

Spin Relaxation of Optically Aligned Rubidium Vapor*

W. FRANZEN

Arthur D. Little, Incorporated, Cambridge, Massachusetts

(Received March 23, 1959)

A new optical method for studying the spin relaxation of optically aligned rubidium vapor is described. In this method, the pumping radiation, consisting of circularly polarized D_1 resonance radiation, is suddenly shut off and then turned on again after a known time interval. The relaxation which takes place during the interval of darkness causes the vapor to become more opaque to the pumping radiation at a rate which is determined by the relaxation time. A large degree of alignment, as well as a relaxation time of about 80 milliseconds, were observed in a closed-off evacuated cylindrical glass cell completely lined, except for 1/200 of the wall area, with a thin film of tetracontane ($C_{40}H_{82}$). The variation of relaxation time with buffer gas pressure was studied

in this cell and in an unlined glass cell. From the observations with the unlined cell, diffusion coefficients for rubidium in neon and argon of 0.31 cm^2/sec and 0.24 cm^2/sec , respectively, can be deduced. Observed cross sections for disorientation collisions between aligned ground-state rubidium atoms and neon, argon, krypton, and xenon atoms are $5.2 \times 10^{-22} \text{ cm}^2$, $3.7 \times 10^{-22} \text{ cm}^2$, $5.9 \times 10^{-21} \text{ cm}^2$, and $1.3 \times 10^{-20} \text{ cm}^2$, respectively. In the evacuated tetracontane-lined cell, the relaxation time decreased by 30% for a tenfold increase in rubidium vapor pressure. An explanation for this relatively weak dependence is suggested. The longest observed relaxation time was approximately 0.4 seconds in a tetracontane-lined cell filled with neon to a pressure of 3 cm Hg.

INTRODUCTION

A STUDY of the relaxation of alkali metal vapors aligned by optical pumping is particularly interesting for several reasons. In the first place, a relatively large population of oriented atoms is present at temperatures of the order of 300–400°K, corresponding to a degree of alignment achieved by other methods of spin orientation at liquid helium temperatures.^{1–5} Furthermore, since the oriented atoms are in the vapor state, they interact with each other and with other gas atoms in the course of isolated binary collisions. The relaxation process is therefore a somewhat more straightforward physical problem than relaxation in condensed systems.

By varying the experimental conditions, such as the partial pressure of an inert buffer gas, or the alkali vapor pressure, the relative frequency of different types of collisions leading to relaxation can be changed and the disorienting interactions can be studied separately. Such a procedure has been followed in the experiment to be described here. The principle of the experimental method can be described as follows.

When circularly polarized resonance radiation is passed through the vapor of an alkali metal, the strongly absorbing magnetic sublevels in the ground state of the alkali atoms tend to get depopulated at the expense of the weakly absorbing levels. This effect is particularly striking when the D_1 line only is present in the pumping radiation.^{4,5} As a result of this process, the vapor becomes more transparent to the pumping radiation. By applying a sudden perturbation to the system, it is then possible to obtain information on the relaxation of the vapor by observing its optical transparency as a function of time. Such a method was first

used by Dehmelt,² who observed the effect on the transmitted light of suddenly reversing a small longitudinal magnetic field. The field reversal reverses the sign of the polarization of the vapor, causing it to become momentarily more opaque. The decay rate of the inverted polarization under the combined effects of relaxation and continued pumping can then be used to deduce the relaxation time of the vapor by separating out the contribution of relaxation.

However, a more reliable measurement of relaxation time is achieved by allowing an aligned vapor to relax in the dark. The change in alignment with time is then determined by relaxation alone, and it is not necessary to separate out any competing effects. To carry out a measurement of this type, we have constructed a mechanical shutter that interrupts the pumping light beam suddenly, and then turns it on again after a variable time interval. The actual interruption time can be measured directly by triggering the sweep of an oscilloscope with the output signal from a photomultiplier tube which is illuminated by light passing through the vapor cell.

When the shutter opens after a short interval of closing, the transparency of the vapor will have changed as a consequence of the partial relaxation of the vapor. This change is reflected in a decreased output signal from the photomultiplier an instant after the re-opening of the shutter. By superimposing the output signals from the photomultiplier corresponding to a series of shutter closing times on a single oscilloscope photograph, the approximately exponential decay of the polarization of the vapor is plotted out directly.

In the case of the rubidium vapor cell used in our experiment, under the most favorable conditions the transmitted light intensity changed by as much as twelve percent as a result of relaxation in the dark. The corresponding amplitude of the Dehmelt-type field reversal transient was somewhat more than twenty percent of the total amount of light passing through the cell. The effects measured here are therefore relatively

* Supported by the U. S. Army Signal Corps Research and Development Laboratory, Fort Monmouth, New Jersey.

¹ A. Kastler, Proc. Phys. Soc. (London) A67, 853 (1954).

² W. B. Hawkins, Phys. Rev. 98, 478 (1955).

³ H. G. Dehmelt, Phys. Rev. 105, 1487 (1957).

⁴ W. E. Bell and A. L. Bloom, Phys. Rev. 107, 1559 (1957).

⁵ W. Franzen and A. G. Emslie, Phys. Rev. 108, 1453 (1957).

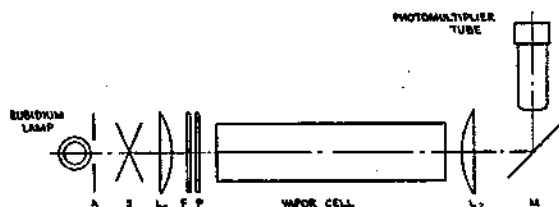


Fig. 1. Schematic diagram of optical system. The symbols have the following significance: *A*-aperture; *S*-shutter; *L*₁-condensing lens; *F*-interference filter; *P*-circular polarizer; *L*₂-collimating lens; *M*-mirror.

large and easily observable, except when the relaxation time is quite short.

APPARATUS

A schematic picture of the optical system employed in this experiment is shown in Fig. 1. As can be seen from this diagram, light from a rubidium spectral lamp passes through an aperture which is in the focal plane of a condensing lens. A mechanical shutter is mounted between the aperture and the lens. The light collected by the lens passes successively through an interference filter and through a circular polarizer and then enters a cylindrical glass cell containing the rubidium vapor. After traversing the cell along its axis, the pumping radiation falls on the face of an infrared-sensitive photomultiplier tube. The entire setup is directed along a magnetic meridian and is surrounded by two rectangular Helmholtz coils which allow both the vertical and the longitudinal magnetic fields to be adjusted at will. The rectangular framework holding the coils is covered with black paper on all sides except one, where an opening is left to allow manipulation of the shutter.

The construction of the mechanical shutter is illustrated in Fig. 2. As shown in this picture, a black paper flag approximately $3\frac{1}{2}$ inches long and $2\frac{1}{2}$ inches wide is fastened to the end of an 8-inch long thin steel blade. The blade is fastened to a pivot at its other end, around which a strong steel spring tends to rotate it. The rotational motion of the blade is arrested, however, by an adjustable metal cam which can slide sideways. There are three stable positions of the steel blade, depending on the position of the cam. In the first position, the paper flag is out of the light beam and below it; in the second position, the flag is directly in the beam, and in the third position, the flag is out of the beam and above it. In operation, the cam is moved from left to right by a modified Atwood's machine, as shown in Fig. 2. By adjusting the position of the middle portion of the cam, the flag will spend a variable length of time in the light beam. In practice, a variation of shutter closing times ranging from 20 to 500 milliseconds could be achieved. To obtain still longer closing times, the cam was moved manually.

Both Philips and Osram spectral lamps operated on direct current were employed as light sources. A three-

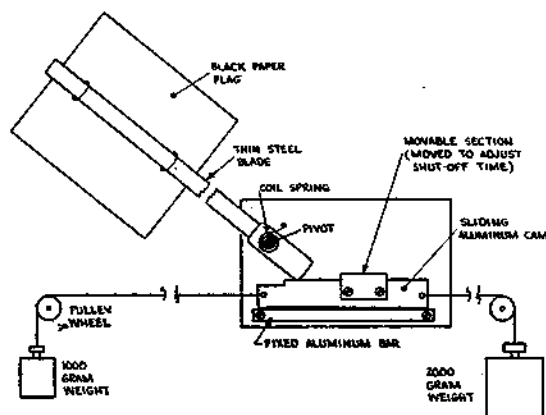


Fig. 2. Construction of mechanical shutter.

inch diameter interference filter⁶ was used to eliminate the D_2 component from the rubidium resonance radiation. The circular polarizer consisted of a type HN-7 polarizing sheet and a 200-m μ retardation plate.⁷

The vapor cell itself was a cylindrical Pyrex tube, 8 inches long and 2 inches in outside diameter. Both ends of the cell were closed off with flat circular windows cemented to the cylinder with Epoxy resin. The cell was equipped with two 15-mm diam. sidearms projecting vertically upwards and downwards from the center of the cell, respectively. A vacuum and gas filling system was permanently connected to the cell by means of a 2-mm capillary tube attached to the lower sidearm, which contained the rubidium reservoir. The upper sidearm was used to introduce the rubidium metal into the cell, after which the arm was sealed off permanently.

In addition to unlined glass cells, a cell lined with a thin film of tetracontane was used. Tetracontane is a straight-chain saturated hydrocarbon of chemical composition $C_{40}H_{82}$. It therefore belongs in a class with eicosane ($C_{20}H_{42}$) used successfully by Dehmelt recently for a similar purpose.⁸ However, tetracontane has the advantage of a higher melting point (approximately 80°C) and of a negligibly small vapor pressure at rubidium vapor temperatures (40 to 50°C).

The tetracontane was distributed over the inside walls of the cell by melting it in an atmosphere of argon, and random shaking of the cell during the course of cooling and solidification. The coverage obtained by this procedure is quite good, as can be judged by placing a drop of distilled water into the cell and observing its lack of adhesion as it rolls about. (In a cell completely coated with a water-repellent material such as tetracontane or polyethylene, a drop of water will not stick at all, but move about like a drop of mercury on a clean glass slide.) However, as explained

⁶ Spectrolab interference filter type PCB; Spectrolab, Inc., North Hollywood, California.

⁷ Purchased from the Polaroid Corporation, Cambridge, Massachusetts.

⁸ H. G. Dehmelt, *Bull. Am. Phys. Soc. Ser. II*, 3, 9 (1958).

above, in order to install the cell on our optical bench and introduce rubidium metal into it, the upper side arm had to be opened and then sealed off again. As a result, a 15-mm diam. circle at the top of the cell was not covered with tetracontane, comprising approximately 1/200 of the total area of the cell.

The main body of the cell was enclosed in a black-anodized heavy aluminum housing through which warm air was passed in order to maintain an appropriate temperature. The rubidium reservoir in the lower side arm projected out of the housing into a glass beaker filled with warm silicone oil. Thermocouples were used to measure temperatures in various parts of the system.

The glass capillary projecting from the lower side arm could be closed off by means of a Hoke bellows valve. The other side of the valve was attached to a glass gas filling and pressure measuring manifold, which in turn was connected to a metal vacuum system. The glass manifold was equipped with both octoil and mercury manometers. All the rare gases used in the experiment were spectroscopically pure grades obtained from the Linde Air Products Company. No attempt was made to purify these gases any further in the belief that the rubidium vapor itself would be an extremely effective getter for those residual impurities which might shorten the relaxation time.

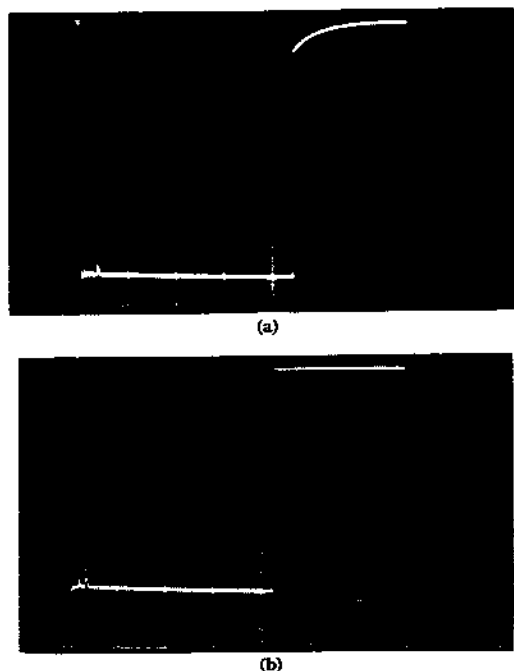


FIG. 3. Photographs of shutter transients to demonstrate the effect of optical pumping and relaxation on the resonance radiation transmitted through a rubidium vapor cell. Experimental conditions were as follows: cell lining, tetracontane; buffer gas, neon at a pressure of 0.4 cm Hg; cell temperature, 48°C; oscilloscope sweep speed, 200 msec/scale division. (a) Vertical component of the earth's magnetic field compensated. In this case, there is optical pumping alignment of the vapor. (b) Vertical component of the earth's field not compensated. In this case, there is no optical alignment.

DEMONSTRATION OF METHOD

To demonstrate the effect of spin relaxation on the transparency of optically aligned rubidium vapor, photographs of shutter transients recorded on a Tektronix oscilloscope have been reproduced in Figs. 3 and 4. In Figs. 3(a) and 3(b), the gain of the vertical amplifier of the oscilloscope has been adjusted so that the entire output of the photomultiplier tube is visible on the face of the cathode-ray tube.

In Fig. 3(a), the vertical component of the earth's magnetic field has been compensated, and the horizontal component is parallel to the direction of light propagation. Under these conditions, optical pumping alignment of the rubidium vapor in the cell is brought about by illumination with circularly polarized D_1 radiation.

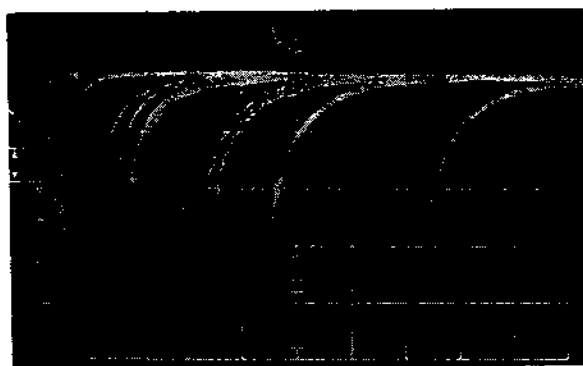


FIG. 4. Enlarged shutter transients to illustrate the approximately exponential decay of the excess transparency of the rubidium vapor, as the vapor is allowed to relax in the dark for a varying length of time. A smooth curve has been drawn with ink through the beginning points of the "recovery" traces. The logarithm of the average decrement of the smooth decay curve is given by $\bar{\delta} = \log\{1/3[(Y_1/Y_2) + (Y_2/Y_3) + (Y_3/Y_4)]\}$. The decay time is then $\tau = T/\bar{\delta}$ where T is the (equal) time interval corresponding to the decrement intervals. (In this photograph, we have used $T = 100$ msec.) This photograph was taken under the following conditions: cell lining, tetracontane; buffer gas, neon at a pressure of 0.58 cm Hg; cell temperature, 48°C; oscilloscope sweep used, 200 msec/scale division.

The sweep of the oscilloscope is triggered by the photomultiplier signal resulting from the sudden decrease of transmitted light intensity at the instant of shutter closing. The electron spot on the cathode-ray tube face thus suddenly moves downward from its previously stationary position in the upper left-hand corner. At the same time, the oscilloscope sweep circuit carries it to the right at a constant rate (thick trace on bottom of photograph). A moment later, the shutter opens again, but the light intensity passing through the cell has now fallen below its pre-closing value. However, the pumping effect of the light gradually realigns the vapor, and the transmitted light intensity returns to its original value after a short time (curved portion of trace in upper right-hand corner of photograph). The vertical motion of the oscilloscope trace at the instants of shutter opening and closing are not visible on this

photograph because of the high writing speed resulting from the motion of the shutter and the relatively small aperture opening of the oscilloscope camera.

Figure 3(b) is a photograph taken immediately after Fig. 3(a), with all conditions of operation unchanged, except that the vertical component of the earth's magnetic field is now left uncompensated. Since the dip angle of the earth's magnetic field is rather large (of the order of 75°) in Cambridge, Massachusetts, where this experiment was performed, the resultant field is nearly vertical, and no pumping alignment of the vapor takes place.² The light intensity therefore returns to its original value when the shutter opens, as indicated by the horizontal trace in the upper right hand corner. (It is also interesting to observe that the maximum deflection of the oscilloscope trace as a result of the closing of the shutter is now *less* than in Fig. 3(a). This corresponds to the fact that the vapor is more opaque in an unpolarized state. The difference between the levels of the traces at left bottom of the two photographs corresponds exactly to the change in transparency brought about by optical pumping.)

In Fig. 4, the gain of the vertical amplifier of the oscilloscope has been increased in order to emphasize the effect of relaxation. Furthermore, a number of shutter transients with a range of closing times are superimposed on a single photograph. We can regard these oscilloscope records as electronic enlargements of the uppermost portion of Fig. 3(a).

Evidently, the loss in transparency of the vapor as a result of relaxation in the dark approaches a limiting value asymptotically, as we would expect. Superimposed on the end points of the photographed shutter transients is an approximate smooth curve which has been drawn with ink through the beginning points of the thick "recovery" traces. The position of these beginning points on the photograph corresponds to the transmitted light intensity at the instant of shutter opening. We have assumed that the decay curve is exponential in every case. To determine the decay time, the logarithm of the average decrement of each curve has been measured, as shown in Fig. 4.

RESULTS

A summary of the most important results of this experiment is presented in Fig. 5. The experimentally determined spin relaxation time is plotted as a function of buffer gas pressure for an unlined glass cell filled with neon, argon, krypton, and xenon at various pressures, and for a tetracontane-lined cell filled with a variable pressure of neon.

In cells filled with neon and argon (both lined and unlined), relaxation times were determined by measuring the logarithm of the average decrement of the experimentally recorded shutter transients, as explained previously. It is estimated that this procedure yields relaxation times accurate to about $\pm 10\%$. A constant

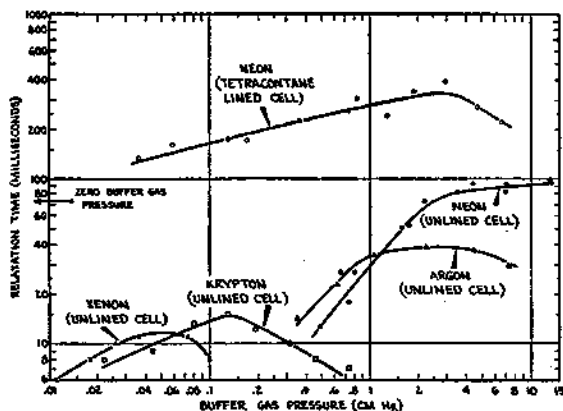


FIG. 5. Rubidium vapor spin relaxation time as a function of buffer gas pressure under various conditions.

logarithmic decrement over the range of shutter intervals recorded on one photograph would be an indication that the relaxation of the vapor is indeed exponential. In practice, the decrement varied in some cases by as much as 20% over the decay curve, indicating some deviation from exponential decay. The series of shutter transients recorded on one photograph were usually taken as quickly as possible, in a time which rarely exceeded one minute. To check the constancy of the light source during this time, field-reversal transients were photographed before and after each series. The amplitude of the observed field-reversal transient is a very sensitive measure of light intensity. (Except for possible variations in light intensity during the process of photographing one series of shutter transients, the measured relaxation time is of course independent of the intensity of the pumping radiation.)

In the case of the unlined cell filled with krypton and xenon, the relaxation times were so short that the shutter transient method could not be employed. In these cases, we therefore photographed field-reversal transients and deduced decay times from the extrapolated slope of such transients, as described by Dehmelt.³

Aside from the large differences observed in the effects of the various inert gases on the spin relaxation time, the effect of the tetracontane lining is particularly noteworthy. Evidently, in a cell lined with this material, the variation of relaxation time with buffer gas pressure has a character entirely different from that observed in an unlined glass cell. Furthermore, a considerable degree of alignment and an appreciable relaxation time are achieved in a high vacuum.

Figure 6 shows the variation of the measured relaxation time with cell temperature in an evacuated tetracontane-lined cell. In this case, as in all our observations, the temperature of the rubidium reservoir was maintained consistently about 2°C below the cell temperature. In the scale of vapor pressures indicated in Fig. 6, it has been assumed that the vapor pressure is given directly by the cell temperature. The relatively

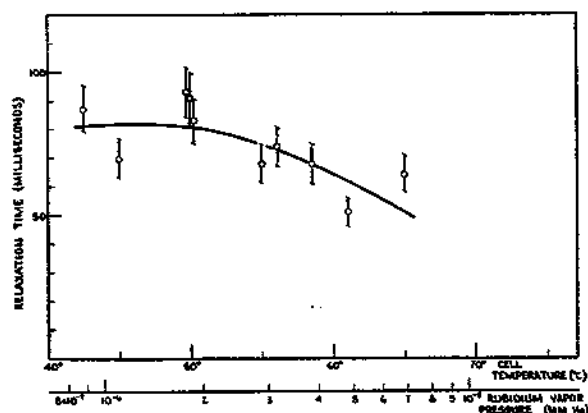


FIG. 6. Variation of relaxation time with rubidium vapor pressure for an evacuated cell lined with tetracontane.

weak dependence of the observed relaxation time on rubidium vapor pressure is remarkable.

It may be of interest to note that a tetracontane-lined evacuated cell was closed off from the gas-filling and vacuum system and operated for several days without observable change in characteristics.

ANALYSIS OF RESULTS AND DISCUSSION

The relaxation of a partially oriented alkali metal vapor in a buffer gas would be expected to take place by electron exchange between colliding alkali atoms, as discussed by Wittke and Dicke⁹ and Purcell,¹⁰ by collisions with buffer gas atoms, and by collisions with the cell walls. Experimental evidence for the influence of electron exchange on the width of the hyperfine resonance line in Rb^{87} has been obtained by the Princeton group,¹¹ who obtained an approximately linear relationship between line width and vapor pressure. From this relationship, they have deduced an effective cross section for exchange collisions σ_{ex} in Rb^{87} of 7 to $10 \times 10^{-14} \text{ cm}^2$. If our cell temperature can indeed be used to compute the rubidium vapor pressure, we would expect a mean time between collisions (corresponding to a relaxation time) of

$$\tau_{ex} = 1/(n\sigma_{ex}\bar{v}_{rel}) = 6.5 \times 10^{-3} \text{ sec}$$

at a cell temperature of 47°C . (This was our usual operating temperature, corresponding to a rubidium vapor pressure of approximately $1.5 \times 10^{-6} \text{ mm Hg}$.) The measured relaxation time in our experiment with an evacuated, tetracontane-lined cell at this temperature was approximately $90 \times 10^{-3} \text{ sec}$, or 14 times as long, as can be seen by inspection of Fig. 6. (Since the cell is in a high vacuum, there is no contribution to the relaxation time from buffer gas collisions in this case, and the only effective relaxation mechanisms are spin

exchange collisions between rubidium atoms and wall collisions. The mean time between wall collisions is of the order of $0.2 \times 10^{-3} \text{ sec}$ in a cell of the dimensions used in this experiment.)

Furthermore, the data of Fig. 6 seem to indicate a relatively small variation of relaxation time with vapor pressure. On increasing the rubidium vapor pressure from $8 \times 10^{-7} \text{ mm Hg}$ to $8 \times 10^{-6} \text{ mm Hg}$, the relaxation time appears to decrease to about $\frac{2}{3}$ of its maximum value, while the relationship observed by the Princeton group would predict a decrease by a factor of 10.

We would like to suggest the following explanation for this discrepancy which is perhaps related to a suggestion made recently by Bender.¹² In a nonradiative binary collision, of which a spin exchange collision between two rubidium atoms is an example, the sum of the z components of the total angular momenta of the colliding atoms must be the same before and after the collision. This means in the first place that in a collision between two atoms which are both in the higher energy hyperfine state ($F = I + \frac{1}{2}$, where I is the nuclear spin) and for which the magnetic quantum number has either its maximum or its minimum value ($m_F = F$ or $m_F = -F$), spin exchange cannot affect the spin orientation of the two atoms. In the second place, if two atoms collide which are in the same hyperfine state both before and after the collision, their combined light absorption probability for D_1 radiation will remain unaffected by the collision. Thus for an atom with nuclear spin $I = \frac{3}{2}$, as Rb^{87} or Na^{23} , the absorption probability for D_1 radiation in the $F = 2$ state is proportional to $2 - m_F$; in the $F = 1$ state it is proportional to $2 + m_F$. For two atoms, both of which are in the $F = 2$ state, the combined absorption probability is therefore proportional to $4 - [m_F^{(1)} + m_F^{(2)}]$, while if they are both in the $F = 1$ state, it is proportional to $4 + [m_F^{(1)} + m_F^{(2)}]$. If $[m_F^{(1)} + m_F^{(2)}]$ is invariant, the amount of light absorbed by the two atoms in the same F state does not change as a result of the collision.

The transmission monitoring technique therefore is not sensitive to Δm -relaxation induced by binary collisions between atoms in the same hyperfine state. Undoubtedly, a certain proportion of the spin relaxation events are of this type, and their occurrence could not be recognized in our experiment. However, such events do affect the $m_F = 0$ states which are of principal interest to the hyperfine resonance experiments.

In view of these observations, we shall attempt to analyze the variation of relaxation time with buffer gas pressure in an unlined glass cell by neglecting the contribution of spin exchange collisions between rubidium atoms to the observed relaxation time. Thus we shall consider only wall and buffer gas collision disorientation in this case.

⁹ J. P. Wittke and R. H. Dicke, *Phys. Rev.* **103**, 620 (1956).

¹⁰ R. M. Purcell and G. B. Field, *Astrophys. J.* **124**, 542 (1956).

¹¹ Dicke, Carver, Alley and Van der Ven, Final Report to the U. S. Army Signal Corps Engineering Laboratory, September 30, 1957 (unpublished).

¹² P. L. Bender, *Proceedings of the 12th Annual Frequency Control Symposium*, Asbury Park, New Jersey, May 8, 1958 (unpublished), p. 593.

Let us assume that every wall collision results in complete disorientation, i.e., an atom is randomly oriented after striking the glass wall of the cell. Let the density of aligned atoms be n_1 at the instant when the shutter closes. (We can regard "alignment" as being defined by the average value of the absorption probability for D_1 radiation at that instant, so that initially the entire population is "aligned".) If n_2 is the density of randomly oriented atoms which are produced by wall collisions, or by disorienting buffer gas collisions, then by definition $n_2=0$ initially. It is easy to show that the excess light transmission through the cell (in excess of the transmission through a cell containing only randomly oriented atoms) is proportional to n_1 .

If only the two relaxation mechanisms mentioned above are operative, then n_1 can be described by a diffusion equation containing an absorption term:

$$\partial n_1 / \partial t = D \nabla^2 n_1 - k n_1. \quad (1)$$

The equation for n_2 is redundant since $n_1 + n_2 = n = \text{constant}$. The constant k is given by

$$k = N_0 \sigma \bar{v}_{\text{rel}} (p/p_0), \quad (2)$$

where N_0 is the density of buffer gas atoms at atmospheric pressure p_0 and at the appropriate rubidium vapor temperature; the actual density at pressure p is $N = N_0 (p/p_0)$. σ is the disorientation cross section which characterizes rubidium-buffer gas collisions, and \bar{v}_{rel} is the mean relative velocity of rubidium and buffer gas atoms.

D is the coefficient of diffusion for rubidium atoms in the buffer gas. The pressure dependence of D has the form

$$D = D_0 (p_0/p). \quad (3)$$

The solution of Eq. (1) in a cylindrical cell which satisfies the boundary condition that n_1 vanish at the walls is

$$n_1(r, z, t) = \sum_{i=1}^{\infty} \sum_{j=1}^{\infty} A_{ij} \exp\{-[(\mu_i^2 + \nu_j^2)D + k]t\} \times J_0(\mu_i r) \cos(\nu_j z), \quad (4)$$

where $\nu_j = (2j-1)\pi/L$ and μ_i is defined by $J_0(\mu_i a) = 0$, and L and a are the length and radius of the cell respectively.

The simplest approximation that can be made in the absence of detailed knowledge of the initial distribution of n_1 is to consider only the first mode of (4).

The relaxation time is then

$$\tau = \frac{1}{(\mu_1^2 + \nu_1^2)D + k} = \frac{1}{1.28 \text{ cm}^{-2} D_0 (p_0/p) + N_0 \sigma \bar{v}_{\text{rel}} (p/p_0)}, \quad (5)$$

where we have set $\mu_1 a = 2.405$; $a = 2.15$ cm; $\nu_1 = \pi/L$

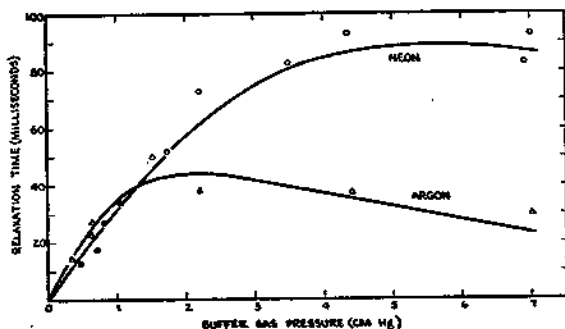


FIG. 7. Relaxation time as a function of buffer gas pressure in an unlined cell filled with neon and argon. The indicated points are experimental points, but the smooth curves are theoretical curves computed on the basis of assumed diffusion coefficients and disorientation cross sections for the two gases, as explained in the text. The solid and open circles refer to the experimental points for neon and the open triangles to those for argon.

and $L = 20.0$ cm, which describes the dimensions of our cell. The values of D_0 and σ which give the best fit to the experimental points for neon are $0.31 \text{ cm}^2/\text{sec}$ and $5.2 \times 10^{-22} \text{ cm}^2$, respectively, and for argon, $0.24 \text{ cm}^2/\text{sec}$ and $3.7 \times 10^{-22} \text{ cm}^2$, respectively. A plot of Eq. (5) using these parameters has been superimposed on the experimental points for neon and argon in Fig. 7. We have assumed a temperature of 47°C , for which $N_0 = 2.29 \times 10^{19} \text{ cm}^{-3}$, and mean relative velocities of $6.5 \times 10^4 \text{ cm/sec}$ for rubidium-neon and $5.0 \times 10^4 \text{ cm/sec}$ for rubidium-argon.

The diffusion coefficients for rubidium diffusing through neon and argon have not been measured previously. The values that we have derived are quite reasonable in comparison with known diffusion coefficients in rare gases. This result, as well as the relatively good fit to the experimental points obtained in Fig. 7, seems to lend strong support to the assumption that complete disorientation is produced in every wall collision in a glass cell.

The disorientation cross section σ for rubidium colliding with neon is astonishingly small; it is smaller than the gas-kinetic collision cross section by a factor of approximately 10^8 . In other words, 10^8 collisions with neon are necessary on the average in order to disorient the spin of an aligned rubidium atom in its electronic ground state.

Equation (5) predicts that the relaxation time in a buffer gas should go through a maximum value at a certain gas pressure. For a cell of our geometry, the maximum occurs at 5.4 cm Hg neon pressure; in argon, it occurs at approximately 2.0 cm Hg pressure.

In view of the extremely short relaxation times in krypton and xenon, it was not possible to make measurements over a wide range of pressures. For this reason, we were not able to fit a calculated curve to the experimental data in these cases. However, diffusion coefficients for rubidium in krypton and xenon can be computed from the coefficient in neon by assuming that D_0 is inversely proportional to the product of the gas

kinetic collision cross section and the square root of the reduced mass, at a given temperature. (This would be true for a gas of hard spheres, which is a reasonable model for monatomic gases.) This argument leads to diffusion coefficients of $0.16 \text{ cm}^2/\text{sec}$ for rubidium in krypton, and $0.13 \text{ cm}^2/\text{sec}$ for rubidium in xenon. (By the same argument, we would calculate a diffusion coefficient of $0.21 \text{ cm}^2/\text{sec}$ for rubidium in argon, as compared to a measured value of $0.24 \text{ cm}^2/\text{sec}$.)

We can then calculate approximate disorientation cross sections in krypton and xenon from the experimentally observed maximum relaxation time by use of Eq. (5). The resulting values are $5.9 \times 10^{-21} \text{ cm}^2$ for krypton and $1.3 \times 10^{-20} \text{ cm}^2$ for xenon. These cross sections are 100 and 200 times larger, respectively, than the value in neon. Such very large differences in the disorienting properties of the various inert gases are quite surprising.

We shall now turn to a discussion of the relaxation time measured in a tetracontane-lined cell with variable neon buffer gas pressure. As can be seen from Fig. 5, the relaxation time slowly increased with increasing neon pressure, reaching a maximum value of about 0.4 second at a pressure of 3 cm Hg. Evidently, the neon is again inhibiting diffusion to the walls, or to some portion of the walls. In view of the fact that about 1/200 of the total wall area of the cell was left uncovered, as a result of the method of sealing-off the cell employed here, we are not able to judge conclusively whether tetracontane itself, or the uncovered portion of the cell, were the principal remaining causes of wall disorientation.

However, since the ratio of the relaxation time observed in a vacuum (about 80 msec) to the mean cell crossing time for rubidium in a high vacuum (0.2 msec) is about 400, while the ratio of covered to uncovered cell wall area is about 200, we are inclined to attribute the remaining wall relaxation to the uncovered glass. In that case, the variation of relaxation time with buffer gas pressure shown in Fig. 5 can be interpreted in terms of the inhibition of diffusion along the axis of the cell (the z direction) by the neon buffer gas.

If this assumption is correct, considerably longer relaxation times should be observed in a completely

lined cell. It is important to emphasize, however, that in view of the need for a rubidium reservoir at one place in the cell, it is not possible to achieve complete coverage in practice; the surface of the liquid alkali metal in the reservoir will certainly always be a cause of complete disorientation. Our cell was constructed so as to enhance the frequency of wall collisions, since this was an important object of our study. In a spherical cell, the ratio of volume to surface area would be more favorable than in our cylindrical cell and still longer relaxation times should be easily attainable.

CONCLUSION

The various rare gases differ considerably in their effect on the spin orientation of ground-state rubidium atoms. This difference in behavior does not appear to have a physical explanation at the present time. Of the gases investigated, neon has by far the smallest disorientation cross section.

The dependence of the observed relaxation time on rubidium vapor pressure is surprisingly weak. An attempt has been made to explain this effect on the basis of a distinction between Δm -relaxation and ΔF -relaxation induced in spin-exchange collisions.

Straight-chain hydrocarbon wall-linings such as tetracontane are very effective in inhibiting relaxation in wall collisions. Tetracontane is a particularly suitable substance in view of its high melting point and very low vapor pressure at rubidium or cesium vapor temperatures. Extremely narrow hyperfine resonance lines should be obtainable in a tetracontane-lined spherical cell filled with neon at a low pressure.

ACKNOWLEDGMENTS

Thanks are due Dr. A. G. Emslie for his sympathetic interest in this work. George Feick and Dr. William E. Cass were very helpful in providing chemical advice in connection with the development of suitable wall coatings. I would like to thank Dr. Ivan Simon for loan of the tetracontane used in the experiment, and William S. Martin for his expert design and construction of the mechanical shutter.