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Rubidium Spin Relaxation in the Rare Gases Under Ultraclean Conditions[*]

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The spin relaxation of optically pumped rubidium vapor induced by rubidium–rare-gas atomic collisions has been investigated in an ultraclean environment. The experiment was performed under conditions such that the partial pressure of nonrare-gas impurities was less than 1×10^{-8} Torr, and that the time between Rb-Rb spin exchange collisions was short compared to the spin relaxation time. The cross sections (in cm^2) for disorientation of rubidium were found to be: He, 3.3×10^{-25}; Ne, 3.3×10^{-24}; Ar, 1.1×10^{-22}; Kr, 7.3×10^{-21}; Xe, 1.3×10^{-19}. The fact that these cross sections are considerably smaller than previously reported values is attributed primarily to the low degree of impurity contamination in the present work. When compared with already existing values for cesium and sodium, the disorientation cross sections of these three alkali metals are seen to have a remarkably similar dependence on buffer-gas atomic number. The new experimental values are also compared with recent theoretical calculations.

INTRODUCTION

An extremely high polarization or orientation of a vapor of paramagnetic atoms can be obtained by the method of optical pumping.[1] A few of the materials most extensively studied by this technique have been isotopes of atomic hydrogen,[2,3] nitrogen,[4–7] mercury,[8] and helium,[9–11] with particular emphasis on cesium,[12] rubidium,[13] potassium,[14] and sodium.[15,16] When vapors of these atoms are subjected to optical pumping, large population differences in the Zeeman magnetic sublevels of the atomic ground state are created through selective absorption and re-emission of circularly polarized resonance radiation. The alkali metals are particularly well suited for this purpose because of their relatively high vapor pressures, strong optical resonance lines, and favorable electronic structure. The degree of polarization that may be obtained is limited in general only by the intensity of available light sources and by the amount of disorientation caused by collision of polarized atoms with impurities or with the walls of the containing vessel. It was realized early that disorientation at the walls could be greatly reduced, either by coating the walls with certain inert hydrocarbon or silicone compounds,[17] or by adding a nonmagnetic "buffer gas" that would retard diffusion of polarized atoms to the walls of the cell, while not in itself causing disorientation.[18] Both techniques have been widely used, and each has led to further interesting physical problems.

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[1] For comprehensive reviews of optical pumping techniques, see G. V. Skrotskii and T. G. Izyumova, Usp. Fiz. Nauk **73**, 423 (1961) [English transl.: Soviet Phys.—Usp. **4**, 177 (1961)]; and A. Kastler, J. Opt. Soc. Am. **47**, 460 (1957) or Nuovo Cimento Suppl. **6**, 1148 (1957).

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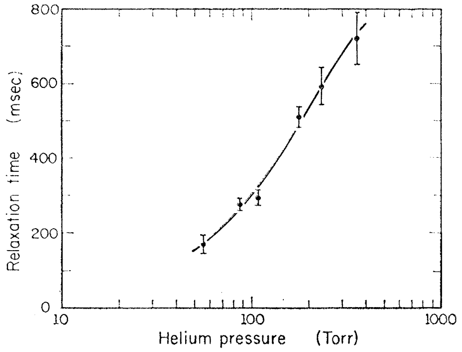

FIG. 1. Relaxation of optically pumped rubidium in helium. In Figs. 1–3 the error bars are equal to one standard deviation from the mean for more than five, but less than ten determinations of the relaxation time. The solid line in each case represents the best fit of Eq. (1) to the data.

In 1959, W. Franzen investigated the relative efficiency of various rare gases as buffers for optically pumped rubidium.[19] By measuring the relaxation time of the polarized vapor as a function of buffer-gas pressure, he was able to evaluate spin-disorientation cross sections for rubidium in neon, argon, krypton, and xenon. He showed that for buffer gases of low atomic number these cross sections were astonishingly small, of the order of 10^{-8} times the gas kinetic cross section, whereas, for a gas of high atomic number such as xenon, the cross section was 10^{-5} times the kinetic cross section. This relatively large variation of the rare-gas disorientation cross sections proved to be of considerable interest and has not yet been fully explained. Franzen's pioneering work has since provided a basis for other researchers who have extended the study of spin relaxation to other buffer gases,[20–22] and to other alkali metals.[23–28]

In recent papers, Franz and Lüscher,[27] and Legowski[28] reported measurements of the disorientation cross sections for cesium in neon and argon that appeared to be inconsistent with the previously reported values for rubidium in these gases. In particular, it was difficult to understand why the disorientation cross section for cesium in neon should be an order of magnitude *smaller* than that for rubidium in neon, since it seemed reasonable to expect that an alkali of larger atomic number would generally have a larger disorientation cross section in any particular buffer gas. In the work on cesium mentioned above,[27] it was observed that under some circumstances a small amount of residual impurity in the optical-pumping cell could have an unexpectedly large effect on the measured relaxation times, and thus could lead to an inaccurate determination of the spin-disorientation cross section. Since a "small amount" can mean as little as 10^{-7}- to 10^{-6}-Torr impurity partial pressure, the utilization of an ultrahigh vacuum system in a spin-disorientation experiment was clearly indicated. Furthermore, the rubidium-rubidium spin-exchange cross section has recently been carefully measured,[29] yielding a value about a factor of 5 smaller than had been previously supposed. This would indicate the possibility that a "spin-temperature equilibrium" in the rubidium vapor may not have existed in Franzen's experiment, as had been assumed. The lack of such an equilibrium can lead to ambiguity in the interpretation of the measured relaxation times. For these reasons we felt it would be worthwhile to remeasure the rubidium disorientation cross sections under ultraclean conditions and at higher rubidium vapor pressure.[30] New values for these cross sections have been obtained that differ in some cases by more than an order of magnitude from previous rubidium measurements, but which are now in much better qualitative agreement with measurements on other alkali metals. It is suggested that the primary difference between the present experiment and the original work by Franzen lies in degree of impurity contamination.

EXPERIMENTAL APPARATUS

Since the bulk of the equipment used in this experiment was similar to that described in our earlier report on cesium,[27] only important modifications to that apparatus will be noted. In the present work an all-metal-and-glass ultrahigh-vacuum system was used both for the optical-pumping cell and for the gas-handling manifold, with bakeable Granville-Phillips ultrahigh vacuum values used throughout. A zeolite trap was placed between the diffusion pump and the rest of the system in order to remove any vapors back-streaming from the pump. Buffer-gas pressures were measured using a null-type capacitance manometer, balanced by an ordinary oil manometer. The entire apparatus was baked at a temperature of 350°C for 24 hours, reaching an ultimate vacuum of 1×10^{-10} Torr as measured by a Bayard-Alpert gauge. When closed off from the pumps, the system was capable of maintaining a vacuum of better than 10^{-8} Torr for an extended period of time. Following bakeout, pure rubidium was distilled from a Pyrex breakseal into the optical-pumping cell.

The rubidium lamp used in this experiment was of

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[27] F. A. Franz and E. Lüscher, Phys. Rev. **135**, A582 (1964).

[28] S. Legowski and E. Lipworth, J. Chem. Phys. **41**, 1313 (1964).

[29] H. W. Sands and R. H. Moos, Phys. Rev. **135**, A591 (1964).

[30] F. A. Franz, Phys. Letters **13**, 123 (1964).

the same type as that employed in the cesium work,[31] with improved intensity and stability obtained through immersion of the radio-frequency coil and bulb in heated Dow Corning #200 silicone oil. This lamp emitted a "broad" D_1 line, with approximately equal intensity in all hyperfine components. The optical-pumping light, having traversed the usual D_2 filter[32] and circular polarizer, was passed in an essentially parallel beam through the optical-pumping cell. Precautions were taken to insure complete and uniform incident illumination. A large condensing lens in back of the cell focused the entire beam on the surface of a 917 phototube. In order to insure the presence of a saturated vapor during the experiment, a small pool of rubidium was deposited in the bottom of the optical-pumping cell. Both the cell and the lamp contained natural rubidium, that is, a mixture of the two common rubidium isotopes.

The transient response of the monitoring photocell was greatly improved by providing constant exposure to a low-intensity dc lamp. The relaxation signal obtained from the photocell upon the closing and opening of a shutter was passed first through a low-noise, wide-band dc amplifier, then through a solid-state clipping circuit, and finally photographed from the screen of a Tektronix 515 oscilloscope. Between 5 and 10 photographs (i.e., determinations of the relaxation time) were made at each pressure indicated in Figs. 1–3, with between 20 and 30 data points per picture. The method of data reduction was the same as that described in the cesium paper.

EXPERIMENTAL RESULTS

As has been usual in experiments of this type, the relaxation time τ of the optically pumped rubidium vapor was measured as a function of buffer-gas pressure p. In the present work the dependence of τ upon p is assumed to be[27]

$$\tau=\left[\frac{480D_0}{p}+N_0v_{\mathrm{rel}}\sigma\frac{p}{760}\right]^{-1}, \tag{1}$$

where $N_0=2.15\times10^{19}$ cm^{-3}, and v_{rel} is the mean relative velocity for buffer-gas atoms and rubidium atoms at 67°C. The experimental data for rubidium relaxation in helium, neon, and argon are displayed in Figs. 1–3. The solid line in each figure represents the best fit of Eq. (1) to the data, thus determining the value of the diffusion coefficient D_0, and the spin-disorientation cross section σ for rubidium in each gas. These parameters, along with previously measured values, appear in Tables I and II.

TABLE I. Cross sections for spin disorientation of rubidium in the rare gases. (All cross sections are expressed in cm^2.)

	Present work	Previous work[a]
He	3.3×10^{-25}	6.5×10^{-25}
Ne	3.3×10^{-24}	5.2×10^{-23}
Ar	1.1×10^{-22}	3.7×10^{-22}
Kr	7.3×10^{-21}	5.9×10^{-21}
Xe	1.3×10^{-19}	1.3×10^{-20}

[a] References 19 and 20.

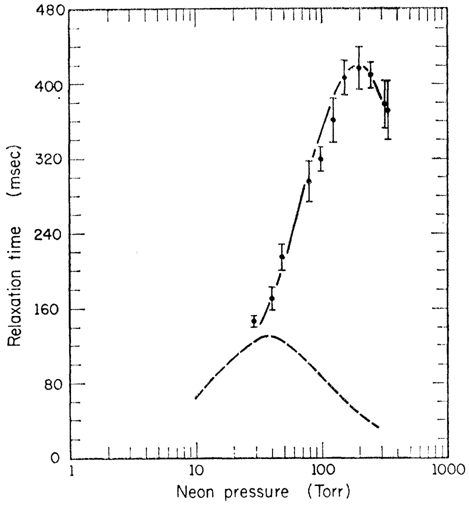

FIG. 2. Relaxation of rubidium in neon. The dashed curve at the bottom of the figure indicates the dependence of the relaxation time upon neon pressure that would have been predicted from previous measurements (Ref. 19).

In order to measure the cross sections for krypton and xenon, small amounts of these gases were mixed in neon, since rubidium relaxation in pure krypton or xenon is too fast to be measured by the present method. Knowing the relaxation time in pure neon, it is possible to evaluate the disorientation cross sections for krypton and xenon from the relaxation times measured for the mixtures.[27] The mixtures employed were 0.725-Torr krypton in 127-Torr neon, 0.725-Torr krypton in 240-Torr neon, 0.128-Torr xenon in 127-Torr neon, and and 0.128-Torr xenon in 164-Torr neon, yielding relaxation times of 114, 120, 55, and 48 msec, respectively. The average cross sections deduced from these values are listed in Table I.

No maximum in the relaxation curve for helium (Fig. 1) was reached due to the impossibility of attaining sufficiently high helium pressures in the present apparatus. The disorientation cross section determined for this gas must therefore be considered relatively

TABLE II. Diffusion coefficients of rubidium in the rare gases. The values given are for the diffusion coefficient at atmospheric pressure. Units are cm^2/sec.

	He	Ne	Ar
Present work (67°C)	0.68±0.20	0.48±0.10	0.37±0.08
Previous work (48°C)	0.54	0.31	0.24

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[31] F. A. Franz, Rev. Sci. Instr. 34, 589 (1963).

[32] I am indebted to Professor Robert Novick and the Columbia Radiation Laboratory for their generous loan of an interference filter suitable for this experiment.

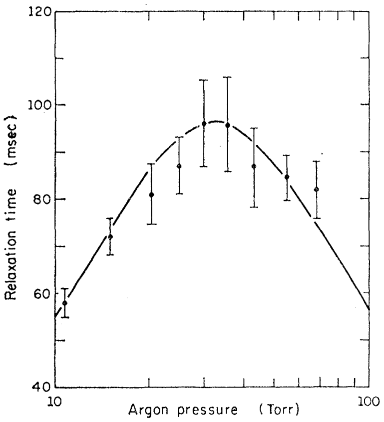

FIG. 3. Relaxation of rubidium in argon.

inaccurate. In Fig. 2, the small dashed curve represents the variation of relaxation time *versus* neon pressure that would be predicted if Franzen's values for D_0 and σ are inserted into Eq. (1). The new value for the neon disorientation cross section is more than an order of magnitude smaller than the value previously reported.[19]

Several additional features of the relaxation-time–versus–buffer-gas-pressure curves should be mentioned. In both the neon and argon curves there is a clear maximum as predicted in Eq. (1), considerably improving the determination of D_0 and σ. Furthermore, although the relaxation times are considerably longer than would be predicted on the basis of previous measurements, at low buffer-gas pressures they seem to fall slightly below these predictions. One thus must explain why both somewhat shorter relaxation times at low gas pressure and amazingly longer relaxation times at higher gas pressure have been measured in the work reported in this paper. It is almost certain that these differences arise from the fact that the present experiment has been performed under ultraclean conditions, whereas in previous work a small amount of contamination in the absorption cell may have had an unexpectedly large effect. This possibility will be further explored in the following section.

DISCUSSION

(A) The Relaxation Signal

Although all measurements were made on a sample of natural rubidium (72.2% Rb^{85}, 27.8% Rb^{87}), for the moment only the isotope Rb^{87} ($I=\frac{3}{2}$) will be considered. In its ${}^2S_{1/2}$ ground state, this isotope has a total of eight m_F sublevels within the two hyperfine levels $F=2,1$. At room temperature the occupation probabilities of all eight levels are essentially equal. Franzen and Emslie,[33] and Dehmelt,[34] were the first to suggest that a radical change in the thermal-equilibrium population distribution would be produced by the absorption of circularly polarized D_1 light, resulting in a "pumping" of the vapor to a state of net orientation or polarization. This method of polarization has been used in the present work and in many previous experiments.

The degree of absorption from the light transmitted through an optical-pumping cell is closely related to the spin polarization of the optically pumped vapor. Let a beam of left-circularly-polarized D_1 photons be passed through a cell containing the alkali vapor plus buffer gas. If the intensity of the light transmitted through the cell is monitored, strong initial absorption will be observed, followed by a gradual increase of intensity of transmitted light as the vapor is "pumped" to its polarized state. If K represents the absorption of light at any time, with the vapor in any state of polarization, then

$$K=\sum_i AK_i\rho_i\,, \tag{2}$$

where A is a function of the incident light intensity, and K_i and ρ_i are the absorption and occupation probabilities for the ith state. The initial absorption of light by an unpolarized vapor is thus

$$K_0=\sum_i AK_i\rho_i^0\,, \tag{3}$$

where ρ_i^0 is the thermal-equilibrium occupation probability for the ith state. All ρ_i^0 are equal and $\sum_i \rho_i^0 =\sum_i \rho_i = 1$, by definition.

The usual technique followed in experiments of this type is to allow a polarized vapor to relax in the dark for known length of time, and then to record the initial absorption that occurs when the optical pumping light is again passed through the cell. A plot of initial absorption *versus* dark time yields the "relaxation signal" R as a function of dark time, where

$$R=K_0-K=\sum_i AK_i(\rho_i^0-\rho_i)\,. \tag{4}$$

R as defined above is equivalent to the signal "S_m" in Ref. 36. The absorption probabilities K_i for the case under consideration are listed in Table III, along with the expectation values of S_z, the z component of alkali electron spin, and I_z, the z component of alkali nuclear spin, for the various (F,m_F) states. K_i can be written

TABLE III. Absorption probabilities and expectation values of S_z and I_z for the magnetic sublevels of the ground state of Rb^{87} ($I=\frac{3}{2}$). The absorption probabilities are calculated for the absorption of left circularly polarized D_1 (7948 Å) light. The expectation values of S_z and I_z are calculated in the weak-field limit, i.e., F is a good quantum number.

F	m_F	K_i	$\langle S_z\rangle$	$\langle I_z\rangle$
2	2	0	1/2	3/2
2	1	1	1/4	3/4
2	0	2	0	0
2	−1	3	−1/4	−3/4
2	−2	4	−1/2	−3/2
1	1	3	−1/4	5/4
1	0	2	0	0
1	−1	1	1/4	−5/4

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

[34] H. G. Dehmelt, Phys. Rev. **105**, 1482 (1957).

in the form $4\langle\frac{1}{2}-S_z\rangle_i$. Letting $\chi_i=(\rho_i-\rho_i^0)$,

$$R=-\sum_i A\chi_i 4\langle\tfrac{1}{2}-S_z\rangle_i=4A\sum_i \chi_i\langle S_z\rangle_i. \qquad (5)$$

The relaxation signal R is thus directly proportional to the average electronic spin polarization $\sum_i \chi_i\langle S_z\rangle_i=\langle S_z\rangle$ of the vapor. This implies that relaxation times measured in this experiment are actually measures of the decay of $\langle S_z\rangle$, rather than of the total polarization $P=\sum_i m_i\chi_i$.

(B) The Spin-Temperature Approximation

If an optically pumped vapor is allowed to relax in the dark, the rate of change of the occupation probability ρ_i of the ith ground state sublevel is given by[23]

$$d\rho_i/dt=D_0(p_0/p)\nabla^2\rho_i-N_0(p/p_0)v_{\mathrm{rel}}\sigma\rho_i + c + \text{spin-exchange terms}, \qquad (6)$$

where D_0 is the diffusion coefficient of the alkali in 760 Torr of buffer gas, p_0 is 760 Torr, p is the actual buffer gas pressure, N_0 is the number of atoms at atmospheric pressure and the temperature under consideration, v_{rel} is the relative velocity of alkali and buffer gas atoms, σ is the disorientation cross section, and c is a constant. The various terms on the right-hand side of this equation arise from diffusion of polarized alkali to the walls of the cell, disorientation due to alkali-rare gas collisions, and disorientation-induced scattering *into* the state i. If we multiply both sides of the equation by m_i, and sum over all i, we obtain

$$dP/dt=D_0(p_0/p)\nabla^2 P-N_0(p/p_0)v_{\mathrm{rel}}\sigma P, \qquad (7)$$

where $P=\sum_i m_i\rho_i=\sum_i m_i\chi_i$ is the total polarization of the vapor. The spin-exchange terms do not contribute to the relaxation of P since in a collision between two alkali atoms (1,2) the quantity $[m_F^{(1)}+m_F^{(2)}]$ remains invariant,[19] thus implying that the net polarization of the colliding pair does not change. This lack of dependence of alkali relaxation on spin exchange has been experimentally verified by Bouchiat.[35] The general series solution of Eq. (7), subject to the boundary condition that $P=0$ at the walls of the cell, has been given by several authors,[20,23,27] and will not be reproduced here. It has been customary to assume that only the first term of the series contributes to the relaxation, and this has also been done in the present work, resulting in Eq. (1) relating the measured relaxation time to the buffer gas pressure.

A difficulty now arises in the fact that Eq. (7), which we wish to use to describe the relaxation of the optically pumped vapor, involves the total polarization $P=\sum_i m_i\chi_i$, whereas the experimentally detected relaxation signal involves the z component of electronic spin, $\langle S_z\rangle=\sum_i\langle S_z\rangle_i\chi_i$. Since $\langle S_z\rangle$ differs from P by a term involving the occupation probabilities for several states, these two parameters will not in general follow the same equation of motion. Fortunately, the spin-temperature approximation[4] offers a way out of this dilemma.

If the time τ_{ex} between alkali-alkali spin-exchange collisions is short compared to the thermal relaxation time τ, a "spin-temperature equilibrium" obtains in which the populations ρ_i of the various m_F substates assume a particularly simple form $\rho_i=Ce^{-m_i\beta}$, where C is a normalization constant and β is a spin-temperature parameter. If an optically pumped vapor is allowed to relax in the dark, any disorientation brought about by collisions of polarized atoms with rare gas atoms or cell walls is reflected by a decrease in β. Anderson[36] has shown that when the spin-temperature approximation applies, the polarization P is an essentially linear function of $\langle S_z\rangle$, for spin polarizations up to about 30%. Such a value of spin polarization is about the limit that can be obtained using uncoated optical pumping cells and rare-gas buffers. This means that under normal experimental conditions, provided that $\tau_{\mathrm{ex}}\ll\tau_{\mathrm{relax}}$, the difficulties voiced above do not apply, and the relaxation times measured are representative of the decay of both $\langle S_z\rangle$ and P.

The condition necessary for a spin-temperature equilibrium to exist ($\tau_{\mathrm{ex}}<\tau$) must now be considered. τ_{ex} can be written $\tau_{\mathrm{ex}}=1/(n\sigma_{\mathrm{ex}}v_{\mathrm{rel}})$, where n is the number of rubidium atoms per cm^3, σ_{ex} is the spin-exchange cross section, and v_{rel} is the mean relative velocity of the rubidium atoms. The vapor pressure of rubidium as a function of temperature is given by[37]

$$\log_{10}p(\mathrm{Rb})=4560/T+12.00-1.45\log_{10}T, \qquad (8)$$

resulting in a value of 2.4×10^{11} cm^{-3} for n at 67°C. The selection of an appropriate value for σ_{ex} poses more of a problem. Several workers have recently measured the various Rb-Rb spin-exchange cross sections and have obtained quite different results. The only consistent feature appears to be that each researcher has found the cross sections Rb^{85}-Rb^{85}, Rb^{87}-Rb^{87}, and Rb^{85}-Rb^{87} to be approximately equal in his experiment. Bouchiat and Brossel[38] found values for these cross sections between 6×10^{-14} and 8×10^{-14} cm^2, while Jarrett,[39] and Sands and Moos[29] have found values between 1×10^{-14} and 2×10^{-14} cm^2. If a value of 2×10^{-14} cm^2 is assumed, τ_{ex} at 67°C is approximately 5 msec. Since the shortest relaxation times measured in this experiment were 50 msec, the condition that τ_{ex} be much smaller than τ_{relax} was clearly satisfied. Moreover, since all rubidium-rubidium spin-exchange cross sections appear to be approximately equal, under the present experimental conditions a spin-temperature equilibrium also existed between the two isotopes. The relaxation signal thus

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[35] M. A. Bouchiat and J. Brossel, Compt. Rend. **254**, 3650 (1962).

[36] L. W. Anderson, Nuovo Cimento **31**, 986 (1964).

[37] *Metals Reference Book*, edited by Colin J. Smithells, 3rd ed. (Butterworth, Inc., Washington, D. C., 1962), p. 655.

[38] M. A. Bouchiat and J. Brossel, Compt. Rend. **257**, 2825 (1963).

[39] S. M. Jarrett, Phys. Rev. **133**, A111 (1964).

gave the decay of both $\langle S_z \rangle$ and the polarization for the entire vapor.

In Franzen's experiment, on the other hand, a value of 2×10^{-14} cm^2 for σ_{ex} would indicate a τ_{ex} of about 30 msec. Since the maximum relaxation time measured by Franzen was 100 msec, with most measurements equal to 40 msec or less, a spin-temperature equilibrium may not have existed. The lack of such an equilibrium was surely the case during measurements on krypton and xenon, where relaxation times of 15 msec and less were found. The fact that the polarization is not simply related to the absorption signal when the spin-temperature approximation does not apply may partially explain why Franzen found only a factor of 2 difference in the cross sections for krypton and xenon, whereas in the present experiment a difference of a factor of 18 was found.

It should also be noted that the density of rubidium under actual experimental conditions may be quite a bit lower than that predicted by Eq. (5), since the vapor pressure can be sensitive to an impurity film on the surface of the rubidium reservoir. For example, in his work on the rubidium spin-exchange cross sections, Jarrett, using an interferometric technique,[39] found a rubidium density of 3.33×10^{11} atoms/cm^3 at 90°C, whereas a value 3 times greater is predicted by Eq. (5). The spin-exchange times mentioned above may therefore have been somewhat longer than the values quoted. The condition that $\tau_{\text{ex}} < \tau_{\text{relax}}$ would still be satisfied, however, in the present experiment, due to the very long relaxation times measured.

(C) Effect of Impurities on the Disorientation Cross Section

Standard, nonbaked, diffusion-pumped vacuum systems have been used in virtually all experiments concerned with alkali spin disorientation. As a rule, 10^{-5} to 10^{-6} Torr is the ultimate vacuum obtainable with a system of this type. This background pressure, quite high by ultra-high vacuum standards, is generally comprised of a mixture of water vapor, oxygen, carbon monoxide, carbon dioxide, and hydrocarbon vapors that have backstreamed from the diffusion pump. Franzen reasoned that such impurities would be effectively gettered by the highly reactive alkali present in the absorption cell, and concluded that, to a good approximation, their effect on the alkali relaxation could be neglected. In such a nonbaked system there are, however, tremendous quantities of impurities adsorbed on the cell walls, from where they are continuously evolved. Thus, although the gettering efficiency of the alkali vapor is undoubtedly quite high, there still remains a small partial pressure of background impurities that can interact with the optically pumped alkali, either through spin exchange or by chemical combination. Either of these interactions would introduce another mode of alkali relaxation that has not been included in Eq. (7). The impurity partial pressure would be independent of buffer-gas pressure, and would be constant at any particular temperature. Its effect can be taken into account by adding a constant term to the right hand side of Eq. (7), resulting in

$$dP/dt = D\nabla^2 P - KP - K'P\,, \tag{9}$$

where $K' = N_0 v_{\text{rel}}' \sigma' (p'/p_0)$, and v_{rel}' is the relative velocity of impurity and alkali atoms, σ' is the interaction cross section, and p' is the impurity partial pressure. The approximation for the relaxation time is then modified to be

$$\tau = [D_0(\pi/R)^2(p_0/p) + N_0\sigma v_{\text{rel}}(p/p_0) + N_0\sigma' v_{\text{rel}}'(p'/p_0)]^{-1}. \tag{10}$$

The general effect of the impurity would be to lower and flatten the maximum of the relaxation-time–versus–buffer-gas-pressure curve. For example, if the impurity is assumed to have a molecular weight of about 32, the alkali-impurity relative velocity at 67°C is 5.5 cm/sec. If the interaction cross section is taken to be about 10^{-14} cm^2, of the order of typical spin-exchange cross sections, as little as 5×10^{-7}-Torr impurity partial pressure would result in a measured relaxation time of 95 msec at the maximum of the neon relaxation curve (Fig. 2), rather than the observed 395 msec. It is interesting to note that Franzen's original neon data shows the characteristics predicted by the above hypothesis; that is, a broad and low relaxation-time–versus–pressure curve that, in fact, does not possess any clearly defined maximum. Computer fits of the three-parameter function (7) to both the previous and present sets of neon data tend to substantiate the impurity hypothesis, yielding a 5-times-smaller disorientation cross section from Franzen's data than was previously evaluated, while leaving essentially unchanged the cross section evaluated from the present data.

(D) Effect of Impurities on the Diffusion Coefficient

Since the primary intent of this experiment was to obtain accurate determinations of the rubidium–rare-gas spin-disorientation cross sections, a relatively large (250 cc) spherical optical-pumping cell was used so that relaxation due to alkali-wall collisions would be minimized, while relaxation due to alkali rare-gas collisions would be maximized. This procedure has resulted in data that do not lead to particularly sensitive determinations of the diffusion coefficients of rubidium in the various gases, as mirrored in the relatively high uncertainty (about 20%) attributed to these values. Even so, the values of the diffusion coefficients reported in this paper are considerably larger than those found previously. We believe that the observed differences again can be attributed, at least in part, to the use of an ultraclean vacuum system in the present experiment.

At low buffer-gas pressures, relaxation of the optically pumped alkali is primarily caused by diffusion of the alkali to the walls of the absorption cell. In all experiments of this type it has been assumed that the density of polarized alkali at the walls is zero; that is, that every collision of a polarized atom with the wall results in disorientation. This boundary condition of course does not hold if the cell wall is coated with certain hydrocarbon of silicone compounds, as has been amply demonstrated.[40] It is entirely possible that certain products backstreaming from a diffusion pump, when adsorbed on a glass surface, might have a similar albeit much smaller effect. Methane, for example, is a primary constituent of the hydrocarbon vapors present in a vacuum system. The spin-disorientation cross section for rubidium colliding with methane has been measured by McNeal[21] to be 8×10^{-24} cm^2, classifying it as an extremely effective buffer gas. That a cell wall partially coated with adsorbed methane or some other hydrocarbon might not be completely disorienting would not be surprising. Obviously, contamination of this sort would lead to the observation of somewhat longer relaxation times at low gas pressure than would be found if the walls provided complete alkali disorientation. Such an effect would lead to a determination of the diffusion coefficient D_0 that would be smaller than the true value. In the present experiment, in addition to baking the system at 350°C, efforts were made to effectively trap any backstreaming diffusion oil products, resulting in minimal wall contamination. The presence of the rubidium "puddle" in the bulb also helped, insuring the presence of a saturated rubidium vapor that tended to adsorb gradually on the cell walls, thus maintaining a completely disorienting surface.

(E) Possible Sources of Error

The possibility of impurity contamination of the rare gases and rubidium metal used in this experiment must be considered. In order to prevent contamination of the rubidium a careful handling procedure was followed. First, an ultrahigh-vacuum system consisting of a manifold of Pyrex breakseals was baked at 350°C until an ultimate vacuum of better than 1×10^{-10} Torr was obtained. The system was then closed from pumps, and pure, dry nitrogen admitted at a pressure greater than 760 Torr. A tube was opened, and the rubidium capsule inserted. The system was resealed and immediately pumped out. The resultant vacuum, without another bakeout, was better than 1×10^{-9} Torr. The rubidium capsule was then broken, and the rubidium distilled into breakseals that were finally pulled off. Both of these latter operations were performed under continuous pumping of the system. In order to introduce rubidium into the optical-pumping cell, a filled breakseal was sealed onto that apparatus. As was mentioned earlier in this paper, the optical-pumping cell and associated gas-handling apparatus, with the exception of the section of the breakseal containing rubidium, were baked at 350°C. Since the rubidium was pure to better than one part in 1000, and the Rb vapor pressure encountered in this experiment was of the order of 10^{-6} Torr, any contamination of the optical-pumping cell from this source was minimal.

No additional purification of the spectroscopic-grade rare gases was attempted since the amount of contamination by impurities other than rare gases is less than one part in 10^7, according to the manufacturer. In a clean vacuum system, much of this residual contamination will be adsorbed by the glass walls, or be gettered by the rubidium. The residual impurities in this experiment were thus reduced to a level that could conceivably affect only rubidium relaxation in helium. For this reason the true helium cross section may be even somewhat smaller than the value quoted in Table I.

There are, of course, several approximations inherent in the derivation of the equations basic to this work. For example, in the derivation of Eq. (3), equal intensities in the hyperfine components of the D_1 line were assumed. Strong differential absorption of these components as the light beam traversed the bulb would lead to an uncertain interpretation of what was actually measured. In the present instance a highly intense broad-line light source was used, with the total light absorption by the vapor being only a few percent. Most measurements were made within one relaxation time constant, where still smaller absorption occurred. It is therefore felt that any "hyperfine pumping" effect was small.

At high vapor pressures the condensation of a reflective coating of rubidium on the walls of the optical pumping cell made the *total* fraction of light absorbed by the vapor a difficult quantity to estimate. In general, the intensity of light transmitted through a cell at 67°C was about 80% of that previously measured for the cell at room temperature. The vapor pressure of rubidium changes by a factor of 50 over this temperature range. It must be remembered, however, that the above result is uncorrected for the increased reflection at the higher operating temperature. We estimate that such reflectional losses accounted for about half of the intensity decrease. At 67°C, with the vapor in the polarized state, the transmission of the absorption cell was typically 90% of that at room temperature. The *changes* in transmitted light intensity measured in the experiment rarely exceeded 7%.

(F) Comparison with Other Experiments

In the past few years, Franzen's technique for measuring alkali-metal spin-disorientation cross sections has been applied to sodium by Anderson and Ramsey,[23,24] and to cesium by Franz and Lüscher[26,27] and by Legowski.[28] It is of interest to compare the

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[40] M. A. Bouchiat, J. Phys. Radium 24, 379 (1963); 24, 611 (1963).

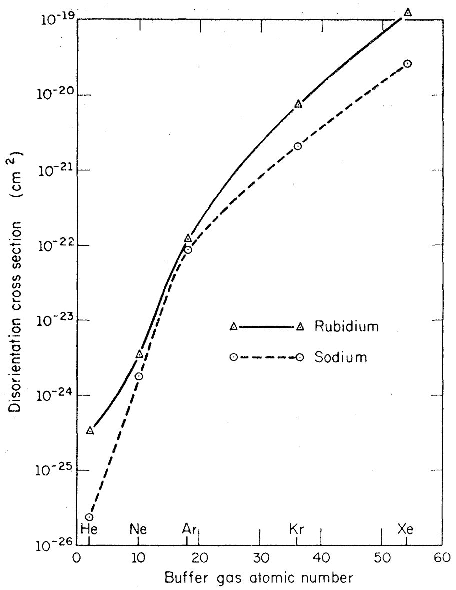

FIG. 4. Comparison of the rubidium and sodium spin-disorientation cross sections in the rare gases as a function of rare-gas atomic number.

values of the cross sections found by these various investigators with the rubidium values found in the present experiment. The variation of disorientation cross section versus buffer-gas atomic number is plotted in Fig. 4 for rubidium and sodium. The disorientation cross sections of cesium in neon and argon found by Franz and Lüscher, if plotted on this graph, would fall very close to the rubidium curve, whereas the values for krypton and xenon would fall somewhat below it. The two latter values must be regarded as highly inaccurate, however, due to the almost certain presence of a high-impurity partial pressure during that phase of the experiment. The relaxation of the various alkalies in the rare gases is thus seen to be remarkably similar. As might be expected, the smallest disorientation cross sections are observed for sodium, with the cross sections for rubidium and cesium proving to be approximately equal. It is reasonable to inquire, however, whether in these latter experiments impurities may have had similar effects as those that are suggested to have occurred in the original experiment on rubidium. This question has already been considered for the case of cesium, with the conclusion that for neon and argon impurity effects were small.[41] It is possible that this may also have been the case for sodium, since most of the impurities may have been driven out of the system due to high operating temperature (150–200°C) of the optical pumping cell. The possibility remains, however, that there may have been an impurity effect, in which case the sodium values should be taken as upper limits on the disorientation cross sections for that alkali. It should also be mentioned that Legowski's values for the disorientation cross sections of cesium in neon and argon differ somewhat from those reported by Franz and Lüscher, particularly in the case of argon. Although in his experiment Legowski was able to detect contributions to relaxation from two diffusion modes, we have found that the description of relaxation by a single decay time is a good approximation in the present experiment. In order to confirm the existence of simple exponential relaxation, some of our data were analyzed graphically by plotting the quantity $\ln[(I_0-I)/I_0]$ versus time,[20,22] where I is equal to the intensity of light transmitted through the cell in its optically pumped state minus the initial intensity of light transmitted through the cell after some dark time, t. I_0 is the value of I for infinite t. In all cases the points lay on straight lines, yielding single decay times. The intercepts of these lines at $t=0$ were not, however, at $\ln(1.0)$ as might be expected, but rather at values ranging from $\ln(0.75)$ to $\ln(0.85)$, indicating the presence of relaxation mechanisms too fast to be measured in the present work. This effect was not observed for cesium,[27] but had been previously reported for rubidium by Bernheim.[20] Since our shutter opening and closing times were about 10 msec each, all times less than 25 msec were rejected in the analysis of data in order to insure that the shutter had indeed been entirely closed. The lack of data for dark times of less than 25 msec appears to be the most probable reason why we did not directly observe higher order (faster) modes of relaxation in the present experiment. All of the other experiments mentioned above have been analyzed under the assumption that the relaxation of the polarized vapor can be described by a single relaxation time.

Quite recently Arditi and Carver[42] reported a highly interesting determination of the relaxation rate between the $F=2$, $m_F=0$ and $F=1$, $m_F=0$ states in Rb^{87} in the presence of various buffer gases. The values they found for the relaxation cross sections were somewhat larger than those found by Franzen for the disorientation cross sections, and hence differ very substantially from those reported in this paper. Their experiment, however, is fundamentally different from the ones described above in that the decay of the observable $\langle \bar{S}\cdot\bar{I}\rangle$ is measured, with $\langle S_z\rangle$ equal to zero. A population difference between the $F=2$, $m_F=0$ and $F=1$, $m_F=0$ states is created, the decay of which yields several parameters, including the relaxation cross section for alkali–buffer-gas collisions. The parameter that Arditi and Carver call T_G, from which the relaxation cross sections are determined, is comparable to our τ defined by Eq. (1). If our assessment of the importance of ultraclean conditions in a spin-disorientation experiment is correct, then the possibility exists that an impurity effect may also have been present in this latter work. The fact that T_G was essentially constant over a wide range of buffer-gas

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[41] F. A. Franz, Coordinated Science Laboratory, University of Illinois, Urbana 1964, Report No. R-202 (unpublished).

[42] M. Arditi and T. R. Carver, Phys. Rev. **136**, A643 (1964).

pressures lends some plausibility to such a view, but does not in itself substantiate it. It is also probable that the relaxation rates between and within the F levels are not equal, making a direct comparison between the Arditi-Carver experiment and the present work difficult. It would be quite interesting, in fact, to measure the relative probabilities for $\Delta F=0$ and $\Delta F=1$ alkali transitions induced by collisions with buffer-gas atoms, since the cross sections reported in this paper should be directly calculable from such data.

(G) Comparison with Theory

Herman recently published a calculation of the rubidium disorientation cross sections that considered deformation and overlap effects arising in alkali–rare-gas collisions, with the disorientation mechanism taken to be a spin-orbit interaction between the alkali valence electron and the combined alkali–rare-gas nuclear fields.[43] In Fig. 5 these calculated values are compared with the experimentally determined spin disorientation cross sections. The theoretical cross sections for He, Ne, and A are all about a factor of 10 larger than the experimental values, while the theoretical cross section for xenon is about a factor of 10 smaller. It is important to note, however, that the dependence of the first 3 cross sections on buffer-gas atomic number predicted by the theory is virtually the same as that obesrved experimentally.

Herman found the collisional deformations to be small for He, Ne, and A, with the rubidium relaxation being caused mainly by spin orbit coupling of the deformed alkali valence electronic orbital to the rubidium ionic core. For Kr and Xe the calculated deformations became quite large, with a resultant increase of the spin-orbit coupling of the alkali electron to the rare-gas nuclear field. Calculations become quite involved in this latter case. It is possible that the failure of the theoretical cross sections for Kr and Xe to follow the dependence of the experimental cross sections on buffer-gas atomic number arises from an underestimate of the coupling to the rare-gas nuclear field.[44] In view of the high order of perturbation theory employed, and the large number of approximations necessary to arrive at numerical values for the various cross sections, better quantitative agreement of theory with experiment might not be reasonably expected.

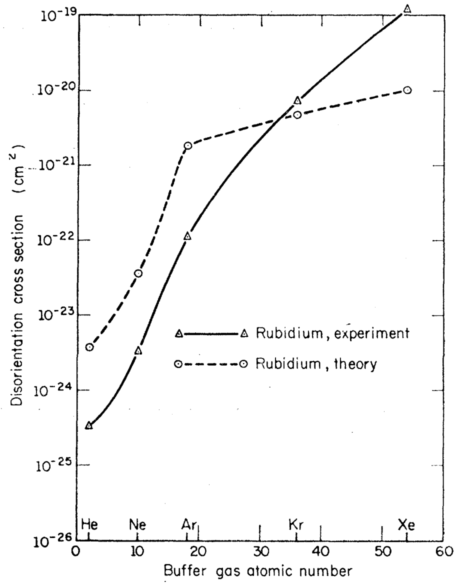

FIG. 5. Comparison of recent theoretical calculations with the experimentally determined spin-disorientation cross sections.

Note added in proof. The appearance of a recent article in the Journal of the Optical Society of America[45] has made me realize that I have ignored in the introduction to this paper the important contributions by Professor Hans Dehmelt to the study of spin relaxation. Indeed, Dehmelt's study of sodium relaxation in argon[16] was the first published work on the spin relaxation of an optically pumped alkali metal vapor in a buffer gas. The cross section for spin disorientation ($\sigma_{\mathrm{Na\text{-}Ar}}$) evaluated from this experiment, 7.0×10^{-23} cm^2, remains in good agreement with subsequent work. Dehmelt was also among the first to intensively study the utility of various wall coatings in optical pumping, and in fact made the initial measurements of rubidium and cesium spin relaxation.[46] I greatly regret the omission of mention of this work in the body of this article.

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[43] R. M. Herman, Phys. Rev. **136**, A1576 (1964).

[44] R. M. Herman (private communication).

[45] H. G. Dehmelt, J. Opt. Soc. Am. **55**, 335 (1965).

[46] H. G. Dehmelt, Proceedings of the 12th Annual Symposium on Frequency Control, Fort Monmouth, 1958, p. 577 (unpublished).