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Relaxation Mechanisms in Optical Pumping*

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The distribution of population in the ground-state sublevels of an optically pumped alkali-metal vapor has been found to be strongly dependent on the mechanisms assumed responsible for relaxation. Two modes of optical pumping zero mixing and complete mixing in the excited state, and three modes of alkali relaxation, uniform, Zeeman, and electron randomization, are considered. Calculations of the sublevel relative populations are made in terms of experimentally measurable parameters for all six combinations of pumping and relaxation modes. Optical-pumping transient signals are then used to demonstrate that alkali relaxation due to wall collisions is of the low-frequency "Zeeman" variety, while relaxation due to alkali–rare-gas collisions takes place through randomization of the spin of the alkali valence electron. Equations for the rate of change of the electronic spin polarization are derived for all cases, and are found to be nonexponential, in contrast with the case of an alkali of zero nuclear spin.

I. INTRODUCTION

THE use of optical pumping to create a large magnetization in a vapor of alkali-metal atoms is now a fairly well-known technique. Through the selective absorption and re-emission of circularly polarized resonance radiation, large differences in population among the various Zeeman magnetic sublevels of the alkali atomic ground state can be obtained. Since each Zeeman sublevel is characterized by a particular orientation of the atomic magnetic moment with respect to the direction of an external magnetic field, differences in sublevel populations can imply the existence of a net magnetization of the vapor.

A magnetization, once produced by optical pumping, should persist for quite a long time, since the lifetime against spontaneous transition between ground-state sublevels is of the order of thousands of years. In practice the atoms of an optically pumped vapor collide with impurities, or with the walls of the containing vessel, losing polarization in such encounters. Two methods that have been commonly used to preserve alkali polarization are to retard the diffusion of the alkali to the cell walls through the use of nonmagnetic buffer gases, or to make the walls nonrelaxing through the use of paraffin or silicone coatings. Even the totally nonmagnetic rare gases, however, have proved to be imperfect buffers. The first experiment on the relaxation of an optically pumped alkali-metal vapor in a buffer gas was performed in 1957 by Dehmelt,[1] who measured the cross section for sodium relaxation in argon. Dehmelt also made initial studies of alkali relaxation in evacuated coated cells, and extended his relaxation studies to other alkali metals.[2] In 1959, Franzen[3] made a systematic study of the efficiency of various rare gases as buffers for optically pumped rubidium, measuring disorientation cross sections in Ne, Ar, Kr, and Xe. Since that time there have been many further contributions to the study of spin relaxation of optically pumped vapors.[4–16]

Although much experimental data is now available, theoretical calculations of the various disorientation cross sections have only recently been performed. In 1962 Bernheim[4] made the first attempt to explain the variation of the rubidium–rare-gas disorientation cross sections with rare-gas atomic number. Bernheim proposed that during an alkali–rare-gas collision the alkali valence electron experiences a spin-orbit coupling in the rare-gas nuclear electric field that induces precession of electronic magnetic moment, with resultant relaxation. Herman[17] has recently modified and extended Bernheim's work, and has arrived at numerical estimates of the rubidium–rare-gas disorientation cross sections. Although Herman's theory appears to predict rather well the dependence of the cross sections on rare-gas atomic number, quantitative agreement with experiment is poor,[12] probably because of the many approximations and high order of perturbation theory required to arrive at final numerical values.

In 1957, Franzen and Emslie[18] calculated both the

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[1] H. G. Dehmelt, Phys. Rev. **105**, 1487 (1957); J. Opt. Soc. Am. **55**, 335 (1965).

[2] H. G. Dehmelt, in Proceedings of the 12th Annual Symposium on Frequency Control, Fort Monmouth, New Jersey, 1958 (unpublished).

[3] W. Franzen, Phys. Rev. **115**, 850 (1959).

[4] R. A. Bernheim, J. Chem. Phys. **36**, 135 (1962).

[5] R. J. McNeal, J. Chem. Phys. **37**, 2726 (1962); **40**, 1089 (1964).

[6] R. G. Brewer, J. Chem. Phys. **37**, 2504 (1962).

[7] L. W. Anderson and A. T. Ramsey, Phys. Rev. **132**, 712 (1963); Nuovo Cimento **32**, 1151 (1964).

[8] F. A. Franz and E. Lüscher, Phys. Letters **7**, 277 (1963); Phys. Rev. **135**, A582 (1964).

[9] S. Legowski, J. Chem. Phys. **41**, 1313 (1964).

[10] M. Arditi and T. R. Carver, Phys. Rev. **136**, 643 (1964).

[11] R. A. Bernheim and M. Korte, J. Chem. Phys. **42**, 2721 (1965).

[12] F. A. Franz, Phys. Rev. **139**, A603 (1965).

[13] M. A. Bouchiat and J. Brossel, Compt. Rend. **254**, 3650 (1962); **254**, 3828 (1962); **257**, 2825 (1963).

[14] M. A. Bouchiat, J. Phys. Radium **24**, 379 (1963); **24**, 611 (1963).

[15] F. Grossetete, Compt. Rend. **258**, 3668 (1964); **259**, 3211 (1964); J. Phys. Radium **25**, 383 (1964).

[16] R. Marrus and J. Yellin, this issue, Phys. Rev. **141**, 130 (1966).

[17] R. M. Herman, Phys. Rev. **136**, A1576 (1964).

[18] W. Franzen and A. G. Emslie, Phys. Rev. **108**, 1453 (1957).

rate of change of the ground-state sublevel populations of an alkali vapor subjected to optical pumping, and the values of these populations in an optically pumped equilibrium. For convenience of calculation, they assumed that relaxation between ground-state sublevels is uniform, that is, that when an atom in the ith sublevel relaxes, it can reach any other sublevel j with equal probability. Uniform relaxation is a rather unphysical mechanism, however, especially for the consideration of alkali relaxation induced by collisional interactions with buffer-gas molecules. Calculations of the state populations based on the more reasonable relaxation model of Bernheim and Herman are quite uninviting because of the complexities involved in arriving at meaningful numerical results.

In the present paper we have used a simplified, semiempirical approach in order to calculate the ground-state sublevel equilibrium populations. We assume that during alkali-rare-gas collisions deformations and overlap occur that allow the alkali valence electron to briefly experience sharp spikes of electric field. As the alkali moves through the interaction region it will see a spectrum of randomly oriented oscillating magnetic fields. If appropriate frequency components are present, reorientation of either the total magnetic moment of the atom, μ_F, or of the magnetic moment of the valence electron, μ_S, can take place. We consider the effect of these two types of magnetic dipole relaxation on the distribution of population in the ground-state Zeeman sublevels. In order to calculate relative transition probabilities between states we assume the simplest possible model of an alkali atom subjected to an oscillating magnetic field $H_1(\omega)$ with equal components H_x, H_y, and H_z. Then using the calculated relative transition probabilities, we compute the steady-state occupation probabilities of the various ground-state magnetic sublevels in terms of macroscopic parameters, the relaxation rate, and the pumping rate. It will be shown that the distribution of population in the ground-state sublevels varies greatly depending on the relaxation mechanism assumed. These differences will then be utilized to demonstrate which modes of alkali relaxation actually occur in an optical-pumping experiment.

II. OPTICAL PUMPING OF A NUCLEAR SPIN-ZERO ALKALI ATOM

Optical-pumping rate equations have sometimes been derived for a hypothetical alkali atom of zero-nuclear spin.[18a] A calculation based on such a model assumes a particularly simple form that in some cases provides an adequate approximation to the behavior of real alkali atoms. This model will thus be a starting point for the calculations of the optical pumping of alkali atoms of nuclear spin $I=\frac{3}{2}$ that will be presented in a later section.

The ground state of a zero-nuclear-spin alkali atom has two sublevels, $m_F=m_S=\pm\frac{1}{2}$, that are split in a weak magnetic field. The occupation probabilities n_1 and n_2 of states (1) ($m_S=-\frac{1}{2}$), and (2) ($m_S=+\frac{1}{2}$), are normalized ($n_1+n_2=1$). In thermal equilibrium, n_1 and n_2 are essentially equal ($n_1=n_2=\frac{1}{2}$).

The probability per atom for absorption of light by a vapor in any state of polarization is $\sum_i AK_in_i$, where A is a constant proportional to both the incident light intensity and the absorption cross section σ_0. K_i is the relative absorption probability of the ith sublevel, and is determined by the state of polarization of the incident light. For alkali atoms it is found that for the absorption of light in which $\Delta m_F=+1$, K_i is always proportional to $\langle\frac{1}{2}-S_z\rangle_i$, $\langle S_z\rangle_i$ being the expectation value of the electronic spin in the ith sublevel of the ground state. All of our calculations will be based on the assumption that the vapor is pumped by $D_1({}^2P_{1/2}\leftrightarrow{}^2S_{1/2})$ left circularly polarized light, for which $\Delta m_F=+1$ in absorption. Thus, for the zero-nuclear-spin model, $K_1=1$, and $K_2=0$. The probability per unit time for excitation out of state (1) will then be An_1; for state (2) it is zero. We further assume that there is complete mixing between levels in the excited state, that is, that once an atom has been excited, it may decay with equal probability to either sublevel of the ground state. For the moment we neglect relaxation effects between sublevels (1) and (2). The rate equations governing behavior of the state populations n_1 and n_2 are then

$$dn_1/dt=-An_1+\tfrac{1}{2}An_1=-\tfrac{1}{2}An_1,$$

$$dn_2/dt=\tfrac{1}{2}An_1.$$

In most experiments, the state of polarization of the optically pumped vapor is monitored by measuring the intensity of light transmitted through the vapor cell, a technique devised by Dehmelt.[1] It is thus convenient to define the net expectation value of electronic spin $\langle S_z\rangle$ for the entire vapor, $\langle S_z\rangle=\sum_i\langle S_z\rangle_in_i$, since, under the experimental conditions assumed, the absorption of light by the vapor is a linear function of this parameter. Then, for the nuclear-spin-zero atom:

$$\langle S_z\rangle=\tfrac{1}{2}n_2-\tfrac{1}{2}n_1,$$

and

$$d\langle S_z\rangle/dt=\tfrac{1}{2}An_1=\tfrac{1}{2}A\left(\tfrac{1}{2}-\langle S_z\rangle\right)=\tfrac{1}{4}A-\tfrac{1}{2}A\langle S_z\rangle. \quad (1)$$

Since $m_{Fi}=m_{Si}=\langle S_z\rangle_i$, the polarization of the vapor, $P=\sum_i m_{Fi}n_i$, follows the same equation,

$$dP/dt=\tfrac{1}{4}A-\tfrac{1}{2}AP. \quad (2)$$

The effects of relaxation between ground-state sublevels may now be considered. Such relaxation might be caused by collision with buffer-gas atoms, impurity atoms, or the walls of the optical-pumping cell. Let us assume that the rate of such relaxation out of a state is given by some rate constant R multiplied by the occupation probability of the state. For the nuclear-

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[18a] S. M. Jarrett, Phys. Rev. 133, A111 (1964).

spin-zero model, this assumption encompasses all modes of relaxation, uniform or not. Then the time variations of the state populations due to relaxation are given by

$$dn_1/dt=-Rn_1+Rn_2,$$
$$dn_2/dt=-Rn_2+Rn_1.$$

It follows that

$$d\langle S_z\rangle/dt=(d/dt)(\tfrac{1}{2}n_2-\tfrac{1}{2}n_1)=-2R\langle S_z\rangle. \tag{3}$$

The polarization P again follows the same equation:

$$dP/dt=-2RP. \tag{4}$$

If the optical-pumping process is now combined with relaxation in the ground state, we obtain the master equations that govern the behavior of the system at any time:

$$d\langle S_z\rangle/dt=\tfrac{1}{4}A-\tfrac{1}{2}A\langle S_z\rangle-2R\langle S_z\rangle, \tag{5}$$

and

$$dP/dt=\tfrac{1}{4}A-\tfrac{1}{2}AP-2RP. \tag{6}$$

The solution to Eq. (5) is

$$\langle S_z\rangle=\langle S_z\rangle_0[1-\exp(-t/\tau)], \tag{7}$$

where

$$\langle S_z\rangle_0=\tfrac{1}{4}A/(2R+\tfrac{1}{2}A) \tag{8}$$

and

$$1/\tau=2R+\tfrac{1}{2}A. \tag{9}$$

Thermal equilibrium ($n_1=n_2$) at $t=0$ has been assumed. An identical equation for the polarization P also obtains. Both $\langle S_z\rangle$ and P thus have a simple exponential time dependence in the optical pumping of the zero-nuclear-spin alkali atom. Equation (9) has sometimes been used to obtain an estimate of the relaxation time of an optically pumped vapor of real alkali atoms. If the time constant of the pumping curve (τ) is measured as a function of light intensity, extrapolation to zero light intensity yields the relaxation rate $2R$. Knowing the relaxation rate, one may determine the pumping rate, A, for any given light intensity. The steady-state spin polarization, $\langle S_z\rangle_0$, is then given by Eq. (8). The beauty of this method is that by using *relative* pumping and relaxation rates one can deduce a wealth of information about the vapor without reference to such quantities as the absolute absorption cross section per atom. Unfortunately, when we consider the pumping of real alkali atoms with nonzero nuclear spin, the simple time dependence of $\langle S_z\rangle$ predicted by Eq. (6) is no longer exactly exponential. Under many conditions, however, the simple technique for measuring pumping and relaxation rates that was described in the paragraph above may provide at least approximate values for these parameters. In the following section we consider the optical pumping of an alkali atom of nuclear spin $\frac{3}{2}$, and attempt to cast the pumping and relaxation equations into forms similar to those obtained for the nuclear-spin-zero model. Calculations of the ground-state sublevel populations are then made for various modes of pumping and relaxation in terms of the macroscopically measurable pumping and relaxation rates.

III. OPTICAL PUMPING FOR NUCLEAR-SPIN-$\frac{3}{2}$ ALKALIES

A. Absorption Probabilities and Excited-State Mixing

The rate equations that were derived for light absorption by the zero-nuclear-spin alkali atom were simplified by the assumption of complete mixing in the excited state. As we now proceed to the consideration of real alkali atoms, it is well to reconsider the meaning of excited-state mixing, and to try to get some idea of the degree of mixing that might occur in an actual experiment.

Many years ago, Wood and co-workers[19] showed that if the isolated sodium D_1 line ($^2P_{1/2}\leftrightarrow{}^2S_{1/2}$) were passed through a cell containing sodium vapor in the presence of more than a few Torr of argon or some other rare gas, the resonance fluorescence contained both the D_1 and D_2($^2P_{3/2}\leftrightarrow{}^2S_{1/2}$) resonance lines. At low gas pressures the D_2 line disappeared. The conclusion drawn was that at higher rare-gas pressures there was an appreciable probability for a sodium atom, while in the excited state, to collide with a rare-gas atom, with an attendant probability of the sodium atom being thrown into the $^2P_{3/2}$ state from the $^2P_{1/2}$ state. The cross section for such a process is of the order of 10^{-14} cm^2 for sodium[20]; thus, when the buffer/gas pressure is more than a few Torr, considerable mixing in the excited state may be expected to occur. When such mixing is present during the optical-pumping process, all coherence between the ground state and excited states is lost. The optical pumping still proceeds due to the continual depletion of low m_F levels, but its efficiency is greatly impaired compared to the case of no mixing.

Very little information exists on the degree of excited-state mixing for alkalies other than sodium. The amount of mixing that may occur *within* a particular hyperfine level of the excited state is likewise unknown. Recent work has indicated that the cross section for mixing in rubidium is many times smaller than that for sodium.[16] Even greater differences might be expected for cesium. In the absence of more detailed information, only two cases can be easily calculated: those of no mixing and of complete mixing in the excited state.

For $I=\frac{3}{2}$ there are eight Zeeman sublevels in the ground state, corresponding to ($F=2$, $m_F=2,1,0,-1,-2$; $F=1$, $m_F=1,0,-1$). For a moment we neglect relaxation between these levels. The optical-pumping transition probabilities between states $|F,m_F\rangle$ and

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[19] See, e.g., R. W. Wood and F. L. Mahler, Phys. Rev. **11**, 70 (1918).

[20] W. Lochte-Holtgreven, Z. Physik **47**, 362 (1928).

$|F',m_F'\rangle$ are particularly easy to calculate under the assumption of complete excited-state mixing. As mentioned in a previous section, K_i, the probability for absorption of left circularly polarized light, is proportional to $\langle \frac{1}{2}-S_z\rangle_i$. The total rate of excitation of the vapor is thus equal to $\sum_i A'K_i n_i = A'(n_{21}+2n_{20}+3n_{2-1}+4n_{2-2}+3n_{11}+2n_{10}+n_{1-1})$, where the subscripts of the n_i are the (F,m_F) quantum numbers of the sublevels and A' is proportional to incident light intensity and includes normalization parameters. If complete mixing is assumed, the repopulation rate of each ground-state sublevel is equal to $\frac{1}{8}\sum_i A'K_i n_i$. We can then immediately write down the set of eight linear differential equations, $dn_i/dt=\sum_j C_{ij}n_j$, $i=1,2,\cdots 8$, that govern the time dependence of the state populations, n_i. The matrix of coefficients for this set of equations has been published previously by Franzen and Emslie.[18]

With appropriate normalization, the equation describing the rate of change of the electronic spin polarization for optical pumping with complete excited-state mixing becomes

$$\begin{aligned} d\langle S_z\rangle/dt=&\tfrac{1}{4}A-\tfrac{1}{2}A\langle S_z\rangle \\ &-\tfrac{1}{2}A[\tfrac{1}{2}n_{21}+\tfrac{1}{2}n_{20}-n_{2-2}+\tfrac{1}{2}n_{10}+\tfrac{1}{2}n_{1-1}]. \end{aligned} \tag{10}$$

The case for no mixing differs only slightly from that above. The absorption probabilities for the various ground-state sublevels of course remain the same as for complete mixing, but now a kind of coherence between ground and excited states is preserved. For example, whereas an atom in the $|2,-2\rangle$ state that absorbed a photon could return to *any* of the eight ground-state sublevels in the case of complete mixing, for zero mixing, it can only return to $|2,-2\rangle$, $|2,-1\rangle$, $|2,0\rangle$, $|1,-1\rangle$, or $|1,0\rangle$. This happens because the excited atom decays before suffering any collisional perturbation. The matrix of coefficients for optical pumping with no excited-state mixing has also been published by Franzen and Emslie. The equation for $\langle S_z\rangle$, again with appropriate normalization, becomes:

$$\begin{aligned} d\langle S_z\rangle/dt=&\tfrac{1}{4}A-\tfrac{1}{2}A\langle S_z\rangle-\tfrac{1}{2}A[-\tfrac{1}{3}n_{21}-(7/24)n_{20} \\ &+\tfrac{1}{12}n_{2-2}-(7/24)n_{10}-\tfrac{1}{2}n_{1-1}]. \end{aligned} \tag{11}$$

Were it not for the terms in the brackets on the right-hand side of Eqs. (10) and (11), the rate of change of $\langle S_z\rangle$ for an alkali vapor with nuclear spin $\frac{3}{2}$ would be identical to that found for the simple nuclear-spin-zero model, Eq. (5). The effect of the extra terms in Eqs. (10) and (11) is not small. In general, the sum of these terms changes by an amount comparable to the net change in $\langle S_z\rangle$, even at low incident-light intensities and high relaxation rates. Still, the method of measuring the pumping rate by varying the light intensity [see discussion following Eq. (9)] provides at least approximate values that may be of use in some experiments. We have, in fact, used this technique to estimate relaxation times and pumping rates in the analysis of experimental results to be described in a later section.

B. Relaxation Processes

The relaxation of optically pumped alkali-metal vapors has been widely studied since the first measurements were made on sodium by Dehmelt in 1957,[1] and on rubidium by Franzen in 1959.[3] Since 1959, most relaxation measurements have been based on Franzen's technique, which permits the measurement of the relaxation of an optically pumped vapor in the absence of the pumping light. Franzen's technique is to polarize the alkali vapor, then to interrupt the light beam, and to allow the vapor to relax in the dark. After some dark time τ' the shutter is reopened, and the initial intensity of the transmitted light recorded. The process is then repeated for a range of values of dark time. Since the absorption of the vapor in any state of polarization is a linear function of the spin polarization $\langle S_z\rangle$, the plot of initial absorption versus dark time yields a curve representative of the relaxation of $\langle S_z\rangle$ for the vapor. Franzen's technique has generally been applied to the measurement of alkali relaxation in buffer gases, where, by measuring the relaxation time as a function of buffer-gas pressure, both the diffusion coefficient D_0 and the disorientation cross section σ of the alkali in the buffer gas can be measured.

The analysis of relaxation data has usually been made with the simplifying assumption that the relaxation is *uniform*, that is, that relaxation from any ground-state sublevel i can reach with equal probability all other sublevels j. Using a notation similar to that adopted by Franzen, let the probability per unit time for a relaxation-induced transition from state i to state j be w_{ij}. Then $w_{ij}=1/8T_1$, where T_1 is the relaxation time of the vapor. The rate equations for the state populations, n_i, are

$$dn_i/dt=-\sum_j{}' w_{ij}n_i+\sum_j{}' w_{ji}n_j\,, \quad i=1,\,2,\,\cdots 8\,,$$

where the first term on the right represents relaxation *out of* state i, while the second term represents relaxation *into* state i. The primes indicate that terms $(i=j)$ are to be excluded from the sums. Letting $(1/T_1)$ equal $2R$ for ease of comparison with the nuclear-spin-zero model, we find

$$dn_i/dt=-2Rn_i+2R/8\,, \quad i=1,\,2,\,\cdots 8\,.$$

Then

$$d\langle S_z\rangle/dt=-2R\langle S_z\rangle\,, \tag{13}$$

and the relaxation is exponential. Likewise,

$$dP/dt=-2RP\,, \tag{14}$$

where $P=\sum_i m_i n_i$.

Although uniform relaxation may have physical meaning in a few special cases, its use as the mode of alkali relaxation in buffer gases is extremely difficult to justify. A more plausible approach is to recognize that when an alkali atom collides with a buffer-gas molecule or cell wall, deformations and overlap occur that allow the alkali to briefly experience a rapidly varying electric field. As the alkali atom moves through the interaction region it is thus subjected to a Fourier spectrum of randomly oriented oscillating magnetic fields that range in frequency up to the order of the inverse of the correlation or collision time. If appropriate frequency components are present, reorientation of either the atomic or the electronic magnetic moment may take place, either process resulting in relaxation. We do not inquire how much relaxation occurs in such a collision, since our measured relaxation rate gives us that information. All we need from our simple model is the relative probability that an atom subjected to the perturbation will undergo transition from $|F,m_F\rangle$ to $|F',m_F'\rangle$. To obtain these probabilities we assume the simple model of an atom subjected to an oscillating field $H_1(\omega)$ of equal components H_x,H_y,H_z. We consider only values of ω near $\omega=\mu_F H_0/\hbar F$ and $\omega=\mu_s H_0/\hbar S$, for which energy conserving transitions are possible.

1. Zeeman relaxation. In this case we assume that only low-frequency components are present in the frequency spectrum of $H_1(\omega)$. This is expected to be the case, for example, when the duration of an alkali–something-else collision is long compared with the hyperfine period, such as when an atom collides with the wall of the cell.[6] Only H_x and H_y components will be effective in causing relaxation. F and m_F remain good quantum numbers; hence the matrix elements for transition from the state $|F,m_F\rangle$ to the state $|F',m_F'\rangle$ may be written

$$\begin{aligned}\langle F',m_F'|\boldsymbol{\mu}_F\cdot\mathbf{H}_1|F,m_F\rangle&=\boldsymbol{\mu}_F\langle F',m_F'|\mathbf{F}\cdot\mathbf{H}_1|F,m_F\rangle\\&=\mu_F H_1\langle F',m_F'|(\tfrac{1}{2}F_{+}+\tfrac{1}{2}F_{-})|F,m_F\rangle,\end{aligned}\tag{15}$$

where F_{+} and F_{-} are the total-angular-momentum raising and lowering operators, and for simplicity the field H_1 has been assumed to be acting in the x direction. The various transition probabilities are readily calculable. The time variations of $\langle S_z\rangle$ and P for an alkali vapor undergoing Zeeman relaxation are then found to be identical to Eqs. (13) and (14). The interesting aspect of this mode of relaxation is that relaxation occurs only between adjacent states; that is, for example, the state $|2,1\rangle$ is coupled only to the states $|2,2\rangle$ and $|2,0\rangle$. It thus appears that under the application of optical pumping the lower sublevels of $(F=1)$ will be depleted, since there is no connection between $(F=2)$ and $(F=1)$ sublevels through relaxation. This conjecture has been confirmed in experimental investigations to be described in a later section.

2. Electron randomization relaxation. Here we assume that $H_1(\omega)$ also has frequency components equal to those characterized by the spin flip of a free electron in the static magnetic field H_0. The interaction begins with the system in a well-defined state $|F,m_F\rangle$. We wish to find what states $|F',m_F'\rangle$ may be reached by the application of the perturbation. In other words, we wish to calculate matrix elements of the form

$$\begin{aligned}&\langle F',m_F'|S_xH_x|F,m_F\rangle\\&\qquad\approx\langle F',m_F'|(\tfrac{1}{2}S_{+}+\tfrac{1}{2}S_{-})|F,m_F\rangle,\end{aligned}\tag{16}$$

and

$$\langle F',m_F'|S_zH_z|F,m_F\rangle.$$

To accomplish this, we express $|F,m_F\rangle$ in terms of a linear combination of the states $|m_I,m_S\rangle$ that are good quantum states in the presence of the perturbation,

$$|F,m_F\rangle=\sum\langle m_I,m_S|F,m_F\rangle|m_I,m_S\rangle.$$

The coupling coefficients are readily calculated from formulas found in the literature. The matrix elements (16) may then be calculated. The rate of change of $\langle S_z\rangle$ for a vapor undergoing relaxation by electron randomization is

$$d\langle S_z\rangle/dt=-2R\langle S_z\rangle+\tfrac{4}{5}R(n_{11}-n_{1-1}).\tag{17}$$

Likewise,

$$dP/dt=-\tfrac{4}{5}RP+(8/5)R(n_{11}-n_{1-1}).\tag{18}$$

In this case neither $\langle S_z\rangle$ nor P is a simple exponential function of time. However, it is possible that under some circumstances the magnitude of the terms in the parentheses may be small, producing approximate exponential behavior of $\langle S_z\rangle$ and P. Even so, we note the fact that whereas for Zeeman and uniform relaxation the rate of change of both P and $\langle S_z\rangle$ was described by the same time constant, for electron randomization the time constants differ.

Relaxation by electron randomization produces other effects quite different from those resulting from Zeeman relaxation. For example, whereas the $(F=1)$ sublevels were found to be depleted in the case of Zeeman relaxation, for electron randomization they maintain relatively high populations, with large population differences between the states, largely because of the extremely strong relaxation coupling between states $|2,2\rangle$ and $|1,1\rangle$. One prediction from this simple model is that when Zeeman relaxation is dominant, one should not see any sizable resonances in the $(F=1)$ hyperfine level, whereas for electron randomization very strong resonances in this level are predicted. This difference in the distribution of state populations offers a tool that can be used to determine which mode of relaxation actually occurs in a given optical-pumping experiment.

C. The Rate Equations for Optical Pumping

The sets of transition probabilities for various modes of pumping and relaxation provide all the information that is needed for a calculation of the equilibrium state populations in optical pumping. All that remains for us to do is to combine relaxation and pumping effects, set dn_i/dt equal to zero for all i, and solve the resulting sets of eight linear equations for the eight sublevel

TABLE I. Equilibrium occupation probabilities for an optically pumped alkali atom of nuclear spin $\frac{3}{2}$, assuming a variety of pumping and relaxation modes.

	$n_{2,2}$	$n_{2,1}$	$n_{2,0}$	$n_{2,-1}$	$n_{2,-2}$	$n_{1,1}$	$n_{1,0}$	$n_{1,-1}$
Electron randomization, no mixing	0.156	0.139	0.124	0.110	0.097	0.145	0.124	0.105
Zeeman, no mixing	0.135	0.131	0.126	0.122	0.118	0.124	0.123	0.122
Uniform, no mixing	0.134	0.129	0.125	0.121	0.117	0.126	0.125	0.124
Electron randomization, complete mixing	0.141	0.132	0.124	0.117	0.110	0.132	0.125	0.118
Zeeman, complete mixing	0.133	0.130	0.126	0.122	0.119	0.119	0.123	0.127
Uniform, complete mixing	0.133	0.129	0.125	0.121	0.118	0.121	0.125	0.128

populations n_i. We have performed the calculations for the following six cases:

(1) Uniform relaxation: optical pumping with complete mixing;

(2) Uniform relaxation: optical pumping with no mixing;

(3) Zeeman relaxation: optical pumping with complete mixing;

(4) Zeeman relaxation: optical pumping with no mixing;

(5) Electron randomization relaxation: optical pumping with complete mixing;

(6) Electron randomization relaxation: optical pumping with no mixing.

All of our calculations have been performed under the assumption that the time between alkali-alkali spin-exchange collisions, T_2, is long compared to the characteristic relaxation time T_1 of the vapor. This means that the distribution of population among the $|F,m_F\rangle$ states is dominated by the particular mode of relaxation assumed, with only second-order effects being contributed by spin exchange between similar atoms. The condition that T_1 be less than T_2 is not at all difficult to realize experimentally. Optical-pumping resonances can be seen, for example, for alkali densities at least as small as 5×10^9 atoms/cm^3. If we take the spin-exchange cross section to be about 2×10^{-14} cm^2,[20] then at the lowest vapor pressures the time between spin-exchange collisions is several hundred milliseconds. There will be, therefore, a considerable range of experimental situations in which our results may prove useful. The equilibrium sublevel populations obtained for the various modes of pumping and relaxation discussed above, assuming a pumping rate A of 40 sec^{-1} and a relaxation rate R of 640 sec^{-1}, are listed in Table I.[21]

The results reported in this paper are not, of course, the first calculations of the equilibrium distribution of population in an optically pumped alkali-metal vapor. Dehmelt, for example, in the original experiment on alkali relaxation, made a calculation of the state populations for a vapor illuminated by a combination of circularly polarized D_1 and D_2 light. Bloom[22] has previously derived equations for optical-pumping signals under various conditions. Franzen and Emslie[18] have made calculations for uniform relaxation that are similar to those presented in this report; however, their results are applicable only in the limit of very long relaxation times and very fast pumping times. Finally, Anderson[23] has considered the interesting case where spin exchange rather than relaxation determines the equilibrium population distribution, finding that the n_i are proportional to $\exp(-m_i\beta)$, where β is a parameter determined by the polarization of the sample. In this case a "spin-temperature equilibrium" is established in the vapor that makes the relaxation of $\langle S_z\rangle$ and P particularly simple, regardless of the relaxation mechanism assumed.

IV. EXPERIMENTAL RESULTS

The experimental results described in this section were observed in a wide variety of optical-pumping cells containing either Rb^{87} ($I=\frac{3}{2}$) or Cs^{133} ($I=\frac{7}{2}$). The Breit-Rabi formula predicts that in a magnetic field of 1 G the Zeeman energy levels of the ground state of an alkali atom are split in such a way that radio frequency resonances in the upper hyperfine level are at a lower frequency than those in the lower hyperfine level. For Rb^{87} these resonances occur at approximately 698.8 and 701.6 kc/sec, while for Cs^{133} they occur at 349.3 and 350.6 kc/sec. Although the resonances in the upper and lower hyperfine levels are split, within each level the resonances overlap. Under these conditions it is difficult to make an accurate definition of the signal obtained when the static magnetic field is swept through resonance. An approximate idea of the expected sizes of the signals can be obtained by assuming that as the field is swept through a particular resonance the populations in that hyperfine level are equalized, without affecting the other level. The relative sizes of the resonance signals can then be related to the initial spin

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[21] More complete tables that consider a wide range of pumping and relaxation rates have been published in Coordinated Science Laboratory Report R-265, available upon request from the Coordinated Science Laboratory, University of Illinois, Urbana, Illinois 61803.

[22] A. L. Bloom, Phys. Rev. **118**, 664 (1960).

[23] L. W. Anderson, Nuovo Cimento **31**, 986 (1964).

TABLE II. Characteristics of unresolved Zeeman resonance signals within the $F=1$ hyperfine level for various combinations of pumping and relaxation.

Relaxation-pumping mode	($F=1$) signal
Zeeman—no mixing	Small, inverted
Zeeman—complete mixing	Small, normal
Electron randomization—no mixing	Large, inverted
Electron randomization—complete mixing	Moderately large, inverted

polarizations existing within each hyperfine level, and hence to the population differences existing between states.

The calculated populations of the sublevels of the $F=1$ hyperfine level are quite sensitive to the pumping and relaxation mechanisms assumed, as a glance at Table I will indicate. For the experiments reported in this paper, the light-absorption probabilities for the eight ground-state sublevels are 0:1:2:3·4:3:2:1. One's first impression might be that under optical pumping the less absorbing levels would become more highly populated at the expense of the more strongly absorbing levels, as is the case, for example, for uniform relaxation with complete mixing. In fact, however, for several combinations of pumping and relaxation modes the reverse is true, that is, in the $F=1$ level the more strongly absorbing $m=1$ level is more highly populated than the less absorbing $m=0$ and $m=-1$ levels. For convenience in the following discussion, we will refer to this latter case as an "inverted" population in the lower hyperfine level.

The various combinations of electron randomization relaxation and Zeeman relaxation, with zero mixing and complete mixing, together with the characteristic signals they produce in the $F=1$ hyperfine level, are summarized in Table II. We have not included uniform relaxation in this table since in all cases the signals obtained are virtually identical to those for Zeeman relaxation.

We have calculated similar results for the $F=3$ level of cesium, with the exception that the Zeeman-no-mixing signal is small and normal. For cesium, then, the analysis of the experimental signals is particularly simple: an inversion in the $F=3$ level always implies relaxation through electron randomization.

The presence of population differences within the hyperfine levels can be detected by sweeping the static magnetic field slowly through the resonances. If resonances in the lower level are detected, there are several ways of telling whether or not the population distribution is inverted. (i) The radio frequency field can be set at resonance for the $F=1$ level and pulsed on. For a strong enough H_1, the magnetization in the $F=1$ level rotates coherently about the effective field in the rotating reference frame,[24] causing a modulation of the light beam. If the initial oscillations are above the equilibrium light-intensity level, the population is inverted [Fig. 1(a)]. (ii) The frequency of the rf field can be swept rapidly through the resonance. If the population is inverted, a "spike" will be seen [Fig. 1(c)]. (iii) The static magnetic field can be modulated, sweeping through the resonances in times fast compared to the spin-exchange time. If the $F=1$ level is normal, a decrease in light intensity will be seen at the position of the $F=1$ resonance. If it is inverted, an increase, or "bump," will be observed.

All of the cells used in this experiment were prepared using the ultrahigh-vacuum technique described elsewhere.[12] The optical-pumping apparatus used was of the standard variety,[8] with all experiments being performed at room temperature in a static magnetic field of 1 G. At 299°K the vapor pressure of rubidium is 1.5×10^{-7} Torr. Assuming a Rb-Rb spin-exchange cross section of 2×10^{-14} cm^2[25] and a relative velocity of 3.1×10^4 cm/sec, the mean time between spin-exchange collisions, T_2, was approximately 330 msec. All cells were designed so that the thermal relaxation time T_1 of the alkali vapor was short, usually 10 msec or less. The condition that T_1 be much less than T_2 was thus satisfied, therefore spin exchange played no role in determining the distribution of polarization in the vapor.

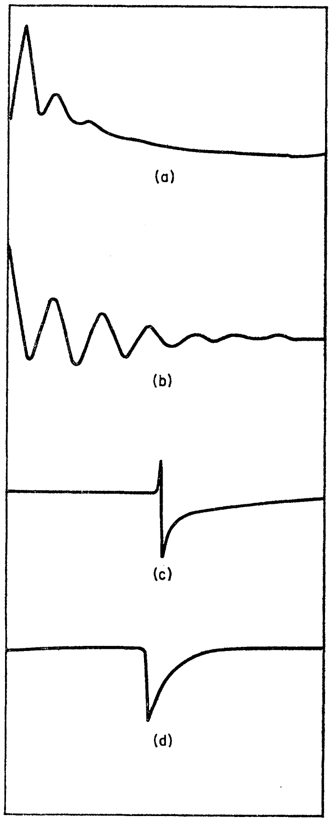

FIG. 1. Typical optical-pumping transient signals for an alkali-metal vapor (Cs). Relaxation and pumping rates were about 80 and 20 sec^{-1} in all cases, but relaxation mechanisms differed due to different buffer-gas-pressures. (a) The signal obtained when the resonant frequency for the lower level is pulsed on. The initial oscillations above the equilibrium level indicate an inverted population. This signal is typical when relaxation by electron randomization is dominant. (b) A similar signal obtained when the population distribution in the lower hyperfine level is "normal," as is the case for uniform or Zeeman relaxation. (c) The signal obtained when the frequency of the radio-frequency field is quickly swept through resonance. Frequency decreases left to right. The upward spike indicates that the population is inverted in the lower level, electron randomization relaxation being dominant in this case. (d) A similar signal for no inversion in the lower level. Zeeman relaxation was dominant.

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[24] C. P. Slichter, *Principles of Magnetic Resonance* (Harper and Row, Publishers, Inc., New York, 1963).

[25] H. W. Moos and R. H. Sands Phys. Rev. **135**, A591 (1964).

We also performed many measurements using a variety of cells containing cesium. At 299°K the vapor pressure of cesium is 1.5×10^{-6} Torr, indicating that the time between spin-exchange collision was about 35 msec. The condition that $T_1 \ll T_2$ was not satisfied as well for these cells as for the rubidium cells. We were able to artificially reduce the cesium vapor pressure by a factor of two or three by introducing a small amount of rubidium or potassium into the cell, an effect also observed by Rozwadowski and Lipworth.[26] The time between spin-exchange collisions was thus lengthened to 70 or 100 msec, better satisfying the $T_1 \ll T_2$ condition. No significant change in the shape of optical-pumping signals was found for the cells that contained a mixture of alkalies.

It is easy to construct optical-pumping cells in which either Zeeman or electron randomization relaxation should be dominant. To demonstrate Zeeman relaxation, we constructed series of rubidium and cesium cells, both coated and uncoated, with pressures of buffer gas ranging from vacuum to a few Torr. Zeeman relaxation with no mixing was expected for all of these cells, and was in fact, detected. For the rubidium cells a very small inverted resonance in the $F=1$ level was observed, whereas for cesium a very small normal resonance in the $F=3$ level was found. Both results agree with the predictions of our calculations. For very fast relaxation times the resonance in the $F=1$ or $F=3$ levels virtually disappeared. If the bulbs were heated, thus increasing the alkali vapor pressure and making the spin-temperature description the appropriate regime, strong resonances appeared in the $F=1$ and $F=3$ levels, as expected. The results are unambiguous, indicating that Zeeman relaxation is the dominant wall relaxation mechanism for both coated and uncoated cells.

Electron-randomization relaxation was observed in cesium and rubidium cells that had been coated and filled to high pressures with neon, nitrogen, argon, or krypton. Inversion of the lower hyperfine level was detected in all cases. The buffer-gas pressure was high enough (greater than 300 Torr) in some bulbs to insure complete excited state mixing; hence for rubidium the inverted signal could only be due to electron-randomization relaxation. For cesium, the inversion of the $F=3$ level clearly indicated dominance of electron randomization, regardless of the degree of excited-state mixing.

The conjectures that alkali wall relaxation takes place through Zeeman relaxation, and that alkali–rare-gas relaxation occurs through electron randomization have thus been verified experimentally. The relaxation probabilities calculated from the highly simplified collisional models assumed in this paper yield equations that provide a fairly accurate description of the behavior of an optically pumped alkali metal vapor. All of the qualitative features of the optical-pumping transient signals predicted by our calculations have been observed experimentally. It may therefore be possible, by creating situations in which the relaxation rate, relaxation mechanism, and pumping rate are known, to study the interesting problem of excited-state mixing, through use of optical-pumping transients similar to those discussed in this paper.

Note added in proof. An important new contribution to the literature, the thesis of Madame M. A. Bouchiat, containing a complete and elegant treatment of many aspects of alkali spin relaxation with particular emphasis on wall relaxation, has recently been published.[27]

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[26] M. Rozwadowski and E. Lipworth, J. Chem. Phys. 43, 2347 (1965).

[27] M. A. Bouchiat, Publications scientifiques et techniques du Ministère de l'Air, Nr. N.T. 146, Paris (1965).