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Analytic Expressions for Transient Signals in the Optical Pumping of Alkali-Metal Vapors*

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Rate equations for the optical pumping of alkali-metal vapors simultaneously subject to pumping, relaxation in the excited state, and relaxation in the ground state are shown to yield analytic solutions for the alkali-metal electronic and nuclear-spin polarizations in the limit of weak pumping. Nuclear-spin and hyperfine-interaction effects are properly included. Analysis of the double-exponential form of the pumping transient of the ground-state electronic-spin polarization is shown to yield new methods for the measurement of cross sections for collisional relaxation in both the ground and excited states. Formulas are derived that relate relaxation cross sections to experimentally measurable parameters. Formulas describing the influence of nuclear spin on signals obtained from standard depolarization of resonance-radiation experiments also are provided. Ambiguities in earlier optical-pumping experiments and calculations arising from oversimplified descriptions of relaxation processes are discussed.

INTRODUCTION

Optical-pumping techniques have received widespread application in the study of collisional relaxation among the Zeeman sublevels of various atomic states.[1] In this paper we derive analytic expressions which describe the production and destruction of electronic- and nuclear-spin polarizations in alkali-metal vapors subject to weak optical pumping. We bring together previous work to show how collisions of pumped atoms with the walls of the experimental cell, simple binary alkali-atom–buffer-gas-atom collisions, and "sticky" alkali-atom–buffer-gas-atom collisions which form van der Waals molecular dimers all contribute to determining the shape of optical-pumping transients. We include rigorous treatments of the effect of the hyperfine interaction on all collisional relaxation processes. We show that in low magnetic fields the pumping transients of the electronic-spin polarization are generally represented by the sum of two exponentials, the rate constants of which depend wholly on relaxation processes in the ground state. We show that the difference of the two rate constants depends only upon the relaxation rate in binary collisions with buffer-gas atoms, and is independent of pumping rate, wall relaxation rate, and molecular formation rate. We further show the the relative contributions of the two rates to the production of the electronic-spin polarization are determined mainly by the degree of collisional relaxation which occurs during the excited-state lifetime. We derive analytic expressions involving the relaxation rates and their relative amplitudes which can be used to determine the cross section for the collisional relaxation of $\langle J_z \rangle$ within the $^2P_{1/2}$ state from experimentally measured ground-state pumping transients. In the course of our calculations, we derive expressions, including all nuclear-spin effects, for the equilibrium values of $\langle J_z \rangle$ and $\langle I_z \rangle$ in the $^2P_{1/2}$ excited state, subject to simultaneous excitation, collisional relaxation, and spontaneous decay. These calculations provide the bases for the analyses of standard depolarization of resonance radiation experiments at low magnetic fields. Finally, we utilize our calculations to show how incomplete knowledge of the mechanics of nuclear-spin effects in collisional relaxation could have contributed to earlier misdeterminations of some ground-state relaxation parameters such as the diffusion coefficients of alkalis in the noble gases.

All of the calculations in this paper are based on the assumption that "weak pumping" prevails, that is, that pumping rates are considerably smaller than ground-state relaxation rates. While such a regime is foreign to that in which the majority of past experiments and calculations have been performed, it is ideally suited for the analysis of optical-pumping transients encountered in experiments utilizing "white-light" pumping sources.[2,3] Appropriate white-light pumping experiments have been in progress in our laboratory throughout the past two years, and will be the subjects of forthcoming publications. The experimental results that we have obtained are consistent with the theoretical predictions of this paper.

PRODUCTION AND DESTRUCTION OF SPIN POLARIZATION

We assume that the alkali-metal vapor to be optically pumped is situated in a weak magnetic

field $\vec{H}_0$. The direction of $\vec{H}_0$ defines the z axis of the system. We further assume that $\vec{F}$, the total atomic angular momentum, and m_F, the projection of $\vec{F}$ upon $\vec{H}_0$, are good quantum numbers both in the $^2S_{1/2}$ ground state and in the $^2P_{1/2}$ excited state. We define n_i to be the occupation probability of the ith $|F, m_F\rangle$ sublevel of the ground state. If the expectation values of the z components of the electronic spin $\vec{S}$ and the nuclear spin $\vec{I}$ for the ith sublevel of the ground state are $\langle S_z\rangle_{gi}$ and $\langle I_z\rangle_{gi}$, respectively, then the ground-state electronic- and nuclear-spin polarizations, $\langle S_z\rangle_g$ and $\langle I_z\rangle_g$, of the vapor are

$$\langle S_z\rangle_g = \sum_i n_i \langle S_z\rangle_{gi} / \sum_i n_i , \tag{1a}$$

$$\langle I_z\rangle_g = \sum_i n_i \langle I_z\rangle_{gi} / \sum_i n_i . \tag{1b}$$

All of our calculations will be concerned with the normal $\sigma^+ D_1$ ($^2S_{1/2} - {}^2P_{1/2}$) optical-pumping technique first introduced by Dehmelt and Franzen and Emslie.[4-6] As usual, we shall normalize the occupation probabilities, and shall assume that the pumping rate is very much smaller than the inverse lifetime of the excited state, ensuring the validity of Eq. (2) at all times:

$$\sum_i n_i \cong 1 . \tag{2}$$

We shall consider the following contributions to the production and destruction of spin polarizations: depopulation pumping due to excitation of atoms out of the ground state owing to the absorption of light, relaxation within the $^2P_{1/2}$ excited state due to collisions of alkali-metal atoms with buffer-gas atoms, repopulation pumping due to spontaneous emission from the excited state, and relaxation within the ground state due to collisions of alkali-metal atoms both with buffer-gas atoms and with the walls of the experimental cell. We shall neglect effects due to spin exchange and effects due to strong absorption of the pumping light as it traverses the experimental cell: We thus assume low alkali densities.

a. *Depopulation pumping.* We shall assume that the pumping light is of equal intensity in all hyperfine components of the alkali absorption line, and that the light is broad band ("white") over all such components at all buffer-gas pressures. We shall neglect all interference terms in excitation and spontaneous emission, an excellent approximation for $\sigma^+ D_1$ pumping.[7,8] If A represents the pumping rate, then the rate of change of n_i due to depopulation pumping alone is

$$\frac{dn_i}{dt} = -Ak_i n_i , \tag{3}$$

where k_i is the relative absorption probability of the ith sublevel. For $\sigma^+ D_1$ pumping, k_i can be written in the following form:

$$k_i = \tfrac{2}{3}[\tfrac{1}{2} - \langle S_z\rangle_{gi}] . \tag{4}$$

Utilizing Eqs. (1a), (3), and (4), we obtain

$$\frac{d\langle S_z\rangle_g}{dt} = -\tfrac{1}{3}A\langle S_z\rangle_g + \tfrac{2}{3}A \sum_i n_i \langle S_z\rangle_{gi}^2 . \tag{5}$$

We now invoke the assumption of "weak pumping"; that is, we assume that the pumping rate is much smaller than the ground-state relaxation rate. This assumption assures us that the second term on the right-hand side of Eq. (5) remains constant at all stages of the optical-pumping process.[9] By explicit calculation we obtain Eqs. (6a)–(6d) for nuclear spins $I = 0, \frac{3}{2}, \frac{5}{2}, \frac{7}{2}$:

$$\frac{d\langle S_z\rangle_g}{dt} = -\tfrac{1}{3}A\langle S_z\rangle_g + \tfrac{1}{6}A \qquad (I=0), \tag{6a}$$

$$\frac{d\langle S_z\rangle_g}{dt} = -\tfrac{1}{3}A\langle S_z\rangle_g + \tfrac{1}{16}A \qquad (I=\tfrac{3}{2}), \tag{6b}$$

$$\frac{d\langle S_z\rangle_g}{dt} = -\tfrac{1}{3}A\langle S_z\rangle_g + \tfrac{19}{324}A \qquad (I=\tfrac{5}{2}), \tag{6c}$$

$$\frac{d\langle S_z\rangle_g}{dt} = -\tfrac{1}{3}A\langle S_z\rangle_g + \tfrac{11}{192}A \qquad (I=\tfrac{7}{2}) . \tag{6d}$$

In a similar manner we obtain an equation for the rate of change of the nuclear spin polarization:

$$\frac{d\langle I_z\rangle_g}{dt} = -\tfrac{1}{3}A\langle I_z\rangle_g + \tfrac{2}{3}A \sum_i n_i \langle S_z\rangle_{gi}\langle I_z\rangle_{gi} . \tag{7}$$

Again, by explicit calculation, we obtain Eqs. (8a)–(8c):

$$\frac{d\langle I_z\rangle_g}{dt} = -\tfrac{1}{3}A\langle I_z\rangle_g + \tfrac{5}{48}A \qquad (I=\tfrac{3}{2}), \tag{8a}$$

$$\frac{d\langle I_z\rangle_g}{dt} = -\tfrac{1}{3}A\langle I_z\rangle_g + \tfrac{35}{324}A \qquad (I=\tfrac{5}{2}), \tag{8b}$$

$$\frac{d\langle I_z\rangle_g}{dt} = -\tfrac{1}{3}A\langle I_z\rangle_g + \tfrac{21}{192}A \qquad (I=\tfrac{7}{2}) . \tag{8c}$$

b. *Repopulation pumping and excited-state relaxation.* We define the following quantities for the $^2P_{1/2}$ excited state:

$$N_k = \text{occupation probability of the } k\text{th } |F, m_F\rangle \text{ sublevel}, \tag{9a}$$

$$\langle J_z\rangle_{ek} = \text{expectation value of } J_z \text{ for the } k\text{th } |F, m_F\rangle \text{ sublevel}, \tag{9b}$$

$$\langle I_z\rangle_{ek} = \text{expectation value of } I_z \text{ for the } k\text{th } |F, m_F\rangle \text{ sublevel}, \tag{9c}$$

$$N = \sum_k N_k \ll 1 , \tag{10}$$

$$\langle J_z\rangle_e = \sum_k \frac{N_k\langle J_z\rangle_{ek}}{N}, \tag{11a}$$

$$\langle I_z\rangle_e = \sum_k \frac{N_k\langle I_z\rangle_{ek}}{N}. \tag{11b}$$

Explicit calculation shows that the repopulation pumping of the ground-state electronic-spin polarization due to spontaneous emission from the excited state can be written in the following forms[10]:

$$\frac{d\langle S_z\rangle_g}{dt} = \frac{-N\langle J_z\rangle_e}{3\tau} \qquad (I=0), \tag{12a}$$

$$\frac{d\langle S_z\rangle_g}{dt} = \frac{N}{6\tau}[\langle I_z\rangle_e - 2\langle J_z\rangle_e] \qquad (I=\tfrac{3}{2}), \tag{12b}$$

$$\frac{d\langle S_z\rangle_g}{dt} = \frac{N}{27\tau}[2\langle I_z\rangle_e - 9\langle J_z\rangle_e] \qquad (I=\tfrac{5}{2}), \tag{12c}$$

$$\frac{d\langle S_z\rangle_g}{dt} = \frac{N}{24\tau}[\langle I_z\rangle_e - 8\langle J_z\rangle_e] \qquad (I=\tfrac{7}{2}). \tag{12d}$$

The repopulation rates of the ground-state nuclear-spin polarization are

$$\frac{d\langle I_z\rangle_g}{dt} = \frac{5N}{6\tau}\langle I_z\rangle_e \qquad (I=\tfrac{3}{2}), \tag{13a}$$

$$\frac{d\langle I_z\rangle_g}{dt} = \frac{25N}{27\tau}\langle I_z\rangle_e \qquad (I=\tfrac{5}{2}), \tag{13b}$$

$$\frac{d\langle I_z\rangle_g}{dt} = \frac{23N}{24\tau}\langle I_z\rangle_e \qquad (I=\tfrac{7}{2}). \tag{13c}$$

In order to complete the calculation of the repopulation pumping rates, we must calculate the quasiequilibrium values of $\langle J_z\rangle_e$ and $\langle I_z\rangle_e$ which exist at any time during the optical-pumping cycle. We shall assume that the rates of excitation of $\langle J_z\rangle_e$ and $\langle I_z\rangle_e$ in the excited state do not change during the optical-pumping process, an excellent approximation for small $\langle S_z\rangle_g$ and $\langle I_z\rangle_g$. We also shall assume that the standard model of "randomization of $\vec{J}$" coupled with nuclear decoupling-recoupling describes collisional relaxation among the Zeeman sublevels of the $^2P_{1/2}$ state.[11-18] This approximation should hold as long as the relaxation rate is less than the inverse of the hyperfine period. If Γ_1 is the relaxation rate for the destruction of "orientation," i.e., of $\langle J_z\rangle_e$, within the $^2P_{1/2}$ state of the nuclear-spin-zero atom, then the relaxation rates for $\langle J_z\rangle_e$ and for $\langle I_z\rangle_e$, taking all nuclear-spin effects into account, are[12]

$$\frac{d\langle J_z\rangle_e}{dt} = -\Gamma_1\langle J_z\rangle_e + 2\Gamma_1(2I+1)^{-2}\langle I_z\rangle_e \tag{14a}$$

and

$$\frac{d\langle I_z\rangle_e}{dt} = -2\Gamma_1(2I+1)^{-2}\langle I_z\rangle_e, \tag{14b}$$

where $\Gamma_1 = n_0\sigma_1 v_{\rm rel}p/p_0$. n_0 is Loschmidt's number, σ_1 is the cross section for the destruction of $\langle J_z\rangle_e$, $v_{\rm rel}$ is the mean relative velocity of alkali atoms and buffer-gas atoms, p_0 is 760 Torr, and p is the actual buffer-gas pressure in Torr. Assuming excitation with σ^+ light under the conditions specified above, we have calculated the following quasiequilibrium values of $\langle J_z\rangle_{e\,\rm eq}$ subject to excitation, collisional relaxation, and spontaneous decay[19]:

$$\langle J_z\rangle_{e\,\rm eq} = \tfrac{1}{2}(1+\Gamma_1\tau)^{-1} \qquad (I=0), \tag{15a}$$

$$\langle J_z\rangle_{e\,\rm eq} = \tfrac{1}{2}(3+\Gamma_1\tau)(1+\Gamma_1\tau)^{-1}\times(8+\Gamma_1\tau)^{-1} \qquad (I=\tfrac{3}{2}), \tag{15b}$$

$$\langle J_z\rangle_{e\,\rm eq} = \tfrac{1}{6}(19+3\Gamma_1\tau)(1+\Gamma_1\tau)^{-1}\times(18+\Gamma_1\tau)^{-1} \qquad (I=\tfrac{5}{2}), \tag{15c}$$

$$\langle J_z\rangle_{e\,\rm eq} = \tfrac{1}{2}(11+\Gamma_1\tau)(1+\Gamma_1\tau)^{-1}\times(32+\Gamma_1\tau)^{-1} \qquad (I=\tfrac{7}{2}). \tag{15d}$$

Similar equations for $\langle I_z\rangle_{e\,\rm eq}$ yield

$$\langle I_z\rangle_{e\,\rm eq} = \tfrac{5}{2}(8+\Gamma_1\tau)^{-1} \qquad (I=\tfrac{3}{2}), \tag{16a}$$

$$\langle I_z\rangle_{e\,\rm eq} = \tfrac{35}{6}(18+\Gamma_1\tau)^{-1} \qquad (I=\tfrac{5}{2}), \tag{16b}$$

$$\langle I_z\rangle_{e\,\rm eq} = \tfrac{21}{2}(32+\Gamma_1\tau)^{-1} \qquad (I=\tfrac{7}{2}). \tag{16c}$$

The equilibrium value of N is the same for all nuclear spins, including $I=0$, and is

$$N = \tfrac{1}{3}A\tau. \tag{17}$$

Equations (15b)–(15d) have significance considerably beyond that of their utilization in the calculations of this paper. These equations provide the bases for the correct extraction of cross sections for collisional relaxation of $\langle J_z\rangle_e$ from experiments measuring depolarization of resonance radiation in low magnetic fields.[20] For atoms with $I\neq 0$ they are the analogs of the Stern–Vollmer equation. They have not been calculated previously. A fit of the appropriate member of this set of equations to the pressure dependence of $(I_{\sigma^+} - I_{\sigma^-})$ in fluorescence yields a cross section for the relaxation of $\langle J_z\rangle_e$ within the $^2P_{1/2}$ state, corrected for nuclear-spin effects. We plot Eqs. (15b)–(15d) in Fig. 1 as a function of $\Gamma_1\tau$ and observe that the main effect of nuclear spin is the lowering of the value of $\langle J_z\rangle_e$ $(\Gamma_1\tau=0)$ from 0.5 for atoms of $I=0$, to approximately 0.25 for atoms of $I\neq 0$. Such an effect would not be observed in a typical depolarization experiment since measurements normally are made in terms of relative rather than absolute units of light intensity. A straightforward fit of the Stern–Vollmer equation $P = P_0(1+\Gamma_1\tau)^{-1}$ to experimental data would yield a value of σ_1 only about 20 to 25% larger than the correct value that would be deduced from Eqs. (15b)–(15d). Nuclear

spin and hyperfine structure therefore affect depolarization experiments to a considerably smaller degree than they affect Hanle-type experiments.[21] The collisional relaxation of the nuclear-spin polarization in the excited state, however, is strongly dependent on the magnitude of the nuclear spin. We provide plots of Eqs. (16a)–(16c) in Fig. 2 demonstrating this effect. The nuclear-spin polarization is not, however, an observable in standard depolarization experiments.

Insertion of the appropriate combinations of Eqs. (15a)–(15d), (16a)–(16c), and (17) into Eqs. (12a)–(12d) and (13a)–(13c) yield the following analytic expressions for the repopulation rates of $\langle S_z\rangle_g$ and $\langle I_z\rangle_g$, including effects of collisional relaxation within the excited state:

$$\frac{d\langle S_z\rangle_g}{dt} = -\tfrac{1}{9}A(1+\Gamma_1\tau) \qquad (I=0), \qquad (18a)$$

$$\frac{d\langle S_z\rangle_g}{dt} = \tfrac{1}{36}A(3\Gamma_1\tau-1)(1+\Gamma_1\tau)^{-1}(8+\Gamma_1\tau)^{-1} \qquad (I=\tfrac{3}{2}), \qquad (18b)$$

$$\frac{d\langle S_z\rangle_g}{dt} = \tfrac{1}{486}A(43\Gamma_1\tau-101)(1+\Gamma_1\tau)^{-1}(18+\Gamma_1\tau)^{-1} \qquad (I=\tfrac{5}{2}), \qquad (18c)$$

$$\frac{d\langle S_z\rangle_g}{dt} = \tfrac{1}{144}A(13\Gamma_1\tau-67)(1+\Gamma_1\tau)^{-1}(32+\Gamma_1\tau)^{-1} \qquad (I=\tfrac{7}{2}) \qquad (18d)$$

and

$$\frac{d\langle I_z\rangle_g}{dt} = \tfrac{25}{36}A(8+\Gamma_1\tau)^{-1} \qquad (I=\tfrac{3}{2}), \qquad (19a)$$

$$\frac{d\langle I_z\rangle_g}{dt} = \tfrac{875}{486}A(18+\Gamma_1\tau)^{-1} \qquad (I=\tfrac{5}{2}), \qquad (19b)$$

$$\frac{d\langle I_z\rangle_g}{dt} = \tfrac{161}{48}A(32+\Gamma_1\tau)^{-1} \qquad (I=\tfrac{7}{2}). \qquad (19c)$$

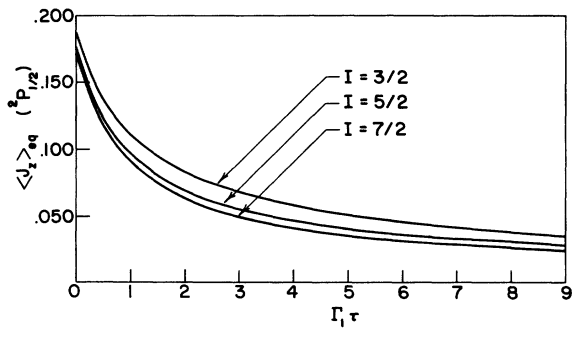

FIG. 1. Dependence of $\langle J_z\rangle_{eq}$ in the $^2P_{1/2}$ state upon degree of collisional relaxation $\Gamma_1\tau$ for nuclear spins 3/2, 5/2, and 7/2. The curves correspond to plots of Eqs. (15b), (15c), (15d). These plots provide the bases for the analyses of standard depolarization experiments performed in low magnetic fields.

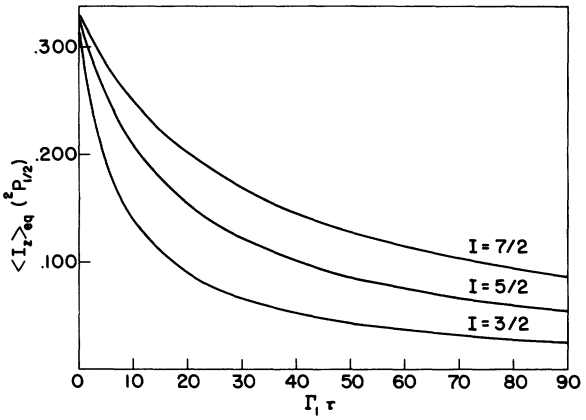

FIG. 2. Dependence of $\langle I_z\rangle_{eq}$ in the $^2P_{1/2}$ state on degree of collisional relaxation $\Gamma_1\tau$ for nuclear spins 3/2, 5/2, and 7/2. The curves correspond to plots of Eqs. (16a), (16b), (16c).

c. *Collisional relaxation in the ground state.* We now shall consider three contributions to rates of change of $\langle S_z\rangle_g$ and $\langle I_z\rangle_g$ due to collisional relaxation within the ground state itself: We consider simple binary collisions of pumped atoms with buffer-gas atoms, "sticky" or molecular-forming collisions of pumped atoms with buffer-gas atoms, and collisions of pumped atoms with the walls of the optical-pumping cell. Our discussion here will be brief since all three relaxation mechanisms have been discussed extensively in the literature.

For simple binary collisions of alkali atoms with buffer-gas atoms, the duration of the collision is short compared to the hyperfine period of the free alkali atom. We shall assume that the time between relaxation events is long compared to the hyperfine period. In such a regime the electron-randomization model with nuclear decoupling-recoupling utilized by Bouchiat and others is valid, leading to the rate equations already presented in Eqs. (14a) and (14b).[11–18] For the description of relaxation in the ground state, replace $\langle J_z\rangle_e$ by $\langle S_z\rangle_g$, $\langle I_z\rangle_e$ by $\langle I_z\rangle_g$, and Γ_1 $(=n_0\sigma_1 v_{rel}p/p_0)$ by $R(=n_0\sigma v_{rel}p/p_0)$. R is the relaxation rate that would be measured for $\langle S_z\rangle_g$ in the absence of nuclear spin, and σ is the cross section for electron-spin relaxation in the ground state. We thus obtain the following equations describing the rates of change of $\langle S_z\rangle_g$ and $\langle I_z\rangle_g$ due to binary collisions of alkali atoms with noble-gas atoms:

$$\frac{d\langle S_z\rangle_g}{dt} = -R\langle S_z\rangle_g \qquad (I=0), \qquad (20a)$$

$$\frac{d\langle S_z\rangle_g}{dt} = -R\langle S_z\rangle_g + \tfrac{1}{8}R\langle I_z\rangle_g \qquad (I=\tfrac{3}{2}), \qquad (20b)$$

$$\frac{d\langle S_z\rangle_g}{dt} = -R\langle S_z\rangle_g + \tfrac{1}{18}R\langle I_z\rangle_g \qquad (I=\tfrac{5}{2}), \qquad (20c)$$

$$\frac{d\langle S_z\rangle_g}{dt} = -R\langle S_z\rangle_g + \tfrac{1}{32}R\langle I_z\rangle_g \qquad (I=\tfrac{7}{2}) \qquad (20d)$$

and

$$\frac{d\langle I_z\rangle_g}{dt} = -\tfrac{1}{8}R\langle I_z\rangle_g \qquad (I=\tfrac{3}{2}), \qquad (21a)$$

$$\frac{d\langle I_z\rangle_g}{dt} = -\tfrac{1}{18}R\langle I_z\rangle_g \qquad (I=\tfrac{5}{2}), \qquad (21b)$$

$$\frac{d\langle I_z\rangle_g}{dt} = -\tfrac{1}{32}R\langle I_z\rangle_g \qquad (I=\tfrac{7}{2}). \qquad (21c)$$

In the presence of some rare gases, bound alkali–rare-gas molecules can form as the result of three-body collisions.[22-25] Such molecules tend to live until struck again by a rare-gas atom. In a pressure regime such that the average lifetime of such a molecule is much longer than the hyperfine period of the alkali atom, i.e., at low pressures, the intensity of the spectral density function of the collisional interaction is negligible at the hyperfine frequency. The appropriate model for the relative relaxation probabilities then is equivalent to those for electron randomization, but with the $F \neq 0$ transitions removed: Magnetic dipole relaxation in this case occurs only among the $|F, m_F\rangle$ sublevels of a given hyperfine state. Such a model yields equal relaxation rates for $\langle S_z\rangle_g$ and $\langle I_z\rangle_g$:

$$\frac{d\langle S_z\rangle_g}{dt} = -R'\langle S_z\rangle_g, \qquad (22a)$$

$$\frac{d\langle I_z\rangle_g}{dt} = -R'\langle I_z\rangle_g, \qquad (22b)$$

where R' is the relaxation rate due to molecular formation and destruction. R' depends upon nuclear spin, as given by Eq. (23):

$$R'(I) = R'(I=0)[2(2I+1)^2]^{-1}. \qquad (23)$$

It is not necessary for our present purposes to display the dependence of R' upon buffer-gas pressure.

The third and final contribution to relaxation in the ground state which we shall consider arises from collisions of pumped atoms with the walls of the optical-pumping cell. This effect was first analyzed by Franzen,[26] and has been the subject of several subsequent publications.[27-30] A rigorous treatment yields a diffusion equation describing the relaxation of polarization of an optically pumped vapor: An infinite number of relaxation rates in principle are involved. Recently, however, it has been verified through extensive computer calculations that the relaxation can be accurately described by a single effective relaxation rate, close in magnitude to that given by the lowest-order diffusion mode.[31] We also note that all available evidence points to the fact that the relaxation of an alkali atom on a glass surface is "uniform," that is, that all transitions between Zeeman sublevels are equally probable in a single relaxation event. The combination of these two facts leads to the following equations, valid for all nuclear spins, which describe the relaxation of $\langle S_z\rangle_g$ and $\langle I_z\rangle_g$ due to collisions of pumped atoms with the walls of the experimental cell:

$$\frac{d\langle S_z\rangle_g}{dt} = -R''\langle S_z\rangle_g \qquad (24a)$$

and

$$\frac{d\langle I_z\rangle_g}{dt} = -R''\langle I_z\rangle_g, \qquad (24b)$$

where

$$R'' = (D_0 p_0/p)[(\pi/L)^2 + (2.045/r)^2]. \qquad (25)$$

D_0 is the "effective" diffusion coefficient, p_0 is 760 Torr, L is the length of the cell, and r is the radius of the cell. The use of the single-exponential approximation for wall relaxation requires a small correction to the buffer-gas relaxation cross section σ. The appropriate correction factors have been calculated elsewhere.[31]

GENERALIZED RATE EQUATIONS FOR WEAK OPTICAL PUMPING

In the most general case of weak optical pumping, all of the relaxation mechanisms that we have discussed in the preceding sections are operative simultaneously. We therefore must consider solutions to equations for the rates of change of $\langle S_z\rangle_g$ and $\langle I_z\rangle_g$ which include appropriate contributions from Eqs. (6), (8), (18), (19), (20)–(22), (24). We note that for all nonzero nuclear spins these generalized rate equations are of the form of Eqs. (26a) and (26b):

$$\frac{d\langle S_z\rangle_g}{dt} = B_1 - B_2\langle S_z\rangle_g + B_3\langle I_z\rangle_g, \qquad (26a)$$

$$\frac{d\langle I_z\rangle_g}{dt} = C_1 - C_2\langle I_z\rangle_g. \qquad (26b)$$

The general solutions to Eqs. (26a) and (26b), assuming $B_2 \neq C_2$, $B_3 \neq 0$, and $\langle I_z\rangle_g(t=0) = \langle S_z\rangle_g(t=0) = 0$, are

$$\langle S_z\rangle_g = D_1(1 - e^{-z_1 t}) + D_2(1 - e^{-z_2 t}) \qquad (27a)$$

and

$$\langle I_z\rangle_g = (C_1/C_2)(1 - e^{-z_1 t}), \qquad (27b)$$

where

$$D_1 = B_3 C_1[C_2(B_2 - C_2)]^{-1} \qquad (28a)$$

and

$$D_2 = B_1/B_2 - (B_3C_1)[C_2(B_2 - C_2)]^{-1} + (B_3C_1/B_2C_2)\,. \tag{28b}$$

The rate constants z_1 and z_2 are

$$z_1 = -C_2\,, \tag{29a}$$

$$z_2 = -B_2\,. \tag{29b}$$

The quantity (D_1z_1/D_2z_2) will prove to be of special significance; we give its form in Eq. (30):

$$D_1z_1/D_2z_2 = B_3C_1(B_1B_2 - B_1C_2 - B_3C_1)^{-1}\,. \tag{30}$$

Examples of the generalized pumping/relaxation equations are given below for $I = \frac{3}{2}$:

$$\frac{d\langle I_z\rangle_g}{dt} = \tfrac{5}{48}A + \tfrac{25}{36}A(8+\Gamma_1\tau)^{-1} - \langle I_z\rangle_g(\tfrac{1}{3}A + \tfrac{1}{8}R + R' + R'')\,, \tag{31a}$$

$$\frac{d\langle S_z\rangle_g}{dt} = \tfrac{1}{16}A + \tfrac{1}{36}A(3\Gamma\tau - 1)(1+\Gamma_1\tau)^{-1}(8+\Gamma_1\tau)^{-1} - \langle S_z\rangle_g(\tfrac{1}{3}A + R + R' + R'') + \langle I_z\rangle_g(\tfrac{1}{8}R)\,. \tag{31b}$$

Equations (31a) and (31b) are wholly compatible with Eqs. (26a) and (26b). The optical-pumping transient for $\langle S_z\rangle_g$ therefore consists of the sum of two exponentials whose rate constants are given by Eqs. (32a) and (32b):

$$z_1 = \tfrac{1}{3}A + \tfrac{1}{8}R + R' + R''\,, \tag{32a}$$

$$z_2 = \tfrac{1}{3}A + R + R' + R''\,. \tag{32b}$$

We obtain from Eqs. (32a) and (32b) the important result that while each of the rate constants z_1 and z_2 depends upon all ground-state relaxation processes, including the pumping rate, the difference between them, $(z_2 - z_1)$, depends only upon the relaxation rate of the electronic-spin polarization. The measurement of $(z_2 - z_1)$ therefore provides a useful new method for the determination of ground-state relaxation cross sections, uninfluenced by the complicating factors present in many earlier experiments. Specifically, for the various nuclear spins, we obtain

$$(z_2 - z_1) = \tfrac{7}{8}(n_0\sigma v_{\rm rel}p/p_0) \qquad (I = \tfrac{3}{2})\,, \tag{33a}$$

$$(z_2 - z_1) = \tfrac{17}{18}(n_0\sigma v_{\rm rel}p/p_0) \qquad (I = \tfrac{5}{2})\,, \tag{33b}$$

$$(z_2 - z_1) = \tfrac{31}{32}(n_0\sigma v_{\rm rel}p/p_0) \qquad (I = \tfrac{7}{2})\,. \tag{33c}$$

The only unknown parameter to be determined from application of Eqs. (31a)–(31c) to experimental data is σ, the cross section for electron-spin relaxation in the $^2S_{1/2}$ ground state.

While the ground-state relaxation rates z_1 and z_2 depend only upon ground-state relaxation processes, their relative contributions, D_1 and D_2, to the transient of $\langle S_z\rangle_g$ depend also upon the degree of collisional relaxation in the excited state. D_1 and D_2 are rather complicated functions of all relaxation rates; we shall not bother to write down the explicit forms. An enormous simplification occurs, however, in the quantity (D_1z_1/D_2z_2). This may be seen by substitution of appropriate terms from Eqs. (31a) and (31b) into Eq. (30). We obtain, for $I = \frac{3}{2}$, and from similar calculations for $I = \frac{5}{2}$ and $\frac{7}{2}$, Eqs. (34a)–(34c):

$$(D_1z_1/D_2z_2) = \tfrac{5}{16}(44 + 3\Gamma_1\tau)(1+\Gamma_1\tau)(8+\Gamma_1\tau)^{-1} \times (2+3\Gamma_1\tau)^{-1} \qquad (I = \tfrac{3}{2})\,, \tag{34a}$$

$$(D_1z_1/D_2z_2) = \tfrac{35}{288}(104 + 3\Gamma_1\tau)(1+\Gamma_1\tau)(18+\Gamma_1\tau)^{-1} \times (2+3\Gamma_1\tau)^{-1} \qquad (I = \tfrac{5}{2})\,, \tag{34b}$$

$$(D_1z_1/D_2z_2) = \tfrac{21}{320}(188 + 3\Gamma_1\tau)(1+\Gamma_1\tau)(32+\Gamma_1\tau)^{-1} \times (2+3\Gamma_1\tau)^{-1} \qquad (I = \tfrac{7}{2})\,. \tag{34c}$$

Equations (34a)–(34c) depend only upon Γ_1, the relaxation rate of $\langle J_z\rangle_e$ in the excited state, and τ, the excited-state lifetime. Within the approximations of this paper, they are independent of the pump rate and independent of all ground-state relaxation processes. D_1, D_2, z_1, z_2 are all experimentally measurable parameters. Eqs. (34a)–(34c) therefore provide a useful new method for

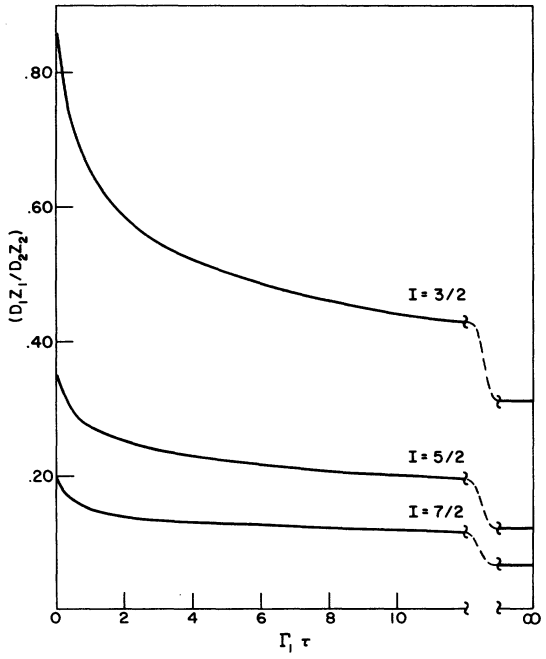

FIG. 3. Plots of (D_1z_1/D_2z_2) vs $\Gamma_1\tau$ for nuclear spins 3/2, 5/2, and 7/2. z_1 is the "slow" ground-state relaxation rate, and D_1 its amplitude; z_2 is the "fast" relaxation rate and D_2 is its amplitude. These plots provide the bases for the determination of the relaxation rate Γ_1 in the $^2P_{1/2}$ excited state through measurement of ground-state pumping transients.

measuring σ_1, the cross section for the destruction of $\langle J_z\rangle_e$ within the $^2P_{1/2}$ excited state. We provide plots of Eqs. (34a)–(34c) as a function of $\Gamma_1\tau$ in Fig. 3.

In deriving Eqs. (34a)–(34c) and Eqs. (15b)–(15c), (16a) and (16b) we have assumed the particular model of electron randomization to describe collisional relaxation within the $^2P_{1/2}$ excited state. While that model should provide an excellent description of the relaxation process throughout the range of buffer-gas pressures most commonly encountered in optical-pumping experiments, it certainly will fail at buffer-gas pressures high enough that $\Delta W/h \ll \Gamma_1$, where ΔW is the energy separation between hyperfine states in the $^2P_{1/2}$ state. In such a case little collisional reorientation of the nuclear spin would occur during the excited-state lifetime, and the repopulation rates of $\langle S_z\rangle_g$ and $\langle I_z\rangle_g$ would be modified. Modifications also would arise if relaxation within the $^2P_{1/2}$ state were dominated by the formation of molecular complexes rather than by binary collisions. The effects of both processes on optical-pumping transients are easily calculated, but lie outside the scope of this paper.

DISCUSSION

Many earlier discussions of optical-pumping rate equations have provided theoretical and experimental bases from which the analytic solutions presented in this paper have evolved.[1,4,6,7,11–18,22–44] Our main contribution in the present paper has been the proper inclusion of the effect of excited-state interactions on determining the shape of ground-state pumping transients. The analytic forms we find for the pumping transients are consistent with the general forms of relaxation transients observed and evaluated by Bouchiat, Gibbs, and others.[12,13,16,28,30,38] Extensive comparisons of the present work with other earlier work are of limited interest, however. Some earlier papers made use of convenient assumptions which we now realize do not correspond to physical reality: The approximation of "uniform" relaxation in alkali–buffer-gas collisions is an example. In other cases, rate equations were solved numerically only in the limit of large pumping-rate–to–relaxation-rate ratios, the regime the opposite of that in which our calculations are valid. Even in those cases where the mechanics of ground-state relaxation were correctly treated and where small pumping-rate–to–relaxation-rate ratios were considered, calculations generally were performed only in the limits of zero or complete mixing in the excited state.

There is previous work on optical-pumping transients that merits special attention. In 1965 Marrus and Yellin measured double-exponential transients in the optical pumping of Rb^{87} and Cs^{133} in the presence of buffer gases.[43,44] They also performed extensive computer evaluations of the pumping equations. Our weak-pumping calculations do not apply to the experiment performed by Marrus and Yellin. Marrus and Yellin worked in the strong-pumping regime: They were concerned with pumping rates generally one to two orders of magnitude greater than ground-state relaxation rates. Moreover, the cause of the double-exponential behavior of the pumping transients in the strong-pumping limit postulated by Marrus and Yellin is fundamentally different from the cause for the double-exponential behavior in the weak-pumping limit. We shall expand on this point below.

In the weak-pumping limit we have obtained—rigorously, within the stated approximations—analytic forms for the pumping transients, and have shown that double-exponential transients occur only if at least some degree of electron randomization relaxation occurs in the ground state. While excited-state interactions influence the relative contributions of the two exponentials to the pumping transient, they do not in themselves induce the double-exponential behavior. In the strong-pumping limit the pumping transients, even in the absence of a buffer gas, are only accidentally and fortuitously approximated by a simple analytic function; the rigorous solutions are sums of exponentials.[43] The complexity of the problem in the strong-pumping limit can be appreciated by reference to Eqs. (5) and (7). For weak optical pumping the magnitudes of the terms $A\sum_i n_i\langle S_z\rangle_{gi}^2$ and $A\sum_i n_i\langle S_z\rangle_{gi}\langle I_z\rangle_{gi}$ remain essentially constant throughout the pumping process. In the strong-pumping regime the magnitudes of these terms change markedly as the spin polarization of the vapor approaches the optically pumped equilibrium: The pump rate itself varies as a function of time. Calculations in the latter situation obviously can be carried out only numerically with the aid of a computer. Marrus and Yellin performed such calculations and attributed the appearance of a second effective exponential to modifications of optical-pumping probabilities induced by collisional relaxation in the excited state. They obtained this result even with the assumption of uniform relaxation in the ground state. Marrus and Yellin thus predicted a cause for the appearance of double-exponential pumping transients which is quite different from that demonstrated by us. The two predictions are not necessarily contradictory, however, since they describe two quite different pumping regimes.

The analytic solutions that we have derived provide insight into the shape of the pumping transients at low buffer-gas pressure, i.e., in the regime where wall relaxation dominates other relaxation processes. They help to explain why many earlier measurements of the collisional relaxation of $\langle S_z\rangle_g$ in the alkalis resulted in misleading determinations of cross sections and diffusion coefficients.[1,29] At low buffer-gas pressures the two relaxation rates z_1 and z_2 approach a common value. The pumping transient then can be approximated by a single exponential. It is not clear, however, without reference to the analytic solutions, to what degree the residual buffer-gas relaxation contributes to this "effective" single-exponential relaxation rate. Equations (34a)–(34c) and Fig. 3 show that, in fact, the "fast" buffer-gas relaxation rate R rather than the "slow" relaxation rate $2R/(2I+1)^2$ predominates in this pressure regime. At low pressures, therefore, the nuclear spin has virtually no "slowing" effect on the ground-state collisional relaxation rate. The effective single-exponential relaxation rate measured at low pressures thus is z_2, consisting of a major contribution from the fast relaxation rate in alkali–buffer-gas binary collisions. "Sticky" collisions also may contribute. At high pressures, of course, both slow and fast relaxation rates arising from binary collisions are much in evidence through the appearance of the double-exponential nature of the transient. Considering the relatively sluggish shutters used in the early experiments, it seems clear that at high pressures only the slow relaxation rate z_1 was measured, with z_2 being neglected. At intermediate pressures the measured relaxation rate was an effective average of z_1 and z_2. The early analyses thus not only neglected nuclear-spin effects, but also suffered from the then unknown fact that the very nature of the relaxation transient changed as a function of buffer-gas pressure. The result was the determination of anomalously high values for diffusion coefficients and values for relaxation cross sections that were neither as large as the nuclear-spin-independent cross section σ nor as small as $2\sigma/(2I+1)^2$. Difficulties such as these can be overcome either through utilization of techniques such as those discussed in this paper, or by measurements of the single-exponential relaxation of $\langle\vec{S}\cdot\vec{I}\rangle$ such as those performed by Beverini *et al.*[30]

Finally, we wish to show that earlier computer calculations of ground-state occupation probabilities made in particular limits of weak optical pumping are consistent with the analytic solutions obtained in this paper.[14] The analytic solutions for $\langle S_z\rangle_{g\,\mathrm{eq}}$ are obtained directly from the formulas derived in the previous sections. For the specific case of $I=\frac{3}{2}$ we obtain Eq. (35):

$$\langle S_z\rangle_{g\,\mathrm{eq}}=\{[\tfrac{1}{16}A+\tfrac{1}{36}A(3\Gamma_1\tau-1)(1+\Gamma_1\tau)^{-1}(8+\Gamma_1\tau)^{-1}]\,[\tfrac{1}{3}A+\tfrac{1}{8}R+R'+R'']+(\tfrac{1}{8}R)[\tfrac{5}{48}A+\tfrac{25}{36}A(8+\Gamma_1\tau)^{-1}]\}$$
$$\times(\tfrac{1}{3}A+R+R'+R'')^{-1}(\tfrac{1}{3}A+\tfrac{1}{8}R+R'+R'')^{-1}. \qquad (35)$$

Equation (35) is a cumbersome expression which depends upon all possible relaxation processes. We shall discuss two limiting cases. Consider first the case in which R, the rate for electron randomization relaxation, dominates all other relaxation processes. In this limit we obtain Eq. (36):

$$\langle S_z\rangle_{g\,\mathrm{eq}}=(A/R)[\tfrac{1}{6}+\tfrac{1}{36}(24+28\Gamma_1\tau)^{-1}(8+\Gamma_1\tau)^{-1}]\,. \qquad (36)$$

We have plotted Eq. (36), together with similar expressions for $I=\frac{5}{2}$ and $I=\frac{7}{2}$ in Fig. 4 as a function of $\Gamma_1\tau$, thus displaying, for fixed pumping-rate–to–ground-state-relaxation-rate ratio, the dependence of $\langle S_z\rangle_{g\,\mathrm{eq}}$ upon relaxation rate in the excited state. The ratio of the spin polarizations obtained in the limits of zero and complete excited-state mixing, for $I=\frac{3}{2}$, in this case is 1.50. In the upper half of Table I we present extrapolated values of equilibrium-state populations, calculated earlier by computer,[14] for the same combination of pumping and relaxation mechanisms. The ratio of the spin polarizations obtained in the limits of zero and complete excited-state mixing in this computer calculation yields the identical result of 1.50. As a second example, consider the case in which R',

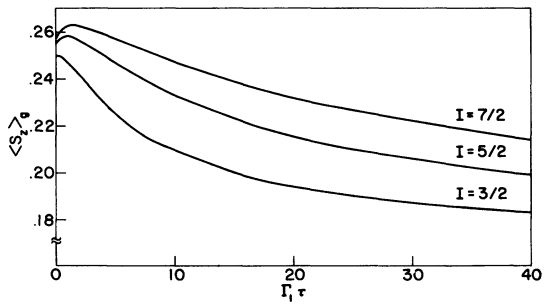

FIG. 4. Dependence of the ground-state equilibrium electron-spin polarization $\langle S_z\rangle_{g\,\mathrm{eq}}$ on relaxation rate within the excited state. Electron randomization relaxation in the ground state has been assumed and, for the purpose of this plot, has been assumed to be of equal magnitude at all values of $\Gamma_1\tau$.

TABLE I. Numerically calculated excess populations $(n_i - \frac{1}{8})$ for ground state $|F, m_F\rangle$ sublevels of $I = \frac{3}{2}$ alkali-metal atoms subject to weak optical pumping plus electron randomization relaxation (E-R) or uniform relaxation (U) in the ground state (Ref. 14). $\Gamma_1 = 0$ corresponds to no mixing in the excited state; $\Gamma_1 = \infty$ corresponds to complete mixing. The computer-generated results summarized here are fully consistent with the analytic solutions for $\langle S_z \rangle_g$ obtained in the present paper (see text).

	$\|2,2\rangle$	$\|2,1\rangle$	$\|2,0\rangle$	$\|2,-1\rangle$	$\|2,-2\rangle$	$\|1,1\rangle$	$\|1,0\rangle$	$\|1,-1\rangle$
E-R, $\Gamma_1 = 0$	2Δ	Δ	0	$-\Delta$	-2Δ	1.4Δ	0	-1.4Δ
E-R, $\Gamma_1 = \infty$	1.2Δ	0.6Δ	0	-0.6Δ	-1.2Δ	0.6Δ	0	-0.6Δ
U, $\Gamma_1 = 0$	$2.34\Delta'$	$1.17\Delta'$	0	$-1.17\Delta'$	$-2.34\Delta'$	$0.17\Delta'$	0	$0.17\Delta'$
U, $\Gamma_1 = \infty$	$2\Delta'$	Δ'	0	$-\Delta'$	$-2\Delta'$	$-\Delta'$	0	Δ'

uniform relaxation, is dominant. Equation (35) then reduces to Eq. (37):

$$\langle S_z \rangle_{g\,eq} = (A/R')[\tfrac{1}{16} + \tfrac{1}{36}(3\Gamma_1\tau - 1)(1+\Gamma_1\tau)^{-1}(8+\Gamma_1\tau)^{-1}] \,. \tag{37}$$

The ratio of limiting values of $\langle S_z \rangle_{g\,eq}$ for zero and complete excited-state mixing in this case is 0.95. Extrapolations of the computer calculations of the equilibrium-state populations for uniform ground-state relaxation subject to zero or complete excited-state mixing are listed in the lower half of Table I. These values yield 0.95 for the ratio of the electronic-spin polarizations in the limits of zero and complete excited-state mixing, wholly in agreement with the predictions of the analytic solutions.

EXPERIMENTAL RESULTS

We have measured and analyzed several hundred transient optical-pumping signals in Cs^{133}, utilizing filtered white light as the pumping source. Our measurements span a range of buffer-gas pressures from 0.5 to 500 Torr, and have been made at Cs vapor pressures as low as 2×10^{-7} Torr. In a future publication we shall give a complete description of our experimental method and results, together with an extension of the present calculations to include effects due to spin exchange. Here we give a brief description of the experimental technique and two specific examples of data in order to demonstrate experimentally the validity of our calculations and the utility of the techniques we have proposed.

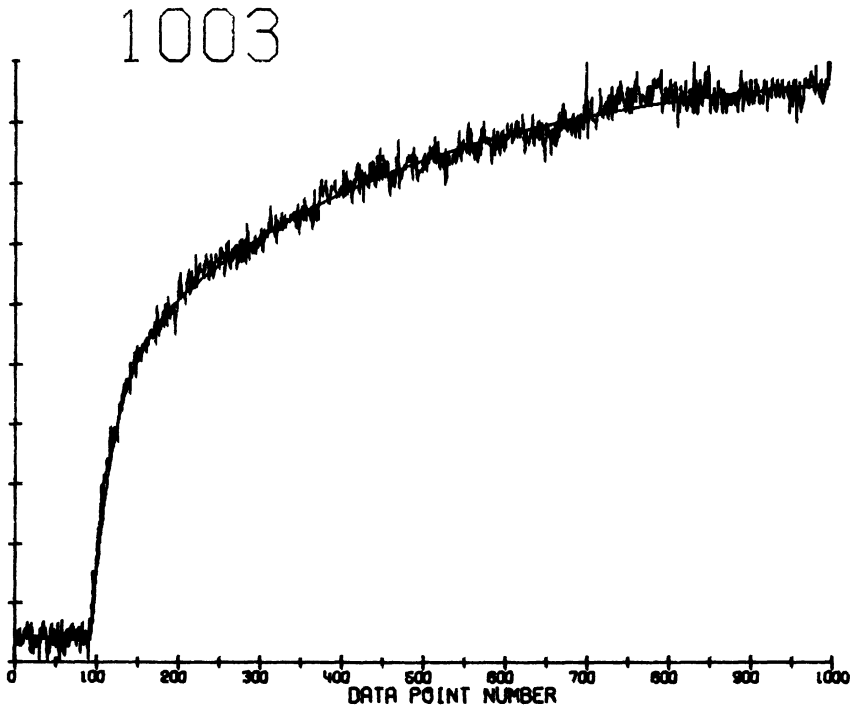

FIG. 5. Experimental optical-pumping transient and double-exponential fit for Cs^{133} in 400 Torr of He at 8°C from white-light optical pumping. The horizontal axis is 1.0 sec full scale.

Aside from our use of white light as the pumping source, our experimental technique is similar to that employed by Marrus and Yellin.[43] We induce pumping transients by pulsing off rf power resonant at the Cs Zeeman frequency. We observe the transients by monitoring the light transmitted through an uncoated cylindrical optical-pumping cell (length 7.4 cm, diameter 6.9 cm) incident on a photodetector connected through a preamplifier to a synchronously triggered Hewlett Packard signal averager. Since the transient is of the order of 10^{-4} to 10^{-6} of the total transmitted light intensity, many sweeps, typically 2^{12} to 2^{15}, of the experimental signal are necessary to achieve optimur reduction of noise. The experimental signals that we display in Figs. 5 and 6 are among the poorer ones that we have obtained. We have chosen to discuss them because they lie at the extremes of very low and very high buffer-gas pressures and because by virtue of their relatively high relaxation rates they are least affected by spin exchange.

We have shown in earlier sections that in the weak-pumping limit optical-pumping transients should in general consist of the sum of two exponentials. At high buffer-gas pressures, where electron randomization relaxation is dominant, the double-exponential behavior should be quite pronounced. In Fig. 5 we display an actual experimental measurement of a pumping transient for Cs in 400 Torr of He at 8°C, as reproduced from digitized data by a Calcomp plotter. For clarity of display the contents of the 1000 data channels have been connected serially by straight lines rather than plotted as points. The horizontal axis corresponds to 1.0 sec full scale. The solid curve represents a computer-generated least-squares fit of a double-exponential function, Eq. (27a), to the experimental data. For this particular curve the following values of parameters have been evaluated: $z_1 = 2.88\ \text{sec}^{-1}$, $z_2 = 39.9\ \text{sec}^{-1}$, $D_1/D_2 = 1.20$. The averages and standard deviations of five such determinations yield the following results: $z_2 - z_1 = 41.7 \pm 5.7\ \text{sec}^{-1}$, and $D_1 z_1 / D_2 z_2 = 0.094 \pm 0.006$. In our calculations in this paper we have ignored effects arising from spin exchange and rapid destruction of possible molecular complexes, and we shall continue to do so for the purpose of this demonstration: At 400 Torr of He and at 8°C such effects are relatively minor. Utilizing Eq. (33c) and the experimental value for $z_2 - z_1$ given above, we find that the nuclear-spin-independent cross section for the collisional relaxation of $\langle S_z \rangle$ in the $^2S_{1/2}$ ground state of Cs is 2.8×10^{-23} cm^2, in good agreement with the measurement of 2.8×10^{-23} cm^2 reported by Beverini *et al.*[30] for the relaxation of $\langle \vec{S} \cdot \vec{I} \rangle$. These two cross sections should be equal, according to theory. A more complete analysis of the data including the effects which we have ignored reduces the value of our cross section somewhat. The experimental value of 0.094 for $D_1 z_1 / D_2 z_2$, through Eq. (34c), leads to the determination of $\Gamma_1 \tau = 40$ at 400 Torr of He.

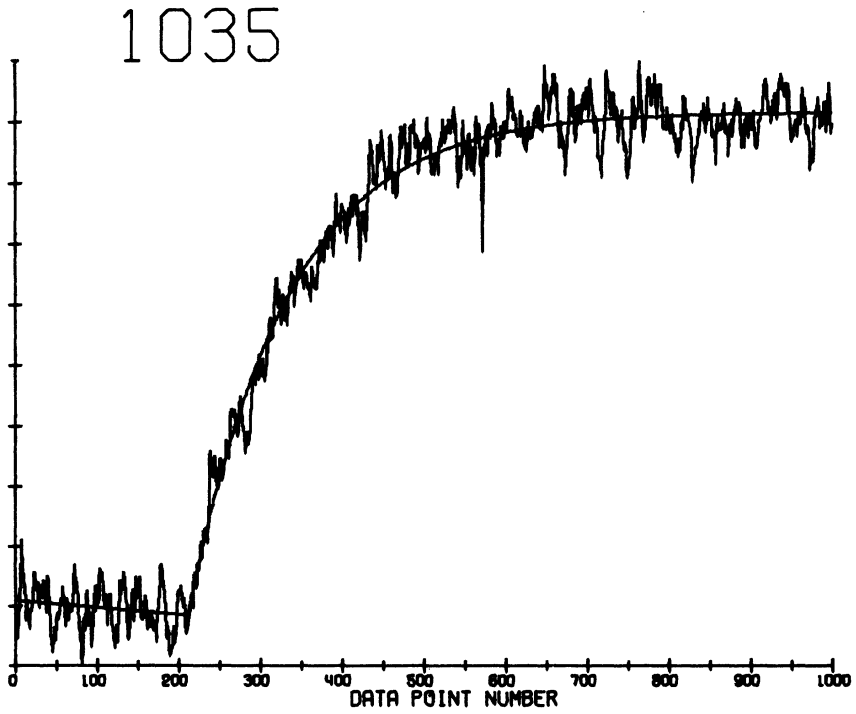

FIG. 6. Experimental optical-pumping transient and single-exponential fit for Cs^{133} in 1.00 Torr of He at 15°C from white-light optical pumping. The horizontal axis is 50 msec full scale.

Taking τ to be 3.4×10^{-8} sec,[45] we find σ_1, the nuclear-spin-independent cross section for the destruction of $\langle J_z\rangle$ in the $^2P_{1/2}$ state of Cs, to be 7×10^{-16} cm^2. This measurement may be compared with the value of 11.8×10^{-16} cm^2 determined by Guiry and Krause[46] using a Zeeman scanning technique at 10 kG and the value of 6.1×10^{-16} cm^2 reported by Bulos and Happer[21] reanalyzing Gallagher's low-magnetic-field Hanle-effect measurement.[47] We consider our determination of σ_1 to be quite rough at the present time: More data is required for a firm determination of this parameter by our technique.

Our calculations predict that at low buffer-gas pressures, where uniform relaxation is dominant, the relaxation rates of the two exponentials in the optical-pumping transient should approach equality, with the pumping transient becoming effectively a single exponential. We demonstrate this effect experimentally in Fig. 6, where we present data taken at 15°C, 1.00 Torr of He. The horizontal axis is 50 msec full scale. The evaluated relaxation rate of the fitted single-exponential curve is 166 sec^{-1}. The average and standard deviation of four such measurements is 171 ± 4 sec^{-1}. Utilizing Franzen's approximation,[26,31] we obtain a value of $D_0=0.33$ for Cs in He at 15°C. Assuming a quadratic dependence of D_0 upon temperature, we obtain a value of 0.30 at 0°C. Measurements at 8°C and at other low pressures lead to essentially the same result. These determinations may be compared to the value of 0.21 reported by Beverini *et al.*[30]

In summary, the analytic expressions derived in this paper constitute the most complete description of the mechanics of the optical pumping of alkali-metal vapors presently available. They include to a high degree of accuracy the effects of all important relaxation mechanisms both in the ground and excited states. They provide new metnods for the determination of relevant cross sections for collisional relaxation. Coupled with the utilization of white-light optical-pumping techniques, they provide a means for unraveling or bypassing many earlier ambiguities which have obscured a full and accurate understanding of the collisional relaxation of electronic-spin polarization.

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†Alfred P. Sloan Fellow.

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[10]This representation is correct only if the hyperfine period is shorter than both the lifetime of the excited state and the mean time between relaxation collisions. More general expressions for the repopulation rates can be derived in terms of $\langle J_z\rangle_F$, the expectation value of J_z within a particular hyperfine state of the excited state.

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