

shallow well (2.65 eV) were probably populated. This probably accounts for the difference in the gross appearance of Figs. 1 and 2 as compared to the corresponding figure^{3,4} for H_2^+ . Thus, in Fig. 1 and 2 for N_2^+ and O_2^+ , the cross sections reach maxima at about 70 eV. For H_2^+ , the cross section is a rapidly rising function with decreasing energy, even down to the lowest observed (12.3-eV) interaction energies.

One must qualify these latter considerations, however, with recognition of the fact that long-lived electronic states of N_2^+ and O_2^+ may be present in the target beams. Effects of such states (generally thought to be primarily quartet states) have been clearly observed^{10,11} in ion-molecule collision studies using beams of ions. Indeed, it has been estimated¹⁰ and shown¹¹ that up to

30% of an O_2^+ beam may be in an excited electronic state (presumably a $^4\Pi_u$ state). The tendency in Fig. 2, of the O_2^+ data to remain high at low energies, may be evidence of the presence of such states in this experiment.

In summary, the data of Figs. 1 and 2 represent measurements, within stated accuracy, of cross section for total dissociation by electron impact on N_2^+ and O_2^+ , respectively, where the N_2^+ and O_2^+ are typical of ions formed by high-energy (150-eV) electron impact on neutral gas at low (10^{-3} Torr) pressure. Though theoretical work has been done for H_2^+ , it does not seem likely that there will be theoretical work for the species reported here for some time.

esses, edited by M. R. C. McDowell (North-Holland Publishing Company, Amsterdam, 1964), p. 847.

¹¹ B. R. Turner, J. A. Rutherford, and D. M. J. Compton, *Bull. Am. Phys. Soc.* **12**, 230 (1966).

¹⁰ R. C. Amme and N. G. Utterback, in *Atomic Collision Proc-*

Cross Sections for Excited-State Mixing in Cesium-Noble-Gas Collisions from D_2 Optical Pumping

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Cross sections for random collisional reorientation of J within the sublevels of the $6^2P_{3/2}$ excited state of cesium have been measured using the D_2 optical-pumping technique. The measured cross sections σ_M^2 are: Cs-He $(3.2 \pm 0.6) \times 10^{-16}$ cm², Cs-Ne $(2.9 \pm 0.6) \times 10^{-16}$ cm², Cs-Ar $(6.0 \pm 1.2) \times 10^{-16}$ cm², Cs-Kr $(9.2 \pm 1.9) \times 10^{-16}$ cm², Cs-Xe $(11.3 \pm 2.3) \times 10^{-16}$ cm². Simplified equations for D_1 and D_2 pumping with zero, partial, and complete excited-state mixing are derived for a hypothetical alkali atom with zero nuclear spin. The calculations are extended to cesium atoms with nuclear spin $\frac{1}{2}$ pumped by σ^+ D_2 radiation. The equilibrium value $\langle S_z \rangle_0$ and the time dependence $\langle S_z(t) \rangle$ of the electronic spin polarization are computed for various degrees of excited-state mixing. $\langle S_z(t) \rangle$ is found to be nearly single-exponential in the zero- and the complete-mixing cases, but shows a distinct double-exponential behavior in the intermediate region. $\langle S_z \rangle_0$ is shown to be dependent on the degree of mixing, and to change sign as the degree of mixing increases. Measurements were performed with a new transmission technique by passing a separate σ^+ -polarized D_2 pumping beam and an alternately σ^+ - and σ^- -polarized D_1 testing beam through the cesium absorption cell. The cross sections for collisionally induced mixing were evaluated by measuring the buffer pressure at which $\langle S_z \rangle_0$ passed through zero.

I. INTRODUCTION

MOST optical pumping experiments have been analyzed either under the assumption that an alkali atom suffers no perturbation while in the excited state,¹ or that it suffers so many perturbations (i.e. collisions) during the excited-state lifetime, that it will

decay with equal probability from any Zeeman sublevel of the excited state, regardless of which one it was originally pumped to.² In a recent article,³ the calculation of optical pumping probabilities was extended to the region of "partial excited-state mixing," where the probability is great that an alkali atom suffers

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¹ W. B. Hawkins, *Phys. Rev.* **98**, 478 (1955).

² H. G. Dehmelt, *Phys. Rev.* **105**, 1487 (1957); J. Brossel, *Les Houches Lectures 1964* (Gordon and Breach Science Publishers Inc., London, 1964), pp. 187-327; T. R. Carver, *Science* **141**, 599 (1963).

³ F. A. Franz and J. R. Franz, *Phys. Rev.* **148**, 82 (1966); F. A. Franz, *Colloq. Intern. Centre Natl. Rech. Sci.* **162** (1967).

only a few collisions with buffer gas atoms before decaying to the ground state. In the present paper, we derive equations for D_1 and D_2 pumping with zero, partial, and complete excited-state mixing applied first to a vapor of hypothetical alkali atoms of zero nuclear spin. We show that the characteristic times describing the rate of change of the electronic spin polarization $\langle S_z \rangle$ and the equilibrium value of this polarization $\langle S_z \rangle_0$ differ in the various cases. We then extend the calculation to cesium atoms with nuclear spin $I = \frac{1}{2}$, and compute the time dependence and the equilibrium values of $\langle S_z \rangle$ obtained for D_2 pumping in a vapor subject to different degrees of excited state mixing. The time dependence of $\langle S_z \rangle$ is shown to be nearly single exponential with zero or complete mixing, but double exponential in the region of partial mixing. $\langle S_z \rangle_0$ is shown to be a sensitive function of degree of excited state mixing, and therefore of buffer gas pressure. At low buffer pressures, $\langle S_z \rangle_0$ is positive, and at high pressures it is negative, as has already been demonstrated experimentally.⁴ We show that by measuring the buffer pressure at which $\langle S_z \rangle_0$ passes through zero,

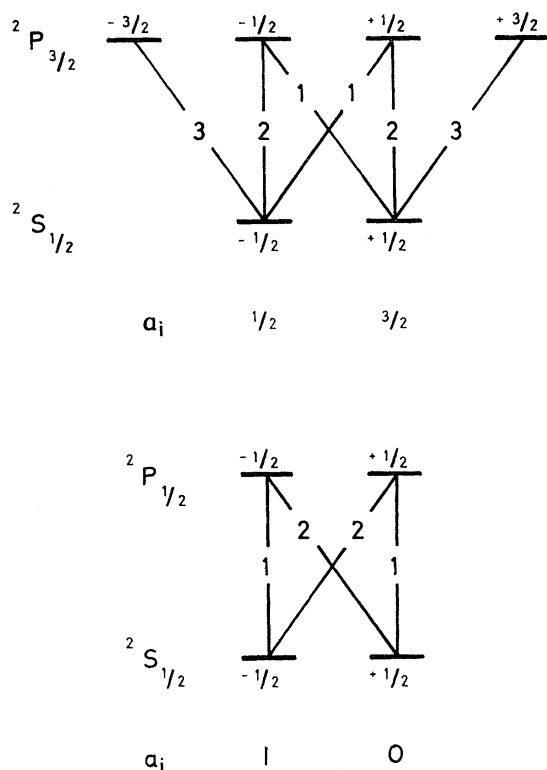


FIG. 1. Relative probabilities for D_2 and D_1 , optical pumping of a hypothetical nuclear spin zero alkali atom. The Zeeman sublevels are labeled by their m_J quantum numbers. The numbers along the vertical and diagonal lines are the relative probabilities connecting the ground- and excited-state sublevels in spontaneous emission. The a_i 's are the relative absorption probabilities for σ^+ resonance radiation.

⁴ J. Fricke and J. Haas, Z. Naturforschg. 21a, 1319 (1966).

the cross section σ_M^2 for collisional random reorientation of \mathbf{J} within an alkali $^2P_{3/2}$ state can be determined. Utilizing this fact, we have used a modification⁵ of the transmission monitoring technique (see Dehmelt, Ref. 2) to determine the cross sections for depolarization within the $6^2P_{3/2}$ excited state of Cs, induced by Cs-atom-noble-gas-atom collisions.

II. PUMPING OF NUCLEAR SPIN ZERO ALKALI ATOMS

We assume that the alkali metal vapor to be optically pumped is situated in a weak magnetic field directed along the optic axis. The total angular momentum \mathbf{F} and m_F , the projection of \mathbf{F} along the field axis, are assumed to be good quantum numbers. For the moment we shall let the nuclear spin \mathbf{I} be zero. A magnetic field thus splits the ground and excited states into $|J, m_J\rangle$ Zeeman sublevels. The absorption of circularly polarized (σ^+) $D_1(^2S_{1/2} \leftrightarrow ^2P_{1/2})$ or $D_2(^2S_{1/2} \leftrightarrow ^2P_{3/2})$ resonance radiation by atoms of the vapor, followed by de-excitation to the ground state through spontaneous emission, causes a pumping of atoms between ground-state sublevels. In Fig. 1 we summarize the relative probabilities relevant for the optical pumping of a nuclear spin-zero alkali atom. The relative probabilities for spontaneous emission from the $|J, m_J\rangle$ sublevels of the $^2P_{1/2}$ and $^2P_{3/2}$ excited states to the $^2S_{1/2}$ ground state are given along the vertical and diagonal lines connecting the sublevels. Along the bottom of the figure we also give the relative probabilities for absorption of $\sigma^+ D_1$ and D_2 light, so normalized that the absorption probability for D_2 light by an unpolarized vapor is twice that for D_1 light. We assume that the difference in energy between the $^2P_{1/2}$ and $^2P_{3/2}$ excited states is large enough that collisionally induced transitions between these two J states can be neglected.^{6,7}

The total electronic spin polarization of the vapor, $\langle S_z \rangle$, is equal to $\sum_i \langle S_z \rangle_i n^{(i)}$, where $\langle S_z \rangle_i$ is the expectation value of the alkali electronic spin in the i th ground-state sublevel, and $n^{(i)}$ is the occupation probability of that sublevel. Since in an optically thin absorption cell the total absorption probability for either D_1 or D_2 σ^+ light is a linear function of $\langle S_z \rangle$, both for the simple $I=0$ model and for real alkali atoms,⁸ it is convenient to derive pumping-rate equations in terms of this parameter. If A is a pumping-rate constant proportional to the incident-light intensity and to the absolute absorption cross section, then the rates of change of the ground-state sublevel populations n^+ and n^- of a vapor of nuclear spin-zero atoms subject

⁵ J. Haas, J. Fricke, and E. Lüscher, Z. Physik, 206 1 (1967).

⁶ M. Czajkowski, D. A. McGillis, and L. Krause, Can. J. Phys. 44, 91 (1966).

⁷ L. Krause, Appl. Optics 5, 1375 (1966).

⁸ Provided that equal hyperfine components are present in the pumping light. For a detailed discussion, see M. A. Bouchiat, Publications scientifiques et techniques du Ministère de l'Air, Nr. N. T. 146, Paris, 1965 (unpublished).

to D_1 optical pumping, with no mixing in the excited state, can be written as shown in Eq. (1). We neglect ground-state relaxation.

$$\begin{aligned} dn^-/dt &= -An^- + \frac{2}{3}An^-, \\ dn^+/dt &= \frac{1}{3}An^-. \end{aligned} \quad (1)$$

Since $\langle S_z \rangle$ is equal to $\frac{1}{2}(n^+ - n^-)$, we obtain

$$d\langle S_z \rangle / dt = \frac{1}{3}A[\frac{1}{2} - \langle S_z \rangle]. \quad (2)$$

If, on the other hand, sufficient buffer gas is present in the absorption cell to produce complete mixing throughout the m_J sublevels of the excited state of the alkali atom before spontaneous decay to the ground state, the rate of change of $\langle S_z \rangle$ is given by

$$d\langle S_z \rangle / dt = \frac{1}{2}A[\frac{1}{2} - \langle S_z \rangle]. \quad (3)$$

For D_2 pumping with no excited-state mixing, we obtain an equation identical to Eq. (2). For D_2 pumping with complete mixing of m_J in the excited state, we obtain Eq. (4).

$$d\langle S_z \rangle / dt = A[-\frac{1}{4} - \langle S_z \rangle]. \quad (4)$$

All four modes of pumping described in Eqs. (2) through (4) show a simple exponential approach to optically pumped equilibrium. For D_1 pumping the maximum value of the electronic spin polarization $\langle S_z \rangle$ is $\frac{1}{2}$, independent of degree of mixing. If the pumping-time constants with zero and complete (m_J) mixing are T_1 and T_1' , respectively, we obtain the following ratio of the pumping times, assuming equal incident-light intensities in both cases.

$$T_1' / T_1 = \frac{2}{3}. \quad (5a)$$

Equation (5a) predicts that equilibrium is approached faster in D_1 pumping if alkali atoms are subject to complete mixing of m_J in the excited state than if they are subject to no mixing at all. This prediction is exactly the reverse of that obtained assuming complete mixing of m_F in a vapor of alkali atoms of nonzero nuclear spin.⁹ There is, therefore, an important qualitative difference between m_J and m_F mixing. The reason that m_J mixing acts to improve rather than to diminish the efficiency of D_1 pumping results from the particular values of the ground-state-sublevel-absorption probabilities, and from the fact that $\Delta m_J = \pm 1$ transitions from the $^2P_{1/2}$ state are more probable than $\Delta m_J = 0$ transitions in spontaneous emission.

A slightly more complicated calculation shows that a vapor of real alkali atoms (nonzero nuclear spin) irradiated by D_1 light also will be pumped faster if the atoms are subject *only* to random reorientation of \mathbf{J} while in the excited state. At low buffer-gas pressures, then, excited-state mixing can actually *increase* the efficiency of the pumping process. It is only when enough collisions occur during the excited state lifetime

to connect all $|F, m_F\rangle$ sublevels that mixing has a detrimental effect.³

Considering now D_2 pumping, the ratio of the time constants T_2 and T_2' for zero and complete mixing, respectively, is

$$T_2' / T_2 = \frac{1}{3}. \quad (5b)$$

As in the case of D_1 pumping, equilibrium is approached faster if spin zero atoms are subject to m_J randomization within the excited $P_{3/2}$ state. The equilibrium electronic spin polarization $\langle S_z \rangle_0$, however, is no longer the same in the cases of zero and complete mixing, but is now predicted to be $\frac{1}{2}$ and $-\frac{1}{4}$, respectively. For intermediate buffer gas pressures, where "partial mixing" occurs, we expect $\langle S_z \rangle_0$ to be between these two extremes. We can find the exact value by combining Eq. (2) with (4). If the lifetime of the excited state is τ and the mean time between mixing collisions is τ_c , where

$$\frac{1}{\tau_c} = N\pi\sigma_M^2 \left[\frac{8RT}{\pi} \left(\frac{1}{M_1} + \frac{1}{M_2} \right) \right]^{1/2}, \quad (6)$$

with N the buffer gas density, σ_M^2 the cross section for mixing of the m_J levels, R the universal gas constant, and M the molecular weights, then the probability that a pumped atom will decay before suffering a mixing collision is $\tau_c / (\tau + \tau_c)$. The corresponding probability that the atom will decay subject to one or more collisions in which m_J randomization occurs is $\tau / (\tau + \tau_c)$. Calling $\tau / \tau_c = \alpha$, the change of the total spin polarization of a vapor of nuclear spin zero atoms subject to partial mixing is given by

$$\begin{aligned} \frac{d\langle S_z \rangle}{dt} &= \frac{A}{3(\alpha+1)} [\frac{1}{2} - \langle S_z \rangle] + \frac{A\alpha}{\alpha+1} [-\frac{1}{4} - \langle S_z \rangle] \\ &= \frac{A}{3} \frac{(1+3\alpha)}{(1+\alpha)} \left[\frac{(2-3\alpha)}{4(1+3\alpha)} - \langle S_z \rangle \right]. \end{aligned} \quad (7)$$

Again we get a single exponential pumping curve, with a time constant T_2'' , where

$$T_2 = \frac{3}{A} \geq T_2'' = \frac{3(1+\alpha)}{A(1+3\alpha)} \geq T_2' = \frac{1}{A}. \quad (8)$$

The corresponding equilibrium electronic spin polarization $\langle S_z(\alpha) \rangle_0$ is

$$-\frac{1}{4} \leq \langle S_z(\alpha) \rangle_0 = \frac{(2-3\alpha)}{4(1+3\alpha)} \leq +\frac{1}{2}. \quad (9)$$

The strong dependence in D_2 pumping of $\langle S_z(\alpha) \rangle_0$ upon degree of mixing [see Fig. 2], especially the pass-through-zero for $\alpha = \frac{2}{3}$, offers a convenient method for the determination of the cross section σ_M^2 for mixing within the $P_{3/2}$ excited level.

⁹ W. Franzen and A. G. Emslie, Phys. Rev. 108, 1453 (1957).

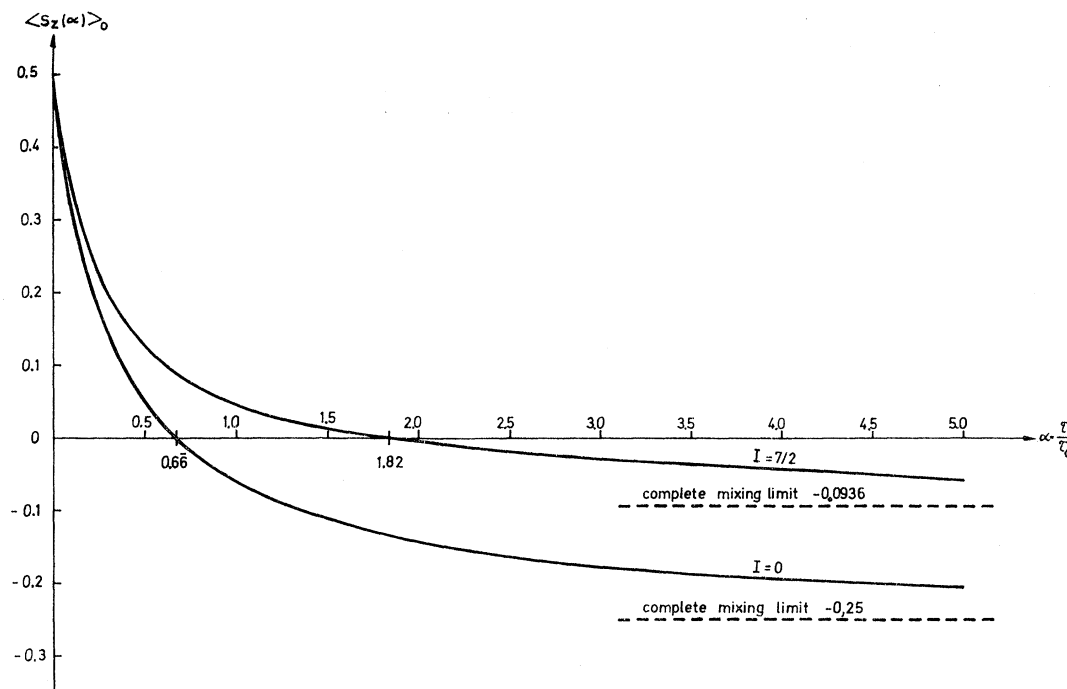


FIG. 2. Expected variation of equilibrium electronic spin polarization, $\langle S_z(\alpha) \rangle_0$, on degree of excited state mixing obtained in D_2 pumping for $I=0$ atoms and for cesium atoms with $I=7/2$. Influence of ground state relaxation is neglected.

III. D_2 PUMPING OF Cs ATOMS SUBJECT TO PARTIAL MIXING

We now proceed to the calculation of the time-dependence and the equilibrium value of the ground-state electronic spin polarization for Cs atoms subject to various degrees of excited state mixing.

We consider a model of a dilute alkali metal vapor (less than 10^{10} atoms/cm³ situated in a buffer of rare-gas atoms. We thus can neglect collisions between alkali atoms and consider only the collisional interaction between cesium and noble-gas atoms. In order that there be an appreciable probability that a collision occurs before the cesium atom decays and, on the other hand, that there is sufficient time for the **J-I** coupling to reestablish between the cesium-noble-gas interactions, the collision frequency is restricted to the range 10^6 to 10^{10} sec⁻¹ corresponding to the pressure range 10^{-2} to 10^2 Torr.

We also neglect wall effects since the shortest average time between collisions of an alkali atom with the wall of the cell (zero buffer-gas pressure) is of the order of 10^{-4} sec, which is long compared to the $^2P_{3/2}$ state lifetime $\tau = (3.05 \pm 0.07) \times 10^{-8}$ sec¹⁰. We assume that the Cs atoms are excited by an ideal source of D_2 light (broad line, not self-reversed, equal intensities in all hyperfine splitting (hfs) components) and that the absorption cell is optically thin. Finally, we neglect ground-state spin relaxation, taking into account the

fact that the experimental result can be extrapolated to a vanishing ratio of relaxation rate to pumping rate.

In Cs, the relatively large energy separation between the $^2P_{1/2}$ and $^2P_{3/2}$ states precludes collisionally induced transitions between these two levels.⁶ We thus can pump through either of two isolated *J* states. We assume that the random reorientation of the *J* vector in each collision, with subsequent reorientation of the nuclear spin, provides an adequate model to describe mixing between sublevels within the $^2P_{3/2}$ state.³

To describe optical pumping with D_2 light and partial excited-state mixing, we use the following optical pumping probability matrix³

$$P = \sum_{N=0}^{\infty} \frac{\tau^N \tau_c}{(\tau + \tau_c)^{N+1}} D \cdot M^N \cdot U. \quad (10a)$$

τ and τ_c have been defined in Sec. II; *U* is a probability matrix for electric dipole transitions induced by absorption of D_2 light with σ^+ polarization; *D* is the equivalent matrix for spontaneous transitions from the excited state to the ground state; and *M* is a mixing matrix producing random reorientation of **J**. The sum is extended over pumping events with 0, 1, 2, and more cesium-rare-gas collisions, all of which are weighted by statistical factors. Interference effects between overlapping excited-state sublevels which might occur in the emission process are neglected in the derivation of Eq. (10a). With $\alpha = \tau/\tau_c$, the above infinite geometric sum

¹⁰ J. K. Link, J. Opt. Soc. Am. 56, 1195 (1966).

is equal to

$$P = \frac{1}{1+\alpha} \left[D \left(E - \frac{\alpha M}{\alpha+1} \right)^{-1} U \right], \quad (10b)$$

where E is the unit matrix.

In the case of Cs, P has 16×16 elements, E and M have 32×32 , and D and U have 32×16 elements. The use of an electronic computer provides the only practical way of evaluating P , and of solving the system of 16 pumping equations for the 16 ground-state occupation probabilities, $n^{(i)}(\alpha)$. We have performed these computations for a number of values of α . $\langle S_z(\alpha) \rangle_0$ for various degrees of excited state mixing was determined (see Fig. 2) by use of the equation

$$\langle S_z(\alpha) \rangle_0 = \sum_i \langle S_z \rangle_i n_0^{(i)}(\alpha), \quad (11)$$

where $n_0^{(i)}(\alpha)$ is the equilibrium value of the occupation probability of the sublevel i for pumping subject to the degree of mixing specified by α . For $\alpha=0$ (no mixing), $\langle S_z(\alpha) \rangle_0$ is equal to $\frac{1}{2}$. As α increases, $\langle S_z(\alpha) \rangle_0$ decreases, finally becoming negative and approaching the complete mixing limit $\langle S_z(\alpha \rightarrow \infty) \rangle_0 = -0.0936$.

From comparison of the pass-through-zero of the curves $\langle S_z(\alpha) \rangle_0$ (Fig. 2) for the model $I=0$ atom ($\alpha_0=0.67$), and for the Cs atom with $I=\frac{7}{2}$ ($\alpha_0=1.82$), we find that about three times more collisions must occur to send the spin polarization for the real alkali atom to zero than for the $I=0$ atom. The decoupling of \mathbf{I} and \mathbf{J} during the collision allows the nuclear spin to act as a reservoir of angular momentum. The collision frequency ν_0 that is necessary to produce zero equilibrium spin polarization for a nuclear spin- $\frac{7}{2}$ atom, assuming random reorientation of \mathbf{J} in every collision is

$$\nu_0 = \frac{1}{\tau_c(\alpha=\alpha_0)} = \frac{1.82}{\tau} = \frac{1.82}{3.05 \times 10^{-8}} = 5.96 \times 10^7 \text{ sec}^{-1}. \quad (12)$$

We also computed the time dependence of $\langle S_z \rangle$ for various degrees of excited-state mixing (see Fig. 3). The curves describing the cases of no mixing and complete mixing show single exponential behavior to within 10% and 5%, respectively. The time constants differ in the two cases by about a factor of 6. If there are enough collisions to produce complete mixing of the excited $|F, m_F\rangle$ levels within the excited state lifetime, the pumping speed to equilibrium is thus greatly increased—even more than in the $I=0$ case.

In the intermediate region, especially near the pass-through-zero, a distinct double exponential behavior in the pumping curve arises, which should be experimentally detectable.

This double exponential behavior results even if one considers the purely academic model in which all atoms are subject to one and only one collision with randomi-

zation of \mathbf{J} [see Fig. 4]. The level $|3,3\rangle$ with $\langle S_z \rangle_{3,3} = -0.375$ is most quickly populated causing the steep slope of $\langle S_z(t) \rangle$. At a later time, levels with $\langle S_z \rangle_i > 0$ are favored, yielding the larger time constant which is connected to the decrease of $|\langle S_z(t) \rangle|$.

IV. EXPERIMENTAL PROCEDURE

In the past several methods have been developed to sample ground state spin polarization of optically pumped vapors (see Dehmelt, Ref. 2).^{11,10} In this work we used a new transmission technique that will be described in detail elsewhere.⁵ The essential features of this method are the following.

The vapor was pumped and maintained in an optically pumped equilibrium by passing $\sigma^+ D_2$ light through the absorption cell. A weak D_1 sampling beam coming from a second resonance lamp was passed in the same direction through the cell. Using a special chopper, the sampling beam was polarized alternately σ^+ , σ^- , at a frequency of about 500 cps. An interference filter passing only the D_1 beam was located behind the absorption cell. By sampling this radiation with a multiplier the difference in ground-state absorption for σ^+ and σ^- polarized D_1 light could be determined. This difference is zero if the vapor is unpumped (as, for example, when the D_2 pumping light source is cut off) or if the pumped equilibrium is one in which the spin polarization vanishes. In all other cases the difference is nonzero.

The main advantage of this method is to yield periodic signals, allowing one to use a phase locked amplifier. Thus one can continuously detect spin polarizations and also improve the signal-to-noise ratio. Even small signals (for example, in pure-rare-gas atmospheres of krypton and xenon with very strong relaxation) were determined quickly and exactly. By placing a D filter behind the absorption cell only the sampling D_1 beam hits the multiplier, providing a further lowering of the noise level.

With the above method we measured the absorption change ΔA between σ^+ and σ^- polarized D_1 light of a cesium vapor pumped by σ^+ polarized D_2 radiation for all rare gases at different pressures. The measured values ΔA are proportional to the electronic spin polarization $\langle S_z \rangle$ of this vapor, as one can see from the following. For σ^+ and σ^- polarized D_1 light, the ground state absorption probabilities a_i^+ and a_i^- , respectively, of the sublevels i are

$$a_i^\pm \sim \left[\frac{1}{2} \mp \langle S_z \rangle_i \right]. \quad (13)$$

Under the assumption of an ideal light source and an optically thin absorption cell one gets the following relation:

$$\Delta A = \sum_i (a_i^+ - a_i^-) n^{(i)} \sim \langle S_z \rangle, \quad (14)$$

¹¹ M. A. Bouchiat et F. Grossetête, J. Physique 27, 353 (1966).

¹² W. Happer and B. S. Mathur, Phys. Rev. Letters 18, 577 (1967).

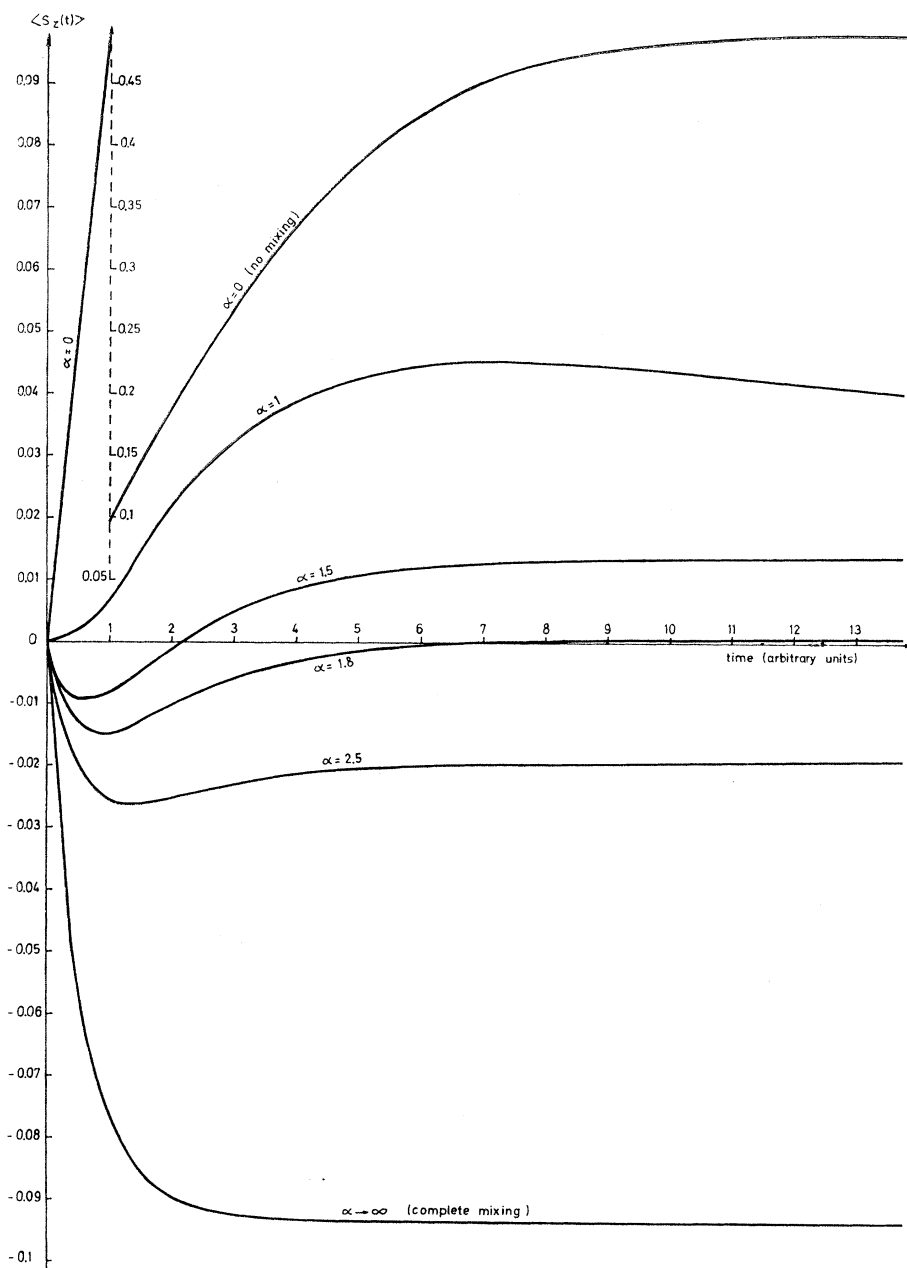


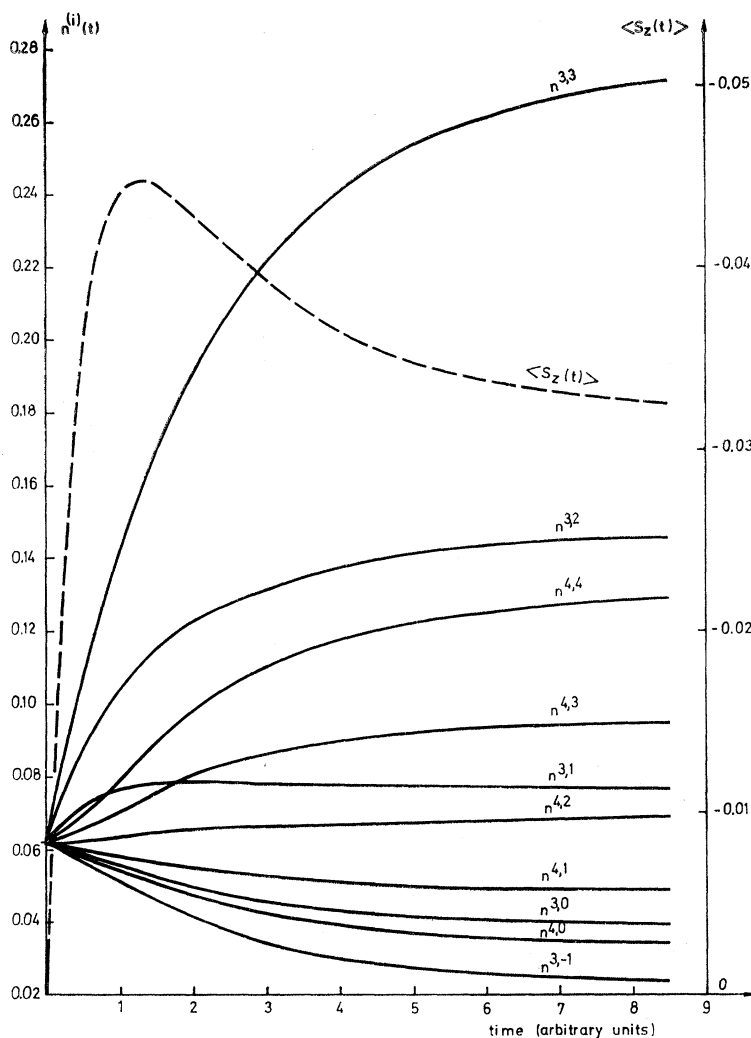
FIG. 3. Time dependence of electronic spin polarization $\langle S_z(t) \rangle$, of a vapor of cesium atoms ($I = \frac{7}{2}$), subject to D_2 pumping, with various degrees of excited state mixing. In the no mixing case two different scale factors are used. Ground state relaxation and inter- \mathbf{J} -transitions are neglected.

where $\langle S_z \rangle$ and ΔA will simultaneously vanish if all $n^{(i)}$ are equal, i.e., if the vapor is unpumped. Therefore we shall define ΔA as a pumping signal. As shown in Sec. III, both values again can vanish, if the vapor is pumped by circularly polarized D_2 radiation subject to a certain degree of excited state mixing ($\alpha = \alpha_0$). The measurement of p_s , the buffer gas pressure at which ΔA vanishes, yields a value for the excited state mixing cross section, σ_M^2 [See Fig. 5].

The experimental arrangement was similar to that of a conventional optical pumping apparatus.¹³ The cesium absorption bulb (about 8 cm in diam) was thoroughly baked and then coated with dotriacontane under high vacuum. A small amount (50 mg) of highly purified cesium metal was distilled into a side arm. The cell was connected to a continuous gas handling system from

¹³ W. W. Holloway, Jr., E. Lüscher, and R. Novick, Phys. Rev. **126**, 2108 (1962).

FIG. 4. Time dependence of ground-state occupation probabilities $n^{(i)}$ and spin polarization (belonging to the negative scale at the right side of the drawing) in the case of $I = \frac{1}{2}$ for a purely academic model in which all atoms are subject to one mixing collision with randomization of J . Some $n^{(i)}$ on the bottom of this drawing are omitted.



which buffer gases at pressures up to 30 Torr could be added. In this way pumping subject to any degree of excited-state mixing could be investigated.

The intensity of the D_2 pumping beam could be varied by more than a factor of 10, yielding values of p_z that were nearly independent of ground-state relaxation for all noble gases within a wide range of pumping light intensity [see Fig. 6].

By varying the cesium absorption-bulb temperature between 25 and 0°C we measured a shift of p_z that was strong at higher temperatures, but vanished at a few degrees centigrade [see Fig. 7], this temperature corresponding to a cesium vapor pressure of about $7 \cdot 10^{-8}$ Torr. The shift was due to a change in the exciting line profile, as was proved by placing an additional cesium absorption cell between the light source and the cell to be optically pumped. By heating the additional bulb, we measured a dependence of p_z upon temperature similar to that described above.

The temperature shift of p_z can be different in different cells, as Fig. 7 shows. The dependence of p_z on temperature is generally less if the cesium metal is situated in a side tube than if it is distilled directly into the cell. This effect can be explained by the assumption¹⁴ that cesium atoms coming from the reservoir can be continuously absorbed by a clean wall coating, thus depressing the Cs density in the cell. However, if Cs metal covers the wall coating, the Cs density at any temperature will be given by the saturated vapor pressure. Even at a few degrees centigrade this appears to make the cell nonoptically-thin, causing a strong shift of p_z .

The values of p_z reported in Table I are asymptotic values at low density and large ratio of pumping rate to relaxation rate. The cross sections for m_J randomization, σ_{M^2} , are calculated using the theoretical result that $\alpha = 1.82$ at p_z .

¹⁴ M. A. Bouchiat and J. Brossel, Phys. Rev. 147, 41 (1966).

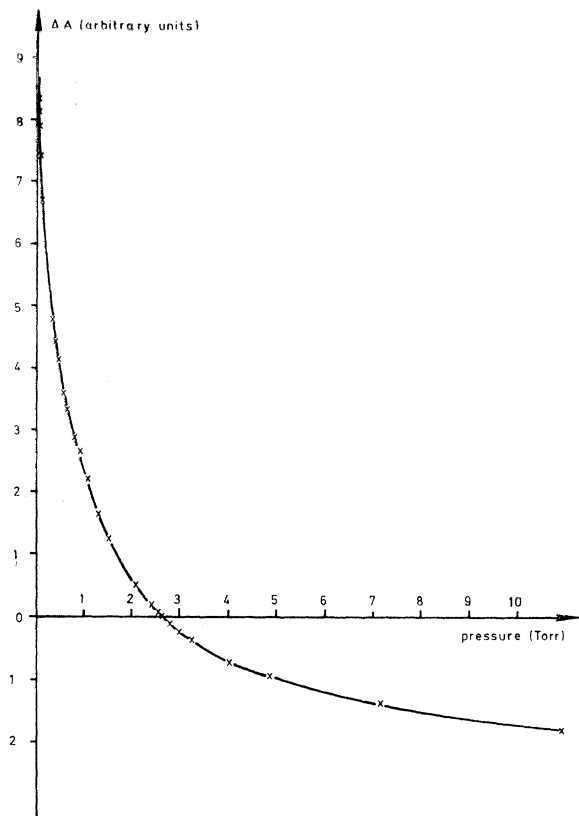


FIG. 5. Measured dependence of the cesium pumping signal upon argon buffer gas pressure using σ^+ polarized D_2 light at about 12°C . p_z lies at a few Torr for all rare gases.

V. ERROR IN DETERMINATION OF σ_M^2

The measured pressure values p_z , where the pumping signals passed through zero could be determined to better than 5%. The influence of ground-state relaxation and vapor pressure in the absorption cell could be eliminated by use of intense pumping light, good wall coatings, and by measuring at temperatures as low as

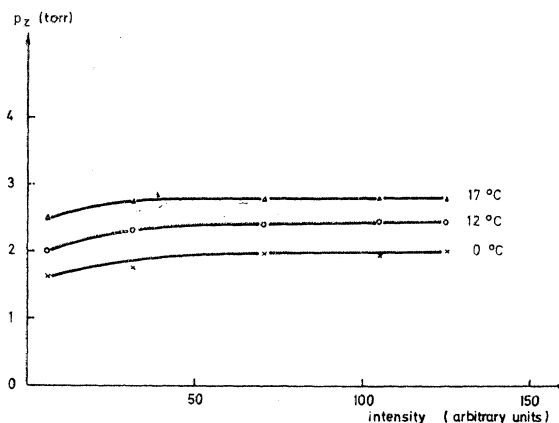


FIG. 6. The dependence of p_z on light intensity. Different asymptotic values of p_z are found for different cell temperatures. Argon was used as buffer gas.

0°C . The excited $P_{3/2}$ state lifetime $\tau = (3.05 \pm 0.07) \times 10^{-8} \text{ sec}^{10}$ that was used to determine the collision frequency ν_0 is accurate within about 3%.

The greatest uncertainty in the determination of σ_M^2 (about 10–15%) arises from small deviations of the exciting line profile from the ideal. This profile has been mapped earlier and showed only two lines with nearly equal intensities and a small amount of self reversal in the case of D_2 light. Both lines were separated by the ground state hyperfine energy of 9192 Mc/sec.¹⁵ The excited $P_{3/2}$ state hyperfine levels (energy separation 152, 203, and 252.5 Mc/sec)¹⁶ are not resolved because of Doppler broadening.

Summing up all errors the total uncertainty of σ_M^2 should not exceed 20%.

VI. DISCUSSION

The cross sections for collisionally induced mixing within the $6^2P_{3/2}$ state of cesium reported in this paper have been evaluated using a model in which J is as-

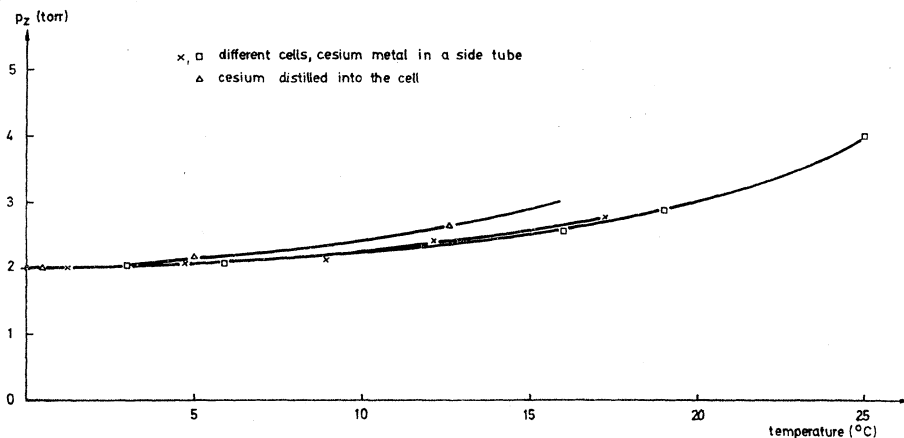


FIG. 7. The dependence of p_z on cell temperature (i.e. on Cs-vapor pressure) for different cells with argon as buffer gas. At a few centigrade an asymptotic value of p_z versus temperature was reached in all cases investigated.

¹⁵ E. C. Beaty, P. L. Bender, and A. R. Chi, Phys. Rev. 112, 450 (1958).

sumed to be randomly reorientated in every alkali-noble-gas atom collision.^{8,17} It has been suggested, however, that this reorientation may not be completely random, but may be restricted by a selection rule on Δm_J .^{18,19} Evidence of such an effect is found in recent measurements of collisional depolarization in Rb and Cs $^2P_{1/2}$ states.²⁰ In the case of collision of "one-electron" atoms, such as the alkalis or Tl, with noble-gas atoms, a simple argument involving time reversal invariance shows that in the adiabatic approximation transitions of the form $m_J \leftrightarrow -m_J$ within the same J multiplet should be forbidden in all orders of perturbation theory.²¹ This selection rule holds not only in the collision frame, but in any convenient frame of interest, in particular, in the lab frame. It therefore predicts that J reorientation in the lab frame is *not* totally random.

In this case $\langle S_z \rangle_0$ is computed to pass through zero

¹⁶ P. Buck, I. I. Rabi, and B. Senitzky, Phys. Rev. **104**, 553 (1956).

¹⁷ P. L. Bender, thesis, Princeton University, 1956 (unpublished). Here an analogous model involving randomization of J was used in order to describe excited-state mixing in sodium.

¹⁸ Selection rules on Δm_J concerning inter- J -level transitions are derived and discussed by P. L. Bender, (Ref. 17) and J. A. Jordan, thesis, University of Michigan, 1964 (unpublished).

¹⁹ Selection rules for mixing within a J -level are suggested by Franz and Franz, Ref. 3 ($\Delta m_J = 0, \pm 2$) and by A. Gallagher, Phys. Rev. Letters **18**, A1 (1967); Bull. Am. Phys. Soc. **12**, 131 (1967) (selection rule $m_J \leftrightarrow m_J$).

²⁰ A. Gallagher, Phys. Rev. Letters **18**, A1 (1967).

²¹ F. A. Franz, G. Leutert, and R. T. Shuey, Helv. Phys. Acta (to be published).

TABLE I. Values of p_z and σ_M^2 for the noble gases.

Nobel gas	He	Ne	Ar	Kr	Xe
p_z (Torr)	1,36	3,12	2,02	1,69	1,56
σ_M^2 (\AA^2)	32 ± 6	29 ± 6	60 ± 12	92 ± 19	113 ± 23

at $\alpha = 2.76$ requiring the cross sections in Table I to be multiplied by a factor of 1.5.

Gallagher's Hanle effect measurements²⁰ of depolarization within the $^2P_{3/2}$ state of Rb are consistent with ours, and would be affected in a similar way by the lab frame $m_J \leftrightarrow -m_J$ selection rule. At the present time, we are not able to offer conclusive proof that such adjustments should be made. Further experiments in which the validity of the $m_J \leftrightarrow -m_J$ rule will be tested are under way.

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