With the same assumptions as before about LS coupling and the matrix elements taken and using the notation and expressions given by Trees,[12] we obtain for the ^5D state of Fe

$$E_l = r_J a_l \mathbf{I}\cdot\mathbf{J} \tag{14}$$

$$a_l = g_e g_I \mu_e \mu_I \langle 3d\beta | 1/r^3 | 3d\beta \rangle , \tag{15}$$

where r_J depends only on J, L, and S. Using the value of $\langle 3d\beta | 1/r^3 | 3d\beta \rangle$ given in Table II, we obtain $a_l = 78.4$ Mc/sec. The value obtained from experimental data by Childs and Goodman[3] is $a_l = 74.8$ Mc/sec; the error of the UHF value is 5%.

Because the UHF wave function is not an eigenfunction of S^2, equivalent expressions for E_l will give different results when evaluated with an UHF function.[17] The results will involve different combinations of $\langle 3d\alpha | 1/r^3 | 3d\alpha \rangle$ and $\langle 3d\beta | 1/r^3 | 3d\beta \rangle$ in the expression for E_l. However, since these integrals have nearly the same value (see Table II), the numerical results for E_l will be nearly the same, and we will not pursue the matter further.

III. CONCLUSION

Good agreement between the magnetic dipole hyperfine-interaction constants obtained from an UHF calculation and from experimental data[4] has been found. In particular, the agreement for the Fermi contact interaction constant (14%) supports the model of exchange core-polarization used in the UHF method.

ACKNOWLEDGMENTS

The authors would like to thank Dr. Leonard Goodman and Dr. Brian Wybourne for informative and helpful discussions. In particular, they would like to thank Dr. Goodman for having suggested this calculation.

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Excited-State Mixing in the Optical Pumping of Alkali-Metal Vapors

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The effect of excited-state mixing on the optical pumping of alkali-metal vapors is considered for the case where the energy separation between the $^2P_{1/2}$ and $^2P_{3/2}$ first excited states is relatively large, allowing the isolation of mixing effects within a particular J level. Two models for the mixing process are proposed, one a random reorientation of the total electronic angular momentum $\mathbf{J}$, and the other a reorientation of $\mathbf{J}$ subject to the selection rule $\Delta m_J = 0, \pm 2$. The probabilities for mixing transitions among J-state sublevels have been calculated for an alkali atom of nuclear spin $\frac{3}{2}$, and can be used to calculate the optical-pumping transition probabilities for a vapor subject to any degree of excited-state mixing. Several possible experiments suggested by these calculations are discussed.

I. INTRODUCTION

THE primary purpose of this paper is to analyze the role that excited-state interactions play in the optical pumping of alkali-metal vapors. In an experiment typical of those to be considered,[1] a beam of circularly polarized $D_1(^2S_{1/2} \leftrightarrow {}^2P_{1/2})$ photons is passed through a cell containing the vapor to be studied. Since the prevailing selection rules are $\Delta m_F = +1$ for absorption, and $\Delta m_F = \pm 1$, 0 for re-emission, the vapor is gradually pumped from ground-state sublevels of low to high (F, m_F), with all atoms ultimately being forced into the highest sublevel if there is no ground-state relaxation. In practice, of course, relaxation exists, being caused by collisions of the alkali atoms with buffer gas molecules, impurity atoms, or the walls of the cell. Collisional interactions can also disrupt the optical pumping process by transferring or mixing atoms among excited-state sublevels prior to de-excitation. The equilibrium population distribution in the ground state is thus determined both by the strengths and characteristics of the relaxation mechanisms involved, and by the various perturbations that the alkali atoms may suffer while in the excited state.

In order to calculate the equilibrium electronic and nuclear spin polarizations, and to describe the transient

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[1] Comprehensive surveys of optical pumping techniques can be found in: G. V. Skrotskii and T. G. Izyumova, Usp. Fiz. Nauk 73, 423 (1961) [English transl., Soviet Phys.—Uspekhi 4, 177 (1961)]; and R. Benumof, Am. J. Phys. 33, 151 (1965).

behavior of the system as it approaches equilibrium, the relative probabilities with which an atom in a given ground-state sublevel can be pumped to other sublevels must be calculated. The simplest situation obtains when the alkali atoms are not subject to any interactions while in the excited state, and hence decay from the particular sublevel to which they were excited. The optical pumping probabilities can be readily calculated in this case, and have been published in matrix form by several authors.[2,3] The opposite extreme in which an atom suffers many collisional perturbations before decaying to the ground state is also amenable to solution if it is assumed that the effect of many collisions is to mix completely the sublevels of the excited state. In this case, even though an atom may have been pumped to a particular excited-state sublevel, it will with equal probability decay from any sublevel. Dehmelt[4] first introduced this concept of complete excited-state mixing in order to derive rate equations to describe the optical pumping of sodium in the presence of a relatively great amount of argon gas. It has since been used by many workers to describe generally the optical pumping of other substances in the presence of more than a few Torr of buffer gas.

During the past few years there has developed an increasing tendency to misinterpret Dehmelt's approximation as implying that in *each* collision of an alkali atom with a rare gas atom there is some probability that the alkali will suffer complete mixing, that is, that after *one* mixing collision the alkali atom will be found with equal probability in any $|F,m_F\rangle$ sublevel. Let us assume that in a given experiment there is a 10% probability that an atom will suffer a mixing collision in the excited state before decaying to the ground state. Then although one can make the approximation that about 90% of the atoms decay before suffering any collisional perturbations, it is *not* correct to say that about 10% decay subject to complete mixing. Dehmelt's approximation can be valid only in the pressure range where the probability is great that every atom suffers many collisions during the excited-state lifetime, and cannot be extrapolated to the region of partial mixing. Moreover, as Dehmelt has pointed out,[5] it also cannot be used in the limit of infinitely many collisions during the excited-state lifetime, but serves best in an intermediate region where the collision frequency is of the order of the hyperfine frequency.

On purely kinematical grounds, one would expect the cross sections for excited-state mixing to be quite sensitive to the energy splittings between the states involved. In sodium the splitting between the $^2P_{1/2}$ and $^2P_{3/2}$ levels is small enough that sufficient kinetic energy is available in virtually all sodium–rare-gas collisions to effect transitions between these states. Mixing therefore occurs throughout all 24 J-state sublevels, with the probability for the process effectively given by the cross section for sensitized fluorescence in the appropriate buffer gas.[6–13] In cesium and rubidium the splittings between J-levels are considerably larger than in sodium, and the alkali–rare-gas relative velocities are smaller. The probabilities for $^2P_{1/2}\leftrightarrow{}^2P_{3/2}$ collisionally induced transitions should thus be much smaller in Rb and Cs than in Na. This expectation is verified in the measurements of cesium–rare-gas sensitized fluorescence cross sections that yield values 10^6 times smaller than the corresponding sodium values.[10] On the other hand, for all alkalies the Zeeman and hyperfine splittings within a given J-level remain negligibly small compared to the energies available in alkali–buffer-gas collisions. It appears, therefore, that although the probability for mixing *between* J states in Rb and Cs may be quite small compared to that in Na, the probability for mixing *within* a J level still should be comparable. Since such mixing is our primary concern in the present paper, we shall confine our discussion to systems in which inter-J-level transitions can be neglected. In the following paragraphs, we attempt to construct a model consistent both with these ideas, and with Dehmelt's original suggestions that may be useful to describe the optical pumping process in the experimentally interesting region of partial excited-state mixing.

II. MIXING MODELS

In the discussion that follows, we shall assume the model of a dilute alkali-metal vapor in which interactions between alkali atoms can be neglected. We thus consider alkali densities of less than 10^{11} atoms/cc, conditions under which optical pumping experiments are often performed. We shall often refer to the angular momentum vectors $\mathbf{L}$ (electronic orbital angular momentum), $\mathbf{S}$ (electronic spin), $\mathbf{I}$ (nuclear spin), $\mathbf{J}$ (total electronic angular momentum$=\mathbf{L}+\mathbf{S}$), and $\mathbf{F}$(total angular momentum$=\mathbf{L}+\mathbf{S}+\mathbf{I}$). In all numerical calculations we shall assume a nuclear spin of $\frac{3}{2}$.

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

[3] W. B. Hawkins, Phys. Rev. **123**, 544 (1961).

[4] H. G. Dehmelt, Phys. Rev. **105**, 1487 (1957).

[5] H. G. Dehmelt (private communication). Dehmelt points out that if the collision frequency is high compared to the hyperfine frequency, $\mathbf{J}$ will suffer successive reorientations in times so short that the nucleus will feel nothing but short-duration random torques whose net effect tends to zero. In the present paper we shall assume that there is sufficient time between mixing collisions for the hyperfine interaction to reorient the nuclear spin; thus our results will not be applicable in the limit of infinitely high-buffer gas pressures.

[6] In this case, sensitized fluorescence refers to transitions between alkali $P_{1/2}$ and $P_{3/2}$ first excited states, induced by nonresonant collisions with buffer gas atoms. The classic experiment on sodium was performed by Wood and Mohler, Phys. Rev. **11**, 70 (1918). More recent work can be found in Refs. 7 through 13.

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

[8] R. Seiwert, Ann. Physik **18**, 54 (1956).

[9] G. D. Chapman and L. Krause, Can. J. Phys. **43**, 563 (1965).

[10] M. Czajkowski, D. A. McGillis, and L. Krause, Can. J. Phys. **44**, 91 (1966).

[11] B. Pitre, A. G. A. Rae, and L. Krause, Can. J. Phys. **44**, 731 (1966).

[12] T. J. Beahn, W. J. Condell, and H. I. Mandelberg, Phys. Rev. **141**, 83 (1966).

[13] J. A. Jordan and P. A. Franken, Phys. Rev. **142**, 83 (1966).

The quantum number m has the usual meaning of the projection of an angular momentum vector upon a fixed axis. We further assume that the alkali vapor is situated in a magnetic field weak enough that F and m_F remain good quantum numbers, but strong enough that the $|F,m_F\rangle$ sublevels of the ground and first excited states are of distinct energies. For alkalies such a condition generally implies a magnetic field of several gauss, again a common experimental situation.

The simplest model that one can assume which remains consistent with Dehmelt's limiting approximation of complete $|F,m_F\rangle$ mixing is that during an alkali–rare-gas collision *some* angular momentum vector of the alkali is completely randomized. We can immediately rule out the direct randomization of m_S or m_I since reorientation of **S** or **I** requires the presence of a magnetic interaction between the buffer gas and alkali atoms. From measurements of ground-state relaxation for rubidium and cesium in the rare gases, we know that for argon, neon, and helium, between 10^6 and 10^9 collisions are required to produce electronic spin depolarization. The magnetic interaction responsible for this mode of disorientation should be of comparable magnitude in the excited state, hence for any mixing to be caused by this means would require buffer gas pressures of the order of 10^4 atm. The only quantity that can be directly affected in a collision, therefore, is the electronic orbital angular momentum **L**.

The question now arises whether a perturbation of **L** can be reflected in a randomization of **J** or **F**. The answer lies in a comparison of some of the characteristic times involved, all of which are assumed to be short compared with the lifetime of the excited state. These characteristic times are the hyperfine period, the fine structure period, and the duration of the collision; about 10^{-10}, 10^{-13}, and 10^{-12} sec, respectively, for rubidium and cesium. We immediately see that a collision lasts only a fraction of a hyperfine period, indicating that no matter what reorientation occurs, the nuclear spin **I** "stands still" during the collision; the hyperfine structure cannot follow such a rapid perturbation. The fine structure period, on the other hand, is shorter than the duration of the collision, hence any change in the orbital motion can be immediately reflected in a reorientation of **J**. In this case, it appears that the random reorientation of **J** might be a valid approximation. If, however, the collision time were shorter than both the hyperfine and fine structure periods, then the maximum randomization that could occur would be that of **L**. This latter case could be true for potassium, for example, whereas the random reorientation of **J** should hold for rubidium and cesium.[14]

Let us assume that the collision frequency is sufficiently high that there is an appreciable probability that a collision occurs before an atom decays, but not as high as the hyperfine frequency. This assumption restricts the time between collisions to the range 10^{-7} to 10^{-10} sec, which corresponds in fact to the range of buffer gas pressures in which optical pumping experiments are often performed. The purpose of this restriction is to allow us to assume that between collisions the $|F,m_F\rangle$ states remain a valid representation for the alkali atom. We have shown above that the reorientation of **J** is the *most* that can happen in a collision of a rubidium or cesium atom with a rare-gas atom. We also recall that we are assuming that transitions *between* J levels are energetically disallowed. The effect of mixing, assuming random reorientation of **J**, can then be described as follows. Before a collision the atom is in a well-defined $|F,m_F\rangle$ excited-state sublevel. During the collision, the coupling between **J** and **I** is broken, making the $|I,J,m_I,m_J\rangle$ representation appropriate. With the aid of the usual vector coupling coefficients,[15] we obtain Eq. (1).

$$|F,m_F\rangle=\sum_{m_I,m_J}\langle I,J,m_I,m_J|F,m_F\rangle|I,J,m_I,m_J\rangle. \quad (1)$$

We now let a mixing operator A act on the atom during the collision. We define A by

$$A|I,J,m_I,m_J\rangle=\sum_{m_J'}\frac{A(m_I,m_J')}{(2J+1)^{1/2}}|I,J,m_I,m_J'\rangle, \quad (2)$$

where $A(m_I,m_J')$ is a phase factor. Not knowing the exact form of the mixing operator A, we cannot predict the phase factors $A(m_I,m_J')$. We make the assumption that at the time another collision occurs all phases are equally probable. The effect of the operator A is to randomly reorient **J**, that is, to make transitions from a particular $|I,J,m_I,m_J\rangle$ state to other states of the same (I,J,m_I) equally probable. The interaction A applied to $|F,m_F\rangle$ yields,

$$A|F,m_F\rangle=\sum_{m_I,m_J}\langle I,J,m_I,m_J|F,m_F\rangle \times\sum_{m_J'}\frac{A(m_I,m_J')}{(2J+1)^{1/2}}|I,J,m_I,m_J'\rangle. \quad (3)$$

After a collision the $|F,m_F\rangle$ states are again a valid representation for the system. In order to find with what probabilities an atom originally in the excited-state sublevel $|F,m_F\rangle$ has reached other sublevels $|F',m_F'\rangle$, we multiply Eq. (3) by $|F',m_F'\rangle^*$, square, and average over phases. We thus obtain a probability matrix, each element of which is equal to the phase averaged square of the interaction matrix element of A. This matrix is given in Table I for the $^2P_{1/2}$ level, and in Table II for the $^2P_{3/2}$ level. It is important to note that the results obtained here pertain to a random, un-

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[14] An analogous model involving randomization of **J** was suggested by Bender in order to describe excited-state mixing in sodium. P. Bender, thesis, Princeton University, 1956 (unpublished).

[15] E. U. Condon and G. H. Shortley, *Theory of Atomic Spectra* (Cambridge University Press, Cambridge, England, 1963).

TABLE I. Probability matrix for mixing of $|F,m_F\rangle$ sublevels in the $^2P_{1/2}$ excited state, assuming random reorientation of **J**. The initial $|F,m_F\rangle$ sublevel is given along the top, and the final sublevel along the side.

(F,m_F) $\diagdown$ (F,m_F)	2,2	2,1	2,0	2, −1	2, −2	1,1	1,0	1, −1
2,2	0.5000	0.1250	0	0	0	0.3750	0	0
2,1	0.1250	0.3125	0.1875	0	0	0.1875	0.1875	0
2,0	0	0.1875	0.2500	0.1875	0	0.0625	0.2500	0.0625
2, −1	0	0	0.1875	0.3125	0.1250	0	0.1875	0.1875
2, −2	0	0	0	0.1250	0.5000	0	0	0.3750
1,1	0.3750	0.1875	0.0625	0	0	0.3125	0.0625	0
1,0	0	0.1875	0.2500	0.1875	0	0.0625	0.2500	0.0625
1, −1	0	0	0.0625	0.1875	0.3750	0	0.0625	0.3125

correlated process. A different approach is required if averages must be made over nonrandom phases.

Subject to the approximations that we have made, the matrix P_{kn} that gives the probabilities for optical pumping transitions from ground-state sublevel n to ground-state sublevel k is of the form

$$P_{kn}\propto\sum_{l,m}|H''_{kl}|^2|H'_{lm}|^2|H_{mn}|^2, \qquad (4)$$

where H_{mn} is the dipole matrix element for absorption of σ^+ light between ground-state sublevel n and excited-state sublevel m; H_{lm}' is the mixing matrix element between excited-state sublevels m and l; and H_{kl}'' is the matrix element for spontaneous emission from excited-state sublevel l to ground-state sublevel k. For the sake of brevity we shall refer to the matrices $|H_{mn}|^2$ as U("up"), $|H_{lm}'|^2$ as M ("mixing"), and $|H_{kl}''|^2$ as D ("down"). The U and D matrices are readily calculable.[15] For the case of *no* mixing in the excited state, the probability matrix P is of the form

$$P_0=DU, \qquad (5)$$

which is identical to the matrix published by Franzen and Emslie.[2] For one and only one mixing collision per atom, the matrix P is of the form

$$P_1=DMU, \qquad (6)$$

and for the case of N mixing collisions per atom,

$$P_N=DM^NU. \qquad (7)$$

We are now in a position to calculate the optical pumping transition probabilities for the case of partial excited-state mixing. The mean time between mixing collisions τ_c can be written as

$$\tau_c=(n\sigma_M v_{\text{rel}})^{-1}, \qquad (8)$$

where n is the number of buffer gas molecules per cc, σ_M is the cross section for mixing, and v_{rel} is the average relative velocity of an alkali-atom–buffer-gas-atom pair. Assuming the lifetime of the excited state to be τ, the probability that an alkali atom suffers *at least* N collisions before decaying to the ground state is

$$[\tau/(\tau+\tau_c)]^N. \qquad (9)$$

The probability that an atom suffers N and only N collisions before decaying is thus

$$[\tau/(\tau+\tau_c)]^N-[\tau/(\tau+\tau_c)]^{N+1}. \qquad (10)$$

For example, if the probability that an atom suffers at

TABLE II. Probability matrix for mixing of $|F,m_F\rangle$ sublevels in the $^2P_{3/2}$ excited state, assuming random reorientation of **J**. The initial $|F,m_F\rangle$ sublevel is given along the top, and the final sublevel along the side.

(F,m_F) $\diagdown$ (F,m_F)	3,3	3,2	3,1	3,0	3, −1	3, −2	3, −3	2,2	2,1	2,0	2, −1	2, −2	1,1	1,0	1, −1	0,0
3,3	0.2500	0.1250	0.0500	0.0125	0	0	0	0.1250	0.1250	0.0625	0	0	0.0750	0.1125	0	0.0625
3,2	0.1250	0.1250	0.1000	0.0625	0.0250	0	0	0.1250	0.0625	0.0625	0.0625	0	0.0875	0.0625	0.0375	0.0625
3,1	0.0500	0.1000	0.1100	0.0925	0.0600	0.0250	0	0.1000	0.0500	0.0625	0.0750	0.0250	0.0900	0.0325	0.0650	0.0625
3,0	0.0125	0.0625	0.0925	0.1025	0.0925	0.0625	0.0125	0.0625	0.0625	0.0625	0.0625	0.0625	0.0825	0.0225	0.0825	0.0625
3, −1	0	0.0250	0.0600	0.0925	0.1100	0.1000	0.0500	0.0250	0.0750	0.0625	0.0500	0.1000	0.0650	0.0325	0.0900	0.0625
3, −2	0	0	0.0250	0.0625	0.1000	0.1250	0.1250	0	0.0625	0.0625	0.0625	0.1250	0.0375	0.0625	0.0875	0.0625
3, −3	0	0	0	0.0125	0.0500	0.1250	0.2500	0	0	0.0625	0.1250	0.1250	0	0.1125	0.0750	0.0625
2,2	0.1250	0.1250	0.1000	0.0625	0.0250	0	0	0.1250	0.0625	0.0625	0.0625	0	0.0875	0.0625	0.0375	0.0625
2,1	0.1250	0.0625	0.0500	0.0625	0.0750	0.0625	0	0.0625	0.1250	0.0625	0	0.0625	0.0750	0.0625	0.0500	0.0625
2,0	0.0625	0.0625	0.0625	0.0625	0.0625	0.0625	0.0625	0.0625	0.0625	0.0625	0.0625	0.0625	0.0625	0.0625	0.0625	0.0625
2, −1	0	0.0625	0.0750	0.0625	0.0500	0.0625	0.1250	0.0625	0	0.0625	0.1250	0.0625	0.0500	0.0625	0.0750	0.0625
2, −2	0	0	0.0250	0.0625	0.1000	0.1250	0.1250	0	0.0625	0.0625	0.0625	0.1250	0.0375	0.0625	0.0875	0.0625
1,1	0.0750	0.0875	0.0900	0.0825	0.0650	0.0375	0	0.0875	0.0750	0.0625	0.0500	0.0375	0.0850	0.0425	0.0600	0.0625
1,0	0.1125	0.0625	0.0325	0.0225	0.0325	0.0625	0.1125	0.0625	0.0625	0.0625	0.0625	0.0625	0.0425	0.1025	0.0425	0.0625
1, −1	0	0.0375	0.0650	0.0825	0.0900	0.0875	0.0750	0.0375	0.0500	0.0625	0.0750	0.0875	0.0600	0.0425	0.0850	0.0625
0,0	0.0625	0.0625	0.0625	0.0625	0.0625	0.0625	0.0625	0.0625	0.0625	0.0625	0.0625	0.0625	0.0625	0.0625	0.0625	0.0625

least one collision is $\frac{1}{2}$ (i.e., $\tau=\tau_c$), the probabilities that it suffers 0, 1, 2, $\cdots$ collisions before decaying are $\frac{1}{2}$, $\frac{1}{4}$, $\frac{1}{8}$, $\cdots$, respectively. The optical pumping transition probabilities for this degree of mixing can then be calculated assuming that $\frac{1}{2}$ of the atoms decay subject to no mixing, $\frac{1}{4}$ subject to a single mixing collision, etc. The optical pumping probability matrix for the particular case where $\tau=\tau_c$ would be

$$P=\tfrac{1}{2}DU+\tfrac{1}{4}DMU+\tfrac{1}{8}DM^2U+\cdots. \tag{11}$$

In general

$$P=\sum_{N=0}^{\infty}\frac{\tau^N\tau_c}{(\tau+\tau_c)^{N+1}}DM^NU, \tag{12}$$

For $\tau_c \ll \tau$, P approaches the complete mixing limit. Effects of ground-state relaxation can be included in a straightforward manner.

Before proceeding to a discussion of several possible experiments, we consider yet another model of the mixing process that under some circumstances may provide a closer approximation to physical reality. Recently several authors[16–20] have made theoretical calculations of various cross sections for inelastic collisions between alkali and rare gas atoms. The calculation of the cross sections for sensitized fluorescence was the immediate goal of these papers, but the results also include information on allowed transitions within J levels. The general approach has been to assume a modified van der Waals' interaction potential, and then to calculate scattering cross sections to various orders of perturbation theory. A selection rule for the change in the alkali angular momentum, $\Delta m_J=0, \pm 2$, results. The relative strengths of the $\Delta m_J=0$ and $|\Delta m_J|=2$ transition probabilities depend in detail on the properties of the colliding atoms, but are generally of the same order of magnitude. We arbitrarily have assumed them to be equal, and have calculated probability matrices analogous to those given in Tables I and II, but subject to the $\Delta m_J=0, \pm 2$ selection rule. Once again we have assumed that inter-J-level transitions are energetically disallowed. The results are given in Tables III and IV.

Several intriguing predictions result from this model:

(*i*) *Excited-state mixing within the* $P_{1/2}$ *level has very little influence on the pumping process, regardless of the magnitude of the mixing cross section and the magnitude of the buffer gas pressure.* Within the $P_{1/2}$ level no $|\Delta m_J|=2$ transitions are possible, hence only states of the same m_F are coupled. An interaction that leaves the m_F quantum number of the alkali unchanged has little effect on the optical pumping cycle. There are slight changes in the optical pumping probabilities, however, due to redistribution of excited-state populations among sublevels of the same m_F. It is intriguing to find that this form of mixing actually aids the optical pumping process rather than hinders it. In Table V we have calculated optical pumping probabilities between ground-state sublevels, assuming that each atom is subject to many $\Delta m_J=0$ mixing collisions. A comparison of Table V with the probability matrix for no mixing[21] shows that atoms originally in certain ground-state sublevels acquire more angular momentum on the average if they are subject to $\Delta m_J=0$ mixing than if they are subject to no mixing at all.

(*ii*) *Whatever degree of detrimental mixing remains results from small second-order contributions to the scattering and from inter-J-level transitions.* The model implies that the cross sections for sensitized fluorescence of the alkalies in the rare gases may give an estimate of the degree of excited-state mixing of the type that is detrimental to the optical pumping process. It appears that such mixing should be virtually nonexistent in some alkalies. For cesium, for example, 10^7 Torr of neon would be required to produce even 10% mixing. Long before this point is reached neglected effects such as quenching and pressure broadening of the absorption line become important.

(*iii*) *Mixing within the* $P_{3/2}$ *level is very strong, and*

TABLE III. The probability matrix for mixing within the $^2P_{1/2}$ level, assuming reorientation of **J**, subject to the selection rule $\Delta m_J=0$. The initial $|F,m_F\rangle$ sublevels are given along the top, and the final sublevels along the side.

(F,m_F) ╲ (F,m_F)	2.2	2.1	2.0	2, −1	2, −2	1,1	1.0	1, −1
2,2	1.000	0	0	0	0	0	0	0
2,1	0	0.625	0	0	0	0.375	0	0
2,0	0	0	0.500	0	0	0	0.500	0
2, −1	0	0	0	0.625	0	0	0	0.375
2, −2	0	0	0	0	1.000	0	0	0
1,1	0	0.375	0	0	0	0.625	0	0
1,0	0	0	0.500	0	0	0	0.500	0
1, −1	0	0	0	0.375	0	0	0	0.625

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[19] J. Callaway and E. Bauer, Phys. Rev. 140, A1072 (1965).
[20] J. A. Jordan, thesis, University of Michigan, 1964 (unpublished).
[21] See Table II of Ref. 2.

TABLE IV. The probability matrix for mixing within the $^2P_{3/2}$ level, assuming reorientation of **J** subject to the selection rule $\Delta m_J=0, \pm 2$. The initial $|F,m_F\rangle$ sublevels are given along the top, and the final sublevels along the side.

$(F,m_F) \backslash (F,m_F)$	3,3	3,2	3,1	3,0	3, −1	3, −2	3, −3	2,2	2,1	2,0	2, −1	2, −2	1,1	1,0	1, −1	0,0
3,3	0.5000	0	0.1000	0	0	0	0	0	0.2500	0	0	0	0.1500	0	0	0
3,2	0	0.2500	0	0.1250	0	0	0	0.2500	0	0.1250	0	0	0	0.1250	0	0.1250
3,1	0.1000	0	0.2200	0	0.1200	0	0	0	0.1000	0	0.1500	0	0.1800	0	0.1300	0
3,0	0	0.1250	0	0.2050	0	0.1250	0	0.1250	0	0.1250	0	0.1250	0	0.0450	0	0.1250
3, −1	0	0	0.1200	0	0.2200	0	0.1000	0	0.1500	0	0.1000	0	0.1300	0	0.1800	0
3, −2	0	0	0	0.1250	0	0.2500	0	0	0	0.1250	0	0.2500	0	0.1250	0	0.1250
3, −3	0	0	0	0	0.1000	0	0.5000	0	0	0	0.2500	0	0	0	0.1500	0
2,2	0	0.2500	0	0.1250	0	0	0	0.2500	0	0.1250	0	0	0	0.1250	0	0.1250
2,1	0.2500	0	0.1000	0	0.1500	0	0	0	0.2500	0	0	0	0.1500	0	0.1000	0
2,0	0	0.1250	0	0.1250	0	0.1250	0	0.1250	0	0.1250	0	0.1250	0	0.1250	0	0.1250
2, −1	0	0	0.1500	0	0.1000	0	0.2500	0	0	0	0.2500	0	0.1000	0	0.1500	0
2, −2	0	0	0	0.1250	0	0.2500	0	0	0	0.1250	0	0.2500	0	0.1250	0	0.1250
1,1	0.1500	0	0.1800	0	0.1300	0	0	0	0.1500	0	0.1000	0	0.1700	0	0.1200	0
1,0	0	0.1250	0	0.0450	0	0.1250	0	0.1250	0	0.1250	0	0.1250	0	0.2050	0	0.1250
1, −1	0	0	0.1300	0	0.1800	0	0.1500	0	0.1000	0	0.1500	0	0.1200	0	0.1700	0
0,0	0	0.1250	0	0.1250	0	0.1250	0	0.1250	0	0.1250	0	0.1250	0	0.1250	0	0.1250

TABLE V. The optical pumping probability matrix for D_1 pumping, assuming $\Delta m_J=0$ mixing in the excited state. The initial $|F,m_F\rangle$ ground-state sublevel is given along the top, and the final ground-state sublevel along the side.

$(F,m_F) \backslash (F,m_F)$	2,2	2,1	2,0	2, −1	2, −2	1,1	1,0	1, −1
2,2	0	0.3333	0.6667	0	0	1.0000	0.6667	0
2,1	0	0.1667	0.3333	0.7500	0	0.5000	0.3333	0.2500
2,0	0	0	0.3333	0.5000	0.6667	0	0.3333	0.1667
2, −1	0	0	0	0.7500	0.6667	0	0	0.2500
2, −2	0	0	0	0	1.3333	0	0	0
1,1	0	0.5000	0.3333	0.2500	0	1.5000	0.3333	0.0833
1, −0	0	0	0.3333	0.5000	0.6667	0	0.3333	0.1667
1, −1	0	0	0	0.2500	0.6667	0	0	0.0833

does disrupt the optical pumping process. When circularly polarized D_2 light is present in the pumping radiation, atoms in the $|2,2\rangle$ ground-state sublevel are strongly pumped to the $|3,3\rangle$ sublevel in the $P_{3/2}$ excited state. If there is no mixing within this level, they can return only to $|2,2\rangle$, destroying no ground-state spin polarization. Since the earliest experiments it has been observed that D_2 pumping is efficient only at the lowest buffer pressures,[22] indicating a large cross section for mixing in the $P_{3/2}$ level. According to the modified van der Waals' model, both $\Delta m_J=0$ and $|\Delta m_J|=2$ transitions are possible within this level. Since the latter transitions connect sublevels of different m_F, alkali angular momentum can be lost, disrupting the optical pumping cycle. When the collision frequency is high compared with the inverse excited-state lifetime, many $|F,m_F\rangle$ sublevels of the $P_{3/2}$ state are connected, and the mixing approaches a limit similar to the "uniform" or "complete" mixing model, in agreement both with experiment, and with earlier expectations.

(*iv*) *Dehmelt's model for the mixing process remains valid for* Li, Na, *and* K. For these alkalies, transitions between J levels cannot be neglected and are, in fact, as probable as transitions within the levels. In this case, even though mixing within the $^2P_{1/2}$ level may be small, a large degree of mixing between J levels remains. A limit similar to the complete mixing model is approached as the collision frequency approaches the hyperfine frequency.

III. SUGGESTED EXPERIMENTS AND DISCUSSION

In the previous sections we have suggested two possible models for mixing within a single excited state. Both models assume a random reorientation of the total electronic angular momentum **J**, one restricted by the selection rule $|\Delta m_J|=0, 2$. Aside from the measurement of the mixing cross sections, which are as yet unknown, it is of interest to determine experimentally which of the two models provides the closer approximation to physical reality.

The measurement of the degree of polarization of resonance radiation reemitted by an alkali-vapor–buffer-gas cell should provide the most direct determination of the degree of mixing within a J level, regardless of which model for the mixing process is correct. It is well known that if an alkali vapor is illuminated by unpolarized or linearly polarized D

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[22] For the most recent work, see S. M. Jarrett, thesis, University of Michigan, 1962 (unpublished).

radiation, the D_2 resonance fluorescence is partially polarized and the D_1 fluorescence is unpolarized. The partial D_2 polarization arises from unequal population of the $^2P_{3/2}$ excited-state sublevels produced in the absorption of light. Alkali–buffer-gas collisions that tend to equalize the sublevel populations are sufficient to depolarize the fluorescence. In a recent experiment, no polarization of rubidium resonance fluorescence was detected at pressures of helium above 25 Torr,[12] indicating a cross section for mixing within the $^2P_{3/2}$ level of at least 10^{-15} cm^2. This value is more than two orders of magnitude larger than the corresponding cross section for inter-J-level transitions, and tempts us to believe that detailed studies may prove intriguing. The particular experiment that we suggest is to pass circularly polarized D_1 and D_2 light separately through an absorption cell, and to measure the degree of polarization of resonance fluorescence. With little or no buffer gas in the cell, both the D_1 and D_2 fluorescence will be partially polarized, but as the gas pressure is increased the polarization will disappear. It should be possible to deduce interaction cross sections from the observed dependence of the degree of polarization on buffer gas pressure. Through a comparison of the mixing cross sections within the two J levels it may be possible to determine the relative strengths of the various Δm_J transitions. Similar experiments have been performed in the past,[23–25] but never, to our knowledge, on systems in which transitions between J levels did not produce the dominant effects.[25a]

Another possible experiment involves the use of the optical pumping process itself to determine the cross sections for excited-state mixing. If σ^+ D_1 light is used to pump the vapor, the relative absorption probabilities of the ground-state sublevels are 0:1:2:3:4:3:2:1. If there is no ground-state relaxation, all atoms are ultimately pumped to the highest $|F,m_F\rangle$ sublevel, $|2,2\rangle$, regardless of the amount of mixing in the excited state. This result obtains because the lower sublevels are continually depleted by the pumping radiation, while $|2,2\rangle$ remains unaffected. The equilibrium electronic spin polarization is equal to $+0.5$. The situation is quite different if circularly polarized D_2 radiation is used to pump the vapor. In this case, the absorption probabilities are 6:5:4:3:2:3:4:5, with $|2,2\rangle$ now having the *strongest* absorption probability, in contrast to zero-absorption probability with D_1 pumping. If there is no excited-state mixing, all atoms are still ultimately pumped to $|2,2\rangle$, again yielding an equilibrium spin polarization of $+0.5$. If there is complete excited-state mixing, however, the $|2,2\rangle$ becomes the least populated, and the sublevel populations are [0.0746, 0.0895, 0.1119, 0.1493, 0.2239, 0.1493, 0.1119, 0.0895], inferring a spin polarization of -0.104. This is a radical change from the no-mixing case, and the difference between the two extremes offers a large "signal" with which to work. Through the use of Tables II or IV and Eq. (12), it is possible to predict the equilibrium spin polarization as a function of the degree of excited-state mixing. By measuring the optical pumping signal as a function of buffer gas pressure, one can then evaluate the mixing cross section with the aid of Eq. (9).

On the basis of the models discussed thus far, one might expect the cross sections for mixing within a particular J level to be roughly the same for all alkalies, and to be of the order of 10^{-15} cm^2 to 10^{-14} cm^2 in magnitude. In a recent experiment, however, Marrus and Yellin,[26] have found that for Rb these cross sections are as small as 10^{-17} cm^2, a rather surprising result. Furthermore, they suggest that a mixing model in which the nuclear spin is also randomized (i.e., a total randomization of **F** in every mixing collision) is more consistent with their results than the random reorientation of **J** that we have proposed in the preceding sections. There are, however, certain assumptions inherent in the analysis of their experiment that we believe are open to question.

Marrus and Yellin attempted to extract information concerning excited-state mixing from a change in shape of the optical pumping signal. They noticed that in a well coated cell containing no buffer gas this curve was a simple exponential, whereas when a buffer gas was admitted the new curve could be represented as a sum of two exponentials. This change in shape of the pumping signal was attributed to partial mixing in the excited state. As we have already remarked, in order to predict the form of optical pumping transient signals, one must calculate relative pumping and relaxation probabilities connecting the ground-state sublevels. In the work under discussion, these calculations were performed assuming a model of uniform ground-state relaxation and a weighted average of zero and complete $|F,m_F\rangle$ mixing in the excited state. The measurements were carried out under conditions of "partial excited-state mixing," where the probability is small that an excited atom will suffer more than one collision before decaying to the ground state. We have already shown by a consideration of the characteristic times involved that in this case it is more reasonable to assume that mixing collisions cause a random reorientation of **J** rather than randomization of **F**. Our primary source of concern,

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[23] G. L. Datta, Z. Physik **37**, 625 (1926).

[24] W. Hanle, Z. Physik **41**, 164 (1927).

[25] W. Ermisch and R. Seiwert, Ann. Phys. (Leipzig) **2**, 393 (1959). References to further work of interest are given in this paper.

[25a] *Note added in proof.* Considerable theoretical and experimental work on excited-state mixing in the $^3P_1$ state of mercury has been performed by A. Omont, J. Phys. Radium **26**, 26 (1965). An extension of Omont's density-matrix formalism to include alkali excited-state mixing would be quite useful, but has not yet been carried out. A model in which the **J** vector of an excited mercury atom (^{199}Hg) is assumed to be randomly reoriented in a collision with a helium atom has recently been experimentally shown to be valid by J. R. Faroux and J. Brossel, Compt. Rend. **262**, 41 (1966).

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

however, arises from the authors' treatment of ground-state relaxation.

Marrus and Yellin suggest that by making the pumping rate ten to one hundred times greater than the relaxation rate the details of ground-state relaxation become unimportant for the analysis of experimental results. This assumption is not necessarily valid. The true parameter of importance is the ratio of the number of atoms pumped per second that decay subject to mixing, to the number of ground-state atoms relaxing per second, since either effect can disrupt the optical pumping process and change the shape of the pumping curve. This ratio is given by

$$A\tau/R(\tau+\tau_c)\,, \tag{13}$$

where A is the pumping rate, R is the ground-state relaxation rate, τ is the lifetime of the excited state, and τ_c is the time between mixing collisions. Using their data relating to the optical pumping of rubidium in neon,[26,27] we find a maximum value of this ratio of about 5:1, making relaxation effects clearly non-negligible. The question that remains is whether ground-state relaxation processes can introduce changes in the pumping signal that are comparable to those produced by excited-state mixing. The answer hinges on whether alkali relaxation induced by collisions with buffer gas atoms can be described by a "uniform" model with a single relaxation time T.

Bouchiat has derived a general Hamiltonian that describes collisionally induced alkali spin relaxation.[28] For alkali–buffer-gas collisions where the collision time is short compared to the hyperfine period, the approximation of a "white" spectral density function might be expected to apply. In simpler terms, this means that the spectrum of oscillating magnetic fields experienced by the alkali during a collision has the same strength at both the hyperfine frequency (ΔW) and the hyperfine Zeeman frequency (ω_F). Under this assumption, the transition probabilities calculated using Bouchiat's Hamiltonian reduce to those calculated by Franz for the case of "electron randomization" relaxation.[29] It has been experimentally demonstrated that the appropriate limits of the Hamiltonian give a valid description of relaxation phenomena, both for wall collisions,[30] and for buffer gas collisions.[31] In the latter case, the equations for the electronic and nuclear spin polarizations of the vapor, $\langle S_z\rangle=\sum_i n_i\langle S_z\rangle_i$ and $\langle I_z\rangle_i=\sum_i n_i\langle I_z\rangle_i$, are given by

$$\begin{aligned} d\langle S_z\rangle/dt &= -C\langle S_z\rangle+\tfrac{1}{8}C\langle I_z\rangle\,,\\ d\langle I_z\rangle/dt &= -\tfrac{1}{8}C\langle I_z\rangle\,, \end{aligned} \tag{14}$$

where the n_i are the populations of the ith ground-state sublevels, and $\langle S_z\rangle_i$ and $\langle I_z\rangle_i$ are the expectation values of the electronic spin and the nuclear spin in these sublevels. The temporal behavior of $\langle S_z\rangle$ is of particular importance, since the pumping signal is a linear function of this parameter, provided that all hyperfine components of the pumping light have equal intensity.[28,31,32]

The solution of the set of equations (14) yields a single exponential time dependence for $\langle I_z\rangle$, but a *double* exponential time dependence for $\langle S_z\rangle$. In the general case, the ratio of the two time constants describing the relaxation of $\langle S_z\rangle$ is a function of the alkali nuclear spin and the ratio $H_1(\Delta W)/H_1(\omega_F)$, ranging from 1:1 to 8:1 as $H_1(\Delta W)/H_1(\omega_F)$ goes from 0 to 1, for nuclear spin $\frac{3}{2}$. The two time constants observed in the pumping curve were in the ratio 5:1. It is important to note that the presence of faster exponential decays has been observed experimentally in Rb,[33,34] and to a lesser extent in Cs.[35] In fact in Legowski's work[36] where the presence of two diffusion modes was detected, the increased importance of electron randomization relaxation undoubtedly contributed to the poor agreement between theory and experiment at high buffer pressures (at low buffer pressures wall relaxation was dominant, while at higher pressures contribution to relaxation from alkali–buffer-gas collisions became important). The *generally* poorer fits[32–35] of high-pressure relaxation data to single exponentials are also likely due to this effect. In view of the double exponential characteristics of alkali relaxation in buffer gases, we question the contention of Marrus and Yellin that the existence of a double exponential pumping curve can be unambiguously attributed to excited-state mixing. Experiments similar to those described at the beginning of this section may shed further light on those problems.

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