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Relative transition probabilities in deexcitation of atomic states by collisional quenching: Cs $6\,^2P_{1/2} \rightarrow 6\,^2S_{1/2}$†

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Nuclear-spin-independent relative probabilities for quenching-induced transitions between the Zeeman sublevels of the $6\,^2P_{1/2}$ and $6\,^2S_{1/2}$ states of Cs have been measured in a new application of optical pumping. The results for Cs-N_2 collisions at 15 °C are $K_1(^2P_{1/2} \rightarrow {}^2S_{1/2}, \Delta m_J = 0) = 0.56 \pm 0.06$, and $K_2(^2P_{1/2} \rightarrow {}^2S_{1/2}, \Delta m_J = \pm 1) = 0.44 \pm 0.06$. The theoretical analysis includes a full treatment of the effect of the hyperfine interaction on relative quenching probabilities, yielding probabilities for $|F', m_{F'}\rangle \rightarrow |F, m_F\rangle$ transitions parametrized in terms of K_1 and K_2. Full solutions to the pumping equations require knowledge of individual populations of excited-state sublevels: Appropriate analytic solutions for these populations have been calculated in the weak-pumping limit. The experimental results indicate that quenching collisions modify atomic de-excitation probabilities in ways which enhance the efficiency of optical pumping.

I. INTRODUCTION

Although extensive literature exists on quenching interactions, atomic collisions which involve the radiationless transfer of energy from excited states of atoms to various degrees of freedom of molecules, virtually nothing is known concerning the effect of these interactions upon the quenched atoms themselves.[1,2] Relative quenching transition probabilities connecting the Zeeman sublevels of excited and ground atomic states have never been measured: The observables in traditional experiments do not depend upon the particular paths by which atoms return to the ground state. In this paper we investigate quenching-induced transitions, with particular emphasis on the practically important case of $^2P_{1/2} \rightarrow {}^2S_{1/2}$ quenching of alkali-metal atoms. We calculate the effect of the hyperfine interaction on this process. We define nuclear-spin-independent $|J', m_{J'}\rangle \rightarrow |S, m_S\rangle$ transition probabilities and parametrize $|F', m_{F'}\rangle \rightarrow |F, m_F\rangle$ transition probabilities in terms of them. We show that the repopulation rates of the electronic and nuclear spin polarizations of an alkali-metal vapor undergoing optical pumping depend rather strongly upon the routes for deexcitation from the excited state. We exploit this dependence to determine the relative transition probabilities in $6\,^2P_{1/2} \rightarrow 6\,^2S_{1/2}$ quenching of Cs by N_2 from experimental measurements of pumping transients in white-light optical pumping of Cs. Our results indicate that quenching modifies atomic deexcitation in ways which enhance the efficiency of optical pumping.

II. RELATIVE PROBABILITIES FOR ATOMIC DEEXCITATION BY QUENCHING

We wish to investigate the relative probabilities by which an atom initially in a well-defined Zeeman sublevel of an atomic excited state can undergo quenching transitions to the various Zeeman sublevels of the ground state. We are particularly interested in quenching from the lowest-lying P states of a heavy alkali-metal atom to the S ground state. We therefore restrict our discussion to situations in which quenching occurs between electronic states of well-defined angular momentum $\vec{J}$, and in which the excited state is reasonably well separated in energy from other excited states. The question immediately arises whether the effects of the quenching interaction should be viewed from a $|J, m_J\rangle$ or a $|m_l, m_s\rangle$ basis within the excited state. The answer depends primarily upon the duration τ^* of the quenching interaction relative to the fine-structure period τ_F. If τ^* is long compared to τ_F, $\vec{L}$ and $\vec{S}$ remain effectively coupled during the interaction, and the $|J, m_J\rangle$ basis is appropriate. For the heavy alkalies such as Rb and Cs, the duration of an alkali-atom–buffer-gas-atom binary collision is of the order of 10^{-12} sec, while τ_F is of the order of 10^{-13} sec. It is clear that the $|J, m_J\rangle$ basis is the most appropriate in the present situation, provided that τ^* can be taken as roughly equal to the duration of the collision.

In the absence of nuclear spin, the relative probabilities $P_Q(J', m_{J'} \rightarrow S, m_S)$ connecting the $|J', m_{J'}\rangle$ sublevels of the excited state with the $|S, m_S\rangle$ sublevels of the ground state are defined by Eq. (1):

$$P_Q(J', m_{J'} \rightarrow S, m_S) = \frac{|\langle S, m_S|Q|J', m_{J'}\rangle|^2}{\sum_{S, m_S}|\langle S, m_S|Q|J', m_{J'}\rangle|^2}, \quad (1)$$

where Q is the quenching operator. For $^2P_{1/2} \rightarrow {}^2S_{1/2}$ quenching we shall define

$$\frac{|\langle S, m_S|Q|J', m_{J'}\rangle|^2}{\sum_{S, m_S}|\langle S, m_S|Q|J', m_{J'}\rangle|^2} = \begin{cases} K_1 & (\Delta m_J = 0) \\ K_2 & (\Delta m_J = \pm 1), \end{cases} \quad (2)$$

and shall utilize the normalization

$$\sum_{S, m_S} |\langle S, m_S | Q | J', m_{J'}\rangle|^2 = (K_1 + K_2) = 1 \,. \tag{3}$$

K_1 and K_2 as defined above are the nuclear-spin-independent relative transition probabilities for quenching.

We now shall consider the role that the relative transition probabilities K_1 and K_2 play in describing quenching in the presence of a hyperfine $(\vec{J}\cdot\vec{I})$ interaction between the electronic magnetic moment and the nuclear spin. We wish to calculate relative quenching probabilities from a well-defined $|F', m_{F'}\rangle$ sublevel of the excited state to a well-defined $|F, m_F\rangle$ sublevel of the ground state. The relative probability $P(F', m_{F'} \to F, m_F)$ for such a transition, is given by Eq. (4):

$$P_Q(F', m_{F'} \to F, m_F) = \frac{|\langle F, m_F | Q | F', m_{F'}\rangle|^2}{\sum_{F, m_F} |\langle F, m_F | Q | F', m_{F'}\rangle|^2} \,. \tag{4}$$

We assume, in analogy with the highly successful model for treating the effect of the hyperfine interaction on electron spin relaxation, that the quenching collision is sudden, that is, that the quenching interaction temporarily decouples the electronic angular momentum from the nuclear spin, and that the nuclear spin does not experience significant reorientation during the collision.[3] We thus have the following representation for the numerator of Eq. (4):

$$|\langle F, m_F | Q | F', m_{F'}\rangle|^2 = \left| \sum_{m_{I'}} C^{I' \, S \, F}_{m_{I'} m_S m_F} C^{I' \, J' \, F'}_{m_{I'} m_{J'} m_{F'}} \times \langle S, m_S | Q | J', m_{J'}\rangle \right|^2 . \tag{5}$$

Since the exact form of the quenching operator Q is unknown, we cannot predict the phases of $\langle S, m_S | Q | J', m_{J'}\rangle$. We shall be dealing with an experimental situation equivalent to a statistical average over many quenching events and one in which quenched atoms are subject to further collisional relaxation upon reaching the ground state. We make the assumption that in this circumstance we may take the phases as effectively random, and average over them, removing cross products in Eq. (5). Since the orthonormality relations for Clebsch-Gordan coefficients reduce the denominator of Eq. (4) to $K_1 + K_2$ $(=1)$, we obtain, for ${}^2P_{1/2} \to {}^2S_{1/2}$ quenching,

$$P_Q(F', m_{F'} \to F, m_F) = \sum_{m_{I'}} \left(C^{I' \, S \, F}_{m_{I'} m_S m_F} C^{I' \, J' \, F'}_{m_{I'} m_{J'} m_{F'}}\right)^2 \times (K_1 \delta_{m_F, m_{F'}} + K_2 \delta_{m_F, m_{F'} \pm 1}) \,. \tag{6}$$

TABLE I. Relative probabilities for quenching-induced transitions between $|F', m_{F'}\rangle$ sublevels of the $\mathrm{Cs}(I=\frac{7}{2})$ ${}^2P_{1/2}$ state and the $|F, m_F\rangle$ sublevels of the ${}^2S_{1/2}$ state. All elements have been multiplied by 64. K_1 and K_2 are defined by Eq. (2).

	4′,4′	4′,3′	4′,2′	4′,1′	4′,0′	4′,−1′	4′,−2′	4′,−3′	4′,−4′	3′,3′	3′,2′	3′,1′	3′,0′	3′,−1′	3′,−2′	3′,−3′
4, 4	$64K_1$	$8K_2$								$56K_2$						
4, 3	$8K_2$	$50K_1$	$14K_2$							$14K_1$	$42K_2$					
4, 2		$14K_2$	$40K_1$	$18K_2$						$2K_2$	$24K_1$	$30K_2$				
4, 1			$18K_2$	$34K_1$	$20K_2$						$6K_2$	$30K_1$	$20K_2$			
4, 0				$20K_2$	$32K_1$	$20K_2$						$12K_2$	$32K_1$	$12K_2$		
4, −1					$20K_2$	$34K_1$	$18K_2$						$20K_2$	$30K_1$	$6K_2$	
4, −2						$18K_2$	$40K_1$	$14K_2$						$30K_2$	$24K_1$	$2K_2$
4, −3							$14K_2$	$50K_1$	$8K_2$						$42K_2$	$14K_1$
4, −4								$8K_2$	$64K_1$							$56K_2$
3, 3	$56K_2$	$14K_1$	$2K_2$							$50K_1$	$6K_2$					
3, 2		$42K_2$	$24K_1$	$6K_2$						$6K_2$	$40K_1$	$10K_2$				
3, 1			$30K_2$	$30K_1$	$12K_2$						$10K_2$	$34K_1$	$12K_2$			
3, 0				$20K_2$	$32K_1$	$20K_2$						$12K_2$	$32K_1$	$12K_2$		
3, −1					$12K_2$	$30K_1$	$30K_2$						$12K_2$	$34K_1$	$10K_2$	
3, −2						$6K_2$	$24K_1$	$42K_2$						$10K_2$	$40K_1$	$6K_2$
3, −3							$2K_2$	$14K_1$	$56K_2$						$6K_2$	$50K_1$

We give the explicit form of the P_Q matrix for Cs ($I=\frac{7}{2}$) in Table I. We note that with the normalization in Eq. (3), all elements in the P_Q matrix can be reduced to functions of the single parameter K_1.

III. EFFECT OF QUENCHING ON OPTICAL PUMPING

The generation of spin polarization in optical pumping depends upon depopulation pumping (absorption of light), collisional relaxation within the excited state, repopulation pumping (deexcitation from the excited state), and various modes of relaxation within the ground state. All of these contributions to the pumping process have been considered in detail in previous publications dealing with the comprehensive rate equations for the weak $\sigma^+ D_1$ optical pumping of alkali-metal vapors. It has been shown that[4,5]

$$\langle \dot{S}_z\rangle_g = B_1 - B_2\langle S_z\rangle_g + B_3\langle I_z\rangle_g\,, \qquad (7a)$$

$$\langle \dot{I}_z\rangle_g = C_1 - C_2\langle I_z\rangle_g + C_3\langle S_z\rangle_g\,, \qquad (7b)$$

where for Cs,

$$C_1 = \tfrac{21}{192}A + \tfrac{161}{48}A(\Gamma_1\tau + 32)^{-1}\,, \qquad (8a)$$

$$B_1 = \tfrac{11}{192}A + \tfrac{1}{144}A(-67+13\Gamma_1\tau)(\Gamma_1\tau+32)^{-1}(\Gamma_1\tau+1)^{-1}\,, \qquad (8b)$$

$$C_2 = \tfrac{1}{3}A + \tfrac{1}{32}R + R' + R'' + \tfrac{1}{32}R_s\,, \qquad (8c)$$

$$B_2 = \tfrac{1}{3}A + R + R' + R'' + \tfrac{21}{32}R_s\,, \qquad (8d)$$

$$C_3 = \tfrac{21}{32}R_s\,, \qquad (8e)$$

$$B_3 = \tfrac{1}{32}R_s + \tfrac{1}{32}R\,. \qquad (8f)$$

In the equations above, A is the pumping rate, Γ_1 is the nuclear-spin-independent rate for collisional relaxation of $\langle J_z\rangle$ in the $^2P_{1/2}$ state, τ is the mean lifetime of the $^2P_{1/2}$ state, R is the nuclear-spin-independent rate for relaxation of $\langle S_z\rangle_g$ in the ground state due to binary Cs–buffer-gas-atom collisions, R'' is the effective relaxation rate due to Cs collisions with the walls of the experimental cell, R' is the relaxation rate due to "sticky" or molecular-complex-forming collisions of Cs atoms with buffer-gas atoms, and R_s is the Cs-Cs spin-exchange rate. More specifically,

$$\Gamma_1 = n_0\sigma_1 v_{\rm rel}\, p/p_0\,, \qquad (9a)$$

$$R = n_0\sigma v_{\rm rel}\, p/p_0\,, \qquad (9b)$$

$$R'' = [(\pi/L)^2 + (2.405/r)^2]D_0 p_0/p\,, \qquad (9c)$$

$$R_s = n_0\sigma_s V_{\rm Cs\text{-}Cs}\, p({\rm Cs})/p_0\,, \qquad (9d)$$

where σ_1 is the nuclear-spin-independent cross section for the destruction of $\langle J_z\rangle$ in Cs–buffer-gas-atom collisions, $v_{\rm rel}$ is the mean relative velocity of Cs atoms and buffer-gas atoms, p is the buffer-gas pressure, σ is the nuclear-spin-independent cross section for the destruction of $\langle S_z\rangle_g$ in binary Cs–buffer-gas-atom collisions, L and r are the length and radius of the (cylindrical) cell, D_0 is the diffusion coefficient of Cs in the buffer gas, σ_s is the nuclear-spin-independent cross section for Cs-Cs spin exchange, and $v_{\rm Cs\text{-}Cs}$ is the mean relative velocity of Cs atoms.

Equations (7a) and (7b) yield the following solution for $\langle S_z\rangle_g(t)$, assuming that $\langle S_z\rangle_g = 0$ at $t=0$:

$$\langle S_z\rangle_g(t) = D_1(1-e^{-Z_1 t}) + D_2(1-e^{-Z_2 t})\,, \qquad (10)$$

where

$$D_1 = \frac{B_3C_1Z_2 + B_1C_2Z_2 - B_1B_2C_2 + B_1B_3C_3}{[B_2C_2 - B_3C_3][Z_2 - Z_1]}\,, \qquad (11a)$$

$$D_2 = \frac{B_1B_2C_2 - B_1B_3C_3 - B_3C_1Z_1 - B_1C_2Z_1}{[B_2C_2 - B_3C_3][Z_2 - Z_1]}\,, \qquad (11b)$$

$$Z_1 = \tfrac{1}{2}\{(B_2+C_2) - [(B_2-C_2)^2 + 4B_3C_3]^{1/2}\}\,, \qquad (12a)$$

$$Z_2 = \tfrac{1}{2}\{(B_2+C_2) + [(B_2-C_2)^2 + 4B_3C_3]^{1/2}\}\,. \qquad (12b)$$

Equations (7a)–(12b) also describe optical pumping subject to quenching, provided that the repopulation rates of $\langle S_z\rangle_g$ and $\langle I_z\rangle_g$ are properly reformulated. With the aid of Table I, we obtain the following equations for the repopulation rates due to quenching alone:

$$\begin{aligned}\langle \dot{S}_z\rangle_g|_{\rm repop\ quench} = {}& (512)^{-1}(\tau_q)^{-1}\{N(4',4')[256K_1 - 144K_2] + N(4',3')[108K_1 - 24K_2] + N(4',2')[32K_1 + 24K_2]\\ &+ N(4',1')[4K_1 + 24K_2] + N(4',-1')[-4K_1 - 24K_2] + N(4',-2')[-32K_1 - 24K_2]\\ &+ N(4',-3')[-108K_1 + 24K_2] + N(4',-4')[-256K_1 + 144K_2] + N(3',3')[-108K_1 + 216K_2]\\ &+ N(3',2')[-32K_1 + 104K_2] + N(3',1')[-4K_1 + 40K_2] + N(3',-1')[4K_1 - 40K_2]\\ &+ N(3',-2')[32K_1 - 104K_2] + N(3',-3')[108K_1 - 216K_2]\}\end{aligned} \qquad (13a)$$

$$\langle \dot{I}_z\rangle_g = (\tau_q)^{-1}(512)^{-1}\{N(4',4')[1792K_1+1680K_2]+N(4',3')[1428K_1+1176K_2]$$
$$+N(4',2')[992K_1+744K_2]+N(4',1')[508K_1+360K_2]+N(4',-1')[-508K_1-360K_2]$$
$$+N(4',-2')[-992K_1-744K_2]+N(4',-3')[-1428K_1-1176K_2]+N(4',-4')[-1792K_1-1680K_2]$$
$$+N(3',3')[1644K_1+1704K_2]+N(3',2')[1056K_1+1176K_2]+N(3',1')[516K_1+600K_2]$$
$$+N(3',-1')[-516K_1-600K_2]+N(3',-2')[-1056K_1-1176K_2]+N(3',-3')[-1644K_1-1704K_2]\}, \quad (13b)$$

where $N(F', m_{F'})$ represents the population of the $|F', m_{F'}\rangle$ sublevel of the $^2P_{1/2}$ excited state, and $(\tau_q)^{-1}$ is the rate for $^2P_{1/2} \to {}^2S_{1/2}$ quenching.

We stress the point that in order to calculate the effect of quenching upon the optical-pumping process, we must know the populations of the individual Zeeman sublevels of the excited state. Equations (13a) and (13b) thus constitute a situation very different from that encountered in normal optical pumping, where the repopulation rates of $\langle S_z\rangle_g$ and $\langle I_z\rangle_g$ are represented by linear combinations of the $N(F', m_{F'})$, which can be described conveniently in terms of $\langle J_z\rangle_e$ and $\langle I_z\rangle_e$, the quasiequilibrium values of the electronic and nuclear polarizations of the excited state.[4] Such a simplification does not occur when deexcitation occurs via quenching rather than via spontaneous emission. Our present need to know the populations of individual Zeeman sublevels implies the necessity of solving 16 simultaneous equations. Previous work fortunately points the way to an ansatz which yields these solutions in the weak-pumping limit. We proceed below to calculate expressions for the quasi-equilibrium values of $N(F', m_{F'})$ subject simultaneously to excitation, relaxation, and deexcitation.

The three primary mechanisms for transfer of alkali atoms out of the $^2P_{1/2}$ state are spontaneous decay to the $^2S_{1/2}$ state, collisional quenching to the $^2S_{1/2}$ state, and collisional transfer to the $^2P_{3/2}$ state. While the rates of these processes determine the effective lifetime, and ultimately the equilibrium population of the $^2P_{1/2}$ state, they have no influence on the relative distribution of population throughout the Zeeman sublevels of that state: Each interaction acts equivalently on all sublevels. On the other hand, relative excitation probabilities and collisional relaxation within the $^2P_{1/2}$ state act differently on different Zeeman sublevels, and thus determine the distribution of population throughout these sublevels, but play no role in determining the effective lifetime of the $^2P_{1/2}$ state. We consider the various interactions in turn.

1. Excitation. We make the following approximations and assumptions. (i) We neglect differences in populations of ground-state Zeeman sublevels, both in thermal equilibrium and in optical pumping. We thus restrict our calculations to the weak-pumping limit. (ii) We assume that the pumping light is of equal intensity over all components of the absorption line: We thus adopt the "white-light" approximation. (iii) We choose the normalization for the ground-state sublevel populations such that $\sum n(F, m_F) = 1$. Under these conditions, the rates of excitation of the $|F', m_{F'}\rangle$ sublevels of the $^2P_{1/2}$ state of Cs ($I = \frac{7}{2}$), in the order $(4', 4')$, $\ldots$, $(4', -4')$, $(3', 3')$, $\ldots$, $(3', -3')$, are $\frac{1}{192}A \times (8, 7, 6, 5, 4, 3, 2, 1, 0, 1, 2, 3, 4, 5, 6, 7)$, where A is the pumping rate.

2. Effective lifetime. We make the following definitions: τ is the natural lifetime of the $^2P_{1/2}$ state. τ_q is the inverse of rate for $^2P_{1/2} \to {}^2S_{1/2}$ quenching, $= (n_0\sigma_q v_{\rm rel} p/p_0)^{-1}$, where σ_q is the nuclear-spin-independent cross section for quenching. τ_J is the inverse of rate for $^2P_{1/2} \to {}^2P_{3/2}$ collisional transfer, $= n_0\sigma_J v_{\rm rel} p/p_0$, where σ_J is the nuclear-spin-independent cross section for collisional transfer from the $^2P_{1/2}$ state to the $^2P_{3/2}$ state. The effective lifetime τ' of the $^2P_{1/2}$ state is given by Eq. (14):

$$(\tau')^{-1} = (\tau)^{-1} + (\tau_q)^{-1} + (\tau_J)^{-1}. \quad (14)$$

Subject to the pumping scheme and normalizations described in 1 above, the total equilibrium population of the $^2P_{1/2}$ state is

$$N = \sum_{F', m_{F'}} N(F', m_{F'}) = \tfrac{1}{3}A\tau'. \quad (15)$$

3. Collisional relaxation. Collisions may lead to relaxation among the Zeeman sublevels of the $^2P_{1/2}$ state rather than to quenching or collisional transfer to other multiplets. The effect of such relaxation upon the optical-pumping process has been fully described in earlier publications.[4,5] From these publications and others we know that (i) at zero relaxation rate the relative populations must be in proportion to the excitation probabilities; (ii) at very high relaxation rates the relative populations must be equal; (iii) for *any* relaxation rate the relative populations must yield the expressions previously derived for the equilibrium electronic and nuclear spin polarizations of the $^2P_{1/2}$ state,

$$\langle J_z\rangle_e = \sum_k \frac{N_k\langle J_z\rangle_{ek}}{N} = \tfrac{1}{2}(11+\Gamma_1\tau)(32+\Gamma_1\tau)^{-1}(1+\Gamma_1\tau)^{-1}, \quad (15a)$$

$$\langle I_z\rangle_e=\sum_k \frac{N_k\langle I_z\rangle_{ek}}{N}=\tfrac{21}{2}(32+\Gamma_1\tau)^{-1}; \qquad (15b)$$

(iv) in weak optical pumping, the distribution of population throughout the individual sublevels of the $^2P_{1/2}$ state should closely parallel the distribution of population found within the sublevels of the $^2S_{1/2}$ ground state. Previous computer calculations have shown for electron randomization relaxation (the correct model for relaxation in alkali-buffer-gas binary collisions) that the "excess" populations of ground-state sublevels are, in the order (4, 4), ..., (3, −3), (4δ), (3δ), (2δ), (δ), (0), $(-\delta)$, (-2δ), (-3δ), (-4δ), $(3\delta')$, $(2\delta')$, (δ'), (0), $(-\delta')$, $(-2\delta')$, $(-3\delta')$, where δ and δ' are numbers small compared to 1.[6]

Combining conditions (i)–(iv), we find that the individual populations of the Zeeman sublevels of the $^2P_{1/2}$ state are given by Table II, where

$$\Delta=\Gamma_1\tau'(25+\Gamma_1\tau')(1+\Gamma_1\tau')^{-1}(32+\Gamma_1\tau')^{-1}, \qquad (16a)$$

$$\Delta'=\Gamma_1\tau'(41+\Gamma_1\tau')(1+\Gamma_1\tau')^{-1}(32+\Gamma_1\tau')^{-1}. \qquad (16b)$$

We stress that these solutions apply *in general* to weak optical pumping; they are not restricted to optical pumping subject to quenching. Similar solutions are easily found for atoms with other nuclear spins.

With Table II, Eqs. (16a) and (16b), and the condition $K_1+K_2=1$, Eqs. (13a) and (13b) for the repopulation rates of $\langle S_z\rangle_g$ and $\langle I_z\rangle_g$ via quenching alone reduce to Eqs. (17a) and (17b):

$$\langle \dot S_z\rangle_g|_{\text{quench repop}}=A(3072)^{-1}(205K_1-92)+A\Gamma_1\tau'(3072)^{-1}(1+\Gamma_1\tau')^{-1}(32+\Gamma_1\tau')^{-1}(-6413K_1-205K_1\Gamma_1\tau'+3196+92\Gamma_1\tau'), \qquad (17a)$$

$$\langle \dot I_z\rangle_g|_{\text{quench repop}}=A(3072)^{-1}(147K_1+252)+A\Gamma_1\tau'(3072)^{-1}(1+\Gamma_1\tau')^{-1}(32+\Gamma_1\tau')^{-1}(-4179-147K_1\Gamma_1\tau'+1764-252\Gamma_1\tau'). \qquad (17b)$$

The repopulation rates of $\langle S_z\rangle_g$ and $\langle I_z\rangle_g$ via spontaneous emission (S.E.) alone have already been calculated, and appear in Eqs. (8a) and (8b). We repeat them here for comparison, taking cognizance of the fact that τ, the natural lifetime, must now be replaced by τ', the effective lifetime:

$$\langle \dot S_z\rangle_g|_{\text{S.E. repop}}=\tfrac{1}{144}A(13\Gamma_1\tau'-67)(1+\Gamma_1\tau)^{-1}\times(32+\Gamma_1\tau')^{-1}, \qquad (18a)$$

$$\langle \dot I_z\rangle_g|_{\text{S.E. repop}}=\tfrac{161}{48}A(32+\Gamma_1\tau')^{-1}. \qquad (18b)$$

The only contribution to repopulation rates which remains to be considered is that arising from transfer of atoms to the $^2P_{3/2}$ state, with subsequent decay to the $^2S_{1/2}$ state via spontaneous emission, quenching, or back transfer to the $^2P_{1/2}$ state. Atoms within the $^2P_{3/2}$ state are subject to rapid relaxation within that state: Typical cross sections are of the order of $10^{-14}\,\text{cm}^2$. It should be a good approximation to assume that on the average all polarization is lost by the time atoms suffer collisional transfer to the $^2P_{3/2}$ state, relaxation within that state, and return to the ground state. We therefore take the repopulation rates of $\langle S_z\rangle_g$ and $\langle I_z\rangle_g$ from this source to be equal to zero.

The total average repopulation rates will be combinations of the various repopulation rates discussed above:

$$\langle \dot S_z\rangle_g|_{\text{repop}}=\alpha_{\text{S.E.}}\langle \dot S_z\rangle_g|_{\text{repop S.E.}}+\alpha_Q\langle \dot S_z\rangle_g|_{\text{repop quench}}+\alpha_J\langle \dot S_z\rangle_g|_{\text{repop coll trans}}, \qquad (19)$$

where

$$\alpha_{\text{S.E.}}=\tau'/\tau, \qquad (20a)$$

TABLE II. Theoretical populations of $|F', m_{F'}\rangle$ sublevels of $^2P_{1/2}$ excited state subject to weak $\sigma^+ D_1$ optical pumping, plus collisional relaxation, quenching, etc. Δ and Δ' are defined by Eqs. (16a) and (16b) in the text. All elements have been multiplied by $192(A\tau')^{-1}$.

$N(4',4')$	$N(4',3')$	$N(4',2')$	$N(4',1')$	$N(4',0')$	$N(4',-1')$	$N(4',-2')$	$N(4',-3')$	$N(4',-4')$
$8-4\Delta$	$7-3\Delta$	$6-2\Delta$	$5-\Delta$	4	$3+\Delta$	$2+2\Delta$	$1+3\Delta$	4Δ
	$N(3',3')$	$N(3',2')$	$N(3',1')$	$N(3',0)$	$N(3',-1')$	$N(3',-2')$	$N(3',-3')$	
	$1+3\Delta'$	$2+2\Delta'$	$3+\Delta'$	4	$5-\Delta'$	$6-2\Delta'$	$7-3\Delta'$	

$$\alpha_Q = \tau'/\tau_q , \tag{20b}$$

$$\alpha_J = \tau'/\tau_J . \tag{20c}$$

Quenching therefore affects the optical-pumping-rate equations only through modification of the terms B_1 and C_1 in Eqs. (8a) and (8b). These now become

$$B_1' = \tfrac{11}{192} A + \langle \dot{S}_z \rangle_g |_{\text{repop}} , \tag{21a}$$

$$C_1' = \tfrac{21}{192} A + \langle \dot{I}_z \rangle_g |_{\text{repop}} , \tag{21b}$$

with $\langle \dot{S}_z \rangle_g |_{\text{repop}}$ and $\langle \dot{I}_z \rangle_g |_{\text{repop}}$ defined as in Eq. (19).

A word of caution is in order. Throughout our description of the optical-pumping-rate equations here and elsewhere we have assumed that the various processes of depopulation pumping, collisional relaxation, and repopulation pumping are incoherent; that is, that they can be treated separately. We have neglected certain interference terms in the excitation process, which is an excellent approximation in general for Cs.[7,8] These interference terms become increasingly important, however, as the lifetime of the $^2P_{1/2}$ state is shortened. As a result, our calculations of repopulation rates cannot be extended to arbitrarily high pressures of a quenching gas. For Cs-N_2 we estimate the range of validity of our calculations to extend to approximately 100-Torr N_2.

IV. EXPERIMENTAL METHOD FOR THE DETERMINATION OF RELATIVE QUENCHING PROBABILITIES

The measurement of relative probabilities for quenching-induced transitions requires the monitoring of an observable which depends both upon the initial sublevel of the atom in the excited state and upon the final sublevel of the quenched atom in the ground state. Standard techniques for the measurement of total quenching cross sections involve observables such as the quenching-induced decrease in fluorescent light intensity, or the shortening of the excited-state lifetime, both of which are independent of the specific final states of the quenched atoms. The transfer of angular-momentum polarization from an excited state to a ground state, however, depends strongly upon the relative transition probabilities connecting initial and final sublevels. In Sec. III we calculated how various modes of this "repopulation pumping" contribute to the rate equations governing weak $\sigma^+ D_1$ optical pumping. In the present section we discuss somewhat further the effect of repopulation pumping upon optical-pumping transients, and show how experimental transient signals may be analyzed to determine the quenching relation probability parameter K_1.

The normal form of the $\langle S_z \rangle_g$ optical-pumping transient is given by Eq. (10). The measurable parameters are the rate constants Z_1 and Z_2, and the relative amplitudes D_1 and D_2. Z_1 and Z_2 depend solely upon ground-state relaxation processes, and hence are not of present interest. D_1 and D_2 depend upon all pumping and relaxation processes, including the effects of repopulation pumping, which are of interest to us. From Eq. (16) of Ref. 5 we obtain Eq. (22), the theoretical expression for the dimensionless ratio D_1/D_2, where we have replaced B_1 and C_1 by the modified parameters B_1' and C_1' calculated in Sec. III:

$$\frac{D_1}{D_2} = [-B_2 B_3 C_1' (B_2 - C_2) - B_3 C_3 (B_3 C_1' + B_1' B_2)] [(B_2 - C_2)(-B_1' B_2 C_2 + B_1' B_3 C_3 + B_3 C_1' C_2 + B_1' C_2^2) - B_3 C_3 (B_3 C_1' + B_1' C_2)]^{-1} . \tag{22}$$

We now shall show that the right-hand side of Eq. (22), despite its cumbersomeness, can be reduced with surprising ease and accuracy to a dependence upon K_1 alone: All other parameters can be fixed by independent measurement. First we note that B_3 and C_3 are calculable if σ and σ_S are known [see Eqs. (9)]. B_2 and C_2 then are calculable from the measured relaxation rates Z_2 and Z_1, using Eqs. (17a) and (17b) of Ref. 5. B_1' and C_1' are specified by Eqs. (21a) and (21b). Assuming that τ, σ_q, σ_J, and σ_1 are known, the only unknown parameters remaining are the pumping rate A and the quenching parameter K_1. Since A multiplies both B_1' and C_1', and since one of these parameters appears as a factor in each term of Eq. (22), A divides out, leaving K_1 as the only unknown parameter. An experimental measurement of D_1/D_2, inserted into Eq. (22), thus provides a determination of K_1. In Sec. V we report such determinations of K_1 from experimental measurements of optical-pumping transients of Cs in N_2.

V. EXPERIMENTAL RESULTS AND DISCUSSION

We have measured $\langle S_z \rangle_g$ pumping transients of Cs in various pressures of N_2 utilizing white-light optical pumping. The experimental technique and method of analysis were the same as described in earlier publications. We obtained the data listed in Table III. The following additional information is nesessary in order to extract experimental determinations of K_1 from the measured values of D_1/D_2:

$$\tau = 3.4 \times 10^{-8} \text{ sec (Ref. 9)}, \quad \sigma_q = 86 \text{ Å}^2 \text{ (Ref. 10)},$$

$$\sigma_J = 5.3 \text{ Å}^2 \text{ (Ref. 10)}, \quad \sigma_S = 2.2 \times 10^{-14} \text{ cm}^2 \text{ (Ref. 11)} .$$

TABLE III. Measured parameters of optical-pumping transients of Cs in N_2 at 15 °C and determinations of the quenching relative probability K_1. The two measurements at 20 Torr were made at significantly different light intensities. Determinations of K_1 from data at pressures of 100 Torr or greater would be invalid for reasons discussed in the text.

P (N_2) (Torr)	Z_1 ($\sec^{-1}$)	Z_2 ($\sec^{-1}$)	D_1/D_2	K_1
20.5	3.25 ± 0.47	35.4 ± 1.8	1.35 ± 0.07	0.53
20.0	3.91 ± 0.20	31.4 ± 0.2	1.20 ± 0.03	0.52
30.2	2.91 ± 0.45	45.6 ± 3.3	1.85 ± 0.16	0.54
40.0	3.15 ± 0.23	57.4 ± 3.2	2.01 ± 0.11	0.57
60.0	3.30 ± 0.05	72.8 ± 1.0	2.49 ± 0.04	0.64
100.3	4.14 ± 0.18	102.8 ± 8.7	2.57 ± 0.05	
151.9	5.62 ± 0.32	162.3 ± 0.2	2.73 ± 0.17	
250.3	7.88 ± 0.14	238.0 ± 8.0	3.03 ± 0.05	

Since σ_1 for Cs-N_2 at present is unknown, we are forced to make an approximation concerning the rate for collisional relaxation within the $^2P_{1/2}$ state: We shall take it to be zero. We have found by actual computation that the accuracy of our results depends very little on this assumption: σ_1 for Cs-N_2 would have to be greater than 75 Å^2 to change our evaluated values of K_1 by as much as 10%. (The change would act to decrease K_1.) The comparable cross sections for Cs-He and Cs-Ar are about 10 Å^2.[12] The reason for the weak dependence of our experimental results upon σ_1 is that because of the shortening of the $^2P_{1/2}$-state lifetime due to quenching, very little relaxation can occur prior to deexcitation, even if σ_1 is relatively large. The resultant determinations of K_1 are listed in the last column of Table III. They yield the result

$$K_1 = 0.56 \pm 0.06\,, \tag{23a}$$

$$K_2 = 0.44 \pm 0.06\,. \tag{23b}$$

The standard deviation of the various measurements of K_1 is 0.04. The uncertainties quoted in Eqs. (23a) and (23b) represent our best estimates of the possible error in K_1 and K_2, obtained by allowing the various parameters to vary over a reasonable range of probable error.

The values of K_1 and K_2 determined above correspond to rates for repopulation of $\langle S_z\rangle_g$ and $\langle I_z\rangle_g$ via quenching which are larger than the corresponding rates for repopulation via spontaneous emission. Quenching thus enhances the efficiency of $\sigma^+ D_1$ optical pumping through actual modification of probabilities for atomic deexcitation. The degree of enhancement of electronic spin polarization depends also upon the relative values of the other relaxation parameters: In typical cases the enhancement due to quenching should be between 10 and 30%. In the extreme case of deexcitation via quenching alone compared to deexcitation via spontaneous emission subject to complete mixing within the $^2P_{1/2}$ state (i.e., at very high buffer-gas pressures) the enhancement factor may approach 75%.

It is of some interest to determine how quenching affects repopulation rates at relatively high N_2 pressures. Although for reasons already represented, our calculations of relative quenching probabilities are not valid for N_2 pressures of 100 Torr or more, we still can obtain the values of C_1' and B_1' from high-pressure data; we just cannot extract meaningful values of K_1 from them. Data from transients measured in N_2 at pressures up to 250 Torr are included in Table III. It can be shown from our lower-pressure data that C_1' remains at 0.21, virtually unchanged as a function of N_2 pressure. There is no reason to expect this behavior to change suddenly at higher pressures. Taking C_1 to be 0.21, we extract the values for B_1' shown in Table IV. It appears that at high N_2 pressures B_1' approaches an asymptotic value greater than 0.08. These values of C_1' and B_1', compared to 0.214 and 0.043 for repopulation via spontaneous emission (no $^2P_{1/2}$-state relaxation), and 0.109 and 0.057 (spontaneous emission, complete $^2P_{1/2}$-state relaxation), imply that significant enhancement of spin polarization due to quenching persists throughout all N_2 pressures.

We can demonstrate rather directly the enhancement of production of spin polarization induced by quenching. The theoretical expression for the equilibrium electronic spin polarization $\langle S_z\rangle_{g\ \mathrm{eq}}$ produced in weak $\sigma^+ D_1$ optical pumping is

TABLE IV. B_1' and C_1' (pumping/repopulation parameters for $\langle S_z\rangle_g$ and $\langle I_z\rangle_g$) for $\sigma^+ D_1$ optical pumping of Cs in N_2, as determined in the present work. [See Eqs. (21a), (21b), (A1).] The values in the table are generally larger than those which can be obtained in a nonquenching buffer gas, and are indicative of quenching-induced enhancement of electronic spin polarization.

P (N_2) (Torr)	B_1'	C_1'
1.0	0.0500	0.213
2.0	0.0537	0.213
3.0	0.0561	0.212
4.0	0.0574	0.212
20.5	0.0625	0.212
30.2	0.0630	0.212
40	0.0633	0.212
60.3	0.0636	0.212
100.0	0.077	0.21
150	0.079	0.21
250	0.081	0.21

$$\langle S_z \rangle_{g\ \mathrm{eq}} = D_1 + D_2 = (B_3 C_1' + B_1' C_2)(B_2 C_2 - B_3 C_3)^{-1} . \tag{24}$$

The values of K_1 and K_2 reported in Eqs. (23a) and (23b) yield values of C_1' and B_1' which are greater than those pertaining to repopulation subject to spontaneous emission. Equation (24) thus predicts that the $\langle S_z \rangle_{g\ \mathrm{eq}}$ actually obtained in N_2 should be anomalously high compared to what it would be if quenching were absent. While we cannot "turn off" quenching to determine whether or not this is true, we can compare the equilibrium polarizations obtained for Cs in N_2 with those obtained in Ne, a nonquenching gas. Taking $D_0(\mathrm{Cs\text{-}Ne}) = 0.185$, $\sigma(\mathrm{Cs\text{-}Ne}) = 4.1 \times 10^{-23}\ \mathrm{cm}^2$, $D_0(\mathrm{Cs\text{-}N_2}) = 0.106$, and $\sigma(\mathrm{Cs\text{-}N_2}) = 57.2 \times 10^{-23}\ \mathrm{cm}^2$, we have calculated the ratios of $\langle S_z \rangle_{g\ \mathrm{eq}}(\mathrm{Cs\text{-}N_2}) / \langle S_z \rangle_{g\ \mathrm{eq}}(\mathrm{Cs\text{-}Ne})$ which would be expected subject to no quenching in either gas (dotted line in Fig. 1).[6] The data points represent actual measurements of $\langle S_z \rangle_{g\ \mathrm{eq}}(\mathrm{Cs\text{-}N_2}) / \langle S_z \rangle_{g\mathrm{eq}}(\mathrm{Cs\text{-}Ne})$ obtained in a white-light optical-pumping experiment at 15 °C. The solid line in Fig. 1 represents the best theoretical fit ($K_1 = 0.54$) to the data, including quenching effects. The experimental results substantiate the prediction of enhanced polarization due to quenching. The predicted and observed quenching enhancement factor at 4-Torr buffer-gas pressure is approximately 26%.

It has been well known prior to our work that optical pumping in the presence of N_2 leads to enhancement of spin polarizations. The effect commonly has been attributed to the quenching-induced suppression of fluorescent photons, since reabsorption of such photons, which otherwise would be emitted in the optical-pumping process, can act as a relaxation mechanism on the ground-state spin polarization.[13-15] We wish to emphasize the fact that the calculations, experiments, and enhancements reported in this paper are quite unrelated to, and distinct from, effects arising from radiation trapping. The relaxation rate due to radiation trapping depends upon the number of fluorescent photons available for reabsorption, and hence is related to the pumping intensity. All of our experimental work has been carried out under conditions such that collisional relaxation rates are far greater than the pumping rate: We have worked in the weak-pumping limit. The effects of radiation trapping thus represent small contributions to large numbers, and can be neglected. This is especially true at high N_2 pressures, where most fluorescent photons have been removed by quenching.

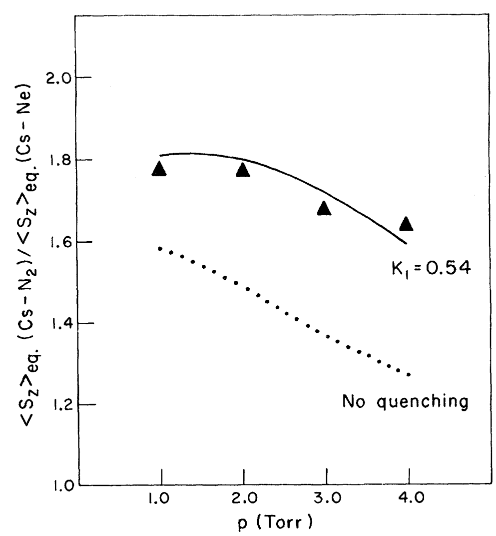

FIG. 1. Measurements and predicted ratios of equilibrium electronic spin polarizations produced in Cs at 15 °C in low pressures of N_2 and Ne.

In summary, we have calculated the effect of the hyperfine interaction on relative probabilities for quenching-induced transitions between the Zeeman sublevels of the excited and ground states of alkali-metal atoms. We have used optical-pumping transients to make the first experimental determination of nuclear-spin-independent relative probabilities for quenching transitions. Quenching in Cs exerts a considerably more beneficial effect on optical-pumping processes than mere removal of fluorescent photons: It alters ${}^2P_{1/2} \rightarrow {}^2S_{1/2}$ relative transition probabilities in such a way that ground-state spin polarizations are enhanced regardless of alkali vapor density. Our work can easily be extended to other situations, studies of enhancements of hyperfine population inversions, for example, and to other systems such as Hg, Tl, Cd, etc., in fact, to any atomic-molecular system which can be optically pumped. Such studies should lead to better understanding of quenching interactions, and of their effect on the performance of optically pumped devices.

APPENDIX

In the main section of this paper we described relative quenching probabilities under the assumption that the fine-structure period was much shorter than the duration of the quenching interaction, $\tau_F \ll \tau^*$: Our discussion was in terms of a $|J, m_J\rangle$ representation for the excited-state Zeeman sublevels. In this appendix we consider the opposite extreme, $\tau_F \gg \tau^*$, in which a $|m_l, m_s\rangle$ representation may seem more appropriate than $|J, m_J\rangle$. We continue to restrict our discussion to cases where the $\vec{\mathrm{L}} \cdot \vec{\mathrm{S}}$ interaction is sufficiently strong that J and m_J are good quantum numbers in the unperturbed atom. We emphasize that the $|m_l, m_s\rangle$ representation is appropriate only during the quenching interaction, with $|J, m_J\rangle$ being appropriate prior to it. We thus still wish to calculate the relative probabilities that an atom initially in a well-defined $|J, m_J\rangle$ sublevel will undergo quenching transitions to the $|S, m_s\rangle$ sublevels of the ground state. The principal difference between our present treatment and that given in Sec. II is that we now assume that the $\vec{L}\cdot\vec{S}$ interaction is too weak to permit reorientation of $\vec{S}$ during the very brief duration of the quenching interaction. (The quenching interaction is assumed to act directly upon only the spatial part of the atomic wave function.) We thus have the following representations for the excited-state sublevels immediately before undergoing quenching:

$$|J', m_{J'}\rangle = \sum_{|m_l', m_s'\rangle} \langle m_l' m_s' | J', m_{J'}\rangle |m_l' m_s'\rangle, \quad \text{(A1)}$$

$$|\tfrac{1}{2}, \tfrac{1}{2}\rangle = \tfrac{1}{2}\sqrt{6}\,|1, -\tfrac{1}{2}\rangle - \tfrac{1}{3}\sqrt{3}\,|0, \tfrac{1}{2}\rangle, \quad \text{(A2a)}$$

$$|\tfrac{1}{2}, -\tfrac{1}{2}\rangle = \tfrac{1}{3}\sqrt{6}\,|-1, \tfrac{1}{2}\rangle + \tfrac{1}{3}\sqrt{3}\,|0, -\tfrac{1}{2}\rangle. \quad \text{(A2b)}$$

We now compute relative transition probabilities to the ground-state sublevels, subject to the restriction that $\Delta m_s = 0$. Since matrix elements $\langle S|Q|P, m_l = \pm 1, 0\rangle$ must all be of equal magnitude, we obtain

$$K_1 = \tfrac{1}{3}, \quad \text{(A3a)}$$

$$K_2 = \tfrac{2}{3}. \quad \text{(A3b)}$$

The relative probability parameter is thus fully specified in this case. Nuclear-spin effects are treated in the same manner as previously.

We note that our original treatment in Sec. II does not predetermine K_1, but allows it to take any value from 0 to 1, and thus includes the present discussion as a particular case. Our experimental result, $K_1 = 0.56$, when compared to the predictions of this appendix, indicates that $\langle S_z\rangle$ is not conserved in ${}^2P_{1/2} \rightarrow {}^2S_{1/2}$ quenching collisions of Cs in N_2. It further suggests that the duration of the quenching interaction must be taken as long compared to τ_F, a finding consistent with our original assumption of the appropriateness of the $|J, m_J\rangle$ representation.

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