

Atomic Orientation by Optical Pumping*

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A variation of the usual method of atomic orientation of alkali metal vapors by optical pumping is proposed. This variation consists of employing a single circularly polarized D_1 line as pumping radiation, instead of a mixture of the two D lines. Under these conditions, one magnetic substate of the ground state is transparent to the pumping radiation. It is shown that for a sufficiently intense light source and relatively weak relaxation, the entire population of the vapor will tend to be pumped into this single state, resulting in nearly one-hundred percent atomic orientation. The pumping process is analyzed in detail for sodium vapor illuminated with $3P_{3/2}-3S_{3/2}$ radiation, and the time dependence of the populations of the eight magnetic sublevels of the ground state is computed. It is shown that in the steady state, the light absorption by the vapor is linear rather than exponential with distance. A simple method of measuring relaxation times based on this observation is suggested. The conditions under which the imprisonment of resonance radiation limits the size of the oriented sample are discussed, and it is suggested that the proposed technique will allow the alignment of larger samples than is possible by the usual method of optical pumping.

INTRODUCTION

THE orientation of alkali metal atoms by optical pumping with circularly polarized resonance radiation has recently attracted wide attention.¹⁻⁹ The usual method consists of illuminating the vapor with circularly polarized resonance radiation consisting of a mixture of two D lines. Under these conditions, only a limited degree of orientation can be achieved, and the size of the vapor sample that can be aligned is small, as discussed by Hawkins.⁵

It has recently been demonstrated by Dehmelt⁸ that it is possible to attain relaxation times of the order of 0.2 sec for optically pumped sodium vapor diffusing through an argon buffer gas atmosphere. Argon-sodium collisions are therefore relatively ineffective as far as disturbing the spin alignment of the sodium atom in its ground state is concerned. The influence of buffer gas collisions on the optical excited state has been investigated by Wood,¹⁰⁻¹³ Lochte-Holtgreven,¹⁴ Seiwert,¹⁵ and Bender.⁷ A review of this subject is to be found in Pringsheim's book.¹⁶ In the earlier experiments in this field, sodium vapor in an argon buffer gas atmosphere was illuminated with resonance light consisting of one

of the two D lines. It was found that when the partial pressure of the buffer gas is increased to a few millimeters of mercury, the relative intensity of the two D lines in the scattered resonance radiation tends toward the equilibrium ratio 1:2, regardless of which of the two lines is used for excitation. Lochte-Holtgreven¹⁴ obtained a cross section of 1.0×10^{-14} cm² for the transfer of sodium atoms from the $3P_{3/2}$ to the $3P_{1/2}$ state in sodium-argon collisions, and a cross section of 0.6×10^{-14} cm² for the inverse process at a temperature of 443°K. These cross sections are of the order of gas-kinetic collision cross sections. One would therefore expect substantially complete mixing of the magnetic sublevels of the excited P states when the buffer gas pressure is raised to such a point that the mean time between collisions approaches the lifetime of the excited state (1.6×10^{-8} sec).¹⁷⁻²⁰

Dehmelt⁸ has pointed out that it is possible to obtain partial orientation of sodium vapor with optical pumping even when there is complete reorientation in the excited state, i.e., complete mixing of the magnetic sublevels in this state, provided there is some difference in the peak intensities of the two D lines emitted by the light source.

We would like to go a step further to suggest that it is possible to approach one-hundred percent orientation of alkali metal atoms by illuminating them with circularly polarized resonance radiation containing only one of the two D lines, namely the one corresponding to an optical transition of the type $nP_{3/2}-mS_{3/2}$. This is true even when $n > m$, that is, when higher members of the principal series of the alkali spectra are employed. Furthermore, the orientation mechanism should be effective regardless of the degree of reorientation that

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¹ A. Kastler, *J. phys. radium* **11**, 255 (1950).² Brossel, Kastler, and Winter, *J. phys. radium* **13**, 668 (1952).³ Brossel, Cagnac, and Kastler, *J. phys. radium* **15**, 6 (1954).⁴ A. Kastler, *Proc. Phys. Soc. (London)* **A67**, 853 (1954).⁵ W. B. Hawkins, *Phys. Rev.* **98**, 478 (1955).⁶ A. Blandin and J. P. Barrat, *Compt. rend.* **243**, 2041 (1956).⁷ P. L. Bender, Ph.D. thesis, Department of Physics, Princeton University, 1956 (unpublished).⁸ H. G. Dehmelt, *Phys. Rev.* **105**, 1487 (1957).⁹ T. Carver and R. H. Dicke, *Proceedings of the Eleventh Annual Symposium on Frequency Control*, Signal Corps Engineering Laboratories, Fort Monmouth, New Jersey, May, 1957.¹⁰ R. W. Wood and L. Dunoyer, *Phil. Mag.* **27**, 1018 (1914).¹¹ R. W. Wood and L. Dunoyer, *Compt. rend.* **158**, 1490 (1914).¹² R. W. Wood and L. Dunoyer, *Radium* **11**, 119 (1914).¹³ R. W. Wood and F. L. Mahler, *Phys. Rev.* **11**, 70 (1918).¹⁴ W. Lochte-Holtgreven, *Z. Physik* **47**, 362 (1928).¹⁵ R. Seiwert, *Ann. Physik* **18**, 54 (1956).¹⁶ P. Pringsheim, *Fluorescence and Phosphorescence* (Interscience Publishers, Inc., New York, 1949), pp. 96-102.¹⁷ A. C. G. Mitchell and M. W. Zemansky, *Resonance Radiation and Excited Atoms* (Cambridge University Press, Cambridge, 1934), p. 36.¹⁸ R. Minkowski, *Z. Physik* **36**, 839 (1926).¹⁹ W. Schuetz, *Z. Physik* **45**, 30 (1927).²⁰ M. Weingeroff, *Z. Physik* **67**, 679 (1931).

may take place in the excited state, or any intermediate excited state, as will be demonstrated.

Consider the case where the direction of rotation of the magnetic vector of the circularly polarized resonance radiation used for pumping is such that the selection rule $\Delta m_F = +1$ applies relative to an axis of quantization defined by a weak longitudinal magnetic field as described by Hawkins.⁵ For a nuclear spin I , the two hyperfine states in the ground state have spins $I - \frac{1}{2}$ and $I + \frac{1}{2}$, respectively. The highest m_F value in the ground state is therefore $m_F = I + \frac{1}{2}$. An identical situation prevails in any of the $P_{\frac{3}{2}}$ excited states for which the two hyperfine states also have $F = I - \frac{1}{2}$ and $F = I + \frac{1}{2}$, the highest m_F value being $m_F = I + \frac{1}{2}$. It is clear that the $m_F = I + \frac{1}{2}$ substate of the ground state cannot undergo transitions subject to the selection rule $\Delta m_F = +1$ since no state having m_F larger than $I + \frac{1}{2}$ is available in the $P_{\frac{3}{2}}$ excited state.

On the other hand, all the other $4I+1$ substates of the ground state hyperfine doublet are able to absorb the circularly polarized resonance radiation. A certain proportion of the excited atoms thus produced will decay into the nonabsorbing $m_F = I + \frac{1}{2}$ sublevel, where they will remain for a time of the order of the relaxation time, undisturbed by the pumping radiation. If the pumping radiation is sufficiently intense and the relaxation time is sufficiently long, the entire population will be thrown into the single nonabsorbing $m_F = I + \frac{1}{2}$ sublevel of the ground state, as we intend to show. This condition corresponds to complete orientation of the alkali atoms, with the coupled nuclear and electron spins both aligned in the direction of the applied magnetic field.

In any actual experimental situation, the relaxation time of course cannot be made indefinitely long, as assumed above. The amount of orientation that can be achieved depends then on the quantity $\rho = 1/\beta_0 T$, where $1/T$ is the relaxation probability per atom per unit time, and β_0 is the average light absorption probability per atom per unit time when the occupation probabilities of the magnetic substates of the ground state are assumed to be equal. The smaller the value of ρ , the nearer the approach of the system to one-hundred percent orientation. This situation is analyzed in detail below.

ANALYSIS OF PUMPING PROCESS

To make the subsequent discussion quite definite, we shall analyze the pumping process as applied specifically to sodium optically pumped with circularly polarized $3P_{\frac{3}{2}} - 3S_{\frac{3}{2}}$ resonance radiation. The choice of this particular case, however, does not restrict the general validity of the method of analysis which can be applied equally well to any of the other alkali metals, or to optical pumping with one of the higher members of the principal series.

Normal sodium consists of a single isotope having a nuclear spin of $\frac{3}{2}$. The hyperfine doublet in the ground

state therefore has $F=1$ and $F=2$, with a total of eight sublevels: $(1, -1)$, $(1, 0)$, $(1, +1)$; $(2, -2)$, $(2, -1)$, $(2, 0)$, $(2, +1)$, $(2, +2)$. The numbers in the parentheses indicate F and m_F , respectively. We shall distinguish these sublevels by using subscripts 1 through 8, in the order stated. Let b_{ij} be the probability per unit time that an atom in the substate i of the ground state has undergone a transition to a substate j of the ground state by absorption and re-emission of a photon. Similarly, we denote by w_{ij} the probability per unit time for the corresponding transition induced by relaxation. The occupation probability $p_k(t)$ of the k th state can be obtained by a solution of the eight simultaneous differential equations

$$\dot{p}_k = -\sum_{j=1}^8 (b_{kj} + w_{kj})p_k + \sum_{i=1}^8 (b_{ik} + w_{ik})p_i; \quad k=1, 2, \dots, 8. \quad (1)$$

Only seven of these equations are independent in view of the relation $\sum_k p_k = 1$. The dot denotes differentiation with respect to time, and the prime is used to indicate that the terms $j=k$ and $i=k$ are to be omitted in the summations.

The omission of the diagonal terms corresponds to the fact that a transition in which an atom in state k absorbs a photon and then returns to the same state does not affect the occupation probability of that state. However, such a transition does contribute to the absorption coefficient of the vapor for the incident resonance radiation. Thus the probability per unit time that an atom in state k will absorb a photon is given by $\sum_j b_{kj}$ and the probability per unit time that any atom will absorb a photon is $\beta = \sum_k \sum_j b_{kj} p_k$. If we assume that the occupation probabilities are all equal at thermal equilibrium (in other words, if we neglect the small differences in the occupation probabilities at sodium vapor temperatures), the average light absorption probability per atom per unit time is

$$\beta_0 = \frac{1}{8} \sum_k \sum_j b_{kj} = \int_0^\infty I_\nu \sigma_\nu d\nu, \quad (2)$$

where I_ν is the spectral density of the incident light in

TABLE I. Relative absorption probabilities $(1/\beta_0) \sum_j b_{kj}$ per unit time of the eight magnetic substates of the ground state of the sodium atom for circularly polarized resonance radiation containing the $3P_{\frac{3}{2}} - 3S_{\frac{3}{2}}$ line only.

| (F, m_F) | k | $(1/\beta_0) \sum_j b_{kj}$ |
|------------|-----|-----------------------------|
| $(1, -1)$ | 1 | $\frac{1}{2}$ |
| $(1, 0)$ | 2 | 1 |
| $(1, +1)$ | 3 | $\frac{3}{2}$ |
| $(2, -2)$ | 4 | 2 |
| $(2, -1)$ | 5 | $\frac{3}{2}$ |
| $(2, 0)$ | 6 | 1 |
| $(2, +1)$ | 7 | $\frac{3}{2}$ |
| $(2, +2)$ | 8 | 0 |

TABLE II. Array of coefficients B_{ik} to be used in the simultaneous differential equations (5) for sodium optically pumped with circularly polarized D_1 radiation. No reorientation in the excited state.

| (F, m_F) \ i | | $(1, -1)$ | $(1, 0)$ | $(1, 1)$ | $(2, -2)$ | $(2, -1)$ | $(2, 0)$ | $(2, 1)$ | $(2, 2)$ |
|------------------|-----|---------------|---------------|------------|---------------|------------|---------------|---------------|----------|
| | | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
| (F, m_F) | k | | | | | | | | |
| $(1, -1)$ | 1 | $-8\rho-11/3$ | 0 | 0 | 2 | 1 | 0 | 0 | 0 |
| $(1, 0)$ | 2 | $2/3$ | $-8\rho-19/3$ | 0 | 2 | 2 | $5/3$ | 0 | 0 |
| $(1, 1)$ | 3 | $1/3$ | $5/3$ | $-8\rho-6$ | 0 | 1 | $5/3$ | 2 | 0 |
| $(2, -2)$ | 4 | 0 | 0 | 0 | $-8\rho-28/3$ | 0 | 0 | 0 | 0 |
| $(2, -1)$ | 5 | 1 | 0 | 0 | $10/3$ | $-8\rho-9$ | 0 | 0 | 0 |
| $(2, 0)$ | 6 | $2/3$ | $5/3$ | 0 | 2 | 2 | $-8\rho-19/3$ | 0 | 0 |
| $(2, 1)$ | 7 | 1 | 1 | 2 | 0 | 3 | 1 | $-8\rho-10/3$ | 0 |
| $(2, 2)$ | 8 | 0 | 2 | 4 | 0 | 0 | 2 | $4/3$ | -8ρ |

photons per cm^2 per sec per unit frequency range, and σ_ν is the cross section for absorption of a photon of frequency ν by a sodium atom when the eight sublevels in the ground state are equally populated. If we take the oscillator strength of the circularly polarized D_1 line as $\frac{1}{8}$, we can employ the dispersion theory relation^{17,21}

$$\int_0^\infty \sigma_\nu d\nu = \frac{1}{6}\pi c r_0 = 4.40 \times 10^{-3} \text{ cm}^2/\text{sec},$$

where $r_0 = e^2/mc^2$ is the classical radius of the electron and c is the velocity of light, to obtain $\beta_0 = 4.40 \times 10^{-3} I_0$ for the layer of sodium vapor first struck by the incident resonance radiation. We have assumed here that the light source emits a spectral line that is considerably broader than the width at half-maximum of the Doppler-broadened absorption line,²² so that we can set $I_\nu = I_0 = \text{constant}$ at the center of the line.

The relative absorption probabilities $(1/\beta_0) \sum_j b_{kj}$ of the eight substates $k=1, 2, \dots, 8$, for the circularly polarized D_1 line are listed in Table I.^{23,24} We note in the first place that the absorption probability of the eighth state ($F=2, m_F=+2$) is zero. This is due to the fact that the transition $3S_{\frac{1}{2}}-3P_{\frac{1}{2}}$ is forbidden for this state by the selection rule $\Delta m_F = +1$. Secondly, we observe that the average absorption probability per atom for a condition where the p_k 's are unequal is given by

$$\beta = \beta_0 \left[\frac{1}{2} p_1 + p_2 + \frac{3}{2} p_3 + 2p_4 + \frac{3}{2} p_5 + p_6 + \frac{1}{2} p_7 \right]. \quad (3)$$

It should be emphasized that these statements are valid

²¹ W. Heitler, *The Quantum Theory of Radiation* (Oxford University Press, New York, 1954), third edition, p. 180.

²² For sodium vapor at 400°K, the Doppler width at half-maximum is $\Delta\nu_D = 1500$ Mc/sec, while a sodium spectral lamp under typical operating conditions emits a D_1 line of width 10⁴ Mc/sec. (See reference 5.) These figures are to be compared with a zero-field hyperfine splitting in the ground state of 1770 Mc/sec and a natural width of 10 Mc/sec. The Lorentz width is negligible at moderate buffer gas pressures.

²³ E. U. Condon and G. H. Shortley, *The Theory of Atomic Spectra* (Cambridge University Press, Cambridge, 1935), Chaps. IX and XII.

²⁴ W. B. Hawkins, Ph.D. thesis, Department of Physics, Princeton University, May, 1954 (unpublished), Appendix D.

regardless of the amount of reorientation of the sodium atom in its excited state.

The simplest assumption that one can make with regard to the relaxation probabilities w_{ij} occurring in Eq. (1) is that all the w 's are equal to each other. This implies that in an individual relaxation event, such as an electron exchange collision between two sodium atoms,^{25,26} or a wall collision, an atom in a given substate has an equal probability for making a transition to any of the other seven substates. If we set $w = 1/8T$ for all the w 's in Eq. (1), then the differential equation satisfied by p_k when no pumping radiation is present is

$$\dot{p}_k = -(1/T) \left(p_k - \frac{1}{8} \right), \quad (4)$$

so that T has the significance of a spin-lattice relaxation time in the usual sense.²⁷

The actual values of the individual transition probabilities b_{ij} of course do depend on the amount of reorientation in the excited state. Two extreme situations can be analyzed simply, namely the case of no reorientation in the excited state, and the case of complete reorientation in the excited state. Any actual physical system would be expected to be intermediate between these two extremes.

In view of (4), the system of Eqs. (1) can be written in the form

$$\dot{p}_k = \left(\frac{\beta_0}{8} \right) \sum_{i=1}^8 B_{ik} p_i + \frac{1}{8T}; \quad k=1, 2, \dots, 8. \quad (5)$$

The coefficients B_{ik} are related to the transition probabilities defined previously by $B_{ik} = (8/\beta_0) b_{ik}$ for $i \neq k$, and $B_{kk} = -(8/\beta_0) [(1/T) + \sum_{j' \neq k} b_{kj'}]$, where the prime again denotes omission of the term $j=k$ in the summation. Normalization of the transition probabilities computed by Hawkins²⁴ leads to the array of coefficients B_{ik} shown in Table II for the case of no reorientation in the excited state.

For the case of complete reorientation in the excited

²⁵ J. P. Wittke and R. H. Dicke, *Phys. Rev.* **103**, 620 (1956).

²⁶ E. M. Purcell and G. B. Field, *Astrophys. J.* **124**, 542 (1956).

²⁷ E. R. Andrews, *Nuclear Magnetic Resonance* (Cambridge University Press, Cambridge, 1954), p. 15.

TABLE III. Array of coefficients B_{ik} to be used in the simultaneous differential Eqs. (5) for sodium optically pumped with circularly polarized D_1 radiation. Complete reorientation in the excited state.

| (F, m_F) \ i | | (F, m_F) | | | | | | | |
|------------------|-----|----------------|--------------|-----------------|---------------|-----------------|--------------|----------------|----------|
| | | (1, -1) | (1, 0) | (1, 1) | (2, -2) | (2, -1) | (2, 0) | (2, 1) | (2, 2) |
| k | i | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
| (1, -1) | 1 | $-8\rho - 3.5$ | 1 | 1.5 | 2 | 1.5 | 1 | 0.5 | 0 |
| (1, 0) | 2 | 0.5 | $-8\rho - 7$ | 1.5 | 2 | 1.5 | 1 | 0.5 | 0 |
| (1, 1) | 3 | 0.5 | 1 | $-8\rho - 10.5$ | 2 | 1.5 | 1 | 0.5 | 0 |
| (2, -2) | 4 | 0.5 | 1 | 1.5 | $-8\rho - 14$ | 1.5 | 1 | 0.5 | 0 |
| (2, -1) | 5 | 0.5 | 1 | 1.5 | 2 | $-8\rho - 10.5$ | 1 | 0.5 | 0 |
| (2, 0) | 6 | 0.5 | 1 | 1.5 | 2 | 1.5 | $-8\rho - 7$ | 0.5 | 0 |
| (2, 1) | 7 | 0.5 | 1 | 1.5 | 2 | 1.5 | 1 | $-8\rho - 3.5$ | 0 |
| (2, 2) | 8 | 0.5 | 1 | 1.5 | 2 | 1.5 | 1 | 0.5 | -8ρ |

state, we assume with Dehmelt⁸ that the rates at which atoms return to the eight magnetic sublevels of the ground state are equal. Using the same normalization procedure applied above, we then get the array of coefficients shown in Table III.

Figure 1 displays graphically solutions of the two sets of simultaneous differential equations (5) that have been obtained by use of an electronic computer for the case $\rho = 1/\beta_0 T = 0.01$. We note the approach of the system to a steady state in which most of the population is in the single substate 8 ($F=2, m_F=+2$). It is also interesting to observe the rapid decrease of the absorption probability $\beta = \beta_0(\frac{1}{2}p_1 + p_2 + \frac{3}{2}p_3 + 2p_4 + \frac{3}{2}p_5 + p_6 + \frac{1}{2}p_7)$ as the steady state is approached.

Of considerable practical interest are analytical solutions of the two sets of equations for the steady state when $\rho = 1/\beta_0 T$ is small. In that case, the steady-state occupation probabilities of the eight states have the approximate values listed in Table IV. We note that the light absorption probability β per unit time per atom approaches the value $7\rho\beta_0 = 7/T$ in the case of complete reorientation in the excited state, and the value $3.63/T$ in the case of no reorientation in the excited state. Remarkably enough, the probability of

light absorption per atom becomes independent of light intensity in the steady state. This follows from the fact that the number of atoms in the seven absorbing states in the steady state is inversely proportional to light intensity. (These statements are valid only when ρ is small compared to unity, i.e., when the light source is sufficiently intense and the relaxation time is long.)

In the practical case where some reorientation in the excited state takes place, the absorption probability β can be written

$$\beta = \left(\frac{1}{N}\right) \frac{\partial}{\partial z} \left[\int_0^\infty I_\nu(z) dz \right] = -\frac{\eta}{T},$$

where η is a dimensionless constant having a value somewhere between 3.63 and 7.00, N is the number of sodium atoms per cm^3 , and z is a distance measured from the front of the vapor sample cell in the direction of light propagation. The integrated light intensity therefore decreases linearly with z in accordance with

$$\int_0^\infty I_\nu(0) dz - \int_0^\infty I_\nu(z) dz = \left(\frac{N\eta}{T}\right) z. \quad (6)$$

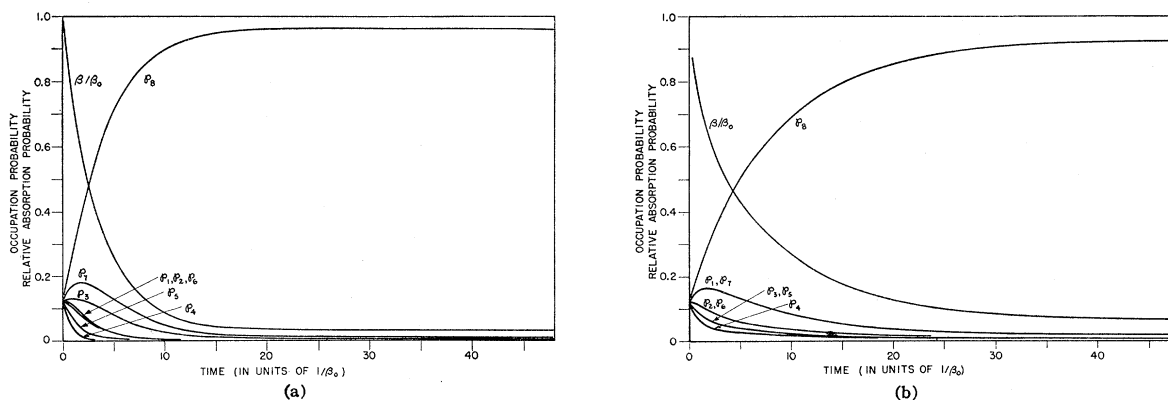


FIG. 1. Predicted rate of change of the occupation probabilities of the eight magnetic sublevels of the sodium atom when illuminated with circularly polarized D_1 radiation. The curves represent solutions of the simultaneous equations (5) obtained by means of an electronic computer for the case $\rho = 1/\beta_0 T = 0.01$. The curve labeled β/β_0 shows the relative light absorption probability per atom per unit time as a function of time. The time $t=0$ corresponds to the instant at which the pumping radiation is suddenly turned on. (a) No reorientation in the excited state of the sodium atom. (b) Complete reorientation in the excited state.

TABLE IV. Steady-state occupation probabilities of the eight magnetic sublevels of the ground state of the sodium atom optically pumped with circularly polarized D_1 radiation. The occupation probabilities are expressed in terms of $\rho = 1/\beta_0 T$ which is assumed to be small compared to unity. The last column gives the steady-state value of the ratio β/β_0 of the average absorption probability per atom per unit time to its value at thermal equilibrium.

| | p_1 | p_2 | p_3 | p_4 | p_5 | p_6 | p_7 | p_8 | β/β_0 |
|------------------------|-------------|-------------|-------------------|-------------------|-------------------|-------------|------------|--------------|-----------------|
| No reorientation | 0.384ρ | 0.398ρ | 0.941ρ | 0.107ρ | 0.194ρ | 0.398ρ | 1.45ρ | $1-3.87\rho$ | 3.63ρ |
| Complete reorientation | 2ρ | ρ | $\frac{2}{3}\rho$ | $\frac{1}{2}\rho$ | $\frac{2}{3}\rho$ | ρ | 2ρ | $1-7.89\rho$ | 7ρ |

The amount of light absorbed by the vapor is thus inversely proportional to the relaxation time T . This observation suggests a convenient method for measuring relaxation times. Evidently, in the steady state the number of photons $N\eta/T$ which are removed from unit area of the incident light beam in unit distance traveled through the vapor just suffices to counteract the effect of relaxation. For a sodium vapor pressure of 7.6×10^{-6} mm Hg, $\eta = 7$ (complete reorientation), and $T = 0.2$ sec (Dehmelt's longest observed relaxation time⁸), we have $N\eta/T = 6.4 \times 10^{12}$ photons/cm²-sec. The condition that $\rho = 1/\beta_0 T$ be small compared to unity requires that $\beta_0 = 4.40 \times 10^{-3} I_0 \gg 1/T$. For $T = 0.2$ sec, this leads to $I_0 \gg 1000$ photons/cm² sec sec⁻¹ as a condition on the spectral density per unit frequency range at the center of the emitted D_1 line.

RELAXATION PROCESSES

The relaxation of a partially oriented alkali metal vapor in a buffer gas would be expected to take place by electron exchange between colliding alkali atoms, as discussed by Dicke²⁵ and Purcell,²⁶ by collisions with buffer gas atoms, and by collisions with the cell walls. The frequency of electron exchange collisions is a function of the alkali vapor pressure. The rates at which the other two types of relaxation events take place is affected by the pressure of the buffer gas, but in an opposite manner for the two cases. An increase in pressure results in an enhanced collision rate with the buffer gas atoms, but it also serves to reduce the diffusion rate of the alkali atoms to the walls. An optimum buffer gas pressure should therefore exist at which the relaxation rate of the oriented alkali atoms is a minimum.

In the case of optical pumping with a single D_1 line, this optimum pressure can be chosen more or less without regard to the effect of disorienting collisions between excited alkali atoms and buffer gas atoms. We have shown that for sodium vapor optically pumped with $3P_{\frac{3}{2}}-3S_{\frac{3}{2}}$ radiation, the pumping rate and the degree of orientation that can be achieved in the steady state, are at the most decreased by a factor of two as the buffer gas pressure is increased from a small value (practically no disorientation collisions) to a large value (complete disorientation in the excited state). On the other hand, in the ordinary method of optical pumping, that is, when a mixture of the two D lines of approximately equal peak intensity is employed, the pumping efficiency goes to zero as the buffer gas pressure is increased, as has been shown by Bender.⁷ It is therefore

necessary to use a value for the buffer gas pressure which is considerably lower than the optimum value discussed above in order to keep the frequency of disorienting collisions between excited alkali atoms and buffer gas atoms to a minimum. Furthermore, a large gas container must be used in order to achieve a reasonably long diffusion time to the walls. Neither of these restrictions apply to the method of pumping proposed here.

The different effect of excited state collisions on the pumping process for the two methods can be explained as follows for the case of sodium. When the intensity of the two circularly-polarized D lines is equal, as would be true for the broad self-reversed lines from a high-intensity spectral lamp, the absorption probabilities of the magnetic substates of the ground state are also equal. The rate at which the absorption of resonance radiation transfers a given atom from the ground state to the excited states is therefore the same for all the substates of the ground state. The pumping process then depends in an essential manner on the preservation, in the excited state, of the change in the z component of the angular momentum brought about by the absorption of the circularly polarized quantum. When the substates of the excited states are completely mixed by collisions with buffer gas atoms, the information contributed by the absorption process is lost, and the pumping efficiency goes to zero.

On the other hand, when a single circularly polarized D_1 line is employed, the absorption probabilities of the substates are unequal. In particular, one of the substates has zero absorption probability. For this reason, a redistribution of the populations of the hyperfine states of the ground state will take place even when the excited substates are completely mixed by collision. The pumping process then depends not so much on the change in magnetic quantum number brought about by the absorption of the circularly polarized quantum, but more on the operation of selection rules on the absorption.

IMPRISONMENT OF RESONANCE RADIATION

In the usual method of optical pumping, the partially oriented vapor remains highly absorbent to the incident radiation and therefore constitutes a strong source of unpolarized scattered resonance radiation. This scattered resonance radiation has a depolarizing effect which makes it impossible to partially orient more than a very small number of atoms,

On the other hand, when the D_1 line alone is used, the absorption probability of the nearly completely oriented vapor decreases to a small value, as we have shown. The vapor therefore represents a comparatively weak source of scattered light. Under these circumstances, it should be possible to extend the aligned sample in the direction of propagation of the collimated pumping radiation, provided its dimensions are kept small in a transverse direction. Thus, a photon of the nearly isotropically emitted scattered light will have a much smaller probability of absorption before escaping from the system than would be the case for the pumping radiation.

In our analysis of the pumping process, the influence of the scattered resonance radiation on the establishment of the steady state has not been taken into account. This influence will depend on the geometry of the sample cell. If the reabsorption probability can be made small enough, we can regard the scattered photons as contributing simply to an effective shortening of the relaxation time. The use of the separated D_1 line gives us considerable freedom of choice as far as the geometry of the sample cell is concerned, as we saw in the previous section, so that this condition can always be fulfilled in a practical case.

The influence of cooperative reradiation, as discussed by Dicke,^{28,29} also has not been considered. In view of the present state of knowledge of this subject, it is not clear to what extent this effect will limit the total number of atoms that can be aligned by optical pumping techniques.

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Note added in proof.—At the meeting of the American Physical Society in Boulder, Colorado, on September 6, 1957, Dr. H. G. Dehmelt independently described the principles of an optical pumping experiment using a single circularly polarized D_1 line.

²⁸ R. H. Dicke, Phys. Rev. **93**, 99 (1954).

²⁹ R. B. Griffiths and R. H. Dicke, Rev. Sci. Instr. **28**, 646 (1957).