

Relaxation and frequency shifts in the ground state of Rb⁸⁵

Jacques Vanier, Jean-F. Simard, and Jean-S. Boulanger

Laboratoire d'Electronique Quantique, Dept du Génie Electrique, Université Laval, Québec G1K 7P4, Canada

(Received 4 June 1973)

Relaxation rates and frequency shifts of the 0-0 hyperfine transition in the ground state of Rb⁸⁵ are studied in some detail at 3.03 GHz. Results on the relaxation rates of the populations and of the coherence introduced in the system by a short microwave pulse are given. Physical parameters are extracted from the data and are interpreted in terms of wall interactions, buffer-gas interactions, and spin-exchange interactions. The data are analyzed in terms of simple theoretical models and are also discussed in relation to published results on other isotopes or alkali-metal atoms.

INTRODUCTION

The interaction of hydrogen and alkali-metal atoms with buffer gases and surfaces in specially coated cells has drawn in the past great interest from many experimenters.¹⁻⁷ This is also true of the spin-exchange interaction between these atoms.⁸⁻¹¹ This interest has been raised for two main reasons. First, hydrogen and the alkalis are atoms with an S ground state. This makes the interpretation of experimental data possible in terms of simple calculations and has led to a rather good understanding of the interaction taking place between a few of these atoms and surfaces such as polyethylene.² Second, these atoms have come to play an important role in the field of atomic frequency standards using hydrogen and rubidium. The accuracy and stability of these standards depend on a good control of the relaxation processes and frequency shifts which take place in these devices. In the hydrogen maser, for example, these shifts may be due to spin-exchange interactions and collisions with the Teflon-wall surface coating of the storage container.^{9,12,13} In a rubidium cell such as those used in frequency standards, spin-exchange interactions and collisions between the rubidium atoms and the buffer gas play an important role.

A fair amount of results have been published on the frequency shifts and relaxation rates observed in hydrogen and Rb⁸⁷. Most of the published data, however, have been concerned with the electronic polarization S_z and the population difference of the hyperfine levels $\langle \vec{S} \cdot \vec{I} \rangle$. Very few experiments have been oriented toward a study of the coherence that can be created inside the ground-state manifold. Furthermore, only fragmentary data have been published on the relaxation rates and the frequency shifts observed in the ground state of Rb⁸⁵. (For an excellent review of the subject of relaxation in alkalis the

reader is referred to W. Happer, Ref. 16.)

In the present paper we give results on the relaxation and the frequency shifts measured for the 0-0 transition of the ground state of Rb⁸⁵ at 3.03 GHz in various physical environments. These results include data on spin-exchange, buffer-gas, and wall interactions.

METHOD OF MEASUREMENTS

The physical system which we have studied experimentally is made up of a vapor of Rb⁸⁵ atoms enclosed in a quartz cell. The perturbation on the rubidium atoms originates from spin-exchange interactions, collisions with a buffer gas, or collisions with the surface of the cell, which may be coated with a substance such as Parafilm. The spherical cell is approximately 7 cm in diameter and is placed at the center of a microwave cavity resonating in the TE₀₁₁ mode, at the hyperfine frequency of the ground state of the rubidium atoms. In this arrangement the atoms are confined to a field of constant phase. Optical pumping of the cell is done through one end of the cavity with a Rb⁸⁵ lamp filtered by a Rb⁸⁷ isotopic filter. This type of pumping, generally called intensity pumping, makes possible the creation of large population differences between the two levels $F=3$ and $F=2$, with the level $F=3$ more populated than the other one. The monitoring of the population inversion and of the coherence existing in the ensemble is done through the observation of stimulated emission signals induced by a short microwave pulse applied to the microwave cavity at the frequency of the transition $F=3, M_F=0 \rightarrow F=2, M_F=0$. In this kind of experiment the pumping light is applied in the form of pulses and the microwave pulse is applied during the time the light is off. This method of measurement, which gives relaxation data in the dark, has been described in some detail in Refs. 5 and 14.

THEORETICAL BACKGROUND

The atomic ensemble may be described by a two-level density matrix of the form

$$\rho = \begin{pmatrix} \rho_{11} & \rho_{12} \\ \rho_{21} & \rho_{22} \end{pmatrix}, \quad (1)$$

where 1 and 2 refer, respectively, to the two levels $F=3, M_F=0$ and $F=2, M_F=0$. At the temperatures considered in this paper both levels 1 and 2 can be considered normally as equally populated; application of the pulse of light creates an overpopulation of level 1 relative to level 2 making $\rho_{11} \gg \rho_{22}$ and the microwave pulse creates off-diagonal elements ρ_{12} and ρ_{21} which are observed as stimulated emission signals.

The decay of the population difference can be described by a term of the form

$$\rho_{11} - \rho_{22} = (\rho_{11} - \rho_{22})_0 e^{-t/T_1}. \quad (2)$$

The stimulated-emission-signal decays in the same way as the off-diagonal elements of the density matrix

$$\rho_{12} = (\rho_{12})_0 e^{-t/T_2}. \quad (3)$$

The time constants T_1 and T_2 are characteristics of the type of interaction taking place in the physical ensemble and are the parameters measured. In this paper we will hold to this definition of T_1 and T_2 so no confusion should arise as to what macroscopic variable is measured. In all cases considered, the decaying signals were very nearly exponential. Only one time constant was observed and the above expressions are considered sufficiently exact for the analysis of the data.

Spin-exchange interactions

The spin-exchange phenomenon in a hydrogen gas as well as in an alkali-metal vapor has received a considerable amount of interest in the past.^{5, 8, 9, 11, 15} Most of the data published for Rb⁸⁵, however, were obtained from measurements on the relaxation of the populations of the two hyperfine levels $F=3$ and $F=2$. Little emphasis has been placed on the measurement of T_2 , the rate of decay of the coherence represented in our context by the off-diagonal elements ρ_{12} and ρ_{21} . Grossetête¹⁵ has obtained an approximate analytical formula giving a relation between T_1 and T_2 in spin-exchange interactions taking place in hydrogen and alkali-metal gases:

$$T_1/T_2 = (6I + 1)/(8I + 4), \quad (4)$$

where I is the nuclear spin and $T_1 = n\bar{v}_r\sigma$. Here, n is the alkali atomic density, \bar{v}_r is the mean relative velocity, and σ is the so-called spin-

exchange cross section. This phenomenon may be thought of as a slowing-down process of the relaxation of the coherence relative to the relaxation of the populations.¹⁶ This factor is most important in the operation of atomic oscillators, such as the rubidium and hydrogen masers, since the atom has a longer lifetime in the radiating state than in the nonradiating state. The factor has been measured for Rb⁸⁷ and found to agree with the theoretical prediction formulated above.⁵

Wall interaction

It is generally assumed that when an atom enters into collision with the surface of a quartz cell it is completely disoriented. Within this hypothesis the lifetime of an atom in a given state is given simply by the inverse of the collision rate with the walls of the cell. In the case of a cell coated with a substance such as paraffin, $(\text{CH}_2)_n$, relaxation is greatly inhibited. In a typical cell, a few inches in diameter, one can in fact observe lifetimes of a few hundred msec corresponding to a few hundred bounces before a change of state takes place. The relaxation of the population and of the coherence may be very different. The populations may relax through physical absorption on the surface, chemical reaction, or nonadiabatic collisions in which the atoms change state. On the other hand, adiabatic collisions act to influence the coherence that may exist in the ensemble. This last interaction can be thought of as introducing a phase shift in the wave function of the atom. If we assume that the main effect comes from mixing in the excited P -state wave function, the shift is given by^{1, 17}

$$\bar{\phi} = 2\pi\nu_0 \frac{E_a}{\nu_s} \left(\frac{1}{\Delta E - I} - \frac{2}{I_a} \right) e^{E_{\text{ads}}/kT}, \quad (5)$$

where ν_0 is the hyperfine frequency, E_a is the adsorption energy of the alkali-metal atom on the wall surface, ν_s is the oscillation period of the atom in the wall potential well, ΔE is the difference in energy between the P state and the ground state, I is the mean ionization energy of the wall surface, and I_a is the ionization energy of the alkali atom. In the case where the radiation lifetime is long compared to the mean time between collision \bar{T}_0 , this phase shift produces an average frequency shift given by

$$\Delta\nu_w = (\bar{\phi}/2\pi)(1/\bar{T}_0). \quad (6)$$

Dispersion in the phase shifts and in the time between collisions introduces a loss of coherence. The dispersion in ϕ may be expressed as,¹

$$\delta(\phi) = [\langle \phi^2 \rangle_{\text{av}} - (\langle \phi \rangle_{\text{av}})^2]^{1/2}. \quad (7)$$

This loss of coherence produces a broadening of the resonance line and we characterize it by a relaxation rate γ_{2w} . Consequently, a simultaneous measurement of the hyperfine frequency and of the coherence relaxation rates should lead to some understanding of the wall interaction through the determination of various parameters such as the mean phase shift per collision and the adsorption energy.

Buffer-gas collisions

Collisions of Rb^{85} atoms with the atoms of a buffer gas such as nitrogen, helium, or other inert gases may be described in the same manner as in the case of the wall surface. One main difference resides in the number of collisions experienced per second by the rubidium atom at the buffer-gas pressure at which measurements are normally made. At low buffer-gas pressures, relaxation on the wall becomes important through the process of diffusion. The diffusion constant of the alkali in the buffer gas is then an important parameter. At high pressures (>10 Torr), relaxation through buffer-gas collisions is predominant. A relaxation cross section which measures the probability of relaxation upon collision is then defined.

Consequently, taking into account the contribution from spin-exchange interactions that may take place at the temperature of interest we write, for an uncoated cell,¹⁸⁻²⁰

$$\frac{1}{T_1} = \gamma_1 = \frac{\pi^2}{R^2} D_0 \frac{P_0}{P} + N_0 \sigma_1 \bar{v}_r \frac{P}{P_0} + \gamma_1^{se}(t_1). \quad (8)$$

Here R is the bulb radius, D_0 is the diffusion constant of the alkali in the buffer gas, P is the buffer-gas pressure, P_0 is the reference pressure (760 Torr), N_0 is the number of buffer-gas molecules/cm³ at atmospheric pressure, σ_1 is the cross section for disorientation, and \bar{v}_r is the relative velocity of the alkali. The term $\gamma_1^{se}(t_1)$ is the contribution from spin exchange at temperature t_1 . We have assumed that a single mode is dominant in the diffusional relaxation.

In an uncoated cell, wall collisions should in principle affect both the population and the coherence at the same rate. Consequently, Eq. (8) should apply for the coherence except that σ_1 must now be reinterpreted as a parameter σ_2 , which measures the loss of coherence owing to adiabatic collisions, and γ_1^{se} must be replaced by γ_2^{se} . In doing this, we neglect a possible broadening caused by the Doppler effect. This approximation will be discussed further in connection with the analysis of the experimental data.

The effect of buffer-gas collisions on the coherence may be interpreted also as producing a phase shift in the wave function of the alkali. In such a model, the same relations as those introduced in the case of the wall interactions apply and we define a phase shift per collision $\bar{\phi}$ which is related to the buffer-gas frequency shift through Eq. (6). The phase shift per collision is small

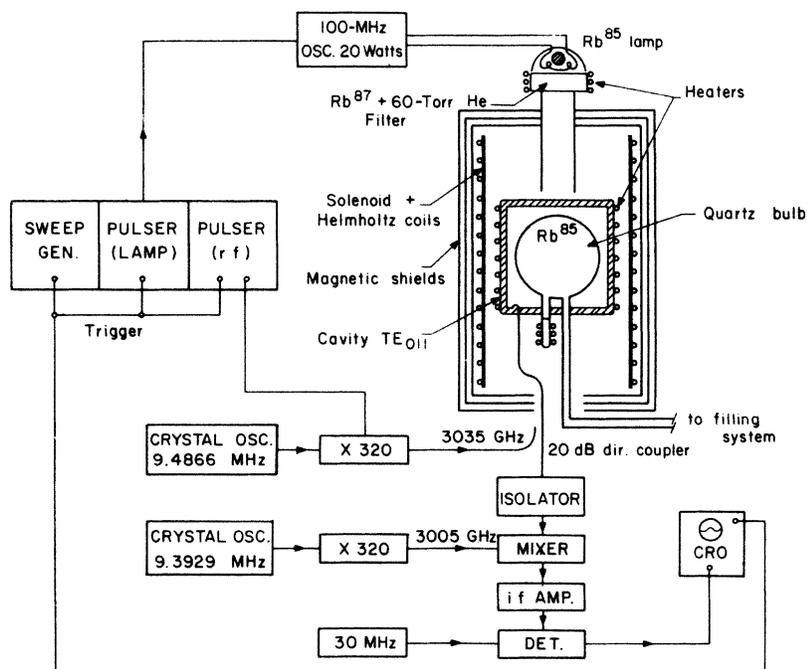


FIG. 1. Experimental setup used to measure the relaxation rates and the frequency shifts in Rb^{85} .

but the collision rate $1/\bar{T}_0$ is very large at the pressures of interest. The frequency shift is of the order of several hundred Hz/Torr. The collision rate is given by the relation

$$n_c = \frac{1}{\bar{T}_0} = \frac{\bar{v}^2}{3D_0} \frac{P}{P_0} S, \quad (9)$$

where \bar{v} is the mean velocity of the rubidium atom, and S is a factor taking into account the anisotropy introduced in the collisions by the difference of mass between the alkali and the buffer-gas atoms. This factor has been calculated by Cohen-Tannoudji.²¹

EXPERIMENTAL RESULTS

The measurements on the 0-0 transition of the ground state of Rb⁸⁵ were carried out with the experimental setup shown in Fig. 1. The relaxation rates were measured in the dark through the technique described in Ref. 5. The frequency was determined with the help of a synthesizer, through a zero-beat technique at the output of the superheterodyne receiver. The synthesizer time base was derived from a rubidium gas-cell passive clock whose frequency was known to better than one part in 10^{10} . The measurements were made during the time of the decay of the stimulated emission signal. It was possible with this technique to obtain an accuracy of a few Hz.

Spin-exchange interaction

Relaxation. The data on spin-exchange relaxation is shown in Fig. 2. These measurements were made in an uncoated cell of 7.6 cm in diameter and containing a buffer gas (nitrogen) at a pressure of 10 Torr. The graph shows the variation of γ_2 as a function of $(\gamma_1 - \gamma_{10})$, where γ_{10} is the relaxation rate measured at a temperature where

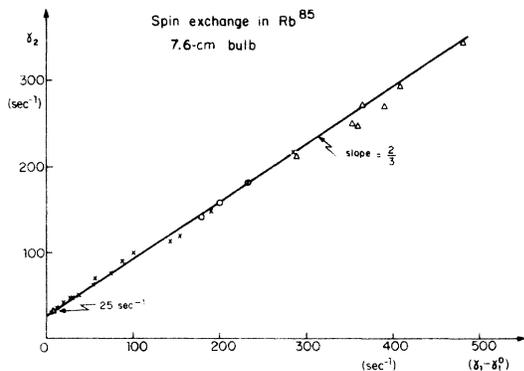


FIG. 2. Relaxation rate γ_2 as a function of $\gamma_1 - \gamma_{10}^0$, a term which is directly proportional to the rubidium density. Various types of points refer to different experiments.

the density of rubidium is negligible. The term $\gamma_1 - \gamma_{10}$ is equal to γ_1^{se} whose value is $n\bar{v}\sigma$ and is thus strictly a measure of the density. Variation of the velocity \bar{v} , over the narrow range of temperature studied has no detectable effect on the data within the accuracy of our measurements and is neglected. Figure 2 shows that the data falls on a straight line with a slope $\Delta\gamma_2^{se}/\Delta\gamma_1^{se}$ equal to $\frac{2}{3}$. This is in agreement with the theoretical predictions made above. The same experiments were repeated for a 6.6-cm cell not containing a buffer gas but coated with Paraflint. The measurements extended over a range of γ_1 from 13 to 45 sec^{-1} . The results obtained confirmed those shown in Fig. 2.

Frequency shifts. We have not been able to detect frequency shifts due to spin-exchange interactions. This is because the shifts expected are small²² ($\sim 10^{-10}$, $\sim 10^{-11}$) and are masked by much larger shifts due to buffer-gas and wall interactions.

Wall interaction (Paraflint)

Relaxation. Wall relaxation was measured as a function of temperature over the range 35–80°C. The cell used had a 6.4-cm diameter and was coated, under vacuum, with Paraflint (Moore and Munger, New York) through a technique similar to that described by Bouchiat and Brossel.² The main difference between this technique and ours was that after the coating was completed the cell was filled with hydrogen, removed from the vacuum system, and reinstalled on another vacuum system. This was necessitated by the physical arrangement of our measuring system. During the measurements a Vacion pump was continuously connected to one arm of the cell and maintained a background residual-gas pressure less than 10^{-8} Torr as measured at the pump. The rubidium was obtained from a breakable glass ampoule and was distilled slowly into another arm of the cell. Care was taken not to contaminate the wall surface of the bulb. We observed no delay in the observation of the resonance signals upon pulsing.

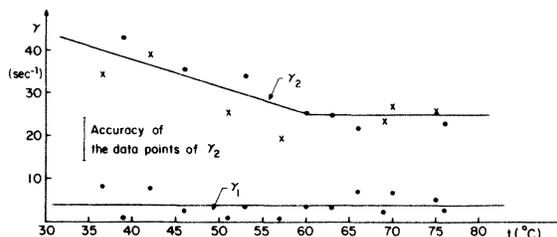


FIG. 3. Relaxation rates γ_2 and γ_1 as a function of the wall temperature (Paraflint) in a 6.6-cm bulb.

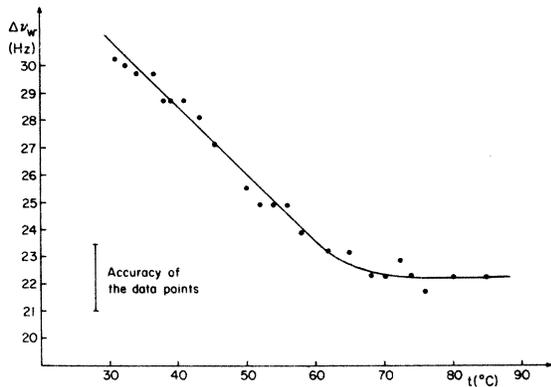


FIG. 4. Frequency shifts $\Delta\nu_w$ as a function of the wall temperature (Paraflint) in a 6.6-cm bulb.

The relaxation rates were measured for fixed cell temperatures while the temperature of the rubidium reservoir was varied. This permitted an extrapolation to zero rubidium density, leaving as relaxation mechanisms only the wall interaction and the effect of the holes of the rubidium reservoir and of the pumping arm. These two holes, however, were made such as to have negligible effects and their contribution was neglected. The results obtained are shown in Fig. 3 for γ_1 and γ_2 . It is found that γ_1 , within experimental errors, is constant in the temperature range over which the measurements were made. On the other hand, γ_2 decreases with temperature up to a temperature of 60° over which it remains practically constant or may slightly increase. The scatter in the data points from an average smooth curve corresponds to a possible error of approximately $\pm 10\%$. This is a little higher than the possible error on each individual measurement at a given reservoir temperature. This may be explained by the fact that the rubidium density in a given cell is a parameter quite difficult to control. The method of extrapolation to zero rubidium density used here is sensitive to this phenomenon through changes in the slope of the data obtained as a function of the rubidium reservoir temperature for a given cell temperature. There is actually a one-to-one correlation between the discrepancy of the points from the average curve traced in Fig. 3 and the difference from the theoretical curve in the slope

TABLE I. Observed values of the phase shift per collision of alkali-metal atoms on a Paraflint surface.

	$\bar{\phi}$ (rad/collision)	t ($^\circ\text{C}$)	References
Rb ⁸⁷	0.04	70 $^\circ\text{C}$	3
Rb ⁸⁵	0.021 ± 0.003	70 $^\circ\text{C}$	This work
Cs	0.09 ± 0.01	...	1

of the relaxation rates measured as a function of rubidium density.

Frequency shifts. The frequency of the 0-0 transition was also measured as a function of temperature. The data are shown in Fig. 4.

Discussion. The results obtained on the wall shift are of the same nature as those obtained by Brewer for the isotope Rb⁸⁷. However, since our measurements have been made below 85°C we have no data on a possible increase in frequency shift above this temperature as observed by Brewer. The lower-molecular-weight constituents of Paraflint start to melt above this temperature. This is concluded from the fact that there is no fixed melting point for this substance, but rather a large softening temperature region around 100°C . It is thus not clear what the data mean in this region.

The average phase shift per collision can be computed from the observed frequency shift through Eq. (6). The result is given in Table I along with data on Cs and Rb⁸⁷ published by other authors.

In principle, for isotopes of the same ionization and adsorption energy, the phase shift is simply proportional to the hyperfine frequency. The results for Rb⁸⁷ and Rb⁸⁵ give $\bar{\phi}_{85}/\bar{\phi}_{87} = 0.56$, while the ratio of the hyperfine frequencies is 0.44. The discrepancy is almost within experimental errors and could originate from differences in the actual surfaces.

Equation (5) can be rearranged in the following way:

$$\ln \Delta\nu = \ln(\text{const}) + E_a/kT.$$

A plot of $\ln \Delta\nu$ against $1/T$ should result in a straight line with a slope equal to E_a/k . This is shown in Fig. 5. For our case we obtain $E_a/k = 9.0 \times 10^2$ and $E_a = 0.078$ eV. Various physical parameters of the surface can be obtained from this data. At 60°C , the hyperfine frequency shift, while the atoms are on the wall, is 1.3×10^8 Hz

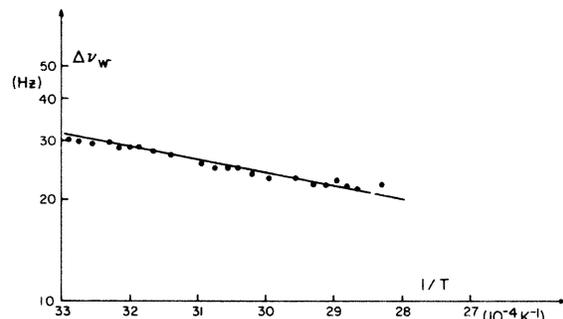


FIG. 5. Frequency shifts $\Delta\nu_w$ as a function of $1/T$ for a Paraflint surface.

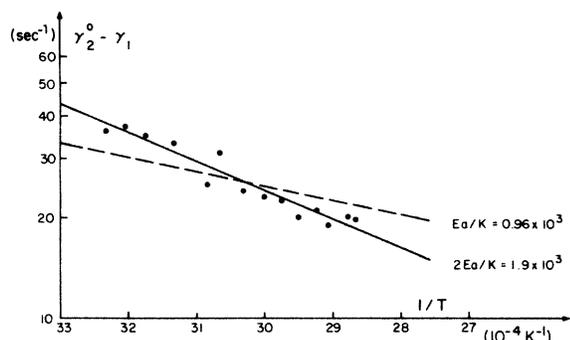


FIG. 6. Relaxation rate γ_2 as a function of the inverse of the wall temperature (Paraflint).

and the adsorption time τ_a is 3.1×10^{-11} sec. This is of the same order of magnitude as the results obtained by Brewer³ for Rb⁸⁷ and as the theoretical prediction of Margenau and co-workers.¹⁷

The data on relaxation can also be analyzed along the same lines, with the interpretation given in Ref. 1. A curve of $\ln\gamma_2$ as a function of the inverse of the wall temperature should have a slope of $2E_a/k$. This has been done on Fig. 6 where the \ln of γ_2 has been plotted against $1/T$. Two corrections however have been made to the data points. First, the extrapolated values γ_2^0 were recalculated by assuming that the original data of γ_2 as a function of the rubidium density must be a straight

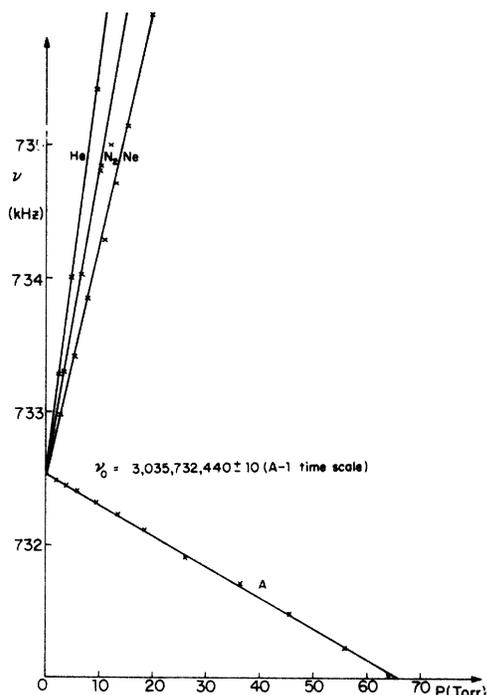


FIG. 7. Frequency shifts observed as a function of buffer-gas pressure.

line with a slope related to the ratio $\gamma_2/\gamma_1 = \frac{2}{3}$. This was done in order to remove some of the scatter in the data points. Second, the γ_2 are corrected for other relaxation mechanisms which were not related to the phase-shift effects. This was done simply by subtracting an average value of γ_1 equal to 4 sec^{-1} from the corrected γ_2^0 . This may be a rather crude method of corrections for nonadiabatic collisions. However, since it is small, there is not much error introduced in this process. In this analysis the effect of the reservoir hole is taken into account automatically through the correction introduced by subtracting γ_1 from the γ_2 values. The solid straight line plotted on Fig. 6 is a theoretical curve with a slope equal to $2E_a/k = 1.8 \times 10^3$ as obtained from the data on the frequency shifts. It appears that this curve is more consistent with the data than the curve with slope E_a/k . Consequently, one might say that the results relative to both the wall shifts and the relaxation of the coherence are well correlated.

As observed before, the relaxation rate γ_1 is found, within our accuracy, to be constant over the range of temperatures studied. A similar observation was made by Bouchiat relative to the relaxation of the observable $\langle \vec{S} \cdot \vec{I} \rangle$.

Buffer-gas interaction

The relaxation rates and the hyperfine frequency shifts were measured in an uncoated cell for various buffer gases. The bulb was connected directly to a clean filling system and the buffer-gas pressure could be varied through a play of valves. The background pressure was of the order of 10^{-7} – 10^{-8} Torr. The impurities in the gases used were less than 10 ppm. The pressure of the buffer gases was measured with a capacitance manometer. This manometer was calibrated against a mercury-column manometer to an accuracy of about 0.5 Torr.

Frequency shifts. The results on the frequency shifts are given in Fig. 7 for argon, helium, neon, and nitrogen as a function of pressure. The measurements were made at room temperature (27°C).

TABLE II. Data on buffer-gas frequency shifts. The accuracy quoted corresponds to a 99% confidence on the values of the slopes. $\nu_0 = 3\,035\,732\,440 \pm 10$ Hz (A time scale).

Gas	$\Delta\nu/\Delta p$ at (27°C) (Hz/Torr)	$\bar{\phi}$ (rad/collision)
He	328 ± 10	1.8×10^{-4}
Ne	179 ± 5	1.8×10^{-4}
N ₂	241 ± 8	2.2×10^{-4}
Ar	-24 ± 0.8	-2.4×10^{-5}

The slope of the various curves has been obtained from a least-squares fit of the experimental points. The crossing of all the curves gave the zero-pressure frequency. The results are summarized in

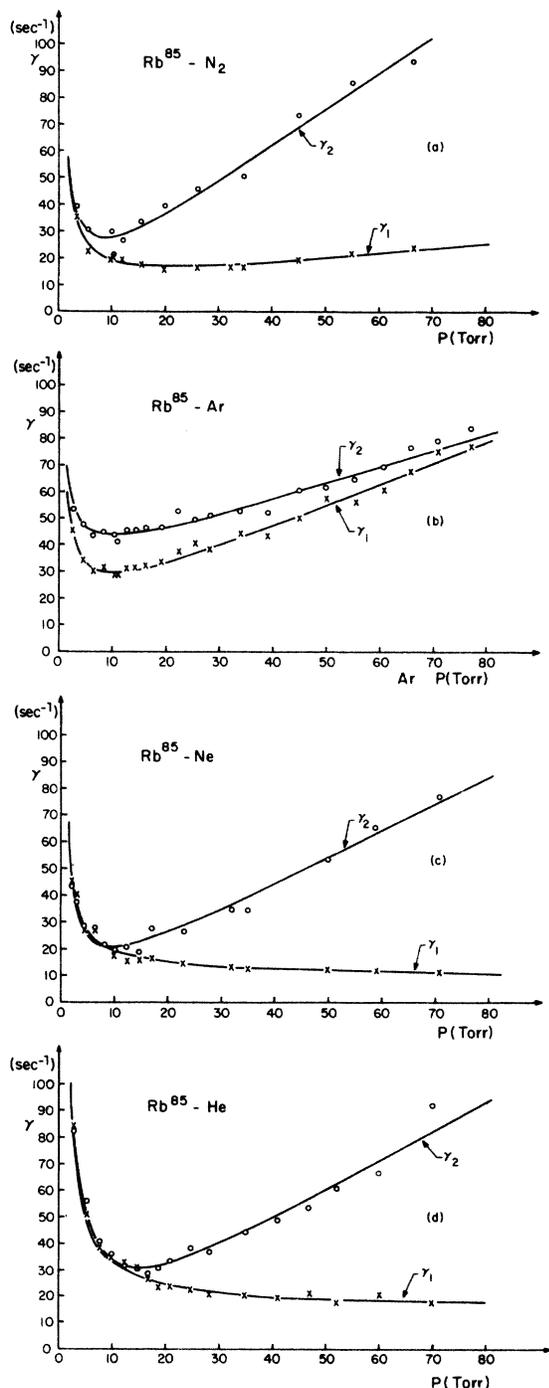


FIG. 8. Relaxation rates γ_1 and γ_2 measured as a function of buffer-gas pressure in a 7.6-cm bulb. The continuous curves are computer fits of Eq. (8) to the experimental data points for (a) N_2 , (b) Ar, (c) Ne, (d) He.

Table II. The average phase shift per collision, given in Table II, has been obtained through Eq. (6). The value of n_c needed in the calculation was obtained from Eq. (9) and the data of Table IV.

We have not measured the temperature coefficient of the frequency variation in these gases due to the limited accuracy of our method of measurement which, as explained above, consisted in measuring the hyperfine frequency during the decay time of the stimulated emission signal.

Relaxation. The relaxation rates γ_1 and γ_2 were also measured in these same gases. The results are shown in Fig. 8 for the four gases studied in a 7.6-cm bulb. It is seen that the shape of the curves are very similar for nitrogen, helium, and neon but differ for argon. These measurements have been repeated either in the direction of increasing pressure or lowering pressure and in different bulbs; the shape of the curves was the same.

Discussion. The pressure shifts given here on Rb^{85} are consistent with the shifts reported in the isotope Rb^{87} by Bender *et al.*²³ Table III gives the ratio of the pressure shifts in Rb^{87} to those in Rb^{85} as compared to the ratio of the hyperfine frequencies. The agreement is good except in the case of argon. It could be that in argon a different type of mechanism takes place which is not the same in both isotopes. The possibility of relatively longlife Rb-heavy buffer-gas molecules has been advanced in the past but it is not clear how this could enter into the picture.²⁴ The zero-pressure value ν_0 is within experimental error, the same one as that reported by Penselin *et al.*²⁵

The results obtained on the relaxation rates γ_1 and γ_2 may be analyzed in terms of the parameters of Eq. (8). This has been done and the continuous smooth curves of Fig. 8 are a computer best fit to the experimental data. The constants D_0 and σ_1 obtained from this exercise on γ_1 are given in Table IV. The value of $\gamma_1^{se}(t_1)$ obtained is of the order of 10 sec^{-1} which is about the value that was expected at the temperature of measurement (27°C).

Values of σ_1 could not be obtained for He and Ne. This is due to the fact that the measurements

TABLE III. Ratio of the pressure shifts of the two rubidium isotopes at 27°C . $\Delta\nu(87)/\Delta\nu(85) = 2.25$.

Gas	$\frac{\Delta\nu(87)}{\Delta\nu(85)}$
He	2.28
N_2	2.23
Ar	2.46
Ne	2.23

were carried out at pressures below 70 Torr. The expected value of σ_1 is small and the disorienting effect of the buffer gas is not important below 100 Torr. In fact, Franz¹⁹ has reported that for these gases a maximum in the relaxation time of the polarization of natural rubidium is observed at pressures above 100 Torr. Although the parameter measured here is not the same as in the case of this author and although the geometry of the cells are not the same, our results are not inconsistent with the existence of such a maximum at this high pressure. For argon and nitrogen, a minimum in the curve of γ_1 versus pressure is observed and a value of σ_1 is obtained. Franz¹⁹ has also observed that the cross section for disorientation is much larger for argon than for the other gases mentioned. Furthermore, it should be mentioned that the strong change in behavior between argon and the other gases shows that the phenomenon observed is really a characteristic of the gases and is not to be associated with stray interactions.

A very interesting aspect of these experiments appears in the inspection of the curve of the coherence relaxation rate γ_2 versus the buffer-gas pressure. There is again a drastic change in behavior between argon and the other gases studied, He, Ne, and N₂. At low pressures for He, Ne, and N₂, where the wall relaxation is predominant, γ_2 are approximately equal to γ_1 . This shows that the collisions with the quartz-uncoated wall are nonadiabatic and that we are in the presence of a type of collision in which the atoms either completely change state or even stick to the wall. In argon it appears that the diffusion is rather slow; at the lowest pressure at which measurements were made, γ_2 is slightly larger than γ_1 . At higher pressures, the phase-shift relaxation is a predominant mechanism in He, Ne, and N₂. The values of the constants D_0 and σ_2 obtained from a computer fit of an equation similar to Eq. (8) to the experimental data are given in Table V. The D_0 values are consistent with those obtained from the data on γ_1 . However, the values are some-

what lower than those reported for data on the relaxation of the polarization $\langle S_x \rangle$ (see, for example, Ref. 16). In the analysis we have neglected the effect of Doppler broadening. This approximation is based on the following considerations. First, our data are taken at buffer-gas pressures above a few Torr, in which case, the Doppler effect is much reduced.^{26,27} Second, all the experiments were done in a bulb placed in a cavity, in a region of constant phase. This has also the effect of reducing Doppler broadening appreciably.²⁸ Finally, the fact that in our experiments $\gamma_1 \approx \gamma_2$ at low pressures justifies this approximation since γ_1 is not affected by the Doppler effect.

The values of σ_2 computed here include, of course, the contribution of nonadiabatic collisions. In this form they are useful for considerations on applications where the relaxation rates have to be controlled.

In the results reported here one notices that although argon gives an average phase shift per collision smaller than the other gases, the relaxation rate γ_2 observed is larger than the rate observed for these other gases. This can be explained by assuming that rubidium atoms experience either negative or positive phase shifts upon collision. The average phase shift ϕ may then be relatively small while the linewidth caused by the dispersion in the phase shifts remains relatively large. In fact, buffer-gas mixtures characterized by a very small value of $\bar{\phi}$ are possible while the linewidth is not decreased by the process of mixing these gases.

In these kinds of experiments questions are often raised relative to the possibility of existence of stray relaxation mechanisms. In our case, we have examined the possibility of relaxation through magnetic field gradients, temperature gradients, or impurities in the buffer gas. The geometry of the solenoid and magnetic shield used made relaxation by magnetic field gradients negligible. A simple experimental test consisting of changing the magnetic field amplitude confirmed this conclusion. Our experiments were

TABLE IV. Values of D_0 and σ_1 obtained from the data on γ_1 . The values have been obtained from a computer fit of Eq. (8) to the experimental data.

Gas	D_0 cm ² /sec	σ_1 10 ⁻²⁴ cm ²
He	0.32	•••
Ne	0.16	•••
N ₂	0.13	80
Ar	0.14	490

TABLE V. Values of D_0 and σ_2 obtained from the data on γ_2 . The method used to obtain these parameters is similar to that used for the data of Table IV.

Gas	D_0 cm ² /sec	σ_2 10 ⁻²⁴ cm ²
He	0.42	294
Ne	0.20	555
N ₂	0.15	743
Ar	0.12	371

done at room temperature and temperature gradients were unlikely to exist. Finally, the vacuum obtained in our system was of the order of 10^{-7} Torr or less and at this pressure impurity relaxation is expected to be negligible. Furthermore, this type of relaxation would affect γ_1 and γ_2 at the same time. The large difference in behavior observed between these two parameters with buffer-gas pressure tends to confirm this conclusion. However, we still consider our results, especially on γ_2 , as preliminary. More experiments are being performed on either Rb⁸⁷ or Rb⁸⁵ and we should be able to further discuss these points in the near future.

CONCLUSION

Of the three mechanisms of relaxation studied in Rb⁸⁵ it appears that spin-exchange relaxation is well understood. We have verified that the ratio of the coherence and population relaxation is in agreement with the theoretical predictions as in the case of Rb⁸⁷. In the case of the interaction of the rubidium atom and a Parafilm-coated surface, we have observed that the ratio of the phase shift in Rb⁸⁵ to the phase shift in Rb⁸⁷ was almost equal to the ratio of the hyperfine frequencies. In the case of buffer-gas interactions we have found that the frequency shifts observed are related to those observed in Rb⁸⁷ through the ratio of the hyperfine frequencies. This is true of He, Ne, and N₂. For Ar, a small difference between the two ratios was observed. From the relaxation rates we have been able to determine the diffusion constant D_0 for various buffer gases as well as the relaxation cross sections. Our D_0 values are smaller than those already published in relation to measurements made on $\langle S_z \rangle$. A similar observation has been made recently by Beverini *et al* in relation to measurements of D_0 for Cs in the same buffer gases.²⁹ These authors have obtained a value of D_0 for $\langle \vec{S} \cdot \vec{I} \rangle$ smaller

than those previously published for $\langle S_z \rangle$. The values of the observed frequency shifts and of the coherence relaxation rates could be correlated only qualitatively and it was not possible to obtain an exact picture of all the interactions taking place. The values of $(T_2)^{-1}$ reported here are of the order of 30 sec^{-1} at a pressure of about 20 Torr. These rates are much smaller than those observed by Arditi *et al.*⁴ in Rb⁸⁷ although their values of $(T_1)^{-1}$ are consistent with ours. On the other hand, the linewidths deduced from our relaxation rates are not consistent with the narrow widths observed by Bender *et al.* in Rb⁸⁷ as can be shown through simple arguments based on the ratio of the hyperfine frequencies.^{30,31} Further experiments in connection with these observations are in progress in our laboratory. For example, we are studying the behavior of Rb⁸⁵ atoms in a coated cell containing a buffer gas at the same time. Theoretical calculations on such a combination have been made by Masnou-Seeuws.³² It would appear that new insight might be obtained about the coherence relaxation mechanism when two types of dephasing agents, well localized in space, are both acting at the same time. This type of experiment will help in answering some of the questions raised by the results reported here, especially those relative to the phase-shift parameter and the absolute value of the coherence relaxation rates.

The above data are of fundamental importance to the realization of a Rb⁸⁵ maser. The construction of such devices has been reported earlier.^{33,34}

ACKNOWLEDGMENTS

We would like to thank J. C. Prince and Y. Chalifour for their technical help. This work has been made possible through grants from the National Research Council, the National Aeronautics and Space Administration, and the Department of Education of the Province of Quebec.

¹H. M. Goldenberg, D. Kleppner, N. F. Ramsey, *Phys. Rev.* **123**, 530 (1961).

²M. A. Bouchiat and J. Brosset, *Phys. Rev.* **147**, 41 (1966).

³R. G. Brewer, *J. Chem. Phys.* **38**, 3015 (1963).

⁴M. Arditi and T. R. Carver, *Phys. Rev.* **136**, A643 (1964).

⁵Jacques Vanier, *Phys. Rev.* **168**, 129 (1968).

⁶P. Zitzewitz, Ph.D. dissertation (Harvard University, 1970) (unpublished); *Rev. Sci. Instrum.* **41**, 81 (1970).

⁷H. C. Berg, *Phys. Rev.* **137**, A1621 (1965).

⁸H. M. Gibbs and R. J. Hull, *Phys. Rev.* **153**, 132 (1967).

⁹S. B. Crampton, *Phys. Rev.* **158**, 57 (1967).

¹⁰M. A. Bouchiat, *Etude par pompage optique de la relaxation d'atomes de rubidium* (Publications Scientifiques et Techniques du Ministère de l'Air, Paris, 1965).

¹¹Jacques Vanier, *Phys. Rev. Lett.* **18**, 333 (1967).

¹²J. Vanier and R. F. C. Vessot, *Appl. Phys. Lett.* **4**, 122 (1964).

¹³J. Vanier and R. F. C. Vessot, *Metrologia* **6**, 52 (1970).

¹⁴Jacques Vanier, *Basic Theory of Lasers and Masers*, (Gordon and Breach, New York, 1971).

¹⁵F. Grossetête, *J. Phys. (Paris)* **29**, 456 (1968).

¹⁶W. Happer, *Rev. Mod. Phys.* **44**, 169 (1972).

¹⁷H. Margenau, P. Fontana, and L. Klein, *Phys. Rev.*

- 115, 87 (1959); R. Herman and H. Margenau, *Phys. Rev.* 122, 1204 (1961).
- ¹⁸F. A. Franz and E. Lüsher, *Phys. Rev.* 135, A582 (1964).
- ¹⁹F. A. Franz, *Phys. Rev.* 139, A603 (1965).
- ²⁰W. Franzen, *Phys. Rev.* 115, 850 (1959).
- ²¹C. Cohen-Tannoudji, *Diplômes d'Etudes Supérieures* (Paris, 1956) (unpublished).
- ²²P. L. Bender, *Phys. Rev.* 132, 2154 (1963).
- ²³P. L. Bender, E. C. Beaty, and A. R. Chi, *Phys. Rev. Lett.* 1, 311 (1958).
- ²⁴M. A. Bouchiat, J. Brossel, and L. Pottier, *Phys. Rev. Lett.* 19, 817 (1967).
- ²⁵S. Penselin, T. Moron, V. W. Cohen, and G. Winkler, *Phys. Rev.* 127, 2 (1962).
- ²⁶R. H. Dicke, *Phys. Rev.* 89, 472 (1953).
- ²⁷L. Galatry, *Phys. Rev.* 122, 1218 (1961).
- ²⁸D. Kleppner, H. M. Goldenberg, and N. F. Ramsey, *Phys. Rev.* 126, 603 (1962).
- ²⁹N. Beverini, P. Minguzzi, and F. Strumia, *Phys. Rev. A* 4, 550 (1971).
- ³⁰P. L. Bender and V. W. Cohen, in *Proceedings of the Sixth International Conference on the Physics of Electronic and Atomic Collisions*, Cambridge, Mass. (MIT Press, Cambridge, Mass., 1969), p. 720.
- ³¹P. L. Bender (private communication).
- ³²F. Masnou-Seeuws and M. A. Bouchiat, *J. Phys. (Paris)* 28, 406 (1967).
- ³³J. Vanier, R. Vaillancourt, G. Missout, and M. Têtu, *J. Appl. Phys.* 41, 3188 (1970).
- ³⁴W. Stern and R. Novick, *Proceedings of the 25th Annual Symposium on Frequency Control*, Atlantic City, N. J. (U. S. Army Electronics Command, Fort Monmouth, N. J., 1971), p. 325.