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Spin relaxation within the 6 $^2P_{1/2}$ and 6 $^2S_{1/2}$ states of cesium measured by white-light optical pumping*

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Collisional relaxation of spin polarization within the Cs atom has been studied using new techniques of white-light optical pumping. Analyses of pumping transient signals have been made including full treatments of effects due to the hyperfine interaction and spin exchange. The nuclear-spin-independent cross sections for relaxation of $\langle S_z\rangle$ in the $6\,^2S_{1/2}$ state of Cs, at 288 °K, are (in 10^{-23} cm^2): Cs-He, 2.43 ± 0.24; Cs-Ne, 4.08 ± 0.40; Cs-Ar, 108 ± 10; Cs-N$_2$, 55.2 ± 5.5. The nuclear-spin-independent cross sections for relaxation of $\langle J_z\rangle$ within the $6\,^2P_{1/2}$ state of Cs, at 288 °K, are (in units of 10^{-16} cm^2): Cs-He, 12.5 ± 4.0; Cs-Ne, 6.9 ± 2.0. The Cs–buffer-gas diffusion coefficients, extrapolated to 273 °K, are (in units of cm^2 sec^{-1}): Cs-He, 0.291 ± 0.030; Cs-Ne, 0.171 ± 0.017; Cs-Ar, 0.111 ± 0.011; Cs-N$_2$, 0.098 ± 0.010. There is no experimental evidence for contributions to low-pressure relaxation rates from the formation of Cs–buffer-gas van der Waals molecules, even in the case of Cs-Ar. There is, however, possible evidence for small contributions to relaxation rates at high buffer-gas pressures from this source.

I. INTRODUCTION

In a recent paper[1] we discussed some of the properties of the rate equations that describe the evolution of ground-state electronic- and nuclear-spin polarizations, $\langle S_z\rangle_g$ and $\langle I_z\rangle_g$, of an alkali-metal vapor subject to optical pumping.[1] We showed in the limit of weak pumping that these equations yield analytic solutions for $\langle S_z\rangle_g$ and $\langle I_z\rangle_g$ which can be used to advantage in the study of the collisional relaxation of alkali-metal atoms, both in the $^2S_{1/2}$ ground state and in the $^2P_{1/2}$ excited state. In the present paper we extend our work to include contributions to the rate equations arising from spin exchange. We utilize these calculations to extract from experimental optical-pumping transients the nuclear-spin independent cross sections for the relaxation of $\langle S_z\rangle_g$, the alkali-atom–buffer-gas-atom mutual diffusion coefficient, the nuclear-spin-independent cross section for collisional relaxation within the $^2P_{1/2}$ state, and the relaxation rate due to the formation and destruction of weakly bound alkali-atom–buffer-gas-atom van der Waals molecules. Our experimental transients span a range of buffer-gas pressures from 1 Torr to more than 600 Torr; they have been obtained using a new white-light optical-pumping technique which defines the experimental conditions with a degree of accuracy seldom attained previously. Our theoretical and experimental results, coupled with the recent results of others, remove many of the ambiguities and inconsistencies which have long clouded a complete understanding of the mechanics of some modes of alkali collisional relaxation. The results also suggest some intriguing puzzles which may merit further investigation.

II. MEASUREMENT OF TRANSIENT SIGNALS IN WHITE-LIGHT OPTICAL PUMPING

Our major experimental innovation in the present work has been the use of filtered white light rather than resonance radiation as the generator of optical pumping. White-light optical pumping was first performed by Bender,[2] who used sunlight as a pumping source in a normal optical-pumping experiment, and by Ensberg and zu Putlitz,[3] who used light from a xenon arc to pump alkali-metal vapors in the presence of buffer-gas pressures ranging up to several atmospheres. Franz, Marshall, and Munarin also used white-light excitation and detection to optically pump Cs in magnetic fields up to 100 kG.[4] The motivation behind using white light in the latter two experiments was that the absorption line of the vapor to be optically pumped was shifted far away from the emission line of a conventional resonance lamp; in Ref. 3 the cause was extensive broadening of the absorption line at high buffer-gas pressures, while in Ref. 4 the cause was the large splitting of Zeeman components of the $^2P_{1/2} \rightarrow {}^2S_{1/2}$ line at high magnetic fields.

While in the present experiment we have neither extremely high buffer-gas pressures, nor high magnetic fields, white-light optical pumping nevertheless is essential for success. The reason is that the character of the optical-pumping transients depends rather critically on the profile of the pumping radiation: correct analyses demand knowledge of that profile. An extreme example can be found in the method of "hyperfine pumping" in which not all hyperfine components of the D_1 (or D_2) line are present in the pumping radiation.[5-9] In most experiments involving normal σ^+ optical pumping it generally either has been *assumed* that the pumping source is "white," that is, that the source emits light or equal intensity at all hyperfine components of the absorption line, or relative intensities have been taken as proportional to the theoretical statistical weights of the lines. Ordinary spectral lamps, due to problems involving self-absorption and mode of excitation, generally fall far short of either ideal. Some experimenters have made careful studies of the profiles of both absorption and emission lines, and have folded this information into analyses of their experiments. This is a difficult and error-prone task however, particularly when measurements are to be made over a wide range of experimental conditions. All of these problems are avoided through the use of filtered white light as the pumping source; the "white-light approximation" in the analysis of pumping rates is then satisfied exactly, provided that the vapor pressure in the optical-pumping cell is sufficiently low that the cell may be considered optically thin. The only advantage of resonance lamps over white-light lamps, in fact, is that under some conditions the resonance lamp may provide several orders of magnitude greater pumping intensity. Such a gain would be illusory in our experiment, however. Our theoretical calculations are valid only in the limit of weak pumping, and hence, through actual measurement, fall ideally within the practicable strengths of white-light sources.

Aside from our use of white light as the pumping source, our experimental setup was very similar to those developed by Marrus and Yellin[10] and by Gibbs et al.[11] Circularly polarized resonance radiation, in our case filtered white light centered at 8944 Å, was passed through a cell containing Cs vapor plus an inert gas situated in a magnetic field of approximately 0.20 G. Optical-pumping transients were induced by first saturating the ground-state Zeeman resonance, then gating off the applied rf. The transients were observed by monitoring the intensity of light transmitted through the optical-pumping cell; they thus represent the evolution of the ground-state electronic-spin polarization $\langle S_z \rangle_g$. In the paragraphs below we summarize some of the more important aspects of the experimental apparatus and technique.

A. Pumping beam

We required a pumping source which would emit light of equal intensity at all hyperfine components of the Cs D_1 absorption line, and which would maintain this condition throughout a wide range of buffer-gas pressures. The xenon arc has the advantages of possessing both relatively high intensity at 8944 Å and a small source size which permits convenient collimation of the pumping beam. It has the disadvantages of relatively high flicker, noise, and drift. The requirements for stability in our experiment were severe: we needed to average transient signals which corresponded to changes as small as 10^{-4}–10^{-6} in the intensity of the transmitted light, and which had characteristic time constants ranging up to several hundred milliseconds. A xenon arc, even when stabilized, provided fluctuations approaching 1% of the total light intensity, rendering it unsuitable for use in the present experiment.

The ideal light source for our purposes proved to be a General Electric DHT 1200-W tungsten projector lamp, powered by three current-regulated Hewlett Packard 6267 dc power supplies connected in series. The tungsten lamp has the advantage of having the peak of its radiation spectrum near the Cs D_1 resonance line. The DHT lamp, in particular, has the advantage of possessing a relatively small (1 cm^2) filament size. Operation at the rated power level tended to produce gradual coating of the Pyrex-glass envelope by vaporized tungsten and occasional bubbling of the envelope itself. Both problems were avoided by making most measurements at reduced power levels, typically 100 V and 9 A. We obtained consistently stable performance by operating the lamp totally unshielded, i.e., without a housing, in a relatively draft-free room.

Of the total energy emitted by the lamp (blackbody spectrum at 3000°K) only a very small portion near 8944 Å is utilized in the optical-pumping process. It is necessary to remove as much of the extraneous radiation as possible from the beam. The intense visible and infrared radiation must be removed in order to avoid thermal destruction of polarizers and narrow-band filters. The D_2 (8521 Å) wavelength must be suppressed for the customary reasons involving pumping mechanics.[12] The beam must be further narrow banded around the D_1 absorption line in order to provide optimum signal to noise ratios in the detection of the pumping transients. In our experiment the light from the DHT lamp was collimated by two 6-in. diam. Pyrex condensor lenses, effective focal length 5-in., and passed through a clear filter through which distilled water was slowly circulated. The water filter removed the large amount of radiation emitted at wavelengths greater than 1.3 μ. The utility of this filter is demonstrated by the fact that without circulation it took only a few minutes for the water to boil. The beam then passed through a Corning 7-69 glass filter which removed most of the visible light. The final filter before the optical-pumping cell was a 50-Å bandwidth, D_1 pass, D_2 reject interference filter, with pass to rejection ratio better than 1000:1. The remaining light was polarized by a Polaroid *HR* linear polarizer, followed by a stress-tuned quarter wave plate of the type designed by Lurio.[13] The quality of circular polarization was measured by rotating a second linear polarizer behind the circular polarizing combination. The quartz plate and the linear polarizer were tuned until intensity variations upon rotation of the second polarizer were 2% or less. Checks of polarization quality were made at the beginning of each experimental run. Shifts proved to be very minor as long as the laboratory temperature remained constant. The smallest aperture in the entire filter-polarizer train was greater than $2\frac{1}{2}$-in., approximately the diameter of the optical pumping cell.

B. Optical pumping cell

The optical pumping cell was a pyrex cylinder 6.9 cm in diameter and 7.4 cm in length. It was situated at the center of a set of three mutually perpendicular Helmholtz coils which provided cancellation magnetic fields of sufficient homogeneity to produce a low magnetic field Zeeman resonance linewidth of 300 Hz. Metallic cesium was distilled under high vacuum into the cell from a side arm which subsequently was drawn off. The side walls of the cell were coated intentionally with a visible layer of Cs in order to ensure effective gettering of trace impurities that could have been present in the ultrapure buffer gases used in the experiment, and to guarantee the presence of a saturated Cs vapor at all buffer-gas pressures and at all temperatures of operation. The windows of the cell, however, were kept clear of visible Cs deposit. The cell was surrounded by a temperature-regulated water bath consisting of a large styrofoam picnic cooler with a plastic garbage-can liner. Optical access was provided by two 3-in.-diam. holes into which evacuated Pyrex cylinders were cemented. Condensation of moisture on elements in the optical path thus was avoided. The temperature of the bath was regulated by circulating chilled water through a copper-tubing heat exchanger. Buffer gases were admitted to the cell from an all metal and glass ultrahigh vacuum gas-handling system. Buffer-gas pressures were measured using a combination of a Granville-Phillips capacitance manometer and a Baratron gauge.

C. Generation and detection of transient pumping signals

The experiment was designed to produce a repetitive transient pumping signal which could be averaged by a Hewlett Packard signal-averager system. The timing of the experiment was controlled by the signal averager. At the end of each sweep the signal averager produced a sync pulse. This pulse triggered a single cycle of a low-frequency square wave from a Wavetek 144 function generator. The square wave gated another Wavetek 144 which throughout the initial half-cycle supplied sinusoidal rf power (68 kHz) to a modified Helmholtz coil mounted on the optical-pumping cell, saturating the ground-state Zeeman resonances in both the $F=4$ and $F=3$ hyperfine sublevels of the ground state. The sweep of the signal averager thus was an initial baseline corresponding to zero polarization (rf power on) followed by the optical-pumping transient. The seemingly cumbersome method of gating rf power described above was the easiest way to ensure that the rf was truly off during the optical-pumping cycle. Ordinary square-wave modulation of rf power, as contrasted with gating, generally permits some leakage of rf during the off portion of the cycle, resulting in an effective shortening of observed relaxation times.

The observed transient signal consisted of a small time-dependent increase in the intensity of the *absorbable* light transmitted through the optical-pumping cell. Since the Cs absorption line is at most a few tenths of an angstrom wide even at buffer-gas pressures approaching 1 atm, it is clear that most of the 50-Å-wide pumping light plays no role in the experiment other than to obscure the transient. We removed much of the inactive light by placing two 5-Å bandwidth 8944-Å pass interference filters in front of the photodetector. Even with this further narrow banding the amplitude of the optical-pumping transients ranged from a few parts in 10^6 to a few parts in 10^4 of the intensity of light incident on the photodetector.

The photodetector itself was a diffused barrier PIN 10D photodiode, carefully selected for low noise, and operated in the unbiased mode. Neutral-density filters were placed in front of the detector to reduce the intensity of light incident upon it to a level at which 50 mV were developed across 500 kΩ. In this mode the detector's response is linear only for very small changes of intensity, a condition easily satisfied in the present work. The 50-mV monitoring signal was fed into one input of a PAR 113 ultralow-noise dc preamplifier. A balancing voltage from a mercury-cell potentiometer was fed into the other input. The amplified (gain of 1000) differential signal was fed to the dc input of the signal averager. Depending on signal size, between 2^{11} and 2^{15} sweeps of the signal were made, with the averaged results finally being punched out on paper tape for later analysis by a CDC 6600 computer.

The extremely small size of the transient signals placed stringent requirements on the stability of the optical-pumping system. Most of the light path between optical components was shielded from dust particles and air currents by 4-in.-diam. black plastic sewer pipe. The entire system was mounted on four Firestone air-ride vibration isolators to eliminate noise induced by building vibration. Care also had to be taken to prevent small air bubbles from developing within the water filter, and occasionally to clean the lamp contacts which tended to oxidize. The sum of the short-term instability and noise of the entire system, as monitored at the input of the signal averager, was less than 1: 10^4 of the signal corresponding to the intensity of the attenuated light incident on the photodetector.

III. COMPREHENSIVE OPTICAL-PUMPING RATE EQUATIONS INCLUDING SELF-SPIN EXCHANGE

In FS we discussed the rate equations which describe the production of spin polarizations in the D_1 σ^+ optical pumping of alkali-metal vapors. We showed that the combined effects of weak depopulation pumping, collisional relaxation within the $^2P_{1/2}$ state, repopulation pumping, and various modes of collisional relaxation within the $^2S_{1/2}$ state, lead to equations which yield analytic solutions for $\langle S_z\rangle_g(t)$ and $\langle I_z\rangle_g(t)$, the electronic- and nuclear-spin polarizations of the alkali ground state. We also showed how measurements of pumping transients can be used to determine nuclear-spin independent cross sections for the collisional relaxation of $\langle S_z\rangle_g$ within the $^2S_{1/2}$ state, and of $\langle J_z\rangle$ within the $^2P_{1/2}$ state. We did not, however, consider contributions to the rate equations arising from spin exchange: we assumed the existence of a regime in which other relaxation rates were considerably greater than the spin-exchange rate. In this section we extend the results obtained in FS for Cs, including now the influence of spin exchange in the ground state.

In 1965 Gibbs calculated explicit expressions for the rates of change of spin polarizations in alkali-metal vapors subject to spin exchange, including rigorously the effects of the hyperfine interaction.[14,15] His calculations are consistent with the density matrix formulation of Grossetête.[16] Gibbs showed that in the limit of small polarizations

$$\langle \dot{S}_z\rangle_g=-\langle \dot{I}_z\rangle_g=\langle S_z\rangle_g\,\frac{[-2I(2I-1)2I-2I(2I-1)2-(2I+2)(2I+3)2I]R_s}{3(2I+1)^3}$$

$$+\langle I_z\rangle_g\,\frac{[-2I(2I-1)+(2I+2)(2I+3)]R_s}{3(2I+1)^3}\,, \qquad (1)$$

where I is the nuclear spin, and $R_s = n_0\sigma_s v_{\text{alk-alk}}p_{\text{alk}}/p_0$. n_0 is Loschmidt's number, σ_s is the nuclear-spin-independent cross section for spin exchange, $v_{\text{alk-alk}}$ is the mean relative velocity of alkali atoms, p_{alk} is the alkali partial pressure, and p_0 is atmospheric pressure. For Cs ($I=\frac{7}{2}$), Eq. (1) reduces to

$$\langle \dot{S}_z\rangle_g=\frac{-21}{32}R_s\langle S_z\rangle_g+\frac{R_s}{32}\langle I_z\rangle_g\,, \qquad (2a)$$

$$\langle \dot{I}_z\rangle_g=\frac{-R_s}{32}\langle I_z\rangle_g+\frac{21}{32}R_s\langle S_z\rangle_g\,. \qquad (2b)$$

Spin-exchange collisions thus provide an interaction whereby electronic- and nuclear-spin polarizations are interconverted. The addition of spin exchange to the interactions already considered in FS leads to the following comprehensive rate equations for $\langle S_z\rangle_g$ and $\langle I_z\rangle_g$:

$$\langle \dot{I}_z\rangle_g=C_1-C_2\langle I_z\rangle_g+C_3\langle S_z\rangle_g\,, \qquad (3a)$$

$$\langle \dot{S}_z\rangle_g=B_1-B_2\langle S_z\rangle_g+B_3\langle I_z\rangle_g\,. \qquad (3b)$$

Equations (3a) and (3b) are of the same form as Eqs. (26a) and (26b) in FS, with one major exception—the term $C_3\langle S_z\rangle_g$ does not appear in the earlier work, i.e., in the absence of spin exchange. Nevertheless, there remains an analytic solution for $\langle S_z\rangle_g$ which still involves the sum of two exponentials:

$$\langle S_z\rangle_g(t)=D_1(1-e^{-Z_1t})+D_2(1-e^{-Z_2t})\,, \qquad (4)$$

where

$$D_1 = \frac{B_3C_1Z_2 + B_1C_2Z_2 + B_1B_2C_2 - B_1B_3C_3}{(B_2C_2 - B_3C_3)(Z_2 - Z_1)}, \qquad (5a)$$

$$D_2 = \frac{-B_1B_2C_2 + B_1B_3C_3 - B_3C_1Z_1 - B_1C_2Z_1}{(B_2C_2 - B_3C_3)(Z_2 - Z_1)}, \qquad (5b)$$

$$Z_1 = \tfrac{1}{2}\{(B_2 + C_2) - [(B_2 - C_2)^2 + 4B_3C_3]^{1/2}\}, \qquad (6a)$$

and

$$Z_2 = \tfrac{1}{2}\{(B_2 + C_2) + [(B_2 - C_2)^2 + 4B_3C_3]^{1/2}\}. \qquad (6b)$$

In the specific case of cesium,[1]

$$C_1 = \frac{21A}{192} + \left(\frac{161A}{48}\right)(\Gamma_1\tau + 32)^{-1}, \qquad (7a)$$

$$B_1 = \frac{11A}{192} + \left(\frac{A}{144}\right)(-67 + 13\Gamma_1\tau) \times (\Gamma_1\tau + 32)^{-1}(\Gamma_1\tau + 1)^{-1}, \qquad (7b)$$

$$C_2 = \tfrac{1}{3}A + \tfrac{1}{32}R + R' + R'' + \tfrac{1}{32}R_s, \qquad (7c)$$

$$B_2 = \tfrac{1}{3}A + R + R' + R'' + 21R_s/32, \qquad (7b)$$

$$C_3 = 21R_s/32, \qquad (7e)$$

$$B_3 = \tfrac{1}{32}R + \tfrac{1}{32}R_s. \qquad (7f)$$

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 owing to binary alkali–buffer-gas-atom collisions, R'' is the effective relaxation rate due to alkali collisions with the walls of the experimental cell, and R' is the relaxation rate due to "sticky" or molecular complex forming collisions of alkali atoms with buffer-gas-atoms. More specifically,

$$\Gamma_1 = n_0\sigma_1 v_{\mathrm{rel}}\, p/p_0, \qquad (8a)$$

$$R = n_0\sigma v_{\mathrm{rel}}\, p/p_0, \qquad (8b)$$

$$R'' = [(\pi/L)^2 + (2.405/r)^2]D_0 p_0/p, \qquad (8c)$$

where σ_1 is the nuclear-spin-independent cross section for the destruction of $\langle J_z\rangle$ in alkali-buffer-gas-atom collisions, v_{rel} is the mean relative velocity of alkali 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 alkali–buffer-gas-atom collisions, L and r are the length and radius of the (cylindrical) cell, and D_0 is the diffusion coefficient of Cs in the buffer gas.

The theoretical expression for the $\langle S_z\rangle_g$ transient can be made less cumbersome than the apparent form provided by Eqs. (5a)–(8c). It is easy to show through reference to Eqs. (7c)–(7f) that the quantity $4B_3C_3(B_2 - C_2)^{-2}$ can assume a value no larger than 0.21, no matter what the magnitudes of R and R_s may be. The square roots in Eqs. (6a) and (6b) thus can be expanded, yielding the simpler expressions for Z_1 and Z_2 given in Eqs. (9a) and (9b):

$$Z_1 = C_2 - B_3C_3(B_2 - C_2)^{-1}, \qquad (9a)$$

$$Z_2 = B_2 + B_3C_3(B_2 - C_2)^{-1}. \qquad (9b)$$

Equations (9a) and (9b) are accurate to better than 99.5%. We shall utilize these approximations in all subsequent work.

The equations derived in this section are highly accurate representations of the transient and equilibrium spin polarizations generated in the white-light optical pumping of cesium. In the limit of zero spin exchange all of them reduce to the equations previously derived in FS, where the various underlying assumptions and approximations are discussed in detail. It is important to keep in mind some limitations of these approximations. Broad-band weak pumping has been assumed throughout, where "weak" is defined in relation to the magnitudes of the ground-state relaxation rates. It is a regime in which a small $\langle S_z\rangle_g$ is created, but in which $\langle \vec{S}\cdot\vec{I}\rangle_g$ remains essentially constant. The nuclear decoupling-recoupling approximation has been used to describe the effects of the hyperfine interaction on relaxation induced in alkali–buffer-gas-atom collisions both in the ground state and in the excited state.[16–26] Due to the relatively large cross sections for excited-state relaxation ($\approx 10^{-16}$ cm^2), this approximation will be strictly valid only for buffer-gas pressures less than a few hundred Torr. At higher buffer-gas pressures the mean time between relaxation events within the $^2P_{1/2}$ state becomes shorter than the hyperfine period, and nuclear reorientation is diminished.[22,26] Finally, a very good but nevertheless still approximate treatment of the effects of diffusion and wall relaxation has been made.[27] Errors of a few percent may be expected from this source.

IV. METHODS OF ANALYSES AND EXPERIMENTAL RESULTS

A. Determination of cross sections for the collisional relaxation of $\langle S_z\rangle_g$

The nuclear-spin-independent cross section for the collisional relaxation of $\langle S_z\rangle_g$ induced in binary encounters of alkali atoms with buffer-gas atoms can be obtained from measurement of the difference of the two rate constants, Z_1 and Z_2, involved in the double-exponential time dependence of the $\langle S_z \rangle_g$ transient. From Eqs. (9a) and (9b) we obtain

$$Z_2 - Z_1 = B_2 - C_2 + 2B_3C_3(B_2 - C_2)^{-1} . \tag{10}$$

For Cs, Eq. (10) has the explicit form

$$Z_2 - Z_1 = \frac{31}{32} R + \frac{20}{32} R_s + 2\left(\frac{R_s}{32} + \frac{R}{32}\right)\left(\frac{21R_s}{32}\right) \times \left(\frac{31}{32} R + \frac{20}{32} R_s\right)^{-1} . \tag{11}$$

While Z_1 and Z_2 individually depend upon the pumping rate, the wall relaxation rate, and the molecular formation rate, their difference is independent of these parameters. Measurement of $(Z_2 - Z_1)$ thus yields a unique determination of R, and therefore of σ, if R_s is known.

It is possible to determine σ even if R_s is not precisely known. At "high" buffer-gas pressures corresponding to $R \geqslant 5 \text{ sec}^{-1}$, and for moderate or small spin-exchange rates corresponding to $R_s \leqslant 10 \text{ sec}^{-1}$, Eq. (12) applies with an accuracy of better than 99%:

$$Z_2 - Z_1 \cong B_2 - C_2 = \frac{31}{32} R + \frac{20}{32} R_s . \tag{12}$$

Measurement of $(Z_2 - Z_1)$ as a function of (high) buffer-gas pressure thus should yield a straight-line graph with slope

$$\frac{d(Z_2 - Z_1)}{dp} = \frac{31}{32} n_0 \sigma v_{\text{rel}} / p_0 , \tag{13}$$

and with extrapolated intercept

$$(Z_2 - Z_1)(p = 0) = \frac{20}{32} R_s . \tag{14}$$

We have utilized the experimental technique discussed in the first section of this paper to make measurements of Cs optical-pumping transients in He, Ne, Ar, and N_2 buffer gases at pressures ranging from 50 to 620 Torr. We have found uniformly excellent agreement between theory and experiment with regard to the double-exponential character of the $\langle S_z \rangle_g(t)$ transient. An example of "poor" data was presented in FS; in Fig. 1 we present an example of typical "good" data. Plots of the measured values of $(Z_2 - Z_1)$ versus buffer-gas pressure are presented in Figs. 2–4, together with fits of Eq. (12) to the experimental data. The error bars represent ± one standard deviation of from three to five measurements. The slopes and intercepts of the fits, together with the evaluated cross sections, are listed in Table I, together with the cross sections for the collisional relaxation of $\langle \vec{S} \cdot \vec{I} \rangle$ reported by Beverini, Minguzzi, and Strumia.[28]

We wish to emphasize the fact that the cross sections reported in Table I are *nuclear-spin-independent cross sections*. They have been extracted from experimental data subject to rigorous analyses of the influence of nuclear spin and the hyperfine interaction on all relaxation processes. They correspond to the cross sections

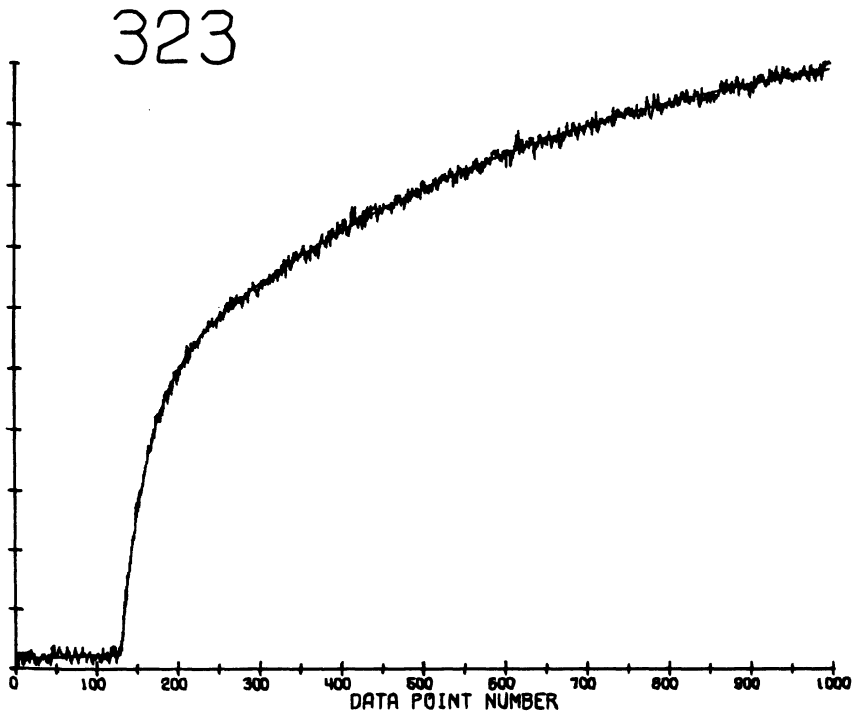

FIG. 1. Experimental optical-pumping transient and double-exponential fit for Cs^{133} in 621 Torr of Ne from white-light optical pumping at 15 °C. The horizontal axis is 500-msec full scale. 2^{12} sweeps were averaged. The evaluated curve parameters are $D_1/D_2 = 1.58$, $Z_1 = 4.53 \text{ sec}^{-1}$, and $Z_2 = 73.9 \text{ sec}^{-1}$.

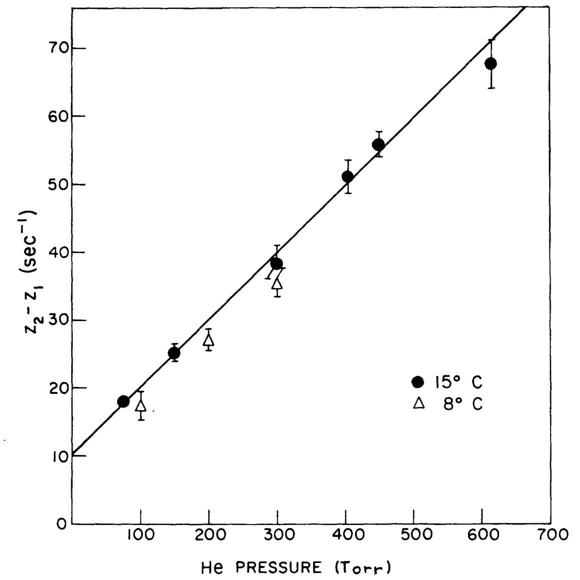

FIG. 2. Plot of measured differences of rate constants, $(Z_2 - Z_1)$ from double-exponential fits to optical-pumping transients of Cs^{133} in high pressures of He.

for collisional relaxation which should be measured in the absence of nuclear spin. They are not directly comparable with cross sections reported in many early papers. In 1964, for example, Legowski[29] and Franz and Lüscher[30] reported cross sections for the relaxation of $\langle S_z \rangle$ of Cs in Ne and Ar which are about an order of magnitude smaller than the cross sections reported in the present paper. These seemingly major disagreements with the present results are accounted for by the fact that in most early papers, including Refs. 29 and 30, data were analyzed subject to the assumption of a model of "uniform" ground-state relaxation and subject to the assumption that spin-exchange contributions to relaxation rates can be ignored. We now know that both assumptions are invalid. Re-analysis of the earlier experimental results with the equations derived in the present paper, coupled with consideration of the optical depth of the experimental cell, satisfactorily remove these discrepancies.[31] This result is gratifying from the points of view both of demonstrating internal consistency among data taken many years apart and of demonstrating the validity of the present calculations also in the limit of very strong spin exchange.

Considering alkali–buffer-gas relaxation alone, theory predicts that for Cs $(I = \frac{7}{2})$ the two relaxation rates Z_2 and Z_1 should be in the ratio 32:1. We have verified this prediction through measurements of pumping transients as a function of light intensity.[31] Theory also predicts that the cross sections for the relaxation of $\langle \vec{S} \cdot \vec{I} \rangle_g$ should be equal to the nuclear-spin-independent cross section for the relaxation of $\langle S_z \rangle_g$. This expectation is well fulfilled, as comparison of our results with those of Beverini *et al.* (see Table I) will show in the cases of He, Ar, and N$_2$. There is, however, an anomaly in the case of Ne where Beverini *et al.* have measured a cross section twice as large as that which we report. We have found no satisfactory explanation for this discrepancy.

There is one significant deviation of our ex-

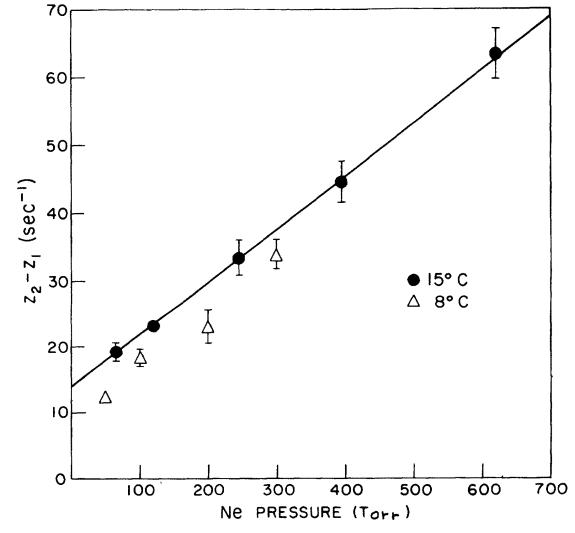

FIG. 3. Plot of measured differences of rate constants, $(Z_2 - Z_1)$ from double-exponential fits to optical-pumping transients of Cs^{133} in high pressures of Ne.

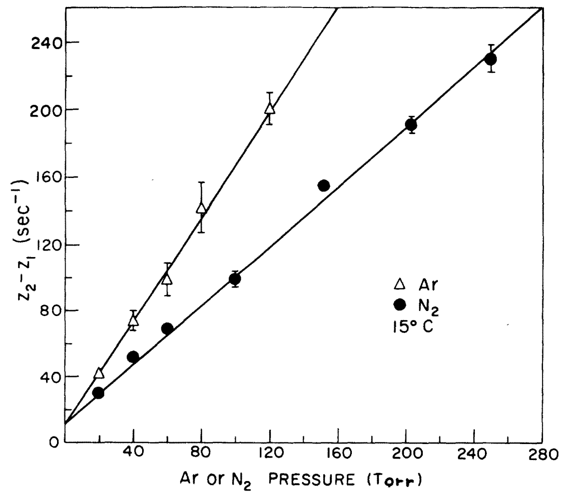

FIG. 4. Plot of measured differences of rate constants, $(Z_2 - Z_1)$ from double-exponential fits to optical-pumping transients of Cs^{133} in high pressures of Ar and N$_2$.

perimental results from our theoretical predictions. The extrapolated intercept of high-pressure $(Z_2 - Z_1)$ data is predicted to lie at $\frac{20}{32} R_s$ [Eq. (14)]. Taking σ_s to be 2.2×10^{-14} cm^2,[28] and p_{Cs} to be 4.6×10^{-7} Torr at 15 °C, we would expect this intercept to occur at 6.4 $\sec^{-1}$. The experimental extrapolations in fact turn out to be higher that this value by 4.2 to 7.4 $\sec^{-1}$, as reference to Table I will show. While this "excess relaxation" has no significant effect on the accuracy of our determinations of the ground-state relaxation cross sections, and merely limits the range of applicability of our technique for determining cross sections for collisional relaxation within the $^2P_{1/2}$ state, it remains of interest to search for its source since in all other respects our pumping equations and solutions appear to describe the characteristics of pumping transients to a high degree of accuracy. In the following paragraphs we consider some possible interactions not included in our rate equations which could lead to such an effect.

First, we wish to demonstrate that the excess relaxation is not accounted for by spin exchange alone. In Figs. 2 and 3 we have included data, marked by triangles, taken at 8 °C rather than at 15 °C. The only experimental parameter which changes markedly within this small-temperature interval is the spin-exchange rate R_s: it falls from 10.3 to 4.5 $\sec^{-1}$. Equation (12) indicates that the 8° $(Z_2 - Z_1)$ data therefore should fall about 3.7 $\sec^{-1}$ lower than the 15° data. Our results are consistent with this prediction. The helium 8° data fall an average of 3.4 ± 0.6 $\sec^{-1}$ lower than the 15° data, while the neon 8° data fall an average of 4.7 ± 1.4 $\sec^{-1}$ lower than the 15° data.

The question arises whether the excess relaxation can be attributed to the formation and destruction of Cs_2 dimers—we have not included the effects of such an interaction in our calculations. Gupta, Happer, Moe, and Park have in fact recently studied the magnetic resonance of such molecules in an optically pumped Cs vapor.[32] The properties of alkali dimers have been extensively studied, however, and their equilibrium concentration is well known. At 298 °K, for example, $n_{\mathrm{Cs}_2}/n_{\mathrm{Cs}} \approx 2.7 \times 10^{-5}$.[33] Since the collision cross section for Cs-Cs_2 cannot be much larger than the Cs-Cs spin-exchange cross section, it is clear that due to the extremely small concentration of Cs_2 at 288 °K, collisions of oriented Cs atoms with Cs_2 dimers cannot account for our observed excess relaxation.

We are left, we believe, with the possibility that the excess relaxation may be due to the formation and destruction of Cs–buffer-gas van der Waals molecules. While both in FS and in the present paper we allowed for contributions to relaxation rates from this source and found that the effect cancelled out in the quantity $(Z_2 - Z_1)$, our treatment is not quite correct at high buffer-gas pressures. We assumed that R', the relaxation rate due to the formation and destruction of van der Waals molecules, made contributions of equal strength to the rate equations for $\langle S_z \rangle_g$ and $\langle I_z \rangle_g$ [see Eqs. (3a), (3b), (7c), (7d)]. This is strictly true only at low buffer-gas pressures where the lifetime of the molecular complex is relatively long, of the order of 10^{-7} to 10^{-8} sec. In that case the spectral density function describing the relaxation interaction has appreciable components only at the Zeeman ($\Delta\omega$, $\Delta F = 0$, $\Delta m_F = \pm 1$) frequency; the amplitude at the hyperfine frequency (ΔW, $\Delta F = \pm 1$, $\Delta m_F = 0, \pm 1$) is effectively zero.[34-39] At buffer-gas pressures of a hundred Torr or more, and for destruction cross sections of the order of 10^{-14} cm^2, however, the amplitude of the spectral density function at ΔW can be several percent of that at $\Delta\omega$. In such a circumstance there can be a greater contribution to the relaxation of $\langle S_z \rangle_g$ than to that of $\langle I_z \rangle_g$, and the relaxation rates corresponding to R'' no longer cancel in $(Z_2 - Z_1)$. Such an effect, coupled with the peculiar characteristic dependence of relaxation rate on buffer-gas pressure, could give rise to our observed excess relaxation. Unfortunately our present data is not of sufficient accuracy to permit a definitive answer on this point. We

TABLE I. Slopes and intercepts of least-squares fits to data in Figs. 2–4. The evaluated nuclear-spin-independent cross sections for collisional relaxation of $\langle S_z \rangle_g$ are listed in column 3, and are compared with previous measurements of the relaxation of $\langle \vec{S} \cdot \vec{I} \rangle$ in column 4.

	$\frac{d(Z_2 - Z_1)}{dp}$ $(\sec\ \mathrm{Torr})^{-1}$	$(Z_2 - Z_1)$ $(p = 0)$ $(\sec^{-1})$	$\sigma(S_z)$ $(10^{-23}\ \mathrm{cm}^2)$	$\sigma(\vec{S} \cdot \vec{I})$ $(10^{-23}\ \mathrm{cm}^2)$ [a]
He	0.098 57	10.59	2.43	2.80 ± 0.3
Ne	0.078 42	13.82	4.08	9.27 ± 0.9
Ar	1.566	10.56	108	104 ± 10
N_2	0.9539	11.75	57.2	55.2 ± 4.4

[a] Reference 28.

TABLE II. Number of alkali–noble-gas van der Waals molecules (n_{AN}) relative to total Cs density (n_A) at 288 °K and 1 Torr of noble gas.[a] n_{AN}/n_A is proportional to noble-gas pressure.

Collision partners	n_{AN}/n_A
Cs-He	1.88×10^{-8}
Cs-Ne	4.83×10^{-8}
Cs-Ar	312×10^{-8}
Rb-Kr	597×10^{-8}

[a] References 40–42.

wish, however, to give an order-of-magnitude argument to show that the explanation is at least feasible.

Mahan has calculated formulas which permit estimation of the equilibrium numbers of Cs noble-gas-atom van der Waals molecules as a function of temperature and pressure of noble gas.[40,41] Using the potential parameters of Baylis,[42] we have calculated the equilibrium numbers of such molecules for Cs in He, Ne, Ar, and Rb in Kr (see Table II). Our largest excess relaxation was found in Ne; we shall consider that case in particular. It is clear from Table II that at 100 Torr of Ne there should be an equilibrium number of Cs-Ne molecules comparable to the equilibrium number of Rb-Kr molecules at 1-Torr Kr. The extraordinary contribution of molecular formation to relaxation rates in Rb-Kr is well known.[34-39] We do not, of course, expect nearly as great a contribution to relaxation rates, even within a hyperfine level, at 100 Torr as at 1 Torr, due to the shortening of the molecular lifetime. Nevertheless there should be some contribution, and we believe it may be sufficient to explain the excess relaxation we have encountered. A detailed analysis is beyond the scope of this paper, but we can draw upon some published experimental data to help demonstrate the plausibility of our contention. Bouchiat, Brossel, and Pottier showed that when 53 Torr of He was added to 0.9 Torr of Kr, the relaxation rate of Rb owing to molecular formation dropped drastically.[35] This effect was attributed to the accelerated breakup of the molecules. Nevertheless there remained a residual relaxation rate of about 10 $\sec^{-1}$ attributable to molecular formation. Thus, the formation and destruction of van der Waals molecules can contribute significantly to relaxation rates, at least within a hyperfine level, even at elevated buffer-gas pressures. While in an experiment such as ours additional information at high buffer-gas pressures should be obtainable from a careful study of the Z_1 rate constant, this cannot be done with our present data since in most cases the pumping rate was not directly measured; the need for such extensive and detailed measurements was not anticipated in that our techniques were specifically designed to circumvent the need for such knowledge. We thus are left with intriguing possibilities regarding the formation of alkali, light noble-gas van der Waals molecules, and their contributions to relaxation rates at high buffer-gas pressures, which stand in need of further investigation.

B. Determinations of cross sections for the collisional relaxation of $\langle J_z\rangle$ within the ${}^2P_{1/2}$ state

In FS we showed how measurements of the relative amplitudes, D_1 and D_2, and of the relaxation rates, Z_1 and Z_2, of the two exponentials making up the $\langle S_z\rangle_g$ pumping transient can be used to determine relaxation cross sections within the ${}^2P_{1/2}$ excited state. We showed that in the absence of spin exchange the theoretical expressions for the quantity D_1Z_1/D_2Z_2 depends only upon $\Gamma_1\tau$, the product of the collisional relaxation rate and the mean natural lifetime of the ${}^2P_{1/2}$ state:

$$\frac{D_1Z_1}{D_2Z_2} = \frac{21}{320}(188+3\Gamma_1\tau)(32+\Gamma_1\tau)^{-1} \times(2+3\Gamma_1\tau)^{-1}\,. \tag{15}$$

Measurements of ground-state transients thus yield determinations of $\Gamma_1\tau$, and therefore of σ_1, the nuclear-spin-independent cross section for the collisional relaxation of $\langle J_z\rangle$ within the ${}^2P_{1/2}$ state.

The simplicity of Eq. (15) arises from the fact that while D_1 and D_2 individually involve the pumping rate and all ground-state relaxation rates, a fortuitous cancellation takes place in the product D_1Z_1/D_2Z_2. This happy circumstance does not continue when contributions due to spin exchange are included in the rate equations. In that case the most convenient expression which permits a determination of $\Gamma_1\tau$ is simply the ratio of amplitudes, D_1/D_2. We obtain, after substitution of Eqs. (9a) and (9b) into (5a) and (5b),

$$\frac{D_1}{D_2} = [-B_2B_3C_1(B_2-C_2)-B_3C_3(B_3C_1+B_1B_2)][(B_2-C_2)(-B_1B_2C_2+B_1B_3C_3+B_3C_1C_2+B_1C_2^2) \times -B_3C_3(B_3C_1+B_1C_2)]^{-1}\,. \tag{16}$$

Application of Eqs. (16) and (7a)–(7f) to determine $\Gamma_1\tau$ from experimental data is a cumbersome but still a tractable task. First note that either C_1 or B_1 appears as a factor in each of the terms of Eq. (16); the pumping rate A thus cancels out of each of these terms. Second, note that R is determined independently from high-pressure measurements of $Z_2 - Z_1$. Since R_s is known from other measurements, it is easy to compute the values of B_3 and C_3 at any particular buffer-gas pressure. Knowing these terms, and taking advantage of the fact that at high pressures $(B_2 - C_2)$ is almost equal to $(Z_2 - Z_1)$, we obtain Eqs. (17a) and (17b) from Eqs. (9a) and (9b):

$$B_2 \cong Z_2 - B_3C_3(Z_2 - Z_1)^{-1} , \tag{17a}$$

$$C_2 \cong Z_1 + B_3C_3(Z_2 - Z_1)^{-1} . \tag{17b}$$

We thus are able to calculate B_2 and C_2 utilizing the experimentally measured values of Z_2 and Z_1. Such an approach circumvents a need to determine the actual magnitudes of the pumping rate and the relaxation rate owing to the possible formation of molecular complexes. All parameters in Eqs. (7a)–(7f) and (16) thus are known, with the exception of $\Gamma_1\tau$. The determination of $\Gamma_1\tau$ therefore reduces to a one-parameter fit of Eq. (16) to experimentally measured values of D_1/D_2.

There are theoretical and empirical limitations on the range of buffer-gas pressures in which Eq. (16) is valid. At buffer-gas pressures so high that Γ_1 exceeds the hyperfine frequency of the $^2P_{1/2}$ state, the nuclear spin does not have sufficient time to undergo reorientation between electron-spin relaxation events. The nuclear decoupling-recoupling approximation, upon which the calculations of the collisional relative transition probabilities among Zeeman sublevels of the $^2P_{1/2}$ state have been based, then becomes inappropriate. Since the hyperfine frequency of the $^2P_{1/2}$ state of Cs is of the order of 10^9 Hz, and the lifetime is 3.4×10^{-8} sec, determinations of values greater than about 30 for $\Gamma_1\tau$ must be considered invalid. Eq. (16) likewise loses accuracy at the lower end of the high-pressure data, that is, at pressures where the unexplained "excess" $Z_2 - Z_1$ intercept is comparable to the relaxation rate R. Fortunately there generally is an intermediate region of buffer-gas pressures stretching over several hundred Torr in which all criteria for validity of Eq. (16) are reasonably met. We report data and results relevant to that region.

The experimental data obtained from measurements of $\langle S_z\rangle_g$ pumping transients in the presence of high pressures of He and Ne, together with the evaluated values of $\Gamma_1\tau$ and σ_1 are summarized in Tables III and IV. The data are the same as those that were used in the determination of the ground-state relaxation cross sections. In the case of He, evaluations of $\Gamma_1\tau$ at pressures greater than 148 Torr were discarded, since $\Gamma_1\tau$ apparently exceeds 30 in those cases. In the case of Ne, evaluations of $\Gamma_1\tau$ were not made at 121 and 66 Torr since at those pressures the unexplained "excess" relaxation discussed above is comparable to R and cannot be neglected. For Cs-He we obtain an average cross section $\sigma_1(\text{Cs-He}) = 12.5 \times 10^{-16}$ cm^2, for Cs-Ne, $\sigma_1(\text{Cs-Ne}) = 6.9 \times 10^{-16}$ cm^2. The internal consistency of the sets of measurements reported in Tables III and IV are probably fortuitous; a realistic estimate of the possible error may be as high as 30%.

In Table V we compare our present measurements of σ_1 with earlier measurements made by Guiry and Krause[43] and by Gallagher,[44] as reinterpreted by Bulos and Happer.[45] Guiry and Krause performed their experiment in a magnetic field high enough (~10 kG) that within the $^2P_{1/2}$ state the nuclear spin was decoupled from the electronic moment; they therefore measured the nuclear-spin-independent cross section directly. The cross sections of Guiry and Krause and ours therefore should be equal. The agreement in fact is quite good. Both measurements show the cross sections to be about an order of magnitude smaller than corresponding cross sections within the $^2P_{3/2}$ state; the cause is the existence of a selection rule based on Kramer's theorem which retards collisional relaxation within an energetically isolated $^2P_{1/2}$ state.[44–48] Baylis has suggested that

TABLE III. Experimental data and evaluated values of $\Gamma_1\tau$ and σ_1 from $\langle S_z\rangle_g$ pumping transients of Cs in helium at 15 °C.

P (Torr)	Z_1 (sec^{-1})	Z_2 (sec^{-1})	D_1/D_2	$\Gamma_1\tau$	σ_1 (10^{-16} cm^2)
618	4.93 ± 0.38	72.3 ± 4.0	1.02 ± 0.06	∞	...
450	4.48 ± 0.49	60.3 ± 2.0	0.93 ± 0.06	~500	...
300	3.66 ± 0.23	42.0 ± 2.6	0.93 ± 0.05	~200	...
148	3.14 ± 0.15	28.5 ± 0.7	0.96 ± 0.06	29	13.7
75	3.30 ± 0.30	21.1 ± 1.0	0.81 ± 0.02	12	11.2

TABLE IV. Experimental data and evaluated values of $\Gamma_1\tau$ and σ_1 from $\langle S_z\rangle_g$ pumping transients of Cs in neon at 15 °C.

P (Torr)	Z_1 (sec^{-1})	Z_2 (sec^{-1})	D_1/D_2	$\Gamma_1\tau$	σ_1 (10^{-16} cm^2)
621	3.73 ± 0.20	67.2 ± 3.3	1.69 ± 0.08	30	7.2
396	2.46 ± 0.09	47.1 ± 2.4	1.94 ± 0.13	20.5	7.7
244	1.90 ± 0.02	35.1 ± 2.5	2.00 ± 0.08	9.5	5.8
121	1.61 ± 0.07	24.7 ± 1.2	2.12 ± 0.13	...	...
6.3	2.02 ± 0.07	21.2 ± 0.8	2.00 ± 0.11	...	...

TABLE V. Nuclear-spin-independent cross sections for the relaxation of $\langle J_z \rangle$ within the $6\,^2P_{1/2}$ state of Cs as measured by optical-pumping transients, Zeeman scanning, and the Hanle effect.

	σ_1 (10^{-16} cm^2) [a]	σ_1 (10^{-16} cm^2) [b]	σ_1 (10^{-16} cm^2) [c,d]
Cs-He	12.5	11.8	6.1
Cs-Ne	6.9	4.7	2.3

[a] Present work.
[b] Reference 43.
[c] Reference 44.
[d] Reference 45.

magnetic fields as small as 10 kG may induce considerable breaking of this selection rule.[49] The agreement between our low-field (0.2 G) results and those of Guiry and Krause at 10 kG, however, suggests that such a breakdown, which certainly should occur at *some* magnetic field, does not yet have any appreciable effect at 10 kG.

The lack of agreement between our results and those reported by Bulos and Happer reanalyzing Gallagher's Hanle-effect work is puzzling. In the absence of nuclear spin our experiment and the Hanle-effect experiment should yield the same values for the relaxation cross sections. While both experiments have been performed under conditions where hyperfine interaction effects are important, both have been carefully analyzed taking these effects into account. It would be useful, we believe, to have measurements of these low-field cross sections by a third independent method. A standard depolarization of resonance radiation experiment with σ^+ excitation, $I_{\sigma^+}-I_{\sigma^-}$ detection, would be of interest. Such an experiment, properly analyzed with regard to the effects of the hyperfine interaction, should yield cross sections equal to those which we report. The relevant equations have already been worked out, and are available in FS.

C. Pumping transients at low buffer-gas pressures: Determinations of diffusion coefficients

At low buffer-gas pressures the relaxation of $\langle S_z \rangle_g$ is dominated by the rate of relaxation owing to collisions of alkali atoms with the walls of the cell. In this regime the rate constants Z_1 and Z_2 approach values which differ mainly by their different dependence on the spin-exchange rate [see Eqs. (7c)–(7f), (9a), and (9b)]; at very low buffer-gas pressures, that is, at high wall relaxation rates, the two rate constants approach a common value. Fits of double-exponential functions to experimental data in such a situation can lead to ambiguous results: different pairs of exponentials can yield fits which are equally good within the limits of experimental accuracy. In fact, a single "effective" exponential reproduces the shape of the true double-exponential transient extremely well, as we indicate in Eq. (18):

$$D_1(1-e^{-Z_1 t})+D_2(1-e^{-Z_2 t}) \cong D_3(1-e^{-Z_3 t}) , \tag{18}$$

where

$$D_3 = D_1 + D_2 , \tag{19}$$

and Z_3 is the effective single-exponential relaxation rate. We have shown through explicit computer calculations that if $1 \leq Z_2/Z_1 \leq 1.5$, then Eq. (20) below applies with an accuracy of 97%, regardless of the D_1/D_2 ratio:

$$Z_3 \cong (D_1 Z_1 + D_2 Z_2)(D_1 + D_2)^{-1} . \tag{20}$$

The parameters D_1, D_2, Z_1, and Z_2 remain as defined by Eqs. (7c)–(7f). The more closely equal the rate constants Z_1 and Z_2 are, the better the approximation in Eq. (20) becomes.

We have taken advantage of the single-exponential approximation to determine the diffusion coefficients of Cs in various buffer gases. Specifically, we have measured pumping transients in He, Ne, Ar, and N_2 buffer gases at pressures ranging from 1.00 to 7.3 Torr, and have extracted effective single-exponential rate constants from fits to the experimental data. An example of a typical low-pressure transient and single-exponential fit is given in Fig. 5. In order to extract the diffusion coefficient from such data, we first note that the value of Z_3 depends upon all possible relaxation rates, including the collisional relaxation rate within the excited state. We have, however, already determined $\Gamma_1 \tau(p)$ and $R(p)$ from measurements of transients at high buffer-gas pressures, as described in Secs. IV A and IV B above. We shall assume for the moment that R'', the relaxation rate due to the formation and destruction of van der Waals molecules, is effectively zero. The only remaining unknown parameters in Eqs. (7c)–(7f), and therefore in Eqs. (9a), (9b), and (20), then are A, the pumping rate, and R', the wall relaxation rate. A is easily determined from measurements of the transient pumping rate as a function of light intensity. (In our low-pressure work A was 1.4 ± 0.4 sec^{-1}.) Experimental measurement of Z_3 thus fixes the value of $R''(p)$; D_0 is then determined from Eq. (8c). In Fig. 6 we present the results of our measurements of effective single-exponential rate constants for Cs relaxation in low pressures of He, Ne, Ar, and N_2 buffer gases. The error bars represent ± standard deviation of three to five measurements. The solid lines are the theoretical predictions of Eq. (20) utilizing values of D_0 chosen for best fit. We emphasize that D_0 is the only adjustable parameter involved in these fits; all other parameters are fixed by independent

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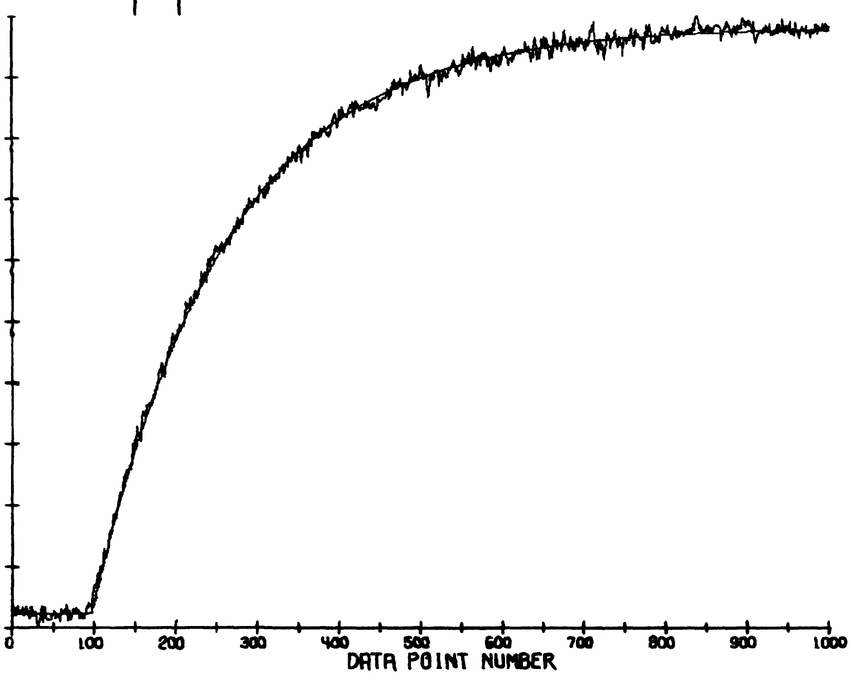

FIG. 5. Experimental optical-pumping transient and single-exponential fit for Cs^{133} in 3.02 Torr of Ar from white-light optical pumping at 15 °C. The horizontal axis is 200-msec full scale. 2^{13} sweeps were averaged. The evaluated effective rate constant Z_3 is 30.4 sec^{-1}.

measurements.

In Table VI we list our determinations of D_0 and compare them with previous measurements and with some approximate theoretical values. The first column contains our measurements made at 288 °K. The second column contains extrapolations of our measurements to 273 °K, assuming a $T^{3/2}$ dependence for D_0. The third column contains the measurements of Beverini *et al.*, obtained from measurement of the relaxation of $\langle \vec{S} \cdot \vec{I} \rangle$. Our major disagreement with the measurements of Beverini *et al.* lies in the determination of the He diffusion coefficient: their experimental value lies 30% lower than ours. We are convinced that our value is the more reliable, however. The data from which our D_0 is evaluated spans a range of relaxation rates from 30 to 162 sec^{-1}, a total variation of 132 sec^{-1}, while the data of Beverini *et al.* spans a range of relaxation rates from 14 to 9.5 sec^{-1}, a total variation of only 4.5 sec^{-1}. Moreover, our results are consistent with those obtained in a very small cell (~12 cm^2) at very high magnetic fields (80 kG).[50]

TABLE VI. Experimental and theoretical diffusion coefficients (at $p = 1$ atm) for Cs in various buffer gases.

	D_0 (15 °C) [a] ($cm^2 sec^{-1}$)	D_0 (273 °K) [b] ($cm^2 sec^{-1}$)	D_0 (273 °K) [c] ($cm^2 sec^{-1}$)	D_0 (273 °K) [d] ($cm^2 sec^{-1}$)
Cs-He	0.315	0.291	0.204	0.264
Cs-Ne	0.185	0.171	0.153	0.104
Cs-Ar	0.120	0.111	0.134	0.095
Cs-N_2	0.106	0.098	0.073	...

[a] Evaluated from present measurements.

[b] Present determinations extrapolated to 273 °K assuming a $T^{3/2}$ dependence.

[c] Measurements of Beverini *et al.*

[d] Theoretical values, calculated as explained in text.

The approximate theoretical values of D_0 listed in Table VI were calculated in the following way. We took Cs noble-gas potentials of Baylis[42] and calculated the approximate internuclear separation r_1 of cesium noble-gas atoms when the (6-8) van der Waals potential is equal to the mean kinetic energy at 273 °K.[51] This value of r should be a reasonable approximation to the hard-sphere collision diameter σ_r. The diffusion coefficients were then calculated from the standard formula.[52]

$$D_0 = \frac{3}{8(n_1+n_2)\sigma_r^2}\left(\frac{kT(m_1+m_2)}{2\pi m_1 m_2}\right)^{1/2} . \qquad (21)$$

There is an additional check which can be made on the consistency of the various D_0 values which we report. The collision diameters of the noble gases are reasonably well established from measurements of the noble-gas self-diffusion coefficients, analyzed with the aid of Eq. (21).[53,54] We list these diameters in column 1 of Table VII. We can extract the noble-gas collision diameters in a similar way from our own diffusion data; these values are listed in column 2. The approximate values of the Cs collision diameters are then easily found: they are listed in column 3. The resultant mean value of the Cs collision diameter is $(4.72 \pm 0.62) \times 10^{-8}$ cm. While the consistency of these collision diameters is not superb, it is considerably better than in any other optical-pumping experiment of which we are aware.

It is important to determine whether the unexplained "excess relaxation" encountered at high buffer-gas pressures persists at low buffer-gas pressures. If that were the case, all of our evaluated diffusion coefficients, particularly that of Ne, would be larger than the true values. Moreover, the predicted equilibrium numbers of van der Waals molecules at low He and Ne pressures are sufficiently small to make molecular formation a negligible contributor to measured relaxation rates in this regime. Indeed, if the excess relaxation were found to persist at low He or Ne pressures, one could rule out the possibility of molecular formation being its cause. We call attention therefore, to the data in Fig. 6 and to the corresponding fits to this data. The agreement of theory with experiment is excellent. We have made additional fits including possible excess relaxation in Z_2 and have found no way to make these fits compatible with the experimental measurements. We are convinced that the "excess relaxation" is *not* present at low buffer-gas pressures; it appears to be strictly a high buffer-gas-pressure phenomenon.

Finally, we return to consider the point that in evaluating D_0 from the low-pressure pumping data we neglected R'', the normal relaxation rate owing to the formation and destruction of van der Waals molecules. This should be an excellent approximation at low pressures of He and Ne, but not for the heavier noble gases. For Rb^{85} in Kr, for example, Bouchiat *et al.* measured a contribution to the relaxation rate of $\langle I_z \rangle_g$ of about 135 sec^{-1} from molecular formation and destruction. From Table II we see that the probability of formation of Cs-Ar molecules is quite comparable to that for Rb-Kr molecules. Extrapolating from the Rb-Kr experimental results, and folding in factors involving the relative velocities and nuclear spins, we would anticipate the contribution to Cs-Ar relaxation from molecular formation to be of the order of 40 sec^{-1} at 4-Torr Ar. In fact, we find experimentally no contribution whatever from this source. If molecular formation were to contribute significantly to our measured relaxation rates, then our evaluated value of D_0 would be anomalously high. We note, however, that our experimental value for D_0 (Cs-Ar) is 0.111, which is lower than the value of 0.134 found by Beverini *et al.* in their experiment on the relaxation of $\langle \vec{S} \cdot \vec{I} \rangle$, in which molecular formation is known not to contribute to relaxation rates. Our measured rate constant of 28 sec^{-1} for Cs in 4-Torr Ar therefore appears to be fully accounted for by ground-state relaxation processes other than molecular formation. We cannot rule out the possibility that there may be *some* contribution to relaxation from this source, but it is most difficult to see how such a contribution could be as much as 4 sec^{-1}. We conclude, therefore, that the contribution to the relaxation of $\langle S_z \rangle_g$ from the formation of van der Waals molecules is at least an order of magnitude smaller that that which would be expected from extrapolation of the results obtained on the Rb-Kr system. There can be little doubt that Cs-Ar molecules should be present in approximately the proportion predicted: the underlying theory is very firmly established. We are left, then, with the rather surprising fact that the formation of Cs-Ar mole-

TABLE VII. Collision diameters evaluated from (a) self-diffusion data, (b) diffusion coefficients evaluated in this experiment, and (c) combination of (a) and (b).

x	(a) $\sigma_r(x)$ (Å)	(b) $\sigma_r(x-\mathrm{Cs})$ (Å)	(c) $\sigma_r(\mathrm{Cs})$ (Å)
He	2.05	3.82	5.59
Ne	2.42	3.43	4.43
Ar	3.47	3.69	3.91
N_2	3.48	4.22	4.96

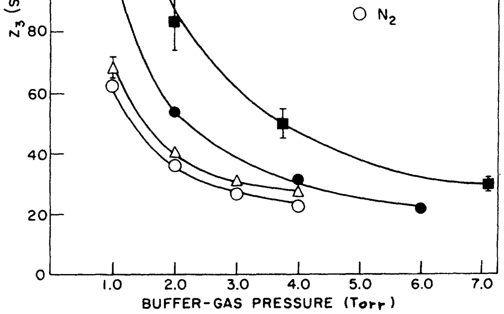

FIG. 6. Fits of Eq. (20) to measured effective single-exponential rate constants of optical-pumping transients of Cs^{133} in low buffer-gas pressures at 15 °C.

cules, in contradistinction with Rb-Kr, has very little effect on the relaxation rates of spin polarization.

V. SUMMARY

The comprehensive pumping equations and solutions presented in this paper, together with the calculations already presented in FS, provide a thorough and complete description of optical pumping in alkali-metal vapors in the weak-pumping limit. We have utilized these calculations to develop new techniques for accurate determinations of the nuclear-spin-independent cross sections for collisional relaxation of spin polarizations in the ground and excited states of the alkali-metal atom, and of the diffusion coefficient of the alkali-metal atom in various buffer gases. While our experimental studies have been restricted to Cs, our techniques are applicable also to other alkali-metal atoms: the appropriate calculations for nuclear spins $\frac{3}{2}$ and $\frac{5}{2}$ have already been published.

Fruitful extensions of white-light pumping techniques can be made, especially in the study of systems for which stable pumping sources are difficult to obtain, such as short-lived or rare isotopes, or in systems possessing relatively fast relaxation times. It would not be difficult, for example, through using Fabry-Perot interferometers to further narrow band the detection, focusing the pumping light within the optical-pumping cell, and working at higher vapor pressures, to improve the detection sensitivity by at least two orders of magnitude over that reported in the present experiment. Other intriguing applications of optical-pumping transient experiments also exist, for example, in the study of relative probabilities for transitions between Zeeman sublevels induced by quenching collisions. The possibilities are many. Some are already in progress in our laboratory and will be reported in future publications.

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