_1$  and  $D_2$  lines.<sup>11</sup> If  $|Q| \ll 1$ , the differences of the populations of adjacent sublevels in weak fields are approximately equal, having the value  $QN/48$  for any combination of levels.

Orientation of sodium atoms under illumination by the  $D_1$  line only has been obtained in reference 9. In this case the degree of orientation was much higher.

The process of optical pumping can be realized not only in weak fields (weak in comparison with the hyperfine interaction), but also in strong fields, in which the coupling between the nuclear angular momentum  $I$  and the electronic angular momentum  $J$  is broken. In this case there is a change of the orientation of only the electronic angular momentum, not of the total angular momentum of the atom. It is interesting to note, however, that along with this there occurs an orientation of the nuclei analogous to that observed in the Overhauser effect.<sup>8</sup>

## II. THE OPTICAL DETECTION OF THE ORIENTATION OF ATOMS

### 1. The Absorption of Light by the Atoms in Optical Pumping

The beam of light of the resonance frequency that has passed through the absorption chamber, and also the light scattered by the atoms of the gas; carry information about the degree of orientation of the atoms. This information can be obtained by observing the changes of the intensity and of the character of the polarization of the light that has passed through the chamber.

Light of the resonance frequency passing through a vapor is absorbed by atoms which are in various sublevels of the ground state. The probability of absorption of light by the gas, calculated on the basis of probability per atom, is given by

$$\beta = \frac{1}{N} \sum_{k,s} P_{ks} N_s = \frac{1}{N} \sum_k P_k N_k. \quad (19)$$

As can be seen from the last expression, the absorption of the light is sensitive to changes of the populations  $N_k$  of the individual sublevels of the ground state. Therefore the intensity of the light after passing through the absorption chamber must change during the process of optical pumping, and also when transitions between the levels are induced by a radio frequency field.

Let  $\beta_0$  be the absorption of light by the system when the populations of the sublevels are the equilibrium values  $N_k^0$ . The coefficient  $\beta_0$  can be calculated easily on the assumption that the equilibrium populations of all the sublevels of the ground state are the same:

$$\beta_0 = \frac{1}{N} \sum_{k=1}^q P_k N_k^0 = \frac{1}{q} \sum_{k=1}^q P_k, \quad (20)$$

i.e., if we neglect the small differences in the populations caused by the Boltzmann factors. Any change of the populations as compared with the equilibrium values is accompanied by a change of the amount of absorption of the light, which can be characterized by the ratio  $\beta/\beta_0$ .

Using the values of  $P_k/\beta_0$  presented in reference 9 for the  $\sigma^+$ -circularly-polarized  $D_1$  line of  $\text{Na}^{23}$ , we find as the expression for  $\beta$

$$\beta = \frac{\beta_0}{N} \left( \frac{1}{2} N_1 + N_2 + \frac{3}{2} N_3 + 2N_4 + \frac{3}{2} N_5 + N_6 + \frac{1}{2} N_7 \right). \quad (21)$$

The absorption of the light by the atoms in the various sublevels of the ground state is not the same for all the levels. As was to be expected, the absorption of circularly polarized  $\sigma^+$  light by atoms in the (2, 2) sublevel is zero. For  $\sigma^-$  light the absorption is given by an expression which differs from Eq. (21) only in that the numbers  $N_k$  are replaced by  $N_{k+1}$ . In this latter case there is zero probability for absorption of the light by atoms in the sublevel (2, -2).

Thus in the process of optical pumping the populations of the sublevels for which the probability of absorption is different from zero are diminished, and the intensity of the light coming through the absorption chamber is correspondingly increased. As the degree of orientation of the atoms of the vapor increases the vapor becomes more transparent for the resonance radiation. With complete orientation of the atoms the light would pass through the chamber without any absorption. Under actual experimental conditions the energy of the light that is absorbed goes to cover the relaxation losses.

Thus by observing the change of intensity of the light coming through the absorption chamber one can judge the degree of orientation of the atoms.

Information about the degree of orientation of the atoms can also be obtained by studying the intensity and polarization of the scattered light. As long as the pumping process has not been completed, the atoms continue absorbing quanta of circularly polarized light. In the emission of light all allowed resonance transitions occur ( $\Delta m_F = 0, \pm 1$ ). Therefore some of the atoms emit linearly polarized light ( $\Delta m_F = 0$ ). As the degree of orientation increases the absorption of the light decreases. The  $\sigma$  component becomes predominant in the light coming through, and the intensity of the  $\pi$  component decreases. By measuring the intensities  $J_\sigma$  and  $J_\pi$  of the scattered light,

we can characterize the degree of orientation by the ratio

$$R = \frac{J_{\sigma} - J_{\pi}}{J_{\sigma} + J_{\pi}}. \quad (22a)$$

If one observes only in the longitudinal ( $z$ ) direction the degree of orientation can be defined by the ratio

$$r = \frac{J_{\sigma^+} - J_{\sigma^-}}{J_{\sigma^+} + J_{\sigma^-}}. \quad (22b)$$

In experiments<sup>5</sup> with  $\text{Na}^{23}$  the ratio  $r$  reached the value 30 percent.

## 2. The Longitudinal and Transverse Signals

Let us agree to call the beam of light that produces the optical orientation (Fig. 3) the longitudinal beam, or the  $z$  beam. The longitudinal beam is directed along the constant magnetic field. As we have seen, by observing the change of intensity of the  $z$  beam one can follow the process of pumping of the atoms. This change of intensity (or "signal") is proportional to the absorption probability  $\beta$ .

In the simplest case of a gas of atoms whose energy in the ground state is characterized by two energy sublevels ( $s = \pm 1/2$ ), we have by Eqs. (3) and (5)

$$\sum_s^2 P_s N_s = \frac{N}{\tau_z} \frac{1}{2} (1 - V_z^P V_z) = s_z, \quad (23)$$

where the index  $z$  reminds us that the quantities in question are determined for the longitudinal  $z$  beam.

The quantity  $s_z$  can be taken as the "signal" of the optical pumping.<sup>8</sup> It is more convenient, however, to take as the measure of the relative signal the expression

$$S_z = J_z V_z^P V_z = J_z - \frac{2}{\alpha_z N} s_z, \quad (24)$$

which is proportional to the intensity of the light that has passed through the absorption chamber, since  $1/\tau_z = \alpha_z J_z$ . For complete orientation of the atoms  $V_z \rightarrow V_z^P \rightarrow -1$  and  $S_z \rightarrow J_z$ .

The orientation of the atoms is accompanied by a magnetization of the gas ( $M_z$ ). In the present case ( $s = \pm 1/2$ )

$$M_z = \mu_a N V_z = -M_0 V_z, \quad (25)$$

where  $\mu_a$  is the magnetic moment of an atom and  $M_0$  is the maximum possible magnetization. Using Eq. (25), we can write the expression (23) for the case  $V_z^P = -1$  in the form

$$s_z = \frac{N}{\tau_z} \frac{1}{2} \left( 1 - \frac{M_z}{M_0} \right) = \frac{N}{\tau_z} \frac{1}{2} (1 - \cos \vartheta), \quad (26)$$

where  $\vartheta$  is the angle between the direction of the magnetization vector and the direction of propagation of the light. A quantum-mechanical derivation of the relation (26) is given in reference 12.

Suppose that besides the longitudinal beam there is light of the resonance frequency propagated perpendicular to the  $z$  axis—a transverse  $\rho$  beam ( $x$  beam or

$y$  beam). Just as we did for the  $z$  beam, we can get an expression for the signal  $S_\rho$

$$S_\rho = J_\rho V_\rho^P V_\rho, \quad (27)$$

where  $J_\rho$  is the intensity of the  $\rho$  beam and  $V_\rho^P$  is defined by Eq. (5), if we use in it the probabilities for transitions under the action of the  $\rho$  beam.

The transverse signal will vary harmonically with the Larmor frequency  $\omega_L$ , since

$$V_\rho = \frac{M_\rho}{M_0} = \sin \vartheta \cos \omega_L t.$$

We note that the  $\rho$  signal is proportional to  $M_\rho$ , and not to  $dM_\rho/dt$ , as occurs in the phenomenon of magnetic resonance.

The transverse beam affects the process of optical orientation produced by the  $z$  beam. There can be two kinds of effects of this sort. The  $\rho$  beam, being circularly polarized, will tend to cause the establishment of orientation in the  $\rho$  direction. This effect is small as long as the intensity of the  $\rho$  beam is not so large that it can produce complete orientation in one period of the Larmor precession. Secondly, it will diminish the degree of orientation produced by the  $z$  beam, by shortening the lifetimes of atoms in the sublevels of the ground state, like any sort of time-dependent perturbation.

Skillman and Bender<sup>13</sup> have experimentally observed a strong increase of the absorption of the light or a decrease of the polarization when the angle between the magnetic field and the direction of propagation of the light is increased. For example, for an angle of  $30^\circ$  the intensity of the light coming through is decreased by a factor of two.

## 3. Multiple Scattering of Light

Under certain conditions multiple scattering of the light can occur in the system of atoms. After being scattered by one atom, a light quantum is then absorbed and reemitted by another atom of the same ensemble. The number of such acts depends on the number of atoms (the density of the gas) in the absorption chamber and on the size and shape of the chamber. A study of multiple scattering shows<sup>7</sup> that the degree of orientation  $R_n$  increases with increase of the number  $n$  of acts of scattering (Table I).

Multiple scattering helps to increase the degree of orientation only provided the photons emitted as the result of the elementary acts of scattering again have the

Table I. Values of  $R_n$  for multiple scattering of photons<sup>7</sup>

$n$	$R_n$
1	0.070
2	0.173
3	0.313

$\sigma^+$  polarization and are propagated in the  $z$  direction. Otherwise they play the role of a  $\rho$  beam. Therefore to increase the degree of optical orientation it is desirable to give the scattering chamber a shape that is elongated in the direction of the propagation of the light and of the constant magnetic field.

### III. THE EFFECT OF RELAXATION PHENOMENA ON THE PROCESS OF OPTICAL PUMPING

#### 1. The Width of the Absorption Lines

The effectiveness of optical pumping is greater when the relaxation processes in the system of atoms go more slowly, i.e., when the widths of the energy levels of the atoms are smaller.

As is well known, the width of an absorption line of a gaseous ensemble of atoms is due to many causes. It can show large changes on account of the Doppler effect, the interactions of the atoms of the ensemble with each other and with the atoms of a buffer gas, collisions with the walls of the vessel in which the gas is contained, and the action of external fields.

The method of optical detection of magnetic resonance opens up new possibilities for the study of the shape of narrow absorption lines in magnetic transitions between sublevels of the fine structure and hyperfine structure. The use of the new method makes it possible to extend and make more precise existing ideas about the causes of the broadening of lines in gases and to bring to light specific features of the dependence of the line widths of fine-structure and hyperfine-structure transitions on pressure, temperature, electric and magnetic fields, and so on, which are not accessible to study by other methods.

Lifetimes against hyperfine-structure transitions of isolated atoms in the ground state are very long. For alkali-metal atoms they are of the order of  $10^6$  years, and for atomic hydrogen even  $\sim 10^7$  years. The natural width of the line, which corresponds to this lifetime, is so small that it can usually be neglected. When a system of atoms is in a resonator the interaction with the radiation field is strengthened, and the width can be increased by two and even three orders of magnitude. For example, in experiments on the hyperfine splitting of atomic hydrogen made with the method of double resonance the natural line width was found to be 80 times that in free space.<sup>14</sup>

A more important case is that of the coherent interaction of atoms. Coherent radiation can decidedly decrease the radiation lifetime of atoms and consequently increase the natural line width. In the most favorable case it is increased by a factor equal to the difference of the populations of the energy sublevels between which the transition occurs. In thermal equilibrium this difference reaches the value  $2 \times 10^{11}$ , which means a radiation lifetime  $\sim 20$  sec. The broadening of lines owing to coherent radiation is significant only for magnetic transitions between sublevels of the fine structure

and especially of the hyperfine structure, for which the wavelength of the radiation is much larger than the mean distance between atoms.<sup>15</sup>

In the optical range of frequencies one of the main causes of line broadening is usually the normal Doppler effect, whose existence follows directly from the conservation laws for the energy and momentum of the system. In this case the line shape is determined by the Maxwellian velocity distribution of the atoms and therefore is Gaussian. The line width is given by the simple expression

$$\Delta\nu_D = 7.2 \cdot 10^{-7} \sqrt{\frac{T^\circ}{A}} \cdot \nu_0, \quad (28)$$

where  $\nu_0$  is the frequency of the transition,  $A$  is the atomic weight, and  $T^\circ$  is the absolute temperature of the gas. It can be seen from Eq. (28) that the line width caused by the normal Doppler effect does not depend on the pressure. Under some conditions, however, this assertion is far from true. Collisions between atoms, and especially collisions with the walls of the containing vessel, can decrease the Doppler width in the radio frequency range to such an extent that it is negligibly small in comparison with the broadening produced by other causes. This problem has been treated theoretically by Dicke.<sup>16</sup>

Let us assume that the radiating atom (but not the radiation) is enclosed in a one-dimensional potential well of width  $a$  and can move back and forth between its walls with the constant speed  $v$ . In this case the radiation emitted by the atoms is modulated in frequency by the various harmonics of this oscillator. Such a radiating system has two types of energy, external and internal. In transitions in which a photon is emitted or absorbed there can be changes of both the internal and the external energy. Therefore the frequency of the emitted photon is given by the expression

$$\nu_{nm} = \nu_0 + \frac{h}{8M_0 a^2} (n^2 - m^2), \quad (29)$$

where  $\nu_0$  is the frequency of the transition for a free atom,  $M_0$  is the mass of the atom, and  $n$  and  $m$  are quantum numbers of levels in the well. The emission spectrum of such a system is a number of lines with intensities proportional to the probabilities of the corresponding transitions.

The introduction of a Maxwellian velocity distribution leads to a continuous distribution of intensity in the emission spectrum, like the normal Doppler distribution, on which there is superposed an undisplaced line emitted by all of the atoms independently of their velocities. The fraction of the energy that corresponds to this line is given by the ratio

$$\left( \frac{\sin \pi \frac{a}{\lambda}}{\pi \frac{a}{\lambda}} \right)^2, \quad (30)$$

where  $\lambda$  is the wavelength of the radiation. If  $a \geq \lambda/2$ ,

the dominant part of the line is the noncentral part, of the Doppler shape and close to the Doppler width. In the case  $a < \lambda/2$  the central line is much widened. If the zero-point energy of the oscillation in the well is  $\ll kT$ , the most intense radiation is that of frequency  $\nu_{\text{mn}}$ . Although the atom is in contact with the wall for an indefinitely short time, the probability for the momentum of the photon to be transferred to the wall and not to another atom is finite and is given by the ratio (30). If  $a \geq \lambda/2$  but the mean free path is small in comparison with  $\lambda$  and the energy of the oscillator is  $\ll kT$ , the line shape can be found classically. We present a simple derivation of the equation that gives the line shape in this case.

Let us consider an atom emitting the plane wave

$$\left. \begin{aligned} E(t) &= E_0 \exp i \left( \Omega_0 t - \frac{x}{\lambda} \right) & (t > 0), \\ E(t) &= 0 & (t < 0), \end{aligned} \right\} \quad (31)$$

where  $\Omega_0 = \omega_0 + i\delta$  is the complex frequency of the radiation, including the damping factor, and  $x(t)$  is the instantaneous value of the coordinate of the moving atom. The spectrum of the radiation is determined by the square of the Fourier component of the expression (31):

$$|E(\omega)|^2 = \frac{E_0^2}{4\pi} \int_0^\infty \int_0^\infty e^{i(\Omega_0 - \omega)t - \frac{x(t)}{\lambda}} e^{-i(\Omega_0 - \omega)t' - \frac{x(t')}{\lambda}} dt dt'. \quad (32)$$

We can calculate the mean value  $\langle |E(\omega)|^2 \rangle$  for the set of atoms of the gas by using the fact that their motion is determined macroscopically by the equation of diffusion. The solution of this equation, normalized to unity,

$$P(\Delta x) = \frac{1}{(4\pi D \Delta t)^{1/2}} \exp \left\{ -\frac{(\Delta x)^2}{4D \Delta t} \right\} \quad (33)$$

gives the probability of a position of the atom. Here  $D$  is the diffusion coefficient of the atoms of the gas. The mean value of  $\exp(-\Delta x/\lambda)$  over the ensemble of noninteracting particles is given by

$$\langle e^{-i\frac{x}{\lambda}} \rangle = \int_0^\infty e^{-i\frac{\Delta x}{\lambda}} P(\Delta x) dx = e^{-\frac{D \Delta t}{\lambda^2}}. \quad (34)$$

Using Eq. (34), we find for the mean spectral density, by Eq. (32),

$$\langle |E(\omega)|^2 \rangle = \frac{\langle E_0^2 \rangle}{2\pi} \int_0^\infty \int_0^\infty e^{-\frac{D \Delta t}{\lambda^2}} e^{i(\Omega_0 - \omega)t - (\Omega_0^* - \omega^*)t'} dt dt'. \quad (35)$$

Assuming  $\delta \ll D/\lambda^2$ , which always holds in the radio region, we find the shape of the line after a direct integration:

$$\langle |E(\omega)|^2 \rangle = \frac{\langle E_0^2 \rangle}{2\pi\delta} \frac{D/\lambda^2}{(\omega_0 - \omega)^2 + (D/\lambda^2)^2}. \quad (36)$$

In this case the line has the Lorentz shape. If we assume that the diffusion coefficient  $D$  is given by

$$D = \left( \frac{\pi}{24} \right)^{1/2} \langle v \rangle_2 L, \quad (37)$$

where  $\langle v \rangle_2$  is the root-mean-square speed of the

atoms and  $L$  is the mean free path, the line width is given by

$$\Delta\nu = 4\pi \frac{D}{\lambda^2} = 2.8 \frac{L}{\lambda} \Delta\nu_D, \quad (38)$$

where  $\Delta\nu_D$  is the normal Doppler width given by Eq. (28). Thus in the radio region the Brownian motion of the atoms leads to a decided alteration of the line shape and line width.

In the derivation it was assumed that the collisions between atoms that occur as the result of elementary acts of diffusion do not affect the internal state of the emitter. Therefore the result is valid only for definite magnetic dipole transitions. These conditions hold in the phenomena of nuclear and electronic magnetic resonance absorption, and also for fine-structure and hyperfine-structure transitions in  $s$  states. In these cases collisions do not interrupt the process of emission from an atom.

Thus there is a decided change in the role of the Doppler effect in the broadening of lines of radio-frequency transitions. For example, for atomic hydrogen which is in an atmosphere of molecular hydrogen at 0.1 mm Hg, a calculation of the line width by Eq. (38) gives 200 kc, whereas  $\Delta\nu_D = 17.4$  kc. The experimentally observed<sup>14</sup> line width of 3 kc shows that in this case the Doppler effect plays a subordinate role and can be neglected.

A spectral line can be broadened on account of various kinds of collisions which occur in gases. In collisions of alkali-metal atoms with each other we must distinguish at least two types of interactions. The presence of unpaired electrons in the atoms leads to a dipole-dipole interaction between them. This gives a very small transition probability per collision. For hydrogen atoms it is of the order of  $10^{-4}$ . This effect is negligibly small in comparison with the electron-exchange interaction between identical atoms. If two atoms with oppositely directed spins pass each other at a distance less than  $10^{-8}$  cm, there is a large probability ( $\sim 0.5$ ) that the spin coordinates of the electrons get interchanged. In reference 14 a calculation is made of the longitudinal and transverse relaxation times  $T_1$  and  $T_2$  for atomic hydrogen associated with the exchange interactions. At room temperature

$$T_2 = 2T_1 = \frac{2}{v \cdot 2N \langle v \rangle \sigma_{\text{exch}}} = \frac{2 \cdot 10^9}{N} \text{ sec}. \quad (39)$$

Here  $\sigma_{\text{exch}}$  is the cross section for an exchange collision between electrons,  $\langle v \rangle$  is the mean relative velocity of the atoms, and  $N$  is the concentration of atomic hydrogen. As is seen from Eq. (39), the absorption line width has a linear dependence on the pressure of the gas. This conclusion is confirmed by experiment.

Among the other causes of broadening of lines we must mention broadening on account of saturation. This is of importance only for sufficiently large power of the radio-frequency field.<sup>18</sup>



## 2. The Role of the Buffer Gas

In the very first experiments on the optical orientation of atoms it was noted that residual amounts of a foreign gas in an absorption chamber filled with alkali-metal vapor ( $\text{Na}^{23}$ ,  $\text{Rb}^{87}$ ) increase the degree of orientation.<sup>1</sup> A systematic study of this matter showed<sup>17</sup> that the degree of orientation of the atoms increases appreciably when the pressure of the buffer gas is increased from 0.3 to 0.5 mm Hg. In the presence of the buffer gas the mean free path  $L$  of the alkali-metal atoms is shorter, which leads, according to Eq. (38), to a decrease of the Doppler line width, and also of the exchange line width. At the same time there is a decrease of the number of collisions of alkali-metal atoms with the walls of the absorption chamber. With increase of the pressure of the buffer gas, however, there begins to be a steadily increasing effect of the relaxation mechanism caused by collisions of the alkali metal with atoms or molecules of the buffer gas. Therefore there is an optimal pressure of the buffer gas at which the relaxation times for the oriented atoms have their largest values.

The optimum pressure can be estimated in the following way.<sup>18</sup> We shall assume that the optical illumination is turned on at the time  $t = t_0$  and acts for a time interval  $\Delta t$ . At the time  $t_0 + \Delta t$  the illumination is terminated, after producing a certain degree of orientation of the atoms.

Let  $N_0(t)$  be the number of oriented atoms and  $N_d(t)$  the number of atoms that have lost their orientation on account of collisions. Obviously

$$N_0(t) + N_d(t) = N.$$

We shall describe the change of the number of oriented atoms by means of the diffusion equation

$$D\Delta N_0 - \kappa N_0 = \frac{\partial N_0}{\partial t}, \quad (40)$$

assuming that collisions with molecules of the buffer gas lead to loss orientation of alkali-metal atoms. Here

$$\kappa = N_0 \sigma \langle v \rangle \frac{p}{p_0}, \quad (41)$$

$N = N_0 p / p_0$  is the number of atoms at atmospheric pressure  $p_0$ ,  $\sigma$  is the effective cross section for collisions between alkali-metal atoms and buffer-gas molecules,  $\langle v \rangle$  is the average relative velocity of the atom and molecule, and  $d$  is the diffusion coefficient of the alkali-metal atoms in the buffer gas:

$$D = D_0 \frac{p_0}{p}. \quad (42)$$

The solution of Eq. (40) for the case of a cylindrical absorption chamber of length  $L$  and diameter  $D$ , under the condition that  $N_0 = 0$  at the walls of the chamber, is of the form

$$N_0(r, z, t) = \sum_{i=1}^{\infty} \sum_{j=1}^{\infty} A_{ij} \exp\{[D(\mu_j^2 + \nu_j^2) + \kappa] t\} J_0(\mu_i r) \cos(\nu_j z). \quad (43)$$

Thus the relaxation time is given by the expression

$$T_j = \frac{1}{D(\mu_j^2 + \nu_j^2) + \kappa}, \quad (44)$$

where  $\mu_j$  are the roots of the equation  $J_0(\mu_0 d) = 0$ ,  $J_0$  is the Bessel function, and  $\nu_j = (\pi/L)/(2j-1)$ . The damping is mainly given by the first term in Eq. (43)

$$T_1 = \left\{ \left( \frac{2.405}{d} \right)^2 + \left( \frac{\pi}{L} \right)^2 D_0 \frac{p_0}{p} + N_0 \sigma \langle v \rangle \frac{p}{p_0} \right\}^{-1}. \quad (45)$$

It is not hard to see that as a function of  $p$  the time  $T_1$  has a maximum at a definite value  $p_m$ . Thus the value of the optimal pressure depends on the geometry of the chamber. The relaxation time is increased if we increase the length of the absorption chamber. Figure 4 shows experimental curves from reference 18 for various buffer gases, from which it can be seen that the relaxation time for a longitudinally extended chamber is longer than for a spherical chamber, for conditions otherwise equal. The optimal pressure of the buffer gas lies in the range 1–10 mm Hg, whereas the pressure of the alkali-metal vapor is of the order of  $10^{-6}$  or even  $10^{-7}$  mm Hg.

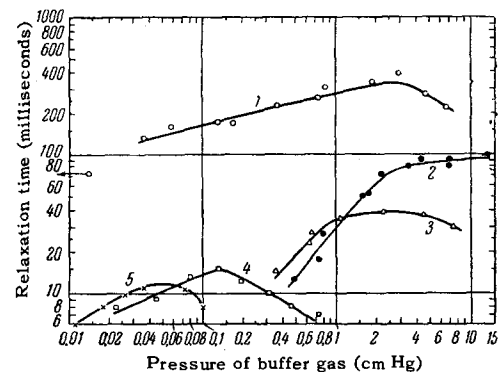


FIG. 4. Dependence of the longitudinal relaxation time  $T_1$  on the pressure of the buffer gas. 1 – neon, cylindrical chamber; 2 – neon, 3 – argon, 4 – krypton, and 5 – xenon, spherical chamber.<sup>18</sup>

## 3. The Role of Disorienting Collisions in the Excited State

We can calculate the effect of relaxation processes on the degree of orientation of the atoms in optical pumping by using the system of equations (11), which describe the changes of the populations of the hyper-fine-structure sublevels of the ground state of an alkali-metal atom.

For the case of two sublevels it follows from Eq. (10) that for the production of a high degree of orientation it is necessary that the time  $\tau$  of the optical transition be much less than the thermal "spin-lattice" relaxation time  $T_1$ . The approach to the stationary state occurs according to Eq. (9) and is characterized by the resultant time  $T_1^*$ .

This treatment, however, in which the effect of re-

laxation phenomena on the process of optical pumping is taken into account by the introduction of a spin-lattice relaxation time for the ground state, does not exhaust the subject.

As has already been noted,<sup>18</sup> atoms that are in the S state do not change their spin orientation in collisions with buffer-gas atoms. In optically excited states, however, such collisions disorient the spin angular momentum relative to the orbital angular momentum. This leads to a change of the probabilities  $P_{ks}$  themselves. The effect of collisions with the buffer gas on atoms that are in optically excited states has been studied in references 19 — 25.

In the very first experiments on this subject it was found that one can observe reorientation in the excited state by means of the light that is producing the pumping. Sodium vapor in an atmosphere of argon was illuminated with the resonance light of one of the D lines. It was found that when the partial pressure of the buffer gas was increased to several mm Hg the scattered resonance radiation as a rule contained both D lines, and the ratio of their intensities would approach the equilibrium value  $1/2$ , independently of which component was producing the excitation. This is due to the fact that as the pressure of argon is raised the number of collisions increases and the populations of the Zeeman sublevels of the states  $3P_{1/2}$  and  $3S_{1/2}$  become equalized, which leads to a definite constant ratio of the intensities of the D lines in the emission spectrum.

Therefore, as we already pointed out, a complete mixing of the magnetic sublevels of the P state on ac-

count of collisions is to be expected if the time between collisions approaches the lifetime of the optically excited states ( $\sim 1.5 \times 10^{-8}$  sec).

Introducing the notations

$$B_{kk} = -\mathcal{F}_k, \quad B_{sk} = P_{sk} \quad (s \neq k), \quad (46)$$

we can rewrite the equations (14) in the form

$$\frac{dN_k}{dt} = \sum_{s=1}^q B_{sk} N_s + \frac{N}{QT_1}. \quad (47)$$

Theoretical calculations of the transition probabilities  $B_{sk}$  can be made for two limiting cases, that in which there is no reorientation in the excited state, and that in which there is complete reorientation. Tables II and III show the values of  $\rho B_{sk}/\beta_0$  so obtained for the case of  $\text{Na}^{23}$  atoms (the  $D_1$  line).

It can be expected that a real system of atoms will be in a state intermediate between these two cases. The assumption of complete reorientation allows us to suppose that the transition probabilities from the excited state to any of the sublevels of the ground state are all the same.

From the solution of the equation (47) for  $\beta_0 T_1 \gg 1$  we can find the ratios  $N_k/N$  shown in Table IV. As can be seen from the table, the pumping process is more effective when there are no disorienting collisions in the excited state. This result is correct in the case in which the pumping is produced by means of only one D line (Figs. 5 and 6).

In the case in which the pumping is produced by the two D lines of approximately equal intensities, the degree of optical orientation goes to zero with increase

**Table II.** Values of the coefficients  $\rho B_{sk}/\beta_0$  for the case of no reorientation in the excited state<sup>9</sup>

$(F, m_F)$		$(1, -1)$	$(1, 0)$	$(1, 1)$	$(2, -2)$	$(2, -1)$	$(2, 0)$	$(2, 1)$	$(2, 2)$
$s$	$h$	1	2	3	4	5	6	7	8
$(1, -1)$	1	$-\frac{8}{\beta_0 T_1} - 11/3$	0	0	2	1	0	0	0
$(1, 0)$	2	$2/3$	$-\frac{8}{\beta_0 T_1} - 19/3$	0	2	2	$5/3$	0	0
$(1, 1)$	3	$1/3$	$5/3$	$-\frac{8}{\beta_0 T_1} - 6$	0	1	$5/3$	2	0
$(2, -2)$	4	0	0	0	$-\frac{8}{\beta_0 T_1} - 28/3$	0	0	0	0
$(2, -1)$	5	1	0	0	$10/3$	$-\frac{8}{\beta_0 T_1} - 9$	0	0	0
$(2, 0)$	6	$2/3$	$5/3$	0	2	2	$-\frac{8}{\beta_0 T_1} - 19/3$	0	0
$(2, 1)$	7	1	1	2	0	3	1	$-\frac{8}{\beta_0 T_1} - 10/3$	0
$(2, 2)$	8	0	2	4	0	0	2	$4/3$	$-\frac{8}{\beta_0 T_1}$

**Table III.** Values of the coefficients  $\rho_{B_{gk}}/\beta_0$  for the case of complete reorientation in the excited state<sup>9</sup>

$(F, m_F)$		$(F, m_F)$							
		$s$	1	2	3	4	5	6	7
$(1, -1)$	1	$-8 \frac{1}{\beta_0 T_1} - 3.5$	1	1.5	2	1.5	1	0.5	0
$(1, 0)$	2	0.5	$-8 \frac{1}{\beta_0 T_1} - 7$	1.5	2	1.5	1	0.5	0
$(1, 1)$	3	0.5	1	$-8 \frac{1}{\beta_0 T_1} - 10.5$	2	1.5	1	0.5	0
$(2, -2)$	4	0.5	1	1.5	$-8 \frac{1}{\beta_0 T_1} - 14$	1.5	1	0.5	0
$(2, -1)$	5	0.5	1	1.5	2	$-8 \frac{1}{\beta_0 T_1} - 10.5$	1	0.5	0
$(2, 0)$	6	0.5	1	1.5	2	1.5	$-8 \frac{1}{\beta_0 T_1} - 7$	0.5	0
$(2, 1)$	7	0.5	1	1.5	2	1.5	1	$-8 \frac{1}{\beta_0 T_1} - 3.5$	0
$(2, 2)$	8	0.5	1	1.5	2	1.5	1	0.5	$-8 \frac{1}{\beta_0 T_1}$

**Table IV.** Stationary relative populations  $N_k/N$  of the sublevels of the ground state<sup>9</sup>

	$N_1/N$	$N_2/N$	$N_3/N$	$N_4/N$
No reorientation . . . . .	$0.384 \frac{1}{\beta_0 T_1}$	$0.398 \frac{1}{\beta_0 T_1}$	$0.941 \frac{1}{\beta_0 T_1}$	$0.107 \frac{1}{\beta_0 T_1}$
Complete reorientation . . . . .	$2 \frac{1}{\beta_0 T_1}$	$\frac{1}{\beta_0 T_1}$	$\frac{2}{3} \frac{1}{\beta_0 T_1}$	$\frac{1}{2} \frac{1}{\beta_0 T_1}$

	$N_5/N$	$N_6/N$	$N_7/N$	$N_8/N$	$B/\beta_0$
No reorientation . . . . .	$0.194 \frac{1}{\beta_0 T_1}$	$0.398 \frac{1}{\beta_0 T_1}$	$1.45 \frac{1}{\beta_0 T_1}$	$1 - 3.87 \frac{1}{\beta_0 T_1}$	$3.63 \frac{1}{\beta_0 T_1}$
Complete Reorientation . . . . .	$\frac{2}{3} \frac{1}{\beta_0 T_1}$	$\frac{1}{\beta_0 T_1}$	$2 \frac{1}{\beta_0 T_1}$	$1 - 7.89 \frac{1}{\beta_0 T_1}$	$7 \frac{1}{\beta_0 T_1}$

of the pressure of the buffer gas.<sup>26</sup> Therefore when the orientation is by the two D lines the pressure of the buffer gas must be less than the optimal pressure.

This difference in the effect of the number of collisions in the excited state in the two cases (one D line and both D lines) can be explained in the following way. When the intensities of the two D lines ( $D_1$  and  $D_2$ ) are about the same, the probabilities of absorption are also the same for all magnetic sublevels. In this case the pumping process depends in an essential way on the preservation in the excited state of the changes of angular momentum that have occurred in the absorption of circularly polarized quanta. In the case of one D line the probabilities of the transitions are unequal, and even losses of information in the excited state do not seriously affect the pumping process, which in this case does not depend so much on the

changes of the magnetic quantum number as on the selection rules.

**4. The Dependence of the Resonance Frequency on the Pressure of the Buffer Gas**

The presence of a buffer gas, which under otherwise equal conditions increases the degree of orientation of the atoms, leads to a shift of the resonance frequency of the radio-frequency absorption lines. A detailed study of the shift of the resonance frequency produced by various buffer gases has been made for  $Na^{23}$  and  $Cs^{133}$  in a paper by Arditi.<sup>49</sup> The results of the experiments show that the resonance frequency of the hyperfine transitions varies linearly with the pressure, as can be seen from Table V.

The lighter gases (hydrogen, helium, nitrogen,

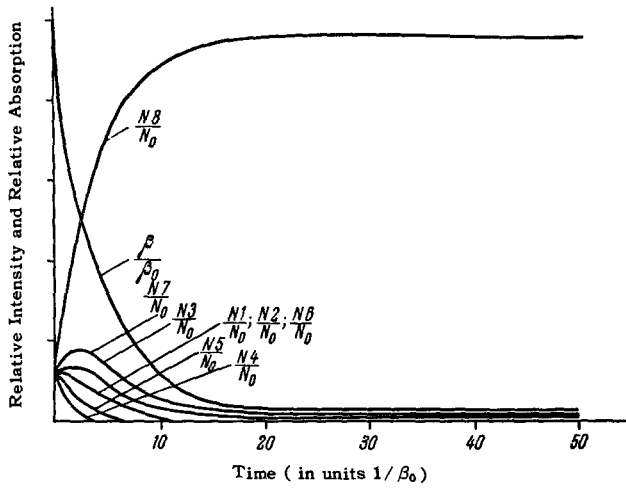


FIG. 5. Time dependences of the population of the Zeeman sub-levels of the ground state of the sodium atom and of the absorption probability  $\beta/\beta_0$ , for sudden turning on of orienting  $\sigma^+$  light, for the case of complete reorientation of the atoms in the excited state.<sup>9</sup>

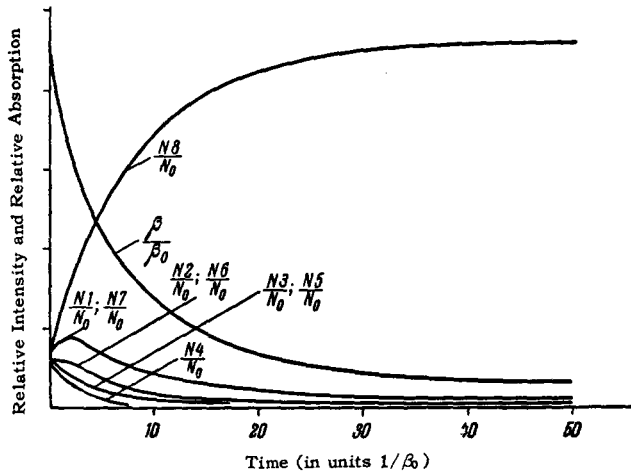


FIG. 6. The same as FIG. 5, but for the case of no reorientation in the excited state.<sup>9</sup>

neon) produce shifts toward higher frequencies, while the heavy gases (argon, krypton, xenon) diminish the resonance frequency. The frequency displacement  $\delta$  is proportional to the pressure of the buffer gas. Therefore for a mixture of gases it is to be expected that

$$\delta = \sum_k p_k^0 \delta_k, \quad (48)$$

where  $\delta_k$  is the value of the shift for the  $k$ -th kind of gas, and  $p_k^0$  is its fractional partial pressure ( $\sum_k p_k^0 = 1$ )

According to Eq. (48) a mixture of two buffer gases for which the frequency of the hyperfine transitions will not depend on the pressure must satisfy the requirements

$$p_1 \delta_1 + p_2 \delta_2 = 0, \quad p_1 + p_2 = 1. \quad (49)$$

As can be seen from Table V, these conditions can be satisfied in several ways, for example by choosing as

Table V. Dependence of resonance frequency of hyperfine transitions on the pressure of a buffer gas (in cps/mm Hg)

Buffer Gas	Frequency Shift
Na <sup>23</sup> Nitrogen	+ 100
Neon	+ 80
Argon	≈ 0
Hydrogen	+ 1900
Helium	+ 1600
Nitrogen	+ 930
Cs <sup>133</sup> Neon	+ 650
Argon	- 250
Krypton	- 1300
Xenon	- 2400

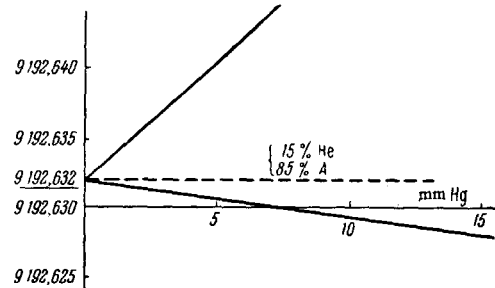


FIG. 7. Dependence of the frequency (in Mc) of the transitions between the hyperfine-structure sublevels of Cs<sup>133</sup> on the pressure of the buffer gas, for helium, argon, and a mixture of the two gases.<sup>49</sup>

the buffer gas a mixture of helium and argon (Fig. 7).

We note that the buffer gas that gives the largest frequency shift also produces the largest disorientation of the atoms. Therefore the intensity of the light which has passed through the absorption chamber depends on the pressure of the buffer gas.

The presence of a buffer gas also causes a shift of the frequencies of optical transitions.<sup>77</sup>

#### IV. PHENOMENOLOGICAL THEORY OF OPTICAL ORIENTATION OF ATOMS

##### 1. The Equations for the Magnetization

The variation of the magnetization that appears when there is optical orientation of the atoms of a paramagnetic gas can be described by means of phenomenological equations<sup>8</sup> which are externally similar to the Bloch equations for the variation of the nuclear magnetization.<sup>27</sup> The solutions of these equations enable us to make calculations to predict for the process of optical pumping the time dependence of the signal, the intensities of the longitudinal and transverse beams, and the required amplitude of the radio frequency field.

For the case in which there are two energy sublevels of the ground state of the atoms ( $s = \pm 1/2$ ), the component  $M_z$  of the magnetization of the gas in the direction of propagation of the longitudinal beam is given by

$$M_z = \mu_a N V_z, \quad (50)$$

where  $\mu_a$  is the magnetic moment of the atom and  $V_z$  is the degree of orientation given by Eq. (3), where  $P_{AB}$  and  $P_{BA}$  are the probabilities of the respective transitions under the action of the  $z$  beam. Using the equation (8) for the variation of  $M_z$  with the time, we find

$$\frac{dM_z}{dt} + \frac{1}{T_1^*} (M_z - M_z^0) = 0, \quad (51)$$

where

$$M_z^0 = \frac{T_1 M_z^P + \tau_z M_z^T}{T_1 + \tau_z}, \quad \frac{1}{T_1^*} = \frac{1}{\tau_z} + \frac{1}{T_1}, \quad (52)$$

and

$$M_z^P = \mu_a N V_z^P, \quad M_z^T = \mu_a N V_z^T. \quad (53)$$

For optical orientation of the atoms  $\tau_z M_z^0 \ll T_1 M_z^P$ . Remembering that the transition probabilities  $P_{AB}$  and  $P_{BA}$  under the action of the  $z$  beam are proportional to its intensity, we get

$$M_z^0 = M_0 \frac{\alpha_z T_1 J_z}{1 + \alpha_z T_1 J_z} V_z^P, \quad (54)$$

where  $M_0 = \mu_a N$ .

The establishment of the stationary orientation of the atoms of a gas which is in the external field  $H_0 = H_z$  and acted on by a  $z$  beam which is turned on at the time  $t = 0$  is described by the solution of Eq. (49)

$$M_z = M_z^0 \left(1 - e^{-\frac{t}{T_1^*}}\right), \quad (55)$$

where  $M_z^0$  is the stationary magnetization. As follows from Eq. (54),  $M_z^0$  increases monotonically with increase of the intensity  $J_z$  of the orienting beam. For  $\alpha_z T_1 J_z \gg 1$  the limiting magnetization is  $M_z = \mp M_0$ . We note that  $M_z$  is negative, i.e., is directed opposite to the magnetic field  $H_0$ , if  $V_z^P < 0$ .

If the direction of the magnetic field  $H_0$  does not coincide with the direction of the  $z$  beam, then in the right member of Eq. (49) we must use the  $z$  component of the torque with which the external field acts on the atom. Denoting by  $\gamma_a$  the absolute value of the gyro-magnetic ratio of the atom, we have:

$$\frac{dM_z}{dt} + \frac{1}{T_1^*} (M_z - M_z^0) - \gamma_a [\mathbf{M}, \mathbf{H}]_z = 0. \quad (56)^*$$

In the absence of an orienting beam ( $J_z = 0$ ), according to Eq. (52),

$$M_z^0 = M_0 V_z^T = \gamma_a H_z \quad (57)$$

and  $T_1^* = \tau_z$ . In this case Eq. (54) goes over into the corresponding Bloch equation.

The equations for the variation with time of the components  $M_x$  and  $M_y$  of the magnetization are obtained in a similar way:

$$\left. \begin{aligned} \frac{dM_x}{dt} + \frac{1}{T_1^*} (M_x - M_x^0) - \gamma_a [\mathbf{M}, \mathbf{H}]_x &= 0, \\ \frac{dM_y}{dt} + \frac{1}{T_1^*} (M_y - M_y^0) - \gamma_a [\mathbf{M}, \mathbf{H}]_y &= 0, \end{aligned} \right\} \quad (58)$$

\* $[\mathbf{M}, \mathbf{H}] = \mathbf{M} \times \mathbf{H}$

where

$$\frac{1}{T_2^*} = \frac{1}{\tau_z} + \frac{1}{T_2}, \quad (59)$$

and  $T_2$  is the time of phase memory of the system of atoms.

If in addition to the orienting  $z$  beam the atoms are also illuminated by a  $\rho$  beam arbitrarily oriented in space, instead of the expressions (50) and (59) we must set

$$\frac{1}{T_1^*} = \frac{1}{\tau_z} + \frac{1}{\tau_\rho} + \frac{1}{T_1}, \quad \frac{1}{T_2^*} = \frac{1}{\tau_z} + \frac{1}{\tau_\rho} + \frac{1}{T_2}, \quad (60)$$

where  $1/\tau_\rho = \alpha_\rho J_\rho$  is the probability of the optical transition under the action of the  $\rho$  beam. In this case, neglecting the paramagnetic magnetization of the gas, we find in analogy with Eq. (54):

$$M_x^0 = M_0 \frac{\alpha_\rho T_2 J_\rho V_\rho^P}{1 + T_1 (\alpha_z J_z + \alpha_\rho J_\rho)}, \quad (61a)$$

$$M_y^0 = M_0 \frac{\alpha_\rho T_2 J_\rho V_\rho^P}{1 + T_1 (\alpha_z J_z + \alpha_\rho J_\rho)}, \quad (61b)$$

$$M_z^0 = M_0 \frac{\alpha_z T_1 J_z V_z^P}{1 + T_1 (\alpha_z J_z + \alpha_\rho J_\rho)}. \quad (61c)$$

If the two beams ( $z$  and  $\rho$ ) are identically polarized, then  $\alpha_z = \alpha_\rho$ .

Thus the problem of calculating the magnetization of a gas in the process of optical orientation reduces to the solution of the system of equations (56) and (58) under suitable conditions.

In the study of the phenomenon of the optical orientation of atoms the need arises to ascertain the nature of the change of the intensity of the  $z$  beam after its passage through the absorption chamber. Such a change can be caused both by the action of a  $\rho$  beam and by a radio frequency field, and is characterized by  $S_z$  and  $S_\rho$  signals.

Using Eqs. (24) and (27), we find for the longitudinal signal ( $S_z$ ) and the transverse signal ( $S_\rho$ ) the expressions

$$S_z = J_z \frac{M_z^P M_z}{M_0^2}, \quad S_\rho = J_\rho \frac{M_\rho^P M_\rho}{M_0^2}. \quad (62)$$

For the case considered above in which the orienting  $z$  beam is suddenly turned on we have according to Eq. (53)

$$S_z = \frac{\alpha_z T_1 J_z}{1 + \alpha_z T_1 J_z} (V_z^P)^2 \left(1 - e^{-\frac{t}{T_1^*}}\right). \quad (63)$$

## 2. The Effect of a Radio-Frequency Field on the Process of Orientation of Atoms

Let us consider the case in which the atoms of the gas in the absorption chamber are in a circularly polarized radio-frequency field

$$h_x = h_0 \cos \omega t, \quad h_y = h_0 \sin \omega t, \quad (64)$$

whose frequency is close to the resonance frequency for transitions between the magnetic sublevels. To

solve the equations (56) and (58) in this case for an arbitrary amplitude of the radio-frequency field it is convenient to go over to a coordinate system which rotates with the frequency  $\omega = \omega_z$  around the z axis. This change of system is made by substituting in Eqs. (56) and (58)

$$\frac{dM}{dt} \rightarrow \frac{dM'}{dt} + [\omega, M'], \quad (65)$$

where  $M'$  is the magnetization relative to the rotating coordinate system. In this system the components of the radio-frequency field are

$$h_x = h_0 \cos \varphi, \quad h_y = h_0 \sin \varphi,$$

where  $\varphi$  is the angle which the stationary vector of the radio-frequency field makes with the axes of this system. Then, setting  $dM'/dt = 0$ , we find a system of inhomogeneous algebraic equations

$$\left. \begin{aligned} -T_2^* [M', \Delta\omega]_x + M'_x &= M_x^0, \\ -T_2^* [M', \Delta\omega]_y + M'_y &= M_y^0, \\ -T_2^* [M', \Delta\omega]_z + M'_z &= M_z^0, \end{aligned} \right\} \Delta\omega = \gamma_a H + \omega, \quad (66)$$

whose solution describes the eventually established motion of the vector (Bloch's case of "slow passage")<sup>27</sup> ( $\omega_L = |\gamma_a| H_0$ ):

$$M_x = \frac{M_x^0 - T_2^* \Delta\omega_z M_y^0}{1 + (T_2^* \Delta\omega_z)^2} + \frac{T_2^* (\Delta\omega_y + T_2^* \Delta\omega_x \Delta\omega_z)}{1 + (T_2^* \Delta\omega_z)^2} M_z, \quad (67a)$$

$$M_y = \frac{M_y^0 + T_2^* \Delta\omega_z M_x^0}{1 + (T_2^* \Delta\omega_z)^2} - \frac{T_2^* (\Delta\omega_x - T_2^* \Delta\omega_x \Delta\omega_z)}{1 + (T_2^* \Delta\omega_z)^2} M_z, \quad (67b)$$

$$M_z = \frac{M_z^0 [1 + T_2^{*2} (\omega_L - \omega)^2] - T_1^* T_2^* (\omega_L - \omega) \gamma_a (M^0 h_0) + T_1^* \gamma_a [M^0, h_0]_z}{1 + T_2^{*2} (\omega_L - \omega)^2 + T_1^* T_2^* \gamma_a^2 h_0^2} \quad (67c)$$

The component  $M'_z$  in the rotating coordinate system is equal to  $M_z$ , and  $M'_x$  and  $M'_y$  are connected with  $M_x$  and  $M_y$  by the simple relations

$$M_x = M'_x \cos \omega t + M'_y \sin \omega t, \quad M_y = M'_x \sin \omega t + M'_y \cos \omega t \quad (68)$$

and vary harmonically with the frequency  $\omega$ . Thus according to Eqs. (67a) and (67b) an x or y beam is modulated in amplitude with the frequency  $\omega$ .

At resonance

$$M_z = \frac{M_z^0 + T_1^* \gamma_a [M^0, h_0]_z}{1 + T_1^* T_2^* \gamma_a^2 h_0^2} \quad (69)$$

decreases with increase of the amplitude of the radio-frequency field. The magnitude of the signal  $S_z$  decreases with approach to resonance. There is also a decrease of  $S_z$  with increase of the amplitude of the radio-frequency field.

From these solutions one can see the competition between the effect produced by the z beam and the thermal relaxation, and also the effect of a  $\rho$  beam on the intensity of the z beam. For small intensities  $J_\rho$  this effect is insignificant. If, however, the beam can produce orientation during the period of the Larmor frequency  $\omega_L$ , it can decidedly diminish the degree of orientation produced by the z beam.

From the expressions that have been given for  $M'$

it follows that in the process of optical pumping there is an increase of the width of the resonance line. If we vary  $J_\rho$  or  $\tau_\rho$  with other conditions kept the same, the condition for the maximum of the signal  $S_z$  is

$$\left(\frac{1}{\tau_0}\right)^2 = \left(1 + \frac{\tau_z}{T_1}\right) \left(1 + \frac{\tau_z}{T_2}\right) \frac{1}{\tau_z^2}. \quad (70)$$

Usually  $\tau_z \ll T_{1,2}$  (slow relaxation), and the largest  $\rho$ -beam signal ( $S_\rho$ ) is observed when the intensities of the  $\rho$  and z beams are equal ( $J_\rho = J_z$ ). In this case the width of the signal  $S_z$  is twice the value it has in the absence of the  $\rho$  beam, and its amplitude is half of the value in the absence of the  $\rho$  beam.

It can be shown<sup>8</sup> that the terms in the expressions (56) that contain  $M_x^0$  and  $M_y^0$  can be omitted, since their only effect on the modulation of the x and y beams is at frequencies that are multiples of the Larmor frequency ( $0, 2\omega_L, 4\omega_L$ ), and they do not change the modulation of the x and y signals with the Larmor frequency.

## V. DETECTION OF RADIO FREQUENCY RESONANCE BY THE OPTICAL METHOD. DETERMINATION OF THE HYPERFINE STRUCTURE CONSTANT AND OF NUCLEAR AND ELECTRONIC g FACTORS

The combination of methods of optical orientation of atoms with the technique of radio-frequency resonance opens up new possibilities for the application of this effect for both scientific and practical purposes.

### 1. The Energy Spectrum of Alkali Metal Atoms in a Magnetic Field

For the quantitative description of the effect of radio-optical double resonance we need a detailed analysis of the energy spectrum of atoms in a magnetic field.

The ground state of atoms which have a single electron in an unfilled shell is a  $^2S_{1/2}$  state. If we neglect the interaction of the optical (valence) electron with the nucleus, the energy spectrum near the ground state has the form shown in Fig. 8. The optical transitions  $P_{3/2} \rightarrow S_{1/2}$  and  $P_{1/2} \rightarrow S_{1/2}$  allowed by the selection rules  $\Delta l = \pm 1$  form a narrow (spin) doublet. If we take into account the interaction of the valence electron with the nucleus the picture is much more complicated. The number of energy levels of the atom in each state is determined by the possible values of the total angular momentum  $F$ ,

$$F = I + J = I + L + S. \quad (71)$$

If we place the gas in a weak external magnetic field  $H_0$  which does not break the coupling between the vectors  $I$  and  $J$ , each energy state of the atom splits up into  $2F + 1$  sublevels, and the distances between them increase with increase of the magnetic field strength. One can find the positions of the energy

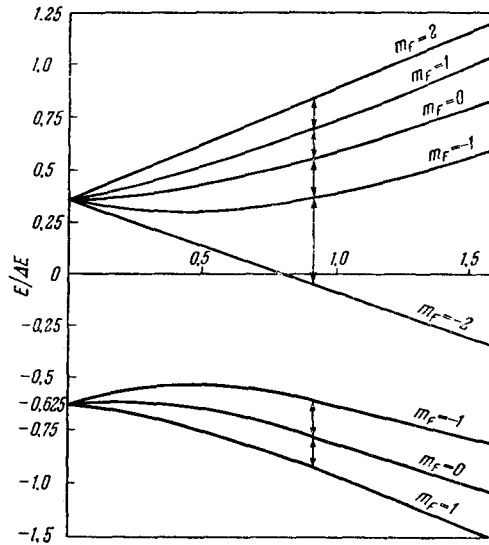


FIG. 8. Energy spectrum of an alkali metal atom ( $I = 3/2$ ) in a magnetic field. The abscissa is the value of the parameter  $\xi$ . The transitions  $\Delta m_F = \pm 1$  between the magnetic sublevels are represented by arrows.

levels by solving the corresponding quantum mechanical problem.

For the ground state of the atom the part of the energy operator that describes the magnetic interaction of the nucleus of the atom with the optical electron and their interactions with the external field is<sup>28</sup>

$$\hat{\mathcal{H}} = a(\mathbf{I}, \mathbf{J}) - \gamma_J \hbar (\mathbf{J}, \mathbf{H}_0) - \gamma_I \hbar (\mathbf{I}, \mathbf{H}), \quad (72)$$

where  $a(\mathbf{I}, \mathbf{J})$  is the hyperfine structure interaction constant and  $\gamma_J$  and  $\gamma_I$  are the gyromagnetic ratios for the electron and the nucleus:

$$\gamma_J \hbar = \frac{\mu_J}{J}, \quad \gamma_I \hbar = \frac{\mu_I}{I}. \quad (73)$$

The presence of the term  $a(\mathbf{I}, \mathbf{J})$  in Eq. (72) leads to the hyperfine splitting  $\Delta E$  of the energy levels even in the absence of the external field. It is convenient to express this splitting in frequency units

$$\Delta E = 2\pi \hbar \Delta \nu. \quad (74)$$

As a measure of the magnitude of the field  $H_0$  it is convenient to take the dimensionless ratio

$$\xi = \frac{|\gamma| H_0}{2\pi \Delta \nu}, \quad \gamma = \gamma_J + \gamma_I. \quad (75)$$

It is agreed to regard<sup>29</sup> the field as weak for  $|\xi| < 0.1$ , as intermediate for  $|\xi| \sim 1$ , and as strong for  $|\xi| > 3$ . For weak fields the vector  $\mathbf{F}$  can be regarded as an integral of the motion.

The energy eigenvalues of the atom for the case  $J = 1/2$  are given by the Breit-Rabi formula,<sup>29</sup> which for  $\mu_I > 0$  has the form:

$$E\left(I \pm \frac{1}{2}, m_F\right) = -\frac{a}{4} - \gamma_I \hbar m_F H_0 \pm \frac{a}{4} (2I+1) \left\{ 1 + \frac{4m_F}{2I+1} \xi + \xi^2 \right\}^{1/2}. \quad (76)$$

In the derivation of Eq. (76) it is assumed that the component of  $\mathbf{F}$  along the direction of the field is an integral of the motion, which is always correct. As can be seen from Eq. (76), in the absence of a field  $\Delta E = a(I + 1/2)$ .

For the alkali metals the hyperfine splitting  $\Delta \nu$  is of the order of magnitude of  $10^{10}$  cps, and  $|\gamma|/2\pi \approx |\gamma_J|/2\pi = 2802552$  cps; therefore  $\xi \approx 10^{-4} H_0$ . In the majority of cases optical orientation is produced in weak fields, and therefore it is sufficient to keep the quadratic terms in the expansion of Eq. (76) in powers of  $\xi$ . Using Eqs. (74) and (75), we find:

$$\begin{aligned} \frac{1}{\hbar} E\left(I + \frac{1}{2}, m_F\right) &= \frac{I}{2I+1} \Delta \nu - \Gamma^- m_F H_0 + \left\{ \frac{1}{4\Delta \nu} \left(\frac{\gamma}{2\pi}\right)^2 - G m_F^2 \right\}, \\ \frac{1}{\hbar} E\left(I - \frac{1}{2}, m_F\right) &= -\frac{I+1}{2I+1} \Delta \nu + \Gamma^+ m_F H_0 - \left\{ \frac{1}{4\Delta \nu} \left(\frac{\gamma}{2\pi}\right)^2 - G m_F^2 \right\}, \end{aligned} \quad (77)$$

where

$$\Gamma^\pm = \frac{1}{2\pi} \left( \frac{\gamma}{2I+1} \pm \gamma_I \right), \quad G = \left( \frac{\gamma}{2\pi} \right)^2 \frac{1}{(2I+1)^2 \Delta \nu}. \quad (78)$$

The frequencies of magnetic transitions between adjacent Zeeman sublevels ( $\Delta m_F = \pm 1$ ) corresponding to the same value of  $F$  are given by

$$\nu^\mp = \nu\left(I \pm \frac{1}{2}, m_F, I \pm \frac{1}{2}, m_F - 1\right) = \Gamma^\mp H_0 - (2m_F - 1) G H_0^2. \quad (79)$$

It is easy to solve Eq. (79) for  $H_0$  in the quadratic approximation, by setting  $\nu^\mp = \Gamma^\mp H_0$  in first approximation. We then get

$$H_0 = \frac{1}{\Gamma^\mp} \nu^\mp + (2m_F - 1) \frac{G}{(\Gamma^\mp)^3} (\nu^\mp)^2. \quad (80)$$

For transitions between sublevels  $I + 1/2 \rightarrow I - 1/2$  we find:

$$\begin{aligned} \nu\left(I + \frac{1}{2}, m_F; I - \frac{1}{2}, m'_F\right) &= \Delta \nu - [\Gamma^- m_F + \Gamma^+ m'_F] H_0 \\ &+ \left[ \frac{1}{2\Delta \nu} \left(\frac{\gamma}{2\pi}\right)^2 - G(m_F^2 + m'^2_F) \right] H_0^2. \end{aligned} \quad (81)$$

The allowed transitions must satisfy the condition  $m_F - m'_F = 0, \pm 1$ . The coefficients  $\Gamma^\pm$  and  $G$  for each concrete case can be calculated if  $\gamma_I$  and  $\Delta \nu$  are known.

For example,<sup>30,45</sup> for  $\text{Na}^{23}$  ( $I = 3/2$ )

$$\frac{\gamma_I}{2\pi} = 1126.7 \text{ cps}, \quad \Delta \nu = 1771.6262 \text{ Mc} \quad (82)$$

from which we find  $|\xi| = 0.0016 H_0$ , and for  $m_F = 2$

$$\Gamma^- = 699793 \text{ cps/oe}, \quad (2m_F - 1)G = 832 \text{ cps/oe}^2. \quad (83)$$

Similarly, for the isotope  $\text{Rb}^{87}$  ( $I = 3/2$ )<sup>30</sup> and  $m_F = 2$

$$\left. \begin{aligned} \frac{\gamma_I}{2\pi} &= 1397 \text{ cps/oe}, \quad \Delta \nu = 6834.1 \text{ Mc}, \\ \Gamma^- &= 699591 \text{ cps/oe}, \quad (2m_F - 1)G = 216 \text{ cps/oe}^2. \end{aligned} \right\} \quad (84)$$

We note that the transition  $(I + \frac{1}{2}, m_F = 0) \rightarrow (I - \frac{1}{2}, m_F = 0)$  has the frequency

$$\nu \left( I + \frac{1}{2}, 0; I - \frac{1}{2}, 0 \right) = \Delta\nu + \frac{1}{2\Delta\nu} \left( \frac{\nu}{2\pi} \right)^2 H_0^2 \quad (85)$$

which has the least dependence on the field. The coefficient of  $H_0^2$  is small. For  $\text{Na}^{23}$  the term is  $2.2 \times 10^3 H_0^2$ , and

$$\nu = (1771.6262 + 0.0022H_0^2) \text{ Mc.} \quad (86)$$

As can be seen from Eqs. (79) and (81), the frequencies of the transitions are somewhat different in the same field  $H_0$ . Therefore on varying the frequency in the neighborhood of  $\Gamma^\pm H_0$  or  $\Delta\nu$  one will observe several lines of radio frequency resonance absorption, their number being determined by the selection rules for the magnetic quantum number ( $\Delta m_F = 0, \pm 1$ ). For the case of nuclear spin  $I = \frac{3}{2}$  there will be  $4 + 2 = 6$  such lines in the neighborhood of the frequency  $\Gamma^\pm H_0$ . The transitions corresponding to these lines are shown in Fig. 8. Their frequencies are

$$\left. \begin{aligned} \nu(2, 2; 2, 1) &= \Gamma^- H_0 + 3GH_0^2, & \nu(2, -1; 2, -2) &= \Gamma^- H_0 - 3GH_0^2, \\ \nu(2, 1; 2, 0) &= \Gamma^- H_0 + GH_0^2, & \nu(1, -1; 1, 0) &= \Gamma^+ H_0 - GH_0^2, \\ \nu(2, 0; 2, -1) &= \Gamma^- H_0 - GH_0^2, & \nu(1, 0; 1, -1) &= \Gamma^+ H_0 + GH_0^2. \end{aligned} \right\} \quad (87)$$

All six lines lie in the frequency interval

$$\delta\nu = \nu(1, -1; 1, 0) = \nu(2, 1; 2, 0) = 2\frac{\gamma_I}{2\pi} H_0 + 4GH_0^2. \quad (88)$$

For  $\text{Na}^{23}$   $\delta\nu = 1628$  cps, and for  $\text{Rb}^{87}$   $\delta\nu = 1685$  cps. Besides these six lines for  $\text{Na}^{23}$  and  $\text{Rb}^{87}$  one can observe four weak lines caused by the quadrupole moments of these nuclei.

The frequencies of the six lines that correspond to the allowed transitions  $I + \frac{1}{2} \rightarrow I - \frac{1}{2}$  can be calculated easily from Eq. (81). The sum of the four frequencies corresponding to the transitions  $(2, m_F) \rightarrow (2, m_F')$  is found from Eqs. (87), (78), and (75) to be

$$\sum \nu = 4\Gamma^- H_0 = \frac{1}{2\pi} (-\gamma + 4\gamma_I) H_0 = \frac{1}{2\pi} (-\gamma_J + 3\gamma_I) H_0. \quad (89)$$

If we denote the frequency of the resonance transition for free electrons by  $\nu_S = |\gamma_S| H_0 / 2\pi$ , the quantity  $(\nu_S - \Sigma\nu) / \nu_S$  does not depend on the field. According to Eq. (89) we easily get

$$\gamma_J = \gamma_S \left( 1 - 3\frac{\gamma_I}{\gamma_S} - \frac{\nu_S - \Sigma\nu}{\nu_S} \right). \quad (90)$$

By measuring the resonance frequency  $\nu_S$  for free electrons and the sum  $\Sigma\nu$  for the nucleus with the gyromechanical ratio  $\gamma_I$  one can use Eq. (90) to find the gyromagnetic ratio of the alkali metal atom with the nuclear spin  $I = \frac{3}{2}$ . As can be seen from Eq. (90),  $|\gamma_J| > |\gamma_S|$ , since  $\gamma_S < 0$ .

## 2. Experiments to Study Radio Frequency Resonance by the Optical Method

If we place an ensemble of optically oriented atoms in a radio frequency field of a frequency corresponding

to transitions between the hyperfine or Zeeman sublevels of the atom, disorientation of the atoms will occur both in the ground state and in the excited state. In the limiting case of saturation of the radio-frequency resonance the populations of the sublevels will be equalized, i.e., the states in which the atoms can absorb light will be repopulated. As a result of this the intensity of light passing through the absorption chamber is diminished. The experimentally observed shape and width of the signal give information about relaxation processes in the system.

Radio-frequency transitions between optically excited states can also be observed by the method of double resonance. This method was first applied to the study of the  $6^3P_1$  state of the mercury atom by Brossel and Bitter.<sup>32,33</sup>

Mercury vapor was illuminated with resonance light  $\lambda = 2537 \text{ \AA}$ , which takes atoms from the ground  $6^1S_0$  state to the triplet  $6^3P_1$ . If the light is polarized so that the electric vector is parallel to the constant magnetic field, it excites atoms only to the sublevel  $m = 0$ . The light emitted by the atoms will be linearly polarized. If a radio frequency field of the resonance frequency is applied perpendicular to  $H_0$ , the radiation from the atoms will also contain  $\sigma$  components. Measurements of the intensity of the emerging light and the character of its polarization in this case give a possibility for detecting radio-frequency resonance. As can be seen from Fig. 9 (curve I), as the radio-frequency resonance is approached the  $\sigma$  component appears, and its intensity reaches a maximum at resonance. The shape of the observed signal is determined by the shape of the magnetic resonance absorption line.

If a constant electric field  $E_0$  is applied parallel to the magnetic field  $H_0$ , there is a new possibility for studying the Stark effect.<sup>34,35</sup> For the  $6^3P_1$  state of mercury the energy intervals  $m = 0 \rightarrow 1$  and  $m = 0 \rightarrow -1$  become unequal in the presence of the electric field (50 kv/cm), and this leads to a distinct splitting of the resonance line (Fig. 9, curve II). One of the maxima corresponds to the absorption of radio-fre-

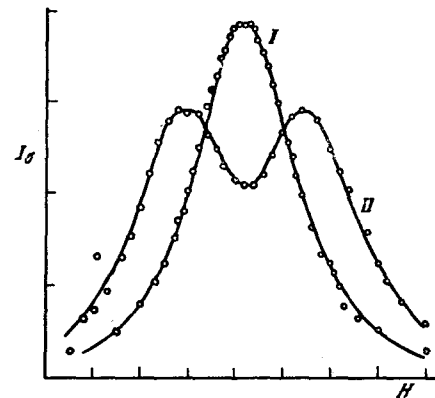


FIG. 9. Curves of the dependence of the optical signal on the magnetic field intensity  $H$  for radio frequency transitions between the sublevels of the  $6^3P_1$  state of mercury. I - without electric field; II - in an electric field  $E \parallel H$  (50 kv/cm).<sup>35</sup>



quency energy and the other to induced emission. The method of detecting the resonance does not enable us to establish a difference between them, and consequently does not determine the sign of the Stark splitting. This sign can be found, however, by studying separately the mercury isotopes which have nonzero nuclear moments and show hyperfine structure.

We call attention to the fact that the Stark splitting, which is easily observed in this case by the radio-optical method is so small that it cannot be detected by the methods of optical spectroscopy. An analysis of the results of the experiments has made it possible not only to confirm that the Stark effect is quadratic in the field, but also to determine the coefficients in the theoretical formula for the separate isotopes and for the mixture.

Dehmelt<sup>36</sup> has made experiments to detect the radio frequency resonance of mercury vapor in the metastable  $6^3P_2$  state in a magnetic field  $H_0 = 0.3$  oe (Fig. 10). Excitation to this state occurred by collisions of

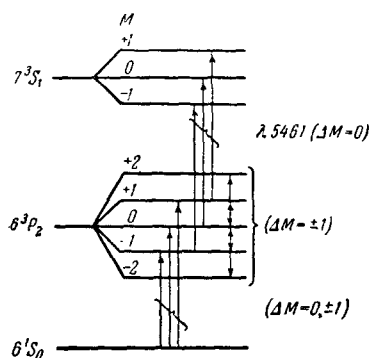


FIG. 10. Diagram to explain the detection of magnetic resonance in the metastable  $6^3P_2$  state of mercury.

the mercury atoms with electrons. Electron collisions produce transitions  $6^1S_0 \rightarrow 6^3P_2$  with the changes  $\Delta m_F = 0, \pm 1$ . The redistribution of the populations caused by the collisions was checked by observing visible radiation  $\lambda = 5461 \text{ \AA}$  which had passed through the absorption chamber; absorption of this light causes transitions  $6^3P_2 \rightarrow 7^3S_1$ . For linear polarization of the light the absorption is mainly through transitions from the level  $m = 0$ . The situation is decidedly changed when there is a radio frequency field ( $\sim 10^{-3}$  oe) perpendicular to  $H_0$ , which induces transitions with  $\Delta m = \pm 1$ . These transitions lead to an increase of the populations of the sublevels  $m_F = \pm 2$ , which take part in the absorption. There is then a decrease of the contribution to the absorption that comes from the sublevels  $m_F = 0, \pm 1$ . The value of the g factor found from measurements of the resonance frequency was  $1.48 \pm 0.01$ , in agreement with the results found by the optical method.

In weak fields the method of optical detection of radio-frequency absorption in a gaseous system of atoms has obvious advantages over the direct method of detecting the effect from the absorption of the en-

ergy of the radio-frequency field. In fact, the amount of energy  $\chi''$  absorbed from the radio-frequency field is proportional to the product of the difference of the populations of the sublevels between which the transition occurs and the thermal relaxation time  $T_1$ , i.e., to the product  $NV^T T_1$ . For rarefied gases, in which  $T_1$  is relatively large ( $T_1 \sim 10^{-5}$  sec) and the interaction of the atoms is mainly through collisions,  $N \approx 10^{16} \text{ cm}^{-3}$ , or at least six orders of magnitude smaller than in condensed media. Therefore because of the small value of the orientation parameter  $V^T$  the absorption signal is much weaker than in solids. To observe an appreciable absorption in the case of transitions  $F = 1 \rightarrow F = 2$  in the ground state in a weak field it is necessary to use considerable quantities of gas (to fill a waveguide with the gas).

It is practically impossible to observe transitions between Zeeman sublevels of the hyperfine structure corresponding to the same value of  $F$  from the absorption of energy from the radio frequency field, because of the smallness of  $V^T$ .

### 3. Many-Quantum Transitions

In experiments on optical detection it has been noted that an increase of the intensity of the radio frequency field not only affects the magnitude of the signal but also causes transitions involving two, three, or more quanta.<sup>6</sup> This phenomenon has been explained theoretically.<sup>37,38,39</sup> For this kind of many-quantum transition the  $n$ -fold transitions correspond to change of the magnetic quantum number by  $\Delta m = n$ .

Barrat, Brossel, and Kastler<sup>6</sup> observed radio frequency resonance between the sublevels of the ground state of  $\text{Na}^{23}$  with orientation by  $\sigma^+$  and  $\sigma^-$  light and with variation of the strength of the constant field. The frequency of the radio frequency field was fixed (108.5 Mc). At small amplitudes of the radio frequency field four absorption lines were observed, corresponding to Zeeman transitions (Fig. 11). As the

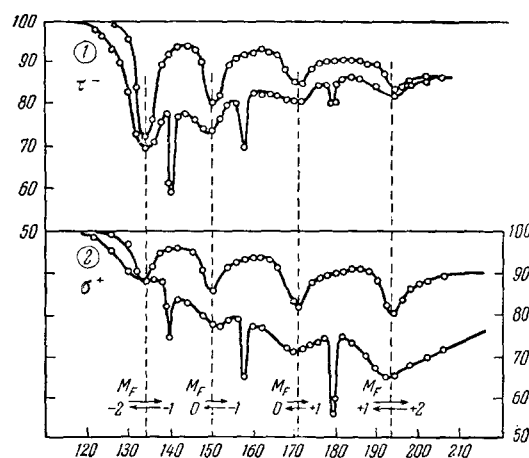


FIG. 11. Variation of the relative magnitude of the signal in  $\text{Na}^{23}$  for different amplitudes of the radio frequency field. The abscissa is the intensity of the constant field, in oersteds. 1 - illumination with  $\sigma^-$  light, 2 - illumination with  $\sigma^+$  light.<sup>6</sup>

amplitude of the radio frequency field was increased the total intensity of the light coming through was diminished. Additional narrow absorption lines then appeared, corresponding to two-quantum transitions, and the lines of the one-quantum transitions were broadened on account of saturation.

Many-quantum transitions of a different type are observed in weak magnetic fields ( $\sim 0.1$  oe). In such fields  $|\xi| \ll 1$ , and all of the Zeeman intervals can be taken to be equal. In this case one expects a single resonance line, as for a system with two sublevels.

A radio frequency field  $h$  rotating with the angular velocity  $\omega$  around  $H_0$  induces transitions with  $\Delta m = +1$  for  $\omega > 0$  and  $\Delta m = -1$  for  $\omega < 0$ . In this case only the one-quantum transition is possible, and in fact only one absorption line is observed experimentally.

If the radio frequency field perpendicular to  $H_0$  is linearly polarized additional absorption lines are observed.<sup>40,41,42,43</sup> The linearly polarized field can be regarded as two circularly polarized fields rotating in opposite directions. In this case, according to the laws of conservation of energy and momentum, the many-quantum transitions correspond to the absorption of several circular quanta of different polarizations, for example  $1\sigma^+ + 1\sigma^+ + 1\sigma^-$ , and so on.

Many-quantum transitions also occur in cases in which higher harmonics of the generator become sufficiently intense as the intensity of the radio-frequency field is increased.<sup>44</sup> Therefore when strong radio-frequency fields are applied additional narrow lines appear in the absorption spectra, while the width of the main lines increases.

Among the various lines in the absorption spectrum the most intense is the one corresponding to the transition from the sublevel to which pumping is occurring. It can always be singled out by this indication.

#### 4. The Determination of Hyperfine Splitting Constants

As is well known, hyperfine splitting constants cannot always be determined by optical methods, primarily because of the inadequate resolving power of optical apparatus.

Methods based on the absorption of microwave energy by a gaseous system of atoms are more promising than optical methods, since in this case the absorption lines have small widths, which permits good resolution of the hyperfine structure. As we have seen, the combination of magnetic resonance methods with optical orientation of atoms makes it possible to secure a large increase in the intensity of the magnetic resonance signal. The detection of the signal by means of a light beam greatly increases the sensitivity of the method.

Arditi and Garver<sup>45</sup> have determined the hyperfine structure constant of  $\text{Na}^{23}$  by exciting the transition  $\Delta F = 1$ ,  $m_F = 0 \rightarrow m_F = 0$  in the ground state  $3S_{1/2}$ . Sodium in a gas chamber of volume about one liter was

kept at a temperature of  $120^\circ$  to  $130^\circ$  C. The buffer gases used were spectroscopically pure argon and neon at pressures from 1 to 50 mm Hg. For the optical orientation these authors used a beam of circularly polarized light ( $\Delta m_F = 1$ ) from a standard sodium lamp, directed along the constant magnetic field. After passing through the gas chamber the light was focused on a photoelectric cell. The homogeneous magnetic field of the order of several gauss was produced by Helmholtz coils. The amplitude of the radio frequency field was large enough to saturate the resonance, i.e., to equalize the populations of the sublevels (1, 0) and (2, 0). The magnitude of the hyperfine splitting in the ground state was determined [cf. Eq. (86)] from a direct measurement of the position of the maximum of the absorption line, which had a width of 400 cps. In this case the width of the absorption line was mainly due to the saturation effect and partly due to noise and instability of the generator. The signal-to-noise ratio in the experiment was 20:1. The accuracy of the frequency measurement was  $\pm 100$  cps. The ratio of the Landé factors for free electrons and  $\text{Na}^{23}$  atoms in the ground state has been determined in references 50 and 51 (cf. Sec. VII).

Bloom<sup>71</sup> has observed the free precession of  $\text{Na}^{23}$  atoms in the earth's magnetic field. The orientation of the atoms was produced by circularly polarized light in the direction of a bias magnetic field perpendicular to the earth's field. By a procedure like that in the method of Packard and Varian,<sup>72</sup> the bias field was suddenly turned off for the observation of the free precession. The subsequent free precession of the atomic angular momenta around the earth's field was detected from the Larmor-frequency modulation of the light beam, which played the part of a  $\rho$  beam relative to the earth's field. The envelope of the signal was a simple exponential with a time constant of 0.5 millisecond. The result obtained shows that the states  $F = 1$  were emptied owing to the optical pumping. Otherwise in the earth's field there would have been beats with frequency  $\sim 1200$  cps, caused by the free precession of the two sets of atoms  $F = 1$  and  $F = 2$  [cf. Eq. (87)].

The study of radio frequency resonance in optically excited states ( $J > 1/2$ ) makes it possible to get information about the magnitudes and signs of the electric quadrupole moments of nuclei. In reference 73 the study of the hyperfine intervals in the  $3^2P_{3/2}$  state revealed the existence of a positive nuclear quadrupole moment  $Q = (1 \pm 0.6) \times 10^{-25}$  cm<sup>2</sup>. In spite of its small size, this moment has made it possible to draw important conclusions about the structure of the  $\text{Na}^{23}$  nucleus.

#### VI. PRACTICAL APPLICATIONS OF THE METHOD OF OPTICAL ORIENTATION OF ATOMS

The phenomenon of optical orientation of atoms is the basis of the functioning of high-sensitivity magne-

tometers for precise measurement of weak magnetic fields. It can be used in making devices with which one can determine orientation in space in relation to an external magnetic field. Possibilities have been studied for producing "atomic clocks" — high-stability frequency standards and optical oscillators in which optical pumping is applied.

The small line width of magnetic resonance, the high sensitivity of the method, and the lack of dependence of the observed optical signal on the intensity of the splitting magnetic field (if it is small in comparison with the hyperfine structure constant) make for the successful competition of these devices with analogous devices based on the application of other physical phenomena.

### 1. The Measurement of Weak Magnetic Fields

The method of optical orientation of atoms is the basis of the functioning of a geomagnetometer<sup>13,31</sup> which can compete successfully with ferromagnetic-probe and nuclear-precession devices.

In this case the measurement of the intensity of a magnetic field is reduced to the measurement of the frequency of the transitions between the magnetic sub-levels of the hyperfine structure of the atoms in vapor of the isotope  $\text{Rb}^{87}$ , which are optically oriented along the earth's field.

A schematic diagram of the magnetometer is shown in Fig. 12. Light from a rubidium lamp containing the isotope  $\text{Rb}^{87}$  passes through an interference filter CF, which singles out the line corresponding to the transition  $5^2P_{1/2} \rightarrow 5^2S_{1/2}$  ( $\lambda = 7943 \text{ \AA}$ ) and stops the line  $\lambda = 7800 \text{ \AA}$ . The light is then circularly polarized by passing through the polaroid P and the quarter-wave plate ( $\lambda/4$ ). The polarized light then goes through the absorption chamber, which contains  $\text{Rb}^{87}$  vapor and an inert gas, the purpose of which is to increase the thermal relaxation time and decrease the Doppler width of the line.

After passing through the absorption chamber the light falls on a photoelectric device (photomultiplier), and after amplification the signal goes to a registering device (oscilloscope or Brown recorder). The apparatus is so oriented that the beam of light is approximately parallel to the earth's magnetic field.

The radio frequency field  $h$  is at right angles with the direction of the light beam. At a frequency close to the resonance frequency of the transition  $S_{1/2}$ ,  $F = 2$  ( $m_F = 2 \rightarrow m_F = 1$ ) the field causes induced transitions which lead to a decrease of the intensity of the light coming through the chamber.

The frequency of the radio frequency field in the constant field 0.565 oe was about 395 kc. The absorption line was observed as a dip in the output of the photoelectric element.

When the axis of the apparatus was turned aside by an angle of  $20^\circ$  from the direction of the earth's field the decrease of the intensity of the line was inappreciable, but for the angle  $30^\circ$  the decrease was already by a factor two. When the absorption chamber was filled with  $\text{Rb}^{87}$  vapor in argon and neon at pressure 1 cm Hg the line width in the frequency scale was 20–25 cps. This made it possible to set the frequency of the generator on the center of the line to accuracy 1 cps, which corresponds to an accuracy of the order of  $10^{-5}$  oe in the measurement of the field.

The inexactness of our knowledge of the atomic constants involved in  $\Gamma$  and  $G$  leads to a small systematic error in the determination of the total vector intensity of the earth's field as calculated from Eq. (79). A comparison with the data obtained in reference 13 with the magnetograph of the magnetic observatory in Fredericksburg showed that this error is  $6 \times 10^{-5}$  oe. It can be taken into account by introducing an empirically corrected value for  $\Gamma^-$  from Eq. (83); this leads to the formula<sup>13</sup>

$$\nu = 699\,632H_0 - 216H_0^2, \quad (91)$$

for the smallest transition frequency.

When the frequency was varied over a range of 1.7 kc six resonance transitions were observed, as expected. The transition  $F = 2$ ,  $m_F = 2 \rightarrow m_F = 1$  from the sublevel to which the pumping occurs gives the most intense line, which can easily be distinguished from the others.

A favorable condition for the use of magnetometers of this type is the fact that the intensity of the observed signal does not depend on the magnitude of the magnetic field if it is small in comparison with the magnitude of the hyperfine structure constant. This is true

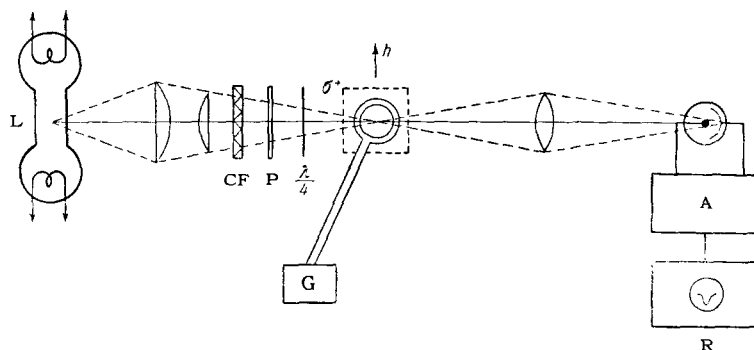


FIG. 12. Schematic diagram of apparatus for observing optical orientation of atoms.<sup>13</sup>

to high accuracy in the case of the earth's field.

Magnetometers based on the phenomenon of optical orientation of atoms can be used to measure not only the earth's magnetic field but also the weaker fields in the space between celestial bodies.

## 2. The Determination of Orientation in Space

Recently there has been developed an extremely simple and sensitive magnetometer designed for installation in rockets and based on the phenomenon of optical pumping in gaseous helium.<sup>46,47,48</sup> The device is highly sensitive, compact, light in weight, of sturdy construction, and low in its power requirements. The magnetometer can detect a component of a small field of less than  $10^{-7}$  oe. The readings of the device are practically independent of the surrounding temperature and of accelerations. Information about the intensity of the field being measured can be easily transmitted by radio.

The authors believe that magnetometers of this kind can be used for the measurement of very weak magnetic fields, for example for the detection of the magnetic field of the moon, and also to prospect for oil and various minerals.

Magnetometers of this type make it possible to measure the component of the magnetic field in the direction of the principal optical axis of the apparatus. They are very sensitive to changes of the orientation of the axis of the apparatus relative to the external magnetic field. Quite recently a prototype of this device has been described, which permits tests of its sensitivity to changes of orientation.<sup>46</sup>

Helium was not chosen accidentally as the working substance of the magnetometer. Unlike the alkali metals, which provide saturated vapors of the required pressure only when the absorption chamber is placed in a thermostat (for  $\text{Na}^{23}$ ,  $t$  is  $120 - 130^\circ \text{C}$ , and for  $\text{Rb}^{85}$   $t$  is about  $47^\circ \text{C}$ ), gaseous helium can be optically pumped at practically any temperature.

The helium atoms can be in two possible states: with the electron spins compensated (parahelium) and uncompensated (orthohelium). Parahelium is diamagnetic, whereas orthohelium is paramagnetic. The ground state  $2^3S_1$  of orthohelium is metastable. The lifetime of an atom in the metastable state is about one millisecond. By exciting helium with a gas discharge one can produce a considerable amount of orthohelium.

The part of the energy spectrum within which the pumping occurs is shown in Fig. 13. In the magnetic field the term  $2^3S_1$  splits into three Zeeman sublevels  $E_m = -g\mu_0 m H_0$  (where  $m = 0, \pm 1$ ); the distance between the sublevels is a linear function of the field  $H_0$

$$\Delta E = g\mu_0 H_0 \quad (92)$$

and the Landé  $g$  factor of the free electron.

When the gas is illuminated with unpolarized light

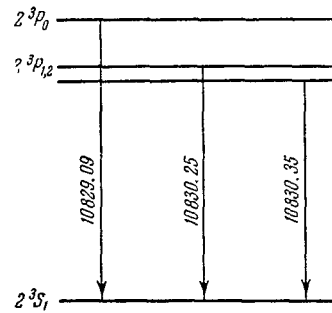


FIG. 13. Energy spectrum of orthohelium near the ground state. The wavelengths of the transitions are shown in Angstroms.

of wavelength  $\lambda = 10829 \text{ \AA}$  helium atoms go from the metastable state  $2^3S$  to the excited state  $2^3P$ . They are in this state about  $10^{-8}$  sec and return to the level  $2^3S_1$ . The levels  $2^3P_{1,2,3}$  are very close to each other; two of them even overlap (see Fig. 13). The lifetime of the excited state is long enough for collisions between the helium atoms to equalize the populations of the sublevels of the excited state, and therefore the probabilities for transitions to the three sublevels of the ground state are equal.

The probability  $P_0$  for absorption of light by atoms that are in the ground state with  $m = 0$  is larger than the probabilities  $P_{+1} = P_{-1}$ . Therefore illumination of helium with unpolarized light of the resonance frequency at  $10829 \text{ \AA}$  leads to a decrease of the population of the level  $m = 0$  and an increase of the populations of the levels  $m = \pm 1$ , and the intensity of the light passing through the absorption chamber increases.

This situation arises, however, only if the beam of light that produces the alignment is propagated along the direction of the external magnetic field. If the direction of the light makes an angle  $\vartheta$  with the direction of the magnetic field, the probabilities of the transitions from the ground-state sublevels  $m = 0, \pm 1$  are changed. As the angle  $\vartheta$  increases the probabilities  $P_{\pm 1}$  increase and the probability  $P_0$  decreases. At the angle  $\vartheta \approx 54^\circ 43'$  the transition probabilities are equal:  $P_{-1} = P_0 = P_{+1}$ . The dependence of the signal strength  $S$  on the angle  $\vartheta$  is given by the formula

$$S = S_0 \left\{ \frac{1}{2} (3 \cos^2 \vartheta - 1) \right\}^2 \quad (93)$$

and is shown in Fig. 14. The dependence of the strength of the observed signal on the angle  $\vartheta$  can be used to determine the orientation of the device relative to the magnetic field.

By placing the absorption chamber in a radio-frequency field of the resonance frequency, which equalizes the populations of the sublevels, one can produce a considerable change of the strength of the signal. By measuring the resonance frequency one can use Eq. (92) to find the intensity of the magnetic field.

Figure 15 shows the block diagram given in reference 46 for a laboratory model of the helium magne-

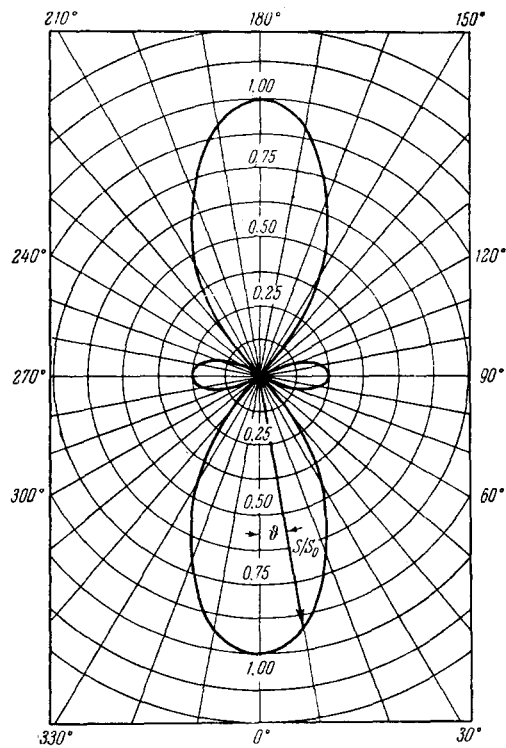


FIG. 14. Dependence of the signal strength  $S/S_0$  on the angle  $\vartheta$  between the direction of the orienting light beam and the external magnetic field.<sup>46</sup>

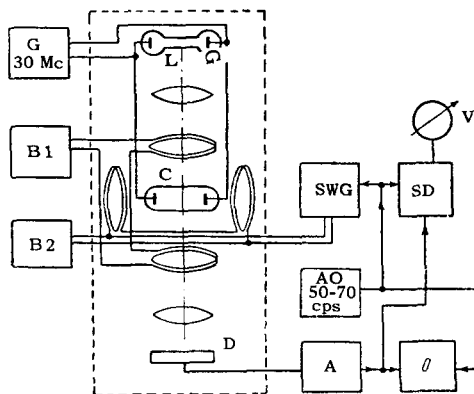


FIG. 15. Block diagram of apparatus for observing the dependence of the signal on the angle  $\vartheta$  in optical pumping in helium.<sup>46</sup>

tometer, which is intended for installation in an airplane or rocket. The generator G supplies power to the helium lamp L and the absorption chamber C, and produces a high concentration of orthohelium and a luminous discharge. Two sources of constant field B1 and B2 produce in the space of the absorption chamber a field which can be arbitrarily varied in magnitude and direction, so as to imitate the earth's magnetic field. The entire apparatus is in a case which screens it from external magnetic fields.

In parallel with the field source B2 there is connected the output of a square-wave generator SWG, which controls the audio oscillator AO. The signal from the output of the vertical deflection amplifier

goes to a synchronous detector SD, to which a reference voltage is supplied from the square-wave generator. The output voltage of the SD is registered by a vacuum tube voltmeter.

If the direction of the constant magnetic field is parallel to the optical axis of the apparatus, the modulation of the magnetic field will be symmetrical. The resultant field is then deflected at audio frequency through equal angles to both sides of the optical axis of the apparatus. In this case no modulation of the light intensity at the output of the device will be observed, since the absorption of the light will be the same as in the absence of the pulses.

If the direction of the earth's field does not coincide with that of the optical axis, the rectangular current pulses cause an asymmetry in the signal. In this case the photosensitive detector registers a modulation of the intensity of the light.

Thus the orientation of the axis of the device relative to the direction of the external field can be checked by the absence of a signal at the output of the device.

Measurements have shown that the device can detect changes of the component of the magnetic field in the direction of its axis which are less than  $10^{-7}$  oe, which gives a possibility for detecting the magnetic field at a distance of more than 80 000 km from the earth.

### 3. An Atomic Frequency Standard

The possibility of using the phenomenon of optical orientation of atoms for making oscillators was first pointed out by Dehmelt.<sup>12</sup> A block diagram of such an oscillator is shown in Fig. 16. The absorption chamber filled with alkali metal vapor is in a magnetic field  $H_0$ . This field is parallel to the direction of the light beam that produces the optical orientation of the atoms. If an alternating radio-frequency field  $h_y$  is present of frequency equal to the frequency of precession of the atomic angular momenta in the earth's field  $H_0$ , and we send through in the direction  $Ox$  another light beam of the same composition as that along the axis  $Oz$ , then after passing through the chamber this beam will be modulated at the frequency of the Larmor precession in the field  $H_0$ . The x beam falls on a photoelectric element, and the signal from this is amplified

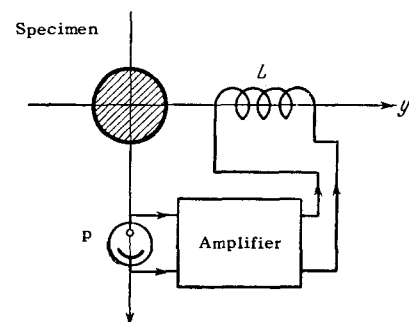


FIG. 16. Block diagram of an oscillator based on optical pumping of atoms.

and fed to the coil  $L$  in which the field  $H_y$  is produced. In this way the generation of undamped oscillations can be accomplished. The frequency  $\nu$  of the oscillations is equal, if we neglect a slight pulling, to the frequency of the transition between the Zeeman sublevels  $(2, 2) \rightarrow (2, 1)$ , and is given by Eq. (79), where  $\Gamma^-$  and  $G$  have the values defined in Eq. (78). For  $\text{Na}^{23}$  the values of  $\Gamma^-$  and  $G$  are given in Eq. (83).

For  $\text{Na}^{23}$  the line width of the oscillator is very small; it is a few cps for an oscillator frequency of the order of 0.35 Mc in a field of 0.5 oe.

The oscillator (maser) based on optical pumping must be regarded as one of the most promising, since in this case one can obtain the greatest excess of atoms in the upper energy sublevel.

In reference 49 we have reports of studies made to see to what extent the phenomenon of optical orientation of atoms can be used to obtain an atomic frequency standard. The atoms  $\text{Na}^{23}$ ,  $\text{Rb}^{87}$ , and  $\text{Cs}^{133}$  have been investigated as working substances.

In order to obtain a frequency standard of high precision, we must satisfy at least three conditions:

1) the frequency of the transitions used for standards must be extremely stable and must be independent of electric and magnetic fields, pressure, temperature, and so on; 2) the width of the resonance line must be as small as possible; 3) the ratio of signal to noise must be large enough.

The authors of these papers were able to choose mixtures of buffer gases (cf. Sec. III) which, while leading to minimum broadening of the line owing to Doppler effect, at the same time give practically no shift of the resonance frequency with change of the buffer gas pressure. For example, under such conditions the line width for  $\text{Rb}^{87}$  was about 70 cps, which made it possible to make frequency measurements with high accuracy.

## VII. ORIENTATION PRODUCED BY EXCHANGE COLLISIONS

### 1. The Effect of Collisions on the Degree of Orientation of Atoms

By the method of optical pumping one can orient the magnetic moments belonging to a system of particles for which the incident light is not resonance radiation. In this case the orientation is produced by spin exchange of electrons, atoms, or nuclei with the optically oriented atoms of an alkali metal vapor.

Experiments on the optical orientation of thermal electrons were first made by Dehmelt.<sup>50,51</sup> The electrons were oriented by means of exchange collisions with optically oriented sodium atoms in which there was transfer of the angular momentum of the atom to the electron. When dynamic equilibrium is reached between the processes of optical pumping and thermal relaxation there is a definite number of oriented elec-

trons in the system. In the presence of a radio frequency field of a frequency close to the Larmor precession frequency of the electrons in the external magnetic field the degree of orientation of the electrons decreases on account of resonance transitions. There is then an increase of the number of sodium atoms giving up their angular momentum to electrons, and this leads to a decrease of the degree of orientation of the sodium atoms. As the frequency approaches the resonance frequency the intensity of the light passing through the absorption chamber is diminished. Thus one can detect the radio frequency resonance of free electrons by an optical method.

An elementary theory of the effect can be developed under assumptions which simplify the problem. Neglecting the velocity distribution, we shall suppose that the speed  $\langle v \rangle_2$  is the same for all electrons and given by

$$\langle v \rangle_2 = \left( \frac{m}{3kT_e} \right)^{1/2}, \quad (94)$$

where  $T_e$  is the electron temperature. We shall take the atoms to be at rest relative to the electrons. We denote by  $N_+$  and  $N_-$  and by  $n_+$  and  $n_-$  the numbers of atoms and of electrons with their magnetic moments directed along the field (+) and opposite to the field (-). Furthermore,

$$N_+ + N_- = N, \quad n_+ + n_- = n. \quad (95)$$

The process of optical pumping of atoms in the absence of free electrons is described by Eq. (7). Since the light is not absorbed by the free electrons, the relaxation of electrons which have got oriented in any way obeys the equation

$$\frac{du}{dt} = -\frac{u}{T_e}, \quad (96)$$

where  $T_e$  is the relaxation time of the free electrons, which is connected with the width of the magnetic-resonance absorption line by the simple relation  $\Delta\nu_e T_e = 1$ , and  $u = (n_+ - n_-)/n$  is the orientation parameter of the electrons.

The changes of the numbers of atoms and electrons oriented along the field that are due only to the mutual collisions can be described by means of the equations

$$\frac{dN_+}{dt} = \sigma_c \langle v \rangle_2 \{n_+ N_- - n_- N_+\}, \quad (97)$$

$$\frac{dn_+}{dt} = \sigma_c \langle v \rangle_2 \{N_+ n_- - N_- n_+\}, \quad (98)$$

where  $\sigma_c$  is the effective cross section for collisions of electrons with atoms. Noting that according to Eq. (95)

$$\frac{dV}{dt} = \frac{2}{N} \frac{dN_+}{dt}, \quad \frac{du}{dt} = \frac{2}{n} \frac{dn_+}{dt}, \quad (99)$$

we find the system of equations

$$\frac{dV}{dt} = \frac{1}{\theta} (u - V), \quad \frac{dV}{dt} = \frac{1}{\theta} (V - u), \quad (100)$$

which describe the change of the orientations of the atoms and electrons with the time owing to the effect of collisions. Here

$$n\theta = N\phi = \frac{1}{\sigma_c \langle v \rangle_2}. \quad (101)$$

Putting together these arguments, we get a system of equations which describe the exchange collisions of the electrons and atoms under the conditions of thermal relaxation and optical pumping:

$$\frac{dV}{dt} = \frac{1}{T^*} (V^* - V) + \frac{1}{\theta} (u - V), \quad \frac{du}{dt} = -\frac{u}{T_e} + \frac{1}{\phi} (V - u). \quad (102)$$

Setting  $dV/dt = du/dt = 0$ , we find the stationary value of the orientation parameter of the atoms, with effects of collisions with electrons included:

$$V^s = \frac{V^*}{1 + \frac{\phi}{\theta + T_e} \frac{T_1^*}{\theta}} \quad (103)$$

in the absence of a radio frequency field. Eliminating  $\phi$  by means of Eq. (101), we can put this last expression in the form

$$V^s = V^* \frac{\theta/N + T_e/n}{(T_1^* + \theta)/N + T_e/n}. \quad (104)$$

If we saturate the electron system by means of magnetic resonance, then  $u = 0$ . Then, according to the first of the equations (102) and the condition (101),

$$\bar{V}^s = \frac{V^*}{1 + T_1^*/\theta} = \frac{V^*}{1 + n\sigma_c \langle v \rangle_2 T_1^*}. \quad (105)$$

Thus as a result of the collisions of the atoms with electrons the degree of orientation of the atoms must be decreased. This decrease depends on the electron concentration  $n$  and the value of the effective collision cross section  $\sigma_c$ , and also on the electron temperature.

A theoretical estimate of the quantity  $\sigma_c$  gives for  $\text{Na}^{23}$  a value of the order of  $10^{-14} \text{ cm}^2$ . In Dehmelt's experiments the other quantities had the values  $\tau = 2 \times 10^{-2} \text{ sec}$ ,  $n = 1.6 \times 10^8 \text{ cm}^{-3}$ ,  $T_e \approx 6 \times 10^{-5} \text{ sec}$ . It is easy to see that in this case  $n\sigma_c \langle v \rangle_2 T_1^* \approx n\sigma_c \langle v \rangle_2 \tau \approx 1$ . Therefore even at small concentrations of the atoms the effect of free electrons on the degree of orientation is easily detectable.

## 2. The Determination of Effective Collision Cross Sections

As a measure of the signal of the optical orientation of atoms in the case of electron resonance registered with a photoelectric detector, Dehmelt takes the expression<sup>51</sup>

$$S = \frac{V^s - \bar{V}^s}{V^*}, \quad (106)$$

which, according to Eqs. (103) and (105), can be written in the form

$$S = \frac{T_e}{\phi} \frac{T_1^*}{\theta} \frac{1}{1 + T_1^*/\theta} \frac{1}{1 + \frac{T_e}{\phi} \frac{T_1^*}{\theta}}. \quad (107)$$

The quantity  $S$  can be determined experimentally. In the experiments of Dehmelt with  $\text{Na}^{23}$  it was found that  $S \approx 0.1$ . According to Eqs. (107) and (101),

$$S < \frac{T_e}{\phi} \frac{T_1^*}{\theta} = T_e T_1^* N n \sigma_c^2 \langle v \rangle_2^2. \quad (108)$$

Setting  $N = 8 \times 10^9 \text{ cm}^{-3}$ , we find from the data given above that  $\sigma_c > 2.3 \times 10^{-14} \text{ cm}^2$ , which is in excellent agreement with the theoretical value.

By measuring the four frequencies of the transitions  $\Delta m_F = \pm 1$  between the sublevels with  $F = 2$  in the hyperfine structure of  $\text{Na}^{23}$  and the resonance frequency  $\nu_S$  of the precession of free electrons, we can determine the ratio  $g_J/g_S = \gamma_J/\gamma_S$  of the Landé factors of the alkali metal atom and the free electron, if the ratio  $\gamma_J/\gamma_S$  is known [see Eq. (90)]. For  $\text{Na}^{23}$  Dehmelt found experimentally the ratio

$$\frac{g_J}{g_S} = 1.000026 \pm 0.00003. \quad (109)$$

We note that other known methods for determining the  $g$  factor of the free electron<sup>52</sup> have accuracy not better than  $5 \times 10^{-3}$ . Measurements with accuracy  $3 \times 10^{-5}$  are sufficient for a further experimental test of the theoretical value of the ratio

$$\frac{\mu_s}{\mu_0} = 1 + \frac{e^2}{hc} + \text{higher-order terms}$$

with relativistic corrections taken into account. The accuracy of the measurement of the ratio  $g_J/g_S$  can evidently be improved by one or two more orders of magnitude.

As can be seen from Eq. (109), the Landé factor of the sodium atom in the ground state is very close to that of the free electron. In reference 81 the method we have described has been applied to measure the ratio of the Landé factors of the free electron and the electron in the hydrogen atom.

The method of Dehmelt has subsequently been used for the orientation of potassium<sup>53</sup> and rubidium<sup>54</sup> atoms by collisions with  $\text{Na}^{23}$  atoms. The radio frequency resonance between the Zeeman sublevels of potassium and rubidium was observed through the change of intensity of the resonance radiation of  $\text{Na}^{23}$  getting through the absorption chamber. Measurement of the shape of the signal made it possible to estimate a lower limit on the effective cross sections for exchange collisions of atoms of these elements with the optically oriented sodium atoms.

In reference 55 the orientation of  $\text{N}^{14}$  and  $\text{N}^{15}$  atoms was accomplished by collisions with  $\text{Na}^{23}$  atoms and the hyperfine structure constants  $a(14)$  and  $a(15)$  in zero field were measured. By determining the ratio of the  $g$  factors of  $\text{N}^{14}$  and  $\text{N}^{15}$  by the method of double electronic and nuclear resonance, the authors found the value of the hyperfine structure anomaly

$$\Delta = \frac{a(15)/a(14)}{g(15)/g(14)} - 1 = 0.000983 \pm 0.000017.$$

### VIII. THE STUDY OF RELAXATION PROCESSES BY THE OPTICAL METHOD

The study of relaxation processes in a gaseous system of atoms oriented by the optical method makes it possible to elucidate many details of these processes which are not accessible to observation by other methods.

The method of optical pumping makes it possible to achieve a high degree of orientation of atoms even at temperatures of 100–200°C. To obtain such a degree of orientation by other methods it is necessary to work at extremely low temperatures, in the helium region. Under the conditions of the experiment the alkali-metal atoms are in the gaseous state, and therefore the interaction between them consists mainly of two-particle collisions. In this case the mechanism of relaxation processes is simpler than in condensed media. One can vary the relaxation times of the atoms being studied over wide ranges by changing the pressure and composition of the buffer gases.

#### 1. Measurement of Relaxation Times of Atoms under Stationary Conditions

As can be seen from Table IV, the probability per unit time  $\beta$  for absorption of light by an atom lies, for the case of sodium, between the two extreme possible values

$$\frac{3.63}{T_1} \leq \beta \leq \frac{7}{T_1}.$$

On the other hand, the probability of absorption of light of the spectral density  $J_\nu(z)$  passing through the absorption chamber in the direction of the  $z$  axis is proportional to the expression

$$-\frac{1}{N} \frac{d}{dz} \int_0^\infty J_\nu(z) d\nu.$$

Therefore we can set

$$\frac{d}{dz} \int_0^\infty J_\nu(z) d\nu = -N \frac{\eta}{T_1}, \quad (110)$$

where  $\eta$  is a dimensionless constant. Integration of this equation gives the total absorption of the light in a chamber of length  $l$  and cross sectional area 1 cm<sup>2</sup>:

$$\int_0^\infty J_\nu(0) d\nu - \int_0^\infty J_\nu(z) d\nu = N \frac{\eta}{T_1} l. \quad (111)$$

The relation (111) enables us to measure the longitudinal relaxation time under stationary conditions by measuring the absorption of light in the gas.

#### 2. Measurement of Relaxation Times under Transitional Conditions

In reference 56 a method is suggested for measuring the longitudinal relaxation time  $T_1$  under transitional conditions, which is suitable for the measurement of relatively long relaxation times.

During the process of establishing the equilibrium orientation of the atoms the intensity of the light passing through the absorption chamber increases from  $J_0$  to  $J_0 + \Delta J$ . If after this one rapidly reverses the direction of the magnetic field  $H_0$  in such a way that the populations of the Zeeman sublevels remain unchanged, the intensity of the light falls to  $J_0 - \Delta J$  and again begins to increase with the time constant  $T_1^*$  under the action of relaxation and optical pumping.

As we see from Eq. (8), the effective relaxation time  $T_1^*$  is connected in a simple way with the longitudinal relaxation time:

$$T_1^* = \frac{T_1}{1 + T_1/\tau_z} = \frac{T_1}{1 + \alpha_z J_z T_1}, \quad (112)$$

where  $\alpha_z$  depends on the transition probabilities. Thus measurements at various values of  $J_z$  make it possible to determine  $T_1$ .

The experiment was made with Na<sup>23</sup> vapor in an atmosphere of argon at various pressures (3 and 40 cm Hg). Relaxation owing to collisions with identical atoms had no appreciable effect because of the very low partial pressure of Na<sup>23</sup> vapor ( $\sim 10^{-7}$  mm Hg). Under these conditions the relaxation time was 0.21 sec with argon at pressure 3 cm Hg and 0.02 sec with argon at 40 cm Hg, so that an unusually narrow absorption line could be observed. The orientation of the atoms was produced with the two D lines of sodium.

The relaxation time was found to be independent of the temperature and of the pressure of the sodium vapor, and to be a linear function of the pressure of the argon.

In reference 18 a method is proposed which makes possible a direct measurement of the time  $T_1$ . Before the equilibrium orientation is reached the light incident on the chamber is interrupted, and then turned on again after a certain time  $\Delta t$ . During the "dark" period the populations of the sublevels approach thermal equilibrium with the time constant  $T_1$ . The turning on of the light finds the system with a definite degree of orientation, which can be determined from the intensity of the light coming through at the instant it is turned on. By changing the length of the dark period one can construct the curve of the thermal relaxation as the envelope of the signals for the different values of  $\Delta t$  (Fig. 17).

This method has been used<sup>18</sup> to measure relaxation times in rubidium oriented with circularly polarized  $\sigma^+$  radiation. The change of the signal owing to the thermal relaxation process was 12 percent. The curves so obtained showing the dependence of the relaxation time on the pressure of the buffer gas, on the type of gas, and on the shape of the absorption chamber have been reproduced in Section III, Fig. 4.

Both the longitudinal relaxation time  $T_1$  and the transverse relaxation time  $T_2$  have been measured<sup>57</sup> for oriented mercury vapor, Hg<sup>199</sup> ( $I = 1/2$ ), in the ground state  $6^1S_0$ . This work was unlike that of ref-



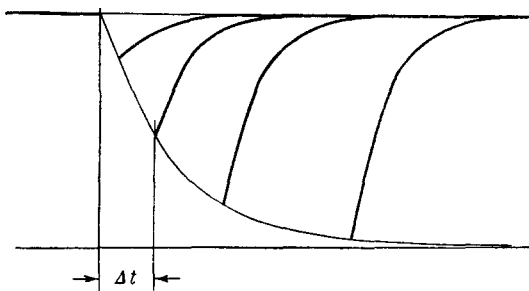


FIG. 17. Illustration of the method for determining the longitudinal relaxation time.<sup>18</sup>

reference 18 in that the measurements were made on the light scattered in a direction perpendicular to the constant magnetic field.

At the instant when the circularly polarized  $\sigma^+$  radiation ( $\lambda = 2537 \text{ \AA}$ ) is turned on, the as yet unoriented vapor strongly scatters the light. As the degree of orientation increases the intensity  $J_S$  of the scattered light falls off, and when the equilibrium orientation is established in the vapor the scattered intensity takes the value  $J_1$ . The change from  $J_S$  to  $J_1$  is an exponential curve with characteristic time  $T_1^* = 1.2 \text{ sec}$ . If  $T_1$  is the longitudinal relaxation time and  $1/T_p$  is the average probability for absorption of a photon by an atom, then

$$\frac{1}{T_1^*} = \frac{1}{T_1} + \frac{2}{3T_p}. \quad (113)$$

From measurements analogous to those described above it was found that  $T_1 = 2 \text{ sec}$ , from which it follows that  $T_p = 2 \text{ sec}$ .

The measurements of the transverse time  $T_2$  were made in the presence of a radio-frequency field with a frequency close to that of the Larmor precession of the mercury atoms in the magnetic field  $H_0$ . The radio-frequency field produced a sinusoidal modulation of the population of the lower level, from which the absorption was larger; that is, it caused a nutation of the nuclear spins. As a result of inhomogeneity of the local field the spins got out of phase. The intensity of the scattered light varied with the frequency  $\frac{1}{2} [\gamma^2 h^2 + (\omega - \omega_L)^2]^{1/2}$  while approaching  $J_S$  with the characteristic time  $T_2$ .<sup>58</sup>

### 3. The Study of Relaxation Times in Optically Excited States

In references 59 and 61 studies have been made on the excited state of the various mercury isotopes. Measurements were made of the lifetime  $T_{\text{exc}}$  of mercury atoms in the excited state, and also of the shape and width of the magnetic resonance between the Zeeman sublevels of this state. Analogous measurements were made in reference 62 on the sublevels of Cd and Zn. It had been observed earlier<sup>34</sup> that  $T_{\text{exc}}$  increases in a paradoxical way with increase of the pressure of mercury vapor in the absorption chamber, and depends on the geometry of the chamber. As

the pressure is lowered it approaches the lifetime of the isolated atom.

A theoretical explanation of the observed dependence of  $T_{\text{exc}}$  on the pressure is given in reference 60, where it is shown that the effect is due to coherent multiple scattering of the photons in the mercury vapor. In fact, the multiple scattering of photons of the resonance frequency increases with the pressure, and this leads to an increase of the effective lifetime of the atoms in the excited state. This is confirmed by the character of the dependence of  $T_{\text{exc}}$  on the geometry of the chamber and by the anomalously large depolarization of the scattered light.

## IX. OPTICAL PUMPING IN SOLIDS

### 1. Special Features of Optical Pumping in Solids

Optical pumping in solids can be obtained with paramagnetic ions that have a discrete energy spectrum in the electric field of the crystal lattice.<sup>63</sup> For the production of a detectable optical pumping it is necessary that the thermal relaxation time of the ions over the magnetic sublevels be at least of the order of the time of a cycle of the optical pumping, or longer than this time. Therefore in order to make successful experiments it is necessary first of all to choose suitable substances.

In recent years the structure of the ground states of paramagnetic ions in various crystalline fields has been successfully studied by the method of paramagnetic resonance. A theory of the optical spectra of the ions has been developed for individual cases.<sup>75</sup> For a number of ions the study of the optical absorption and fluorescence spectra in the crystal lattice reveals the existence of very narrow lines in addition to the absorption bands.<sup>28,76</sup> Very narrow absorption lines are observed, for example, for the rare-earth ions  $\text{Eu}^{+69}$  and  $\text{Cr}^{+++76}$ , and also for phosphors subjected to irradiation, for example, those containing lithium ions.

An analysis of the possibility of optical orientation of ions in solids has been made in reference 74. Optical pumping was first successfully produced with  $\text{Eu}^{++}$  ions in  $\text{CaF}_2$  and  $\text{SrCl}_2$ , and then in synthetic ruby ( $\text{Cr}^{+++}$  in  $\text{Al}_2\text{O}_3$ ).<sup>78,79,81</sup>

The pumping can be observed both from the change of intensity of light passing through the crystal when it is also acted on by a radio frequency field, and also from the change of the intensity and polarization of the fluorescent light. When sufficiently strong magnetic fields are used the relatively high concentration of the ions in a solid makes possible direct detection of the paramagnetic resonance of the ions. It is evidently possible to detect changes in the populations of the magnetic sublevels by observations of the optical Faraday effect.

The technique of double (optical and radio-frequency) resonance can be applied to the study of the

spectra of paramagnetic ions in crystal lattices. In particular, there is a possibility of studying the radio-frequency resonance of paramagnetic ions in the excited state, which is not accessible to other methods.

In the production of optical pumping in solids one must distinguish the cases of fast and slow establishment of thermal equilibrium. In the former case the Boltzmann distribution of the populations in the excited state is reached before the ion emits a light quantum. The difference of the populations is then determined by the thermal relaxation. In the case in which the relaxation processes proceed slowly, the difference of populations is established in a process of optical pumping analogous to that which occurs in gases.

The arrangement of the apparatus for the observation of optical pumping in ruby<sup>68,70</sup> is shown in Fig. 18.

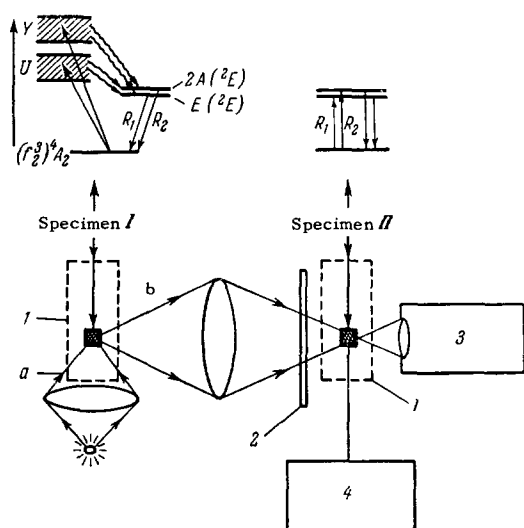


FIG. 18. Arrangement of apparatus for observation of optical pumping in ruby.<sup>68</sup>

The optical spectrum of ruby has been studied thoroughly.<sup>64,65,66</sup> Specimen I, which is the source of radiation, is illuminated by a light beam *a* from a tungsten lamp. The fluorescent light *b* is directed onto the specimen II through the polarizer 2. The illuminated specimen is inside a microwave resonator, which is part of the radiospectrometer 4. The two specimens are enclosed in thermostat 1 and 2, in which the temperature is kept at 2° K, which assures a small width ( $0.6 \text{ cm}^{-1}$ ) of the absorption lines.

The optical transitions cause a disturbance of the distribution of the atoms between the sublevels of the ground state, which is detected by observations of the paramagnetic resonance. By observing the signal from the photomultiplier 3 one can follow the change of intensity of the light coming through the specimen. The change of the signal when the radio frequency field is turned on amounts to one percent.

The optical spectrum of ruby consists of two sharp lines  $R_1$  and  $R_2$ , in which one observes the Zeeman

effect. The R lines appear as fluorescence lines after the absorption of light by the  $\text{Cr}^{+++}$  ions in two broad bands, denoted in Fig. 16 by the letters Y and U. The relaxation from the excited states to the narrow levels  ${}^2E$  is not accompanied by radiation. The transition to the ground state  ${}^4A_2$  is characterized by a lifetime of the order of several milliseconds. This source of light is described in detail in reference 78. The frequencies of the R lines depend on the temperature.

The illumination of specimen II by the light from specimen I leads to a decrease of the population of the ground state and an increase of the populations of the excited sublevels.

## 2. The Method of Selective Reabsorption

Figure 19 shows part of the energy spectrum of  $\text{Cr}^{+++}$  ions in  $\text{Al}_2\text{O}_3$  in a magnetic field at low temperature. The radio frequency field transfers ions from the lower sublevel *a* of the excited state to the upper sublevel *b*. Transitions from the upper sublevel *b* to the ground state give emission of two  $\sigma$  lines  $\delta$  and  $\beta$ , with right and left circular polarizations. Their intensities are in the ratio 3:2. There is a similar situation in the transitions from the lower sublevel *a* of the excited state. Therefore the intensity of the circularly polarized fluorescence does not depend on the distribution of the populations in the excited state, and the magnetic resonance between these sublevels does not affect the intensities of the fluorescence.

At high temperatures the Zeeman sublevels of the ground state are equally populated. In this case resonance reabsorption of the fluorescence does not change the situation. At low temperatures, however, the situation is decidedly changed, since in this case the Boltzmann factor is large, and the populations of the sublevels  $-\frac{1}{2}$  and  $-\frac{3}{2}$  of the ground state are much larger than those of the sublevels  $\frac{1}{2}$  and  $\frac{3}{2}$ . Therefore the resonance radiation that comes from the tran-

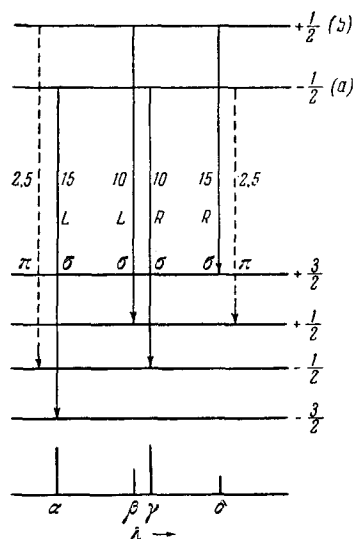


FIG. 19. Energy spectrum of  $\text{Cr}^{+++}$  ions in  $\text{Al}_2\text{O}_3$ .<sup>64</sup>

sitions from the sublevel b ( $\beta$  and  $\delta$ ) is more weakly absorbed than that coming from transitions from the sublevel a ( $\alpha$  and  $\beta$ ). By inducing radio-frequency transitions between a and b one can increase the intensity of the fluorescence and thus detect the radio frequency resonance in the excited state.<sup>67</sup>

In contrast with the ordinary method of double resonance in gases, in which one can detect the resonance from the change of intensity of either linearly or circularly polarized light, the selective-reabsorption method does not allow the use of linearly polarized light. This is because the reabsorption of the linearly polarized fluorescence (Fig. 19) does not affect the intensity of the fluorescence.

The observed line width of the signal in radio-frequency resonance was 17 cps and was comparable with the width obtained in the resonance in the excited state. It was found that this signal arises at a concentration of  $\text{Cr}^{+++}$  ions in the excited state of about  $10^{10}$ . The total increase of the signal of the fluorescence when the Zeeman sublevels of the excited state were saturated was 2.5 percent of the total intensity. This made it possible to measure directly the effective relaxation time  $T_1^*$  in the excited state. The time  $T_1^*$  is determined both by thermal effects and by cross relaxation to the ground state and radiation relaxation effects.

A study of the saturation of the microwave signal gave a determination of the quantity  $(M_{\alpha\delta}H_{\text{rf}}/\hbar)^2 T_1^* T_2^* \sim 1$ . Knowing the times  $T_1^*$  and  $T_2^*$  (the latter from the width of the line), one can determine the value of the matrix element  $M_{\alpha\delta}$  of the magnetic dipole transition.

One can also detect radio-frequency resonance in the ground state by the method of selective reabsorption. Experiments of this kind have been made with ruby.<sup>68</sup> The change of intensity of the light coming through when the radio frequency resonance was saturated amounted to one percent of the total intensity.

The method used in reference 68 is like the method of optical pumping in gases. Since, however, the spectrum of ions in a crystal is more complicated than that of atoms in a gas, additional work is required for the identification and singling out of the required narrow optical lines.

Optical pumping in solids has been the basis of the operation of infrared masers<sup>79</sup> and quantum counters of radiation.<sup>80</sup>

## CONCLUSION

The methods of optical pumping of atoms which have been developed during the past decade have led to the creation of a great new branch of radio spectroscopy. Having decidedly extended the possibilities of optical methods for studying matter, and also of electronic and nuclear magnetic resonance, radio-optical methods have already found many scientific and technical applications.

At the international conference on magnetic resonance in Paris in 1958 about a third of the reports were devoted to various applications of the methods of optical pumping. The first conference on applications of optical pumping methods was held in Ann Arbor in June 1959.

This new and promising branch of physics is now in a period of rapid development.

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