Spin Relaxation of Optically Pumped Cesium*†

F. A. Franz and E. Lüscher‡

Coordinated Science Laboratory and Department of Physics, University of Illinois, Urbana, Illinois

(Received 3 March 1964)

Spin relaxation of optically pumped cesium vapor has been measured as a function of buffer gas pressure for various inert gases. Disorientation cross sections have been found to be 5.3×10^{-24} cm² for neon, 8.0×10^{-23} cm² for argon, 2.1×10^{-21} cm² for krypton, and 4.6×10^{-20} cm² for xenon. The diffusion coefficients of cesium in neon and argon were found to be 0.40 cm²/sec and 0.23 cm²/sec, respectively. Disorientation cross sections and diffusion coefficients for molecular N^{14} and N^{15} have also been measured.

I. INTRODUCTION

FOLLOWING the introduction of optical pumping by Kastler and Bitter in 1949,[1-3] the polarization of alkali metal vapors through optical pumping of their $^2S_{1/2}$ ground states was extensively studied and utilized.[4-8] Since several authors have written at length on this method of polarization,[9-15] only a very brief discussion will be given here.

Basically the process consists of an excitation-deexcitation cycle caused by the absorption of circularly polarized photons from a beam of light passing through an alkali vapor. Through a consideration of the transition probabilities and selection rules involved, it is easy to show that if the absorbing vapor is situated in a weak magnetic field, a high percentage of alkali atoms can be pumped to the highest magnetic substate, $M_F = +|F|$, of the ground state. High population of this state implies a net polarization of the vapor. In the particular experiment described here, the selection rule $\Delta M_F = +1$ attendant with the absorption of a right circularly polarized photon precludes excitation from the $M_F = +|F|$ quantum state; hence, an equilibrium is established in which collisional depolarization is balanced by repumping. In such a case the intensity of light transmitted through the vapor cell is constant and

a maximum. Any decrease in the number of atoms in the polarized state would provide more absorbing atoms, resulting in a corresponding decrease in intensity of the transmitted light.

Inert buffer gases or coated vapor cells have often been used to increase the degree of alkali polarization.[15-22] Important information concerning interactions between oriented atoms and buffer gas molecules can be obtained from a study of the relaxation of a polarized vapor from its oriented state. Initial experiments on relaxation of optically pumped alkali atoms were performed on sodium by Bender[15] and by Dehmelt.[4] The prototype of the work reported in this paper was done by Franzen,[23] who measured the relaxation of oriented rubidium vapor in the presence of neon, argon, krypton, and xenon buffer gases. He showed that two causes of relaxation are dominant: diffusion of oriented atoms to the walls of the containing vessel, and collisions of oriented atoms with buffer gas molecules. By measuring relaxation time as a function of buffer gas pressure, he was able to obtain values both for the diffusion coefficient D_0 of rubidium in the buffer gas, and for the cross section σ for disorientation in collisions between oriented rubidium atoms and buffer gas molecules. Franzen's work on rubidium has been extended by Bernheim[24] and Brewer,[25] while Anderson and Ramsey,[26,27] Bouchiat and Brossel,[28] and Lemmerich and Raith[22] have made further studies on sodium. Preliminary work on cesium has been de-

[1] J. Brossel and A. Kastler, Compt. Rend. **229**, 1213 (1949).
[2] F. Bitter, Phys. Rev. **76**, 833 (1949).
[3] A. Kastler, J. Phys. Radium **11**, 255 (1950); Proc. Phys. Soc. (London) **A67**, 853 (1954).
[4] H. G. Dehmelt, Phys. Rev. **105**, 1487 (1957).
[5] W. B. Hawkins, Phys. Rev. **98**, 478 (1955).
[6] H. Bucka et al., Z. Physik **176**, 45 (1963).
[7] R. Novick and H. E. Peters, Phys. Rev. Letters **1**, 54 (1958).
[8] P. Franken, R. Sands, and J. Hobart, Phys. Rev. Letters **1**, 52 (1958).
[9] W. Franzen and A. G. Emslie, Phys. Rev. **108**, 1453 (1957).
[10] W. E. Bell and A. L. Bloom, Phys. Rev. **107**, 1559 (1957).
[11] W. B. Hawkins, Phys. Rev. **123**, 544 (1961).
[12] A. Kastler, J. Opt. Soc. Am. **47**, 460 (1957); Suppl. Nuovo Cimento **6**, 1148 (1957).
[13] R. L. de Zafra, Am. J. Phys. **28**, 646 (1960).
[14] G. V. Skrotskii and T. G. Izyumova, Usp. Fiz. Nauk **73**, 423 (1961) [English transl.: Soviet Phys.—Usp. **4**, 177 (1961)].
[15] P. L. Bender, thesis, Princeton University, 1956 (unpublished).

[16] C. O. Alley, *Quantum Electronics*, edited by C. H. Townes (Columbia University Press, New York, 1961), p. 146.
[17] W. B. Hawkins, W. R. Bennett, L. Y. Chow, and H. Robinson, Bull. Am. Phys. Soc. **3**, 372 (1958).
[18] H. G. Robinson, E. S. Ensberg, and H. G. Dehmelt, Bull. Am. Phys. Soc. **3**, 9 (1958).
[19] C. O. Alley, in *Advances in Quantum Electronics*, edited by J. R. Singer (Columbia University Press, New York, 1961), p. 120.
[20] F. Hartmann, M. Robinson, J. Brossel, and A. Kastler, Compt. Rend. **246**, 1522 (1958).
[21] J. Brossel, J. Margerie, and A. Kastler, Compt. Rend. **241**, 865 (1955).
[22] J. Lemmerich and W. Raith, Naturwiss. **49**, 127 (1962).
[23] W. Franzen, Phys. Rev. **115**, 850 (1959).
[24] R. A. Bernheim, J. Chem. Phys. **36**, 135 (1962).
[25] R. G. Brewer, J. Chem. Phys. **37**, 2504 (1962).
[26] L. W. Anderson and A. T. Ramsey, Bull. Am. Phys. Soc. **8**, 529 (1963).
[27] L. W. Anderson and A. T. Ramsey, Phys. Rev. **132**, 712 (1963).
[28] M. Bouchiat and J. Brossel, Compt. Rend. **254**, 3829 (1962).

scribed by Legowski and Lipworth[29] and by Franz and Lüscher.[30] Bernheim has attempted a theoretical description of the relaxation mechanism, as more recently has Herman.[31]

In the present experiment the effect of various buffer gases on the spin relaxation of optically pumped cesium has been measured. Spin disorientation cross sections and diffusion coefficients for polarized cesium in nitrogen and in the various noble gases have been evaluated. The need for modification of existing theoretical calculations of disorientation cross sections is pointed out.

II. EXPERIMENTAL TECHNIQUE

A schematic representation of the apparatus used to obtain optically pumped cesium is given in Fig. 1. The heart of the system consisted of a 250 cc uncoated spherical Pyrex bulb, into which a small amount of cesium[32] was distilled under vacuum. One side of the bulb was connected to a gas handling system, from which buffer gases[33] at any desired pressure could be admitted to the bulb. The bulb was enclosed by a massive aluminum furnace that could be heated to provide optimum thermal environment.

The cesium bulb and furnace were surrounded by three mutually perpendicular sets of Helmholtz coils that provided cancellation of the earth's magnetic field and imposed a constant weak magnetic field along the optic axis. Coils were also provided for the cancellation of small field gradients, but, their use seldom proved necessary. A cesium lamp of high intensity in the D_1 (8944 Å) line[34] provided the light flux necessary for optical pumping. A solenoid driven shutter stood between the lamp and the lens system. The opening and closing times of the shutter were approximately 14 msec. An interference filter[35] to block the D_2 line, maintaining maximum D_1 passage was included in the
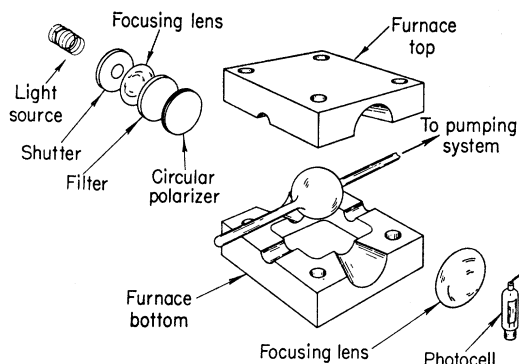

FIG. 1. Diagram of the optical pumping apparatus.

[29] S. Legowski and E. Lipworth, Bull. Am. Phys. Soc. 8, 9 (1963).
[30] F. A. Franz and E. Lüscher, Phys. Letters 7, 277 (1963).
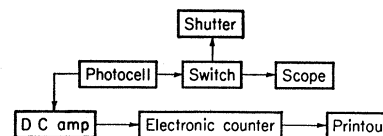[31] R. M. Herman, Bull. Am. Phys. Soc. 9, 11 (1964).
[32] Bram Metallurgical Company, Philadelphia, Pennsylvania.
[33] Linde Company, New York, New York.
[34] F. A. Franz, Rev. Sci. Instr. 34, 589 (1963).
[35] Spectrolab, Sylmar, California.

FIG. 2. Block diagram of the auxiliary electronic apparatus.

lens system. A sheet linear polarizer and quarter wave plate[36] followed the filter. The net purpose of the optical system was to provide a beam of circularly polarized D_1 photons that was then passed through the bulb containing the buffer gas and cesium vapor, finally impinging on a 917 photocell. All measurements were made with the entire bulb illuminated. (Figure 1 is somewhat misleading in this respect.)

With a buffer gas in the bulb, the lamp on, and the shutter open, an equilibrium was soon established in which polarization and depolarization rates of the cesium became equal, a high degree of atomic orientation being attained. The absorption of photons from the light beam thus became constant, and the output of the photocell monitoring the intensity of transmitted light was a maximum, lying at what will be referred to as the equilibrium level.

Sudden closing of the shutter drastically changed this situation. With no light available to continue the pumping process, each disorienting collision of an oriented cesium atom with a buffer gas molecule or cell wall resulted in a decrease in the net polarization of the vapor. The loss of polarization was a function of the time that the shutter remained closed. When the shutter was reopened, optical pumping could again occur. Since during the dark time the cesium vapor had become less polarized, more absorption of light than at the equilibrium level occurred. The intensity of the transmitted light thus jumped to a point somewhat below the equilibrium level, gradually approaching it as the vapor was repumped to its more fully polarized state. The degree of depolarization that occurred during the dark interval was proportional to the difference between these two intensity levels. If this difference were plotted against dark time, a curve representative of the relaxation of polarized cesium vapor would be obtained.

Figure 2 is a block diagram of the remaining elements of the experimental apparatus. Output from the photocell was divided between a wideband dc amplifier and a Tektronix 541 oscilloscope, with type D plug-in unit. The dc amplifier was coupled to a Hewlett-Packard 524B electronic counter set to measure time interval. Both the oscilloscope and the counter were triggered on the negative step caused by the closing of the shutter. The counter was gated off by the positive going step occurring with the reopening of the shutter; hence, the time interval measured by it was approximately equal to the dark time. This number was printed out by a Hewlett-Packard 560A digital recorder slaved to the

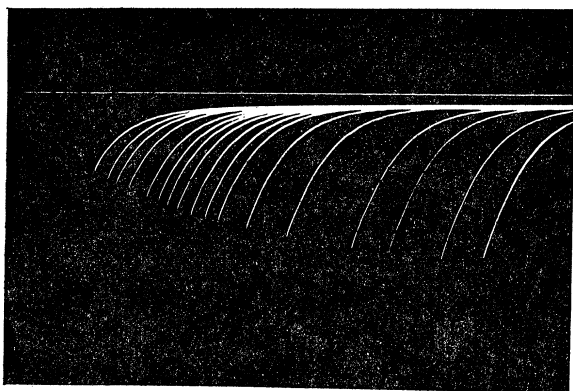[36] Polaroid Corporation, Cambridge, Massachusetts.

FIG. 3. Cesium relaxation in molecular nitrogen.

counter. The oscilloscope trace was recorded on Polaroid type 47 film.

Between 15 and 20 shutter closings of continually increasing dark times were recorded on each photograph. Figure 3 is typical of the data taken in this experiment. The closing and opening of the shutter is not visible due to the high writing speed of the oscilloscope. The curved lines are indicative of the gradual approach of the system back to the equilibrium level caused by the repumping of depolarized cesium. The end points of these lines form the curve that represents the relaxation of the optically pumped cesium. Before removing the photograph from the camera, the trace was raised slightly and triggered manually in order to record a horizontal reference line on the photograph. Measurements of the distances of the end points from this line were later made using a comparator microscope. These measurements, together with the time measurements printed out by the recorder were then fed into an IBM-7094 computer programmed to fit the data to a simple exponential by the method of least squares. This method of data reduction, differing from those previously used, has several important advantages that are discussed below.

If the decay of polarization of optically pumped cesium is an exponential function of the dark time, then the curve formed by the end points of the lines in Fig. 3 is of the form

$$I = I_0[1 - \exp(-t/\tau)],$$

where I is measured from the equilibrium level, and I_0 is the value of I at $t = \infty$. By plotting $\ln[(I_0 - I)/I_0]$ versus time, a straight line, with slope $(-1/\tau)$ is obtained.[24-27] Figure 4 illustrates a sample of our data analyzed in this manner.

The disadvantage of this method of data reduction lies in the fact that absolute measurements of both horizontal and vertical coordinates are necessary. For example, an error in the determination of the exact location of the equilibrium level introduces a systematic error in $\ln[(I_0 - I)/I_0]$. Furthermore, the quantity $\ln[(I_0 - I)/I_0]$ is quite sensitive to any error in the

determination of I_0. Since I_0 is obtained through the measurement of a particular line, one's data reduction is strongly dependent on the accuracy of a single data point.

The greatest uncertainty of all lies in the determination of an absolute time scale. In the past, shutter opening and closing times have been of a magnitude comparable to the relaxation time measured. This, coupled with the lack of knowledge of exactly when the oscilloscope trace was triggered, creates a sizeable uncertainty in both the determination of the dark time duration and the location of the point $t_0 = 0$.

Computer reduction of the data removed these objections. The computer was programmed to make a least-squares fit of the curve $y = A + B \exp(-x/C)$ to the set of data points (x_i, y_i). Thus, the coordinates (x_i, y_i) could be measured from any convenient horizontal and vertical axes, removing the necessity for absolute measurements. The data points were equally weighted, and a measurement of I_0 was not necessary. Accuracy of time measurement was increased by the use of an electronic counter to measure time interval, removing uncertainty caused by any nonlinearity in the horizontal sweep of the oscilloscope.

In practice, the relaxation signal formed only the top 1 to 10% of the total step occurring with the opening of the shutter. To give full scale display to this portion of the step it was necessary to use the most sensitive scales of the oscilloscope with the result that the vertical deflection was overdriven by a factor ten or more. Such abuse resulted in overshoot and drift that were intolerable in this experiment. The problem was solved by placing between the photocell and the oscilloscope a device incorporating a microswitch and mercury battery that shorted the input of the oscilloscope as the shutter began to close, unshorting it just before the shutter reopened. Tests made with square-cornered
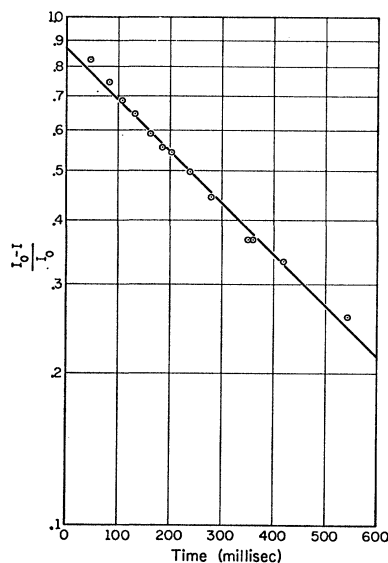

FIG. 4. Plot of $\ln[(I_0 - I)/I_0]$ versus time. These data were taken for cesium relaxing in neon. The relaxation time deduced from this graph was 415 msec, while the value found by the more accurate method described in the text was 360 msec.

signals indicated that no detectable distortion was introduced, while drift and overshoot were eliminated.

Special precautions were taken to insure clean conditions for the experiment. Each Pyrex vapor bulb was carefully washed with hot chromic acid and rinsed with demineralized water and acetone before being sealed into the system. The system was then pumped out and the bulb heated to a temperature of approximately 400°C. A pressure of residual gases of less than 5×10^{-6} Torr was required before proceeding with the distillation of cesium into the bulb. Additional cesium was deposited along the walls of the tube leading into the bulb to act as a getter for residual impurities. A large liquid nitrogen trap was also employed in the system. In general, it was possible to keep the cesium in the bulb quite clean for a period of several weeks. Only when measurements were made on mixtures of krypton or xenon in neon was it necessary to replace the nitrogen trap by a solid CO_2 trap. This, unfortunately, appears to have permitted the presence of a small amount (perhaps 2×10^{-5} Torr) of a residual gas impurity that has affected the data taken for these two gases. This point is discussed more fully in a later paragraph.

Buffer gas pressures were measured with an oil manometer. When mixtures of krypton or xenon in neon were called for, the krypton or xenon was first admitted to the system and its pressure read with the aid of a cathetometer. Neon was then admitted to the system and the mixture allowed to stand for 24 h before measurements were made. In all runs a period of at least 4 h was allowed for the stabilization of the lamp and electronic apparatus and for the bulb to come to thermal equilibrium with the oven. All measurements were made at 44°C±1.0°C in a magnetic field of approximately 0.08 G.

III. EVALUATION AND RESULTS

Following Franzen,[28] we assume that the only depolarizing mechanisms operative are collisions of polarized atoms with buffer gas molecules or with the walls of the cell. The neglect of the effect of spin exchange on alkali relaxation is a nontrivial assumption but can be justified along the lines recently suggested by Anderson.[27,37] In the present experiment, spin exchange would not change the *total* polarization obtained but would affect the population distribution within the magnetic sublevels. Although great care was taken to provide uniform illumination of the bulb, there does remain the possibility that some unpolarized atoms may have diffused into the central area of the bulb from a relatively dark region. This, of course, would affect our measurements. It must be pointed out, however, that the effect of such diffusion, if it existed, would have been to *shorten* the measured relaxation time, whereas we have measured surprisingly *long* relaxation times in this experiment. (Compare the measured disorientation

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

cross sections listed in Table I.) In the following discussion the effects of spin exchange will be neglected.

It is expected that many collisions of polarized cesium atoms with the buffer gas are required to disorient the cesium, while it is fairly well established that a single collision of a polarized cesium atom with a glass surface results in disorientation. The relaxation time of the cesium as a function of increasing buffer gas pressure should first increase as the diffusion of cesium to the cell walls is retarded, reach a maximum, and then decrease as collisions with buffer gas molecules become more frequent.

If n is the number of aligned cesium atoms per unit volume, its time rate of change can be written

$$dn/dt=D\nabla^2n-kn. \tag{1}$$

The first term on the right-hand side of Eq. (1) represents the effect of diffusion to the walls, while the second term arises from the collisions of polarized cesium with buffer gas molecules. The diffusion coefficient D can be written $D_0(P_0/P)$, where D_0 is the diffusion coefficient of cesium in the buffer gas at atmospheric pressure (P_0), and in this experiment, at 44°C. The constant k can be written

$$k=N_0\sigma v_{\rm rel}(P/P_0),$$

where N_0 is the number of buffer gas molecules per cubic centimeter at atmospheric pressure and 0°C; σ is the cross section for spin disorientation; and $v_{\rm rel}$ is the relative velocity between cesium and buffer gas atoms at 44°C.

The solution of this equation, subject to the boundary condition that $n=0$ at the walls of the cell of radius R, is

$$n(r,\theta,\varphi,t)=\sum_{l,m,\alpha} A_{lm\alpha}\frac{J_{l+1/2}}{r^{1/2}}(\alpha r)Y_l^m(\theta,\varphi)$$

$$\times\exp\left[-\alpha^2D_0\left(\frac{P_0}{P}\right)+N_0v_{\rm rel}\sigma\left(\frac{P}{P_0}\right)\right], \tag{2}$$

where l and m are integers, and the summation on α is over the positive roots of $J_{l+1/2}(\alpha R)=0$; for $l=0,\alpha R=n\pi$, where $n=1, 2, 3 \cdots$.

Assuming that only the first term of this series is dominant,

$$n(r,\theta,\varphi,t)\approx A\exp\{-[(\pi/R)^2D_0(P_0/P)$$
$$+N_0v_{\rm rel}\sigma(P/P_0)]t\}. \tag{3}$$

This approximation yields the following expression for the relaxation time τ;

$$\tau=[(\pi/R)^2D_0(P_0/P)+N_0\sigma v_{\rm rel}(P/P_0)]^{-1}. \tag{4}$$

The values of all quantities except D_0 and σ are known. These two parameters may be evaluated by making the best fit of expression (4) to the experimentally observed pressure dependence of the relaxation time. Figures 5 and 6 illustrate this calculation for
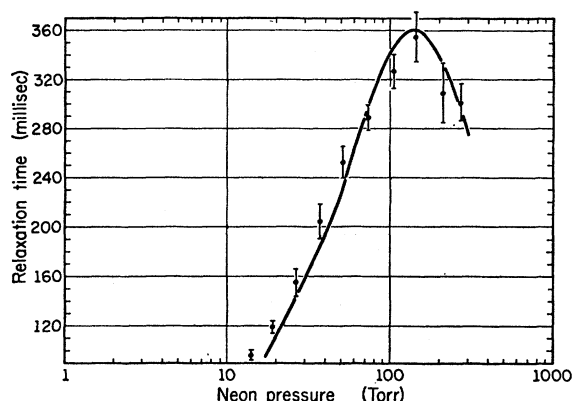
FIG. 5. Relaxation time of polarized cesium as a function of neon pressure. In this graph and those following at least five, but less than ten, determinations of the relaxation time were made at each pressure. The error bars are equal to one standard deviation.

cesium relaxation in neon and in argon, resulting in values of $D_0 = 0.40$ cm²/sec, $\sigma = 5.3 \times 10^{-24}$ cm² for neon; $D_0 = 0.23$ cm²/sec, $\sigma = 8.0 \times 10^{-23}$ cm² for argon.

The previous discussion has assumed the presence of a single buffer gas. If a small amount, perhaps one percent or less, of another gas is present, Eq. (1) must be modified by the addition of another term; that is,

$$dn/dt = D_0(P_0/P)\nabla^2 n - N_0 \sigma v_{rel}(P/P_0)n$$
$$- N_0 \sigma' v_{rel}'(P'/P_0)n, \quad (5)$$

giving

$$\tau \approx [(\pi/R)^2 D_0(P_0/P) + N_0 \sigma v_{rel}(P/P_0)$$
$$+ N_0 \sigma' v_{rel}'(P'/P_0)]^{-1}. \quad (6)$$

P is the total pressure of the mixture, and the primed quantities refer to the second gas. The assumption has been made that the diffusion of the cesium is unaffected by the addition of the second gas.

In order to evaluate the disorientation cross sections for krypton and xenon, we made mixtures of small amounts of these gases in neon, since the relaxation of polarized cesium in the presence of pure krypton or xenon is too fast to be measured by the present method. Knowing D_0 and σ for neon, it was possible to evaluate σ for krypton and xenon by fitting Eq. (6) to the experimental data. Figures 7 and 8 show the results of these

FIG. 7. Relaxation of polarized cesium in a mixture of 0.880% krypton in neon.

calculations that yield cross sections of 5.0×10^{-21} cm² for krypton and 1.1×10^{-19} cm² for xenon.

The lack of agreement between the theoretical Eq. (6), and the experimental data in Figs. 7 and 8 is evident. We believe that the discrepancies can be explained in the following way. When data for these mixtures were taken, it was necessary to remove the liquid-nitrogen trap from the system due to the high temperature of liquefaction of krypton and xenon. This permitted a larger amount of impurities such as CO to collect in the vapor cell upon desorption from the glass. The partial pressure of such an impurity would be independent of the pressure of the krypton-neon or xenon-neon mixture. Assuming that a collision of a cesium atom with a CO molecule would be completely disorienting, a simple calculation shows that an impurity partial pressure of as little as 10^{-5} Torr would account for the discrepancies observed. The position of the *maximum* in the relaxation curve is unaffected by the presence of such impurities, however. By taking these factors into account and by choosing σ to fit the maximum, agreement as good as that in Figs. 5 and 6 is obtained. Values of $\sigma = 2.1 \times 10^{-21}$ cm² for krypton and $\sigma = 4.6 \times 10^{-20}$ cm² for xenon result. We believe these latter values to be correct.

Figure 9 shows the temperature dependence of the cesium relaxation time in a neon atmosphere at a pressure of 56 Torr. The system was first heated to a temperature of 70°C and then allowed to cool gradually. The slope, $d\tau/dT$, of the straight line is 2.72 msec/°C, as determined from a least-squares fit to the data. In
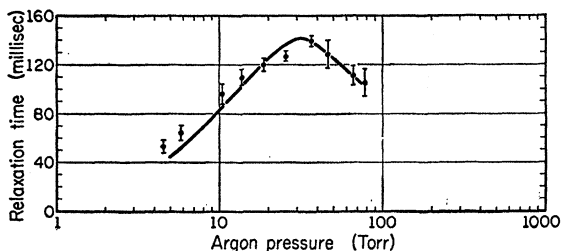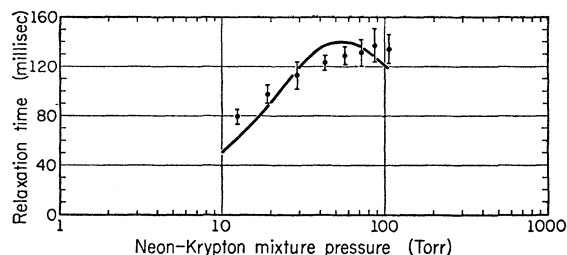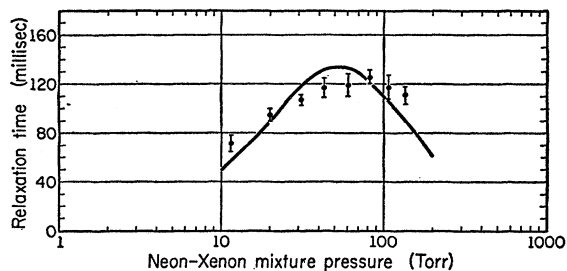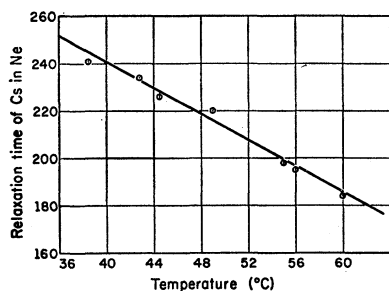

FIG. 6. Relaxation time of polarized cesium as a function of argon pressure.

FIG. 8. Relaxation of polarized cesium in a mixture of 0.061% xenon in neon.

FIG. 9. Temperature dependence of relaxation time.

FIG. 10. Comparison of cesium relaxation in N_2^{14} and N_2^{15}.

the temperature range under consideration, the vapor pressure of cesium changes by a factor of 10.[38]

IV. DISCUSSION

In order to explain the observed variation of disorientation cross sections among the noble gases, Bernheim[24] proposed an interaction involving spin-orbit coupling of the alkali valence electron to the buffer gas molecule. If his explanation is correct, the disorientation cross sections should be proportional to the cube of the atomic number of the buffer gas; that is,

$$\sigma = \kappa Z^3. \qquad (7)$$

Although the disorientation cross sections for rubidium in the noble gases seem to follow this relation, the cesium cross sections reported in this paper do not. Table I summarizes the values of alkali disorientation cross sections that have been measured in the noble gases. For rubidium, κ varies from 0.635×10^{-25} cm^2 (argon) to 1.27×10^{-25} cm^2 (krypton), while for cesium κ varies from 5.3×10^{-27} cm^2 (neon) to 293×10^{-27} cm^2 (xenon). It is interesting to note that the disorientation cross sections for sodium reported by Anderson and Ramsey[26,27,39] also fail to follow relation (7) having values of κ ranging from 1.8×10^{-27} cm^2 (neon) to 160×10^{-27} cm^2 (xenon). It is evident that Bernheim's theory needs modification. Herman[31] recently reported efforts in this direction.

The lack of agreement between Bernheim's theory and the measured values for the cesium spin disorienta-

tion cross section prompted us to look for other possible relaxation mechanisms. The work of Bouchiat, Carver, and Varnum[40] on polarization of He^3 nuclei through spin exchange suggested that a dipolar interaction might be a dominant factor in the disorientation of polarized rubidium. Brewer[25] has investigated this point by measuring rubidium disorientation cross sections in hydrogen and deuterium, finding that dipolar contributions to the rubidium relaxation were negligible. We have obtained further confirmation of this result through the measurement of the disorientation cross sections for N_2^{14} and N_2^{15}.

Dipolar disorientation would occur through interaction of the alkali magnetic moment with magnetic moments of the nitrogen nuclei, and with the rotational moment of the nitrogen nucleus. Since the disorientation probability (and hence the disorientation cross section) is proportional to the square of the magnetic moment, it is clear that the disorientation cross section for N_2^{14} ($\mu_{N_{14}} = 0.4037 \mu_N$) should be larger by about a factor 2 than that for N_2^{15} ($\mu_{N_{15}} = -0.2831 \mu_N$). The rotational moments of N_2^{14} and N_2^{15} have not been measured, but it is expected that the rotational moment of N_2^{14} should be larger than that of N_2^{15}. We may conclude then that if the dipolar mechanism is a dominant mode of disorientation, the disorientation cross section for N_2^{14} should be at least twice that for N_2^{15}.

In Fig. 10 the measured relaxation times of cesium in N_2^{14} and N_2^{15} are compared. The values of D_0 and σ for these two gases are summarized in Table II, where we have also included previously reported data[30] taken for N_2 at 54°C. The disorientation cross sections for N_2^{14} and N_2^{15} at 44°C are approximately equal, ruling out the possibility of a dipolar interaction being dominant

TABLE I. A comparison of the spin disorientation cross sections for cesium, rubidium, and sodium in various noble gases. All cross sections are expressed in cm^2.

	Cs (44°C)	Rb[a,b] (50°C)	Na[c-e] (158°C)
Helium		6.2×10^{-25}	2.2×10^{-26}
Neon	5.3×10^{-24}	5.2×10^{-23}	1.8×10^{-24}
Argon	8.0×10^{-23}	3.7×10^{-22}	8.8×10^{-23}
Krypton	2.1×10^{-21}	5.9×10^{-21}	2.0×10^{-21}
Xenon	4.6×10^{-20}	1.3×10^{-20}	2.5×10^{-20}

a See Ref. 23.	c See Ref. 26.	e See Ref. 39.
b See Ref. 24.	d See Ref. 27.	

[38] *Landolt-Börnstein Tables*, edited by K. H. Hellwege (Springer-Verlag, Berlin, 1960), Vol. 2, pp. 12 and 16.
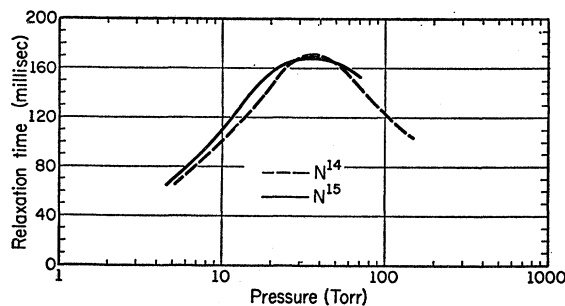[39] L. W. Anderson and A. T. Ramsey, Nuovo Cimento (to be published).

TABLE II. Spin disorientation cross sections and diffusion coefficients for polarized cesium in molecular N^{14} and N^{15}.

	Temp. (°C)	D_0 (cm^2/sec)	σ (cm^2)
N_2^{14}	54.0 ± 1.0	0.29	7.0×10^{-23}
N_2^{14}	44.0 ± 1.0	0.22	4.7×10^{-23}
N_2^{15}	44.0 ± 1.0	0.20	5.3×10^{-23}

[40] M. A. Bouchiat, T. R. Carver, and C. M. Varnum, Phys. Rev. Letters 5, 373 (1960).

in the relaxation of cesium. A slight temperature dependence of the N_2[14] disorientation cross section can also be seen.

A few concluding remarks can be made on the accuracy of the approximations leading to expressions (4) and (6). If higher order terms in Eq. (2) are indeed negligible, then in Fig. 4, $\ln[(I_0-I)/I_0]$ at $t=0$ should be equal to 1.0. A departure from this value would indicate a defect in this approximation. We found that for cesium the values of this intercept ranged from 0.86 to 0.96. This is consistent with the work on sodium, reported by Anderson and Ramsey, but does not agree with the value of 0.70 reported by Bernheim for rubidium in helium. Any further attempt to measure the $t=0$ intercept of $\ln[(I_0-I)/I_0]$ with sufficient accuracy to give information on the spatial distribution of aligned alkali atoms would require the use of a shutter of much faster closing times. Such an experiment might be possible using a solid state shutter based on the Pockels effect.

Calculation of Magnetic Hyperfine Constant of P31

N. Bessis, H. Lefebvre-Brion, and C. M. Moser
Centre de Mécanique Ondulatoire Appliquée, Paris, France

A. J. Freeman
National Magnet Laboratory*, Massachusetts Institute of Technology, Cambridge, Massachusetts

R. K. Nesbet
IBM Research Laboratories, San Jose, California

R. E. Watson
Bell Telephone Laboratories, Murray Hill, New Jersey

(Received 10 March 1964)

The results of different kinds of calculations, which use the concept of spin polarization, all predict a negative sign of the magnetic hyperfine constant of the ^4S ground state of P31 in contradiction with the sign deduced by Lambert and Pipkin from an optical pumping experiment. This result means that either an error in experimental sign has been made or that the first serious breakdown of the exchange polarization model has been found.

I. INTRODUCTION

THE magnetic hyperfine interactions in S state and many other ions having nonzero spin have, in large part, become understood in terms of the spin or exchange polarization of the closed s shells. This polarization yields a net s-electron spin density at the nucleus which interacts with the nucleus via the Fermi contact term.[1] While various objections have been raised to this picture, a series of calculations has emerged involving single-substitution configuration-interaction[2–5] (C.I.) perturbation,[6] and so-called spin-polarized Hartree-Fock[5,7–9] (SPHF) methods.[2,10] One feature of the results is that, with one possible exception

[1] E. Fermi, Z. Phys. 60, 320 (1930).
[2] For a discussion of the relation between single-substitution configuration-interaction and Hartree-Fock theory, see R. K. Nesbet, Proc. Roy. Soc. (London) A230, 312 (1955).
[3] For example, see E. Fermi and E. Segrè, Z. Physik 82, 729 (1933); A. Abragam, J. Horowitz, and M. H. L. Pryce, Proc. Roy. Soc. (London) A230, 169 (1955); and R. K. Nesbet, Phys. Rev. 118, 681 (1960).
[4] N. Bessis, H. Lefebvre-Brion, and C. M. Moser, Phys. Rev. 124, 1124 (1961); 128, 213 (1962).
[5] N. Bessis, H. Lefebvre-Brion, and C. M. Moser, Phys. Rev. 130, 1441 (1963).
[6] For example, see R. M. Sternheimer, Phys. Rev. 86, 316 (1952), and M. Cohen, D. A. Goodings, and V. Heine, Proc. Phys. Soc. (London) 73, 811 (1959).
[7] R. E. Watson and A. J. Freeman, Phys. Rev. 123, 2027 (1961).
[8] For example, see L. M. Sachs, Phys. Rev. 117, 1504 (1960), and D. A. Goodings, ibid. 123, 1706 (1961).
[9] Such calculations have, by common usage, been called "unrestricted Hartree-Fock." As there are other restrictions associated with conventional Hartree-Fock theory (e.g., See Ref. 10) which are not relaxed in such calculations it seems more appropriate to term these "spin-polarized Hartree-Fock" thus indicating the actual restriction being relaxed—the restriction of common radial behavior of orbitals differing only in spin quantum number.
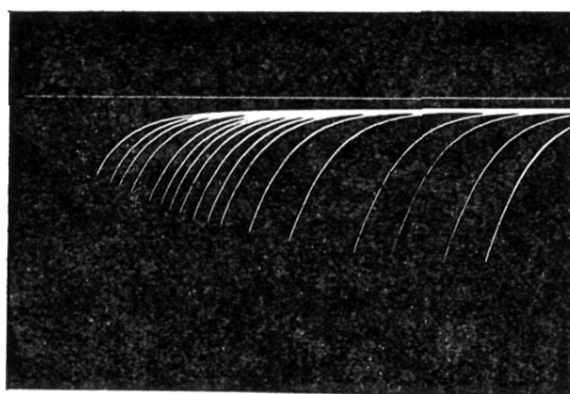[10] For a review and a more complete list of references, see A. J.

FIG. 3. Cesium relaxation in molecular nitrogen.