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Relaxation of Optically Pumped Rb Atoms on Paraffin-Coated Walls

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Relaxation of optically pumped Rb atoms on paraffin-coated walls has been studied using Franzen's sequence (relaxation in the dark) for observables $\langle S_z \rangle$ (mean electronic longitudinal polarization), and $\langle \mathbf{S}\cdot\mathbf{I} \rangle$ (population difference between the two hfs levels). The physical meaning of optical signals under different conditions is analyzed in some detail, and it is pointed out that different observables relax differently. In the interpretation of our results, extensive use has been made of the theoretical analysis of the relaxation of a spin **S** (coupled to a spin **I** in the Rb atom) caused by a weak interaction of the type $\gamma_S H(t)\cdot\mathbf{S}$, $H(t)$ being a random magnetic field acting on S during the dwell time of a Rb atom on the wall. Experimental results are in excellent agreement with this analysis, if one assumes the existence of two uncorrelated interactions of the above type. The first is the dipole-dipole interaction between **S** and the nuclear spins **K** of the protons (or deuterons) of the coating. This interaction has a long correlation time $\tau_{c1} \approx 4\times 10^{-10}$ sec and dominates the relaxation of $\langle S_z \rangle$ in low fields. The second interaction which is independent of spins **K**, has a short correlation time $\tau_{c2} \approx 10^{-12}$ sec, and dominates the relaxation of $\langle \mathbf{S}\cdot\mathbf{I} \rangle$ in low fields, and of $\langle S_z \rangle$ in large fields. The values of these correlation times and of the strengths of the two interactions have been measured, first in low fields by combining results on $\langle S_z \rangle$ and $\langle \mathbf{S}\cdot\mathbf{I} \rangle$ for the two Rb isotopes and for two types of coatings [$(CH_2)_n$ and $(CD_2)_n$], and second, by studying the variations of the "pseudo" relaxation time T_1 of $\langle S_z \rangle$ for magnetic-field values up to 5000 G. We arrive at a detailed picture of physical adsorption of Rb on paraffin-coated walls, and find 0.1 eV for the adsorption energy. These results are compatible with those obtained for the relaxation of oriented Rb atoms in collisions with buffer-gas molecules.

I. INTRODUCTION

TWO ways have been followed to enhance optical-pumping signals in experiments with alkali-metal vapors. In the first, a diamagnetic buffer gas is used at a pressure of several Torr.[1] In the second, the glass walls of the resonance cell are coated with chemically inert substances like saturated paraffins $(CH_2)_n$,[2] or several kinds of silicones (e.g., dimethyldichlorosilane).[3]

The present paper deals with the properties of those coatings and with the behavior of Rb atoms when they bounce from them and get adsorbed on the surface.[4]

Those coatings clearly play a double role. First, the chemical reaction between a Rb atom and the underlying glass is greatly reduced: The lifetime of a Rb atom in the cell is correspondingly increased. Second, one finds that it takes about 10^4 atom-wall collisions to destroy the orientation of a Rb atom; this is shown by the values one obtains for the longitudinal relaxation time T_1 pertaining to $\langle S_z \rangle$ (electronic longitudinal polarization). One gets $T_1 \approx 1$ sec in 6-cm diam. spherical cells.[5] This fact brings to light a very important character of those collisions: They are *weak collisions in which the motion-narrowing condition is fulfilled.*[6]

For a long time the physical nature of this weak, disorienting interaction has been unknown. It seemed important to us to elucidate this point; there was the hope of getting better coatings, and this has, indeed, proved feasible. On the other hand, it was tempting to use optical pumping as a tool to shed some light on the behavior of Rb atoms on a $(CH_2)_n$ surface (i.e., on the process of physical adsorption), and to determine the values of the corresponding parameters.

Difficulties Arising in the Present Study

Many precautions have to be taken in a study of this kind. We now examine this point more closely.

(1) Because of the great complexity of the problem, the experimental conditions have to be made as simple as possible so as to reduce to a minimum the number of relaxation mechanisms. All the results given below have been obtained in *completely evacuated cells* (no buffer gas is present), and in order to eliminate all possible effects of degassing (due for instance to a chemical reaction between the coating and Rb atoms) a getter is permanently attached to the cell (see Fig. 1).

As we shall see, the Rb isotopes ^{85}Rb and ^{87}Rb relax differently. We performed the experiment on *separated isotopes* (purity around 99.5%). Finally, all relaxation times have been measured using Franzen's sequence (*"relaxation in the dark"*).[7] In the above conditions, apart from what happens on the walls, only *exchange collisions between identical atoms* can play a role.

(2) A second class of difficulties exist, which have to do with surface physics: the making of coatings with properties which are reproducible from day to day or in different cells. The behavior of these coatings has been

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[1] J. Brossel, J. Margerie, and A. Kastler, Compt. Rend. **241**, 865 (1955); P. L. Bender, thesis, Princeton University, 1956 (unpublished).

[2] H. G. Robinson, E. S. Ensberg, and H. G. Dehmelt, Bull. Am. Phys. Soc. **3**, 9 (1958); H. G. Dehmelt, in Twelfth Annual Symposium on Frequency Control, Fort Monmouth, 1958, p. 577 (unpublished).

[3] C. O. Alley, in *Advances in Quantum Electronics*, edited by J. R. Singer (Columbia University Press, New York, 1961), p. 120.

[4] M. A. Bouchiat, Publ. Sci. Tech. Min. Air, France, Notes Tech. **146** (1965).

[5] M. A. Bouchiat and J. Brossel, Compt. Rend. **254**, 3828 (1962).

[6] See, for instance, R. Kubo, in *Fluctuation Relaxation and Resonance in Magnetic Systems*, edited by D. Ter Haar (Oliver and Boyd, London, 1962), pp. 29–31.

[7] W. Franzen, Phys. Rev. **115**, 850 (1959).

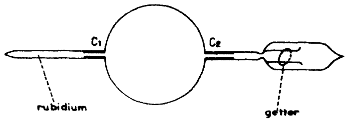

FIG. 1. Type of cell used.

described elsewhere.[4,8] We will recall briefly, later on, some of their properties, and we will stress the precautions one has to take in making them. Let us just say here that contamination by a Rb metal film must be avoided at all costs.

(3) Lastly, many difficulties appear because of the use of optical pumping itself to study relaxation. This point is clearly demonstrated by the range of disagreement among different observers. The problem rests on the physical meaning of optical signals, which are used to monitor the orientation of the vapor; we have always used the amount of light absorbed per unit time from the pumping beam, L_A. Strangely enough, it appears that it is not widely known that L_A can be made to *represent different observables depending on the polarization and on the spectral distribution of the beam within the volume of the cell.* Because different observables relax differently, it is of the utmost importance to know which one is being dealt with. When this is not the case, measurements are of little use. First of all, then, the equivalent opacity[9] of the cell $\nu=\bar{k}l$ must be small in all cases ($\nu<1$). This is because the change in L_A when one goes from a highly polarized to an unpolarized vapor (with opacities ν and ν') is $e^{-\nu'}-e^{-\nu}$. When the conditions $\nu<1$, $\nu'<1$ are not satisfied this cannot be written as $\nu-\nu'$ which is the quantity which lends itself to an easy interpretation. Moreover, if ν is small, the spectral distribution of the beam is about the same everywhere in the cell.

The effect of the spectral distribution of the source has been analyzed elsewhere in some detail.[10,11] The two resonance lines of Rb, D_1 and D_2, are 150 Å apart and are easily separated by interference filters. The hfs of the excited ^2P states are, in this case, smaller than the widths of the lines emitted by most lamps, so that D_1 and D_2 have only two resolved components (due to the hfs ground state) of intensities i_1 and i_2. We will simply state here the conditions under which L_A represents the two observables we have studied, namely, $\langle S_z\rangle$ means electronic longitudinal polarization, and $\langle \mathbf{S}\cdot\mathbf{I}\rangle$ is the population difference of the two hyperfine ground-state sublevels. L_A will represent $\langle S_z\rangle$ at all field values when the detecting beam propagates along the field and is circularly polarized, and when the two hfs components have the same intensity $i_1=i_2$. On the other hand, in low fields, L_A will represent $\langle \mathbf{S}\cdot\mathbf{I}\rangle$ if the detecting beam has an arbitrary direction but is unpolarized, and if the two hfs components have different intensities, $i_1\neq i_2$.

Serious errors arise when the above conditions are not properly fulfilled. For instance, in the study of $\langle S_z\rangle$, if i_1 and i_2 are not equal, L_A is in fact a linear combination of $\langle S_z\rangle$ and $\langle \mathbf{S}\cdot\mathbf{I}\rangle$; The time constant T_H characteristic of $\langle \mathbf{S}\cdot\mathbf{I}\rangle$ will appear in the optical transients. Then one must remember that $\langle \mathbf{S}\cdot\mathbf{I}\rangle$ is affected by exchange collisions between identical atoms, whereas $\langle S_z\rangle$ is practically unchanged. Sensitive tests have been described,[12] to check the condition $i_1=i_2$ which must be satisfied in the lamp itself and in the whole volume of the cell as well. The condition for this is $\bar{k}l\ll 1$, and not only that the total absorption by the cell is small. (Standard lamps emit D lines which are usually many Doppler widths large.) We found that the condition $i_1=i_2$ is very difficult to meet in most lamps; we never found it in D_2. It is also practically impossible to obtain it in D_1 when the lamp is filled with a natural mixture of isotopes because of the coincidences of the hfs components of ^{85}Rb and ^{87}Rb. By using separated isotopes the condition $i_1=i_2$ is nearly achieved in D_1.

The situation is not simple, even when one has managed to actually observe $\langle S_z\rangle$. For instance, when the natural mixture of isotopes is used in the cell, one must remember that exchange collisions between *different* isotopes (unlike those between identical atoms) do change the relaxation of $\langle S_z\rangle$.

Another serious difficulty comes from the fact that, as we shall see, two time constants, T_e and T_n, appear in the relaxation of $\langle S_z\rangle$. In most cases T_n can be much longer than T_e, and the ratio T_n/T_e increases with the nuclear spin I. The relative importance of these constants depends on the initial polarization $\langle S_z\rangle_0$ [see Eq. (11) below]. Depending on conditions of observation, one may very well see one time constant and miss the other. For instance, the method of study of relaxation using optical-pumping transients at lower and lower pumping-light intensities corresponds to initial conditions in which $\langle S_z\rangle_0$ is smaller and smaller. This heavily favors T_n, which is indeed measured by this method.[13] For this reason we used $\langle S_z\rangle_0$ values as large as possible and measured "relaxation in the dark."

Similar, but somewhat smaller, difficulties are met in the study of $\langle \mathbf{S}\cdot\mathbf{I}\rangle$. In this case, one finds that relaxation on the wall is very similar for both isotopes, but electron exchange very quickly becomes the dominant factor when the Rb vapor pressure is raised.[14] The fact that exchange takes place between like or unlike isotopes is of no importance in this case and the natural mixture of isotopes can be used. On the other hand, $\langle S_z\rangle$ and

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[8] M. A. Bouchiat and J. Brossel, Compt. Rend. **260**, 6823 (1965).

[9] A. C. Mitchell and M. W. Zemansky, *Resonance Radiation and Excited Atoms* (Cambridge University Press, New York, 1961), 2nd ed., p. 201.

[10] M. A. Bouchiat, J. Phys. Radium **26**, 415 (1965).

[11] M. A. Bouchiat and F. Grossetête, J. Phys. Radium (to be published).

[12] M. A. Bouchiat and J. Brossel, Compt. Rend. **254**, 3650 (1962); see also Ref. 4, p. 102.

[13] Ref. 4, pp. 87, 93.

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

$\langle \mathbf{S}\cdot\mathbf{I}\rangle$ are coupled by electron exchange: The relaxations of $\langle \mathbf{S}\cdot\mathbf{I}\rangle$ are very different depending on whether or not $\langle S_z\rangle_0$ is zero. It is much slower in the first case, but simpler to interpret in the second case. We used an unpolarized pumping beam in these measurements.

Obviously then, hopeless difficulties arise in the interpretation of the data when the observable at hand is not clearly defined. This is all the more so because, in most instances, several interactions (e.g., two) are simultaneously present to relax the atom. One of them may be the dominant factor for one observable, and the second for another; we saw for instance, that $\langle \mathbf{S}\cdot\mathbf{I}\rangle$ is very sensitive to exchange between identical atoms, whereas $\langle S_z\rangle$ is not.

Similarly we will see below that, in the relaxation of Rb on paraffin-coated walls, two uncorrelated disorienting interactions are indeed present. They have very different correlation times: $\tau_{c1}\approx 4\times 10^{-10}$ sec, and $\tau_{c2}\approx 10^{-12}$ sec. Both interactions play an appreciable role in the relaxation of $\langle S_z\rangle$ in low fields whereas only the one corresponding to τ_{c2} is important in large fields. On the other hand, this last interaction is predominant, in low fields, for the relaxation of $\langle \mathbf{S}\cdot\mathbf{I}\rangle$.

Presentation of Results

In our discussion, we will first (Sec. II) give some experimental details about the production and properties of the coatings, then (Sec. III) describe the general features observed in the relaxation of Rb atoms on $(CH_2)_n$ coatings, and arrive at a microscopic description of the process. We may anticipate the following picture: The nuclear spins $\mathbf{K}$ of the protons in $(CH_2)_n$ produce random magnetic fields $\mathbf{H}(t)$ on the wall. While a Rb atom is adsorbed, the proper Fourier component of $\mathbf{H}(t)$ may flip the spin $\mathbf{S}$ of the valence electron and produce disorientation. The fact that this (magnetic) dipole-dipole interaction is present (in low fields) is shown by the much longer relaxation times which one observes for $\langle S_z\rangle$ on deuterated paraffins $(CD_2)_n$. Nevertheless, this dipole-dipole interaction alone cannot explain all observations, and one has to postulate the existence of a second interaction of the same "magnetic type," with a Hamiltonian of the form $\mathcal{H}_1(t)=\gamma_S\mathbf{S}\cdot\mathbf{H}(t)$. We will then (Sec. IV) recall the theoretical results which have been obtained for an interaction of this type when $\mathbf{S}$ is coupled to $\mathbf{I}$ via the $a\mathbf{S}\cdot\mathbf{I}$ hfs interaction, at all magnetic-field values.[15] Finally (Sec. V), we will show that experimental results fit in very well with the above theory, and give the values of the parameters characteristic of physical adsorption in this case.

II. EXPERIMENTAL DETAILS

The type of cell used is shown in Fig. 1. It is made of Pyrex glass. Two side tubes are attached to the main spherical body (60-mm diam) through two capillaries c_1 (1.2-mm diam), and c_2 (1.8-mm diam), which are 15 mm long. c_1 leads to the reservoir in which 0.5 mg of Rb metal is distilled. The other side tube through which evacuation is made holds a barium getter, which can be flashed by induction heating. The cells are baked at 400°C for several hours, and thoroughly degassed. The paraffin coating is made in the following way.[16] After baking, and cooling, and while the cell is still being pumped, one brings an iron rod (1-mm diam, 60 mm long) through c_1 so that one end, on which has been deposited a drop of paraffin, is placed at the center of the cell. The paraffin is then evaporated *in situ*, by induction heating of the rod. When this is completed, the rod is removed through c_1 (with the help of a permanent magnet) to a side tube, in which it has been stored during baking. This tube is then sealed off.

The coating is very uniform and is hardly visible. No precise control of its thickness is made. It seems to play no role in the final results. Sometimes interference colors can be seen. Thick coatings have a slightly milky appearance. With this method of production the coating is never exposed to air, nor to outside contamination. During the evaporation, long-chain paraffins (polyethylene) are slightly decomposed as can be seen on the vacuum gauge. Rubidium metal is then distilled into the reservoir. In this operation one must avoid any contamination of the coating by a Rb metal film. When this happens, very erratic results are obtained: A clean Rb surface is an area on which complete disorientation occurs, because any Rb atom condensing on such a surface is replaced in the vapor phase by another of the metal deposit. To prevent Rb contamination one operates as follows: While Rb is slowly distilled in the reservoir, capillary c_1 is blocked by an iron rod which has been brought into position through c_2 and which was stored in a side tube on the other end of c_2. After distillation the rod is removed and the cell is sealed off. When prepared in this way and taken from the pumping bench, a cell will *not* resonate or absorb the D lines if no Rb contamination has occurred; this situation will last for periods of 10 days at room temperature, or 4 to 5 days at 40°C. When normal absorption is reached in this way, we heat up the cell to 80°C for 15 h. We then flash the getter. Coatings prepared in this way are "stable", as far as we can see, for periods of several years at temperatures below 60°C. The properties of coatings prepared as stated above are dealt with in the present paper.

What happens during the first few days is not completely clear. It is probably a chemical reaction of Rb with impurities in the paraffin (followed by a small amount of degassing). Diffusion of Rb through the coating to the underlying glass is probably also present. These processes seem to take place at a very slow rate at room temperature on "stable" coatings (i.e., after

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[15] M. A. Bouchiat, J. Phys. Radium 24, 371, 611 (1963).

[16] See Ref. 4, p. 106.

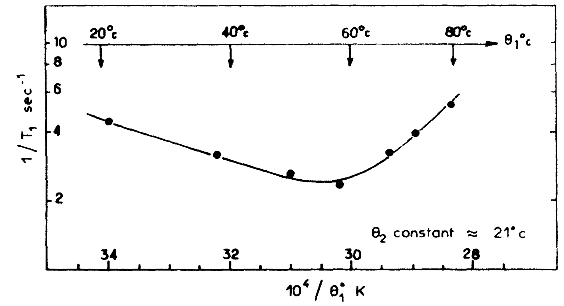

FIG. 2. Wall-temperature dependence of the relaxation time T_1 for observable $\langle S_z \rangle$ in a ^{87}Rb cell coated with $(CH_2)_n$. The temperature θ_2 of the Rb reservoir is kept constant while the wall temperature θ_1 of the spherical bulb is varied ($\theta_1 > \theta_2$).

the period of heating at 80 °C) because, as we explain below, the Rb vapor pressure in uncontaminated cells is always slightly smaller than the pressure of Rb in equilibrium with the molten metal.

In our experiments, the cells are placed in an oven, where the temperatures θ_1 of the wall (in the spherical part), and of the reservoir θ_2 can be separately controlled. One finds indeed that the Rb pressure in the cell is monitored by θ_2 in a reversible way.

The effect of θ_1, temperature of the coating, on wall relaxation (θ_2 being fixed) has been studied in this way. The results have been described elsewhere,[8] and are as follows: *The relaxation time* T_1 *of* $\langle S_z \rangle$ *gets longer when* θ_1 *varies between room temperature and* 60°C (as shown by Fig. 2). This effect is typical of physical adsorption; the dwell time τ_s of the atom on the wall gets shorter at higher temperatures, and the disorienting interactions have less time to flip spin **S**. From the slope of the curve $\log T_1(1/\theta_1)$ (Fig. 2), one can deduce the adsorption energy E_a: One finds 0.1 eV in the present case.

On the other hand, θ_1 being fixed (and kept greater than θ_2), wall relaxation conditions are constant. When θ_2 is varied, one can study the effect of exchange collisions between identical Rb atoms on $\langle S_z \rangle$ and $\langle \mathbf{S}\cdot\mathbf{I} \rangle$. We will describe the results later on; as already mentioned, $\langle S_z \rangle$ is not, or very little, affected, whereas exchange becomes very rapidly the dominating feature in the relaxation of $\langle \mathbf{S}\cdot\mathbf{I} \rangle$[14] (see for instance Fig. 7 below).

One can compare the optical absorption L_A of an uncontaminated cell prepared as described above when the Rb pressure is monitored by the reservoir temperature θ_2, to optical absorption L_A' of another cell which has been deliberately contaminated (a Rb deposit could be seen on the walls in the spherical part). L_A' corresponds to the Rb vapor pressure in equilibrium with the metal at temperature $\theta_1 = \theta_2$. The curves (a) and (b) giving L_A' and L_A versus θ_2 are drawn in Fig. 3. L_A is always smaller than L_A'. Curve (a) can be obtained by multiplying by the factor $\eta = 1.2$ the ordinates of curve (b) at all temperatures below 40°C. This indicates, as mentioned before, that the rubidium coming from the reservoir keeps being absorbed and disappears in the coating.

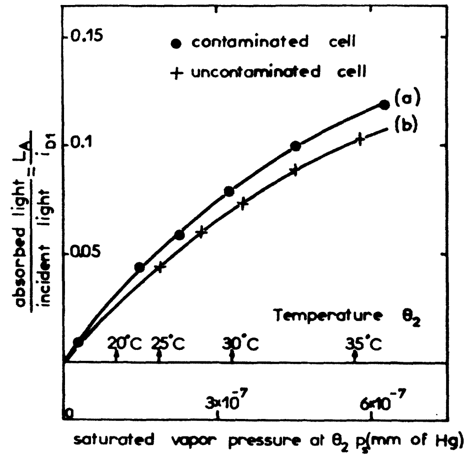

FIG. 3. Amount of D_1 light absorbed by a ^{87}Rb cell (normalized to the incident light intensity i_{D1}). (a) Contaminated cell. L_A' depends on wall temperature θ_1 as indicated by curve a. (b). Uncontaminated cell. L_A depends on reservoir temperature θ_2 (curve b). The vapor-pressure scale corresponds to the vapor pressure of Rb vapor in equilibrium with the metal, p_S, at temperature θ_1 in (a) and θ_2 in (b). Use has been made of the values given in Ref. 30.

From the value of η one can deduce that a Rb atom lives for about 50 sec before being absorbed in the coating. (To obtain this value we take into account the dimensions of cell and capillaries.) This is much longer than any one of the measured relaxation times, which are not affected by this process. η does not vary in a measurable way below 60°C. It increases above that point and becomes very large for temperatures over 80°C, indicating that Rb is then quickly absorbed by the coating; and as shown by Fig. 2, this corresponds to a shortening of relaxation times.[8] We found that all processes were reversible below 80°C. On the other hand, polyethylene molecules break down in the presence of alkali-metal vapor at still higher temperatures, as shown by the existence of degassing and carbon deposits.

The above results show that one can safely determine the absolute number N of Rb atoms in an uncontaminated cell from the measured value of η, provided the vapor pressure N_S of Rb in equilibrium with the metal is itself known. (This is of importance in the determination of absolute values of exchange cross sections.)

In the interpretation of the measurements, another effect must be kept in mind. As can be seen from Fig. 1, a Rb atom will evaporate in the reservoir, go into the main body of the cell through capillary c_1, bounce from wall to wall with a mean flying time τ_v and then go back through capillaries c_1 or c_2 to the Rb deposit, or on the metal surface of the flashed getter. Orientation is then lost in this process in a mean time $\bar{t}$, which represents the duration of the above sequence. This will be called from now on the "reservoir effect." It gives a lifetime $\bar{t}$ to the atom. We have obtained an order of magnitude of $\bar{t}$, of 3 sec, using the Knudesn formula for molecular flow in capillaries c_1 and c_2. $\bar{t}$ can also be determined experimentally by measuring the relaxation time T of an observable having an exponential decay. In the presence of the reservoir effect one measures T' ($T'^{-1}=T^{-1}+\bar{t}^{-1}$). We then measure T'' the time constant of the same observable in a cell having 5 times as many side tubes and capillaries: this reduces $\bar{t}$ by a factor 5 ($T''^{-1}=T^{-1}+5\bar{t}^{-1}$). From the two equations, $\bar{t}$ is obtained, and found to lie between 3 and 4 sec. One must correct all time-constant measurements by the "reservoir effect." All results quoted below have been corrected in this way using $\bar{t}=3.5$ sec.

It is found that, in 60-mm-diam cells, the reservoir effect is of little importance as far as the (rapid) relaxation of $\langle \mathbf{S}\cdot\mathbf{I}\rangle$ is concerned. The same is true for $\langle S_z\rangle$ on $(CH_2)_n$ coatings, but it is not negligible on $(CD_2)_n$ coatings. The situation is even worse with 30-mm-diam cells which we used because of lack of space in the gap of the electromagnet, when we studied the relaxation of $\langle S_z\rangle$ at high fields (5000 G) (see Secs. IV and V). The reservoir effect is very prominent then, and the correction must be made.

III. GENERAL PROPERTIES OF THE RELAXATION PROCESS

We describe now the general features of the relaxation as observed in our experiments. Our purpose is to arrive at a microscopic description of the process which will serve as a basis for the theoretical calculation. The atom flies in a straight line from wall to wall in time τ_v during which no perturbation is present. The atomic Hamiltonian $\mathcal{H}_0$ includes the Zeeman interaction with the dc field H_0 and the hfs term $a\,\mathbf{I}\cdot\mathbf{S}$. Whenever the atom strikes the wall it gets adsorbed for time τ_s (dwell time) during which it is acted upon by the perturbation $\mathcal{H}_1(t)$. This is a random function of time with correlation time τ_c. There is no correlation between the perturbations at two different points on the surface. So that τ_c is at most equal to τ_s. At any given time, the fraction $\tau_s/(\tau_s+\tau_v)$ of all atoms is adsorbed on the wall.

The following results are obtained for $\langle S_z\rangle$ *in low fields.*

(1) As we have already seen, atom-wall collisions are weak and obey the motion-narrowing condition $\langle|\mathcal{H}_1(t)|^2\rangle\tau_c^2\ll 1$.

(2) One finds that the relaxation time is proportional to the diameter of the cell. This so-called "volume effect" is a clear indication that relaxation does take place on the wall, and also that $\tau_s\ll\tau_v$.

(3) Relaxation has been studied for several paraffins $(CH_2)_n$ with widely different n values. Relaxation times are practically independent of n (slightly longer by about 30%, for light paraffins, i.e., small n values). Very similar relaxation times are also obtained with silicone coatings. There seems to be no doubt that it is the CH_2 group, common to all these coatings, which determines the main features of the relaxation.

(4) On deuterated polyethylene $(CD_2)_n$ relaxation times are found to be about 5 times longer than on ordinary polyethylene $(CH_2)_n$ for ^{85}Rb and ^{87}Rb. The nuclear moment of carbon is zero, and its root-mean-square value is larger for the proton than for the deuteron. When one combines results (3) and (4), one arrives at the conclusion that, *at least in part*, the disorienting process involves *the dipole-dipole interaction between the nuclear spin* **K** *of the proton* (*or deuteron*) *on the wall and the electron spin* **S** (*coupled to* **I** *of the Rb atom*. Thus, in the picture given earlier, the field $\mathbf{H}(t)$ is produced by the nuclear moments μ_K of the coating. At this stage, the question arises whether this dipole-dipole interaction including the contact term (we call it from now on the d.d. interaction), is the only one involved. As the detailed discussion of the results will show, the answer is no. For the time being, we will just give a simple argument to that end.

Taking a model in which all the features we have just described are included, the relaxation of a spin **S** (coupled to **I**) due to an interaction of a magnetic type, $\mathcal{H}_1(t)=\gamma_S\mathbf{S}\cdot\mathbf{H}(t)$, has been studied theoretically.[15] (The results of this calculation are given in Sec. IV.) Many processes have been proposed for the possible origin of the magnetic field $\mathbf{H}(t)$, in particular to explain alkali-metal relaxation in collisions against buffer gases.[17] The above theoretical conclusions apply to all those cases. When $\mathbf{H}(t)$ is producted by the d.d. interaction it can be expressed in terms of microscopic parameters like K, μ_K, the average distance of approach of **S** and **K**, etc. Now, one finds [see Eq. (7) below] that the dependence on K and μ_K is such that, if the d.d. interaction were the only one present, all relaxation times would be 16 times longer when D is substituted for H in the paraffin. In the present case, though, there was a 1.7% H impurity in our D polyethylene, so that the factor is only 12.8. As one observes only 5, it is clear that a second interaction is present which does not depend on the nuclear spin of the coating.

Paramagnetic impurities do not seem to be an important cause of relaxation, because we used many paraffins of widely different origins, which all gave very similar results; it seems unlikely that they should not have widely different impurity concentrations. A similar remark holds for polar centers.

The question remains, then, of the physical nature of this "second" interaction. Among the number of those which have been considered to explain the relaxation on buffer gases, the one described by Bernheim[18] (the "spin-orbit" interaction) seems to give a fair account of experimental results in the case of noble gases. During the collision time τ_k, there exists, acting

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[17] See, for instance, Refs. 18, 20, 21, below.

[18] R. A. Bernheim, J. Chem. Phys. **36**, 135 (1962).

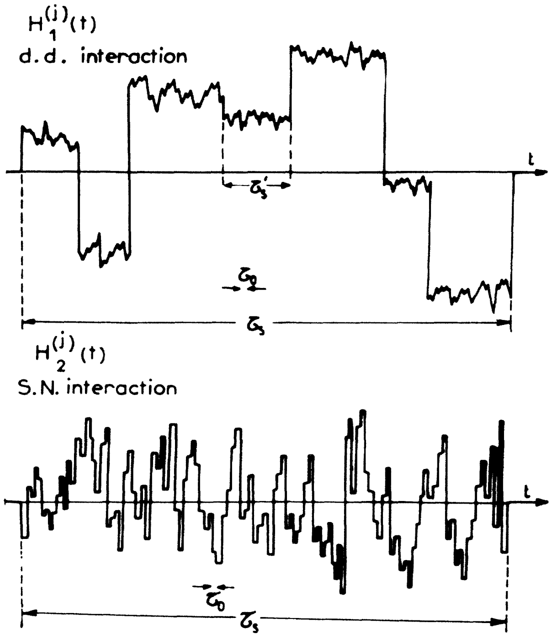

FIG. 4. Variations in time of a component of the random magnetic fields $\mathbf{H}_1(t)$, and $\mathbf{H}_2(t)$ seen by the Rb atom when adsorbed on the wall and produced by the dipole-dipole and spin-orbit interactions. τ_s represents the mean dwell time on the wall, τ_s' the dwell time in a given site, and τ_0 is of the order of 10^{-12} sec (period of thermal vibration).

upon **S**, and interaction of the type $\gamma\mathbf{S}\cdot\mathbf{N}$, **N** being the relative angular momentum of the colliding atoms. This interaction results from the fact that a coupling exists between the orbital motion of the electrons and the rotation of the nuclei; when the wave functions overlap the electron cloud does not rigidly follow the movement of the nuclei (so-called "slipping").[19] The $\mathbf{S}\cdot\mathbf{N}$ interaction is weak and of the same general type considered above $[\gamma_S\mathbf{S}\cdot\mathbf{H}_2(t)]$, with the random magnetic field $\mathbf{H}_2(t)$ being proportional to **N**.[20]

It is legitimate to suppose that the $\mathbf{S}\cdot\mathbf{N}$ interaction is also present in atom-wall collisions. It has the following important feature: The associated field $\mathbf{H}_2(t)$ involves the relative velocities of the colliding atoms; it changes in magnitude and orientation whenever the relative angular momentum of Rb and atoms on the wall changes. In a kind of motion where vibrations exist, $\mathbf{H}_2(t)$ will change sign at every period of the vibration.

The existence of the $\mathbf{S}\cdot\mathbf{N}$ interaction in atom-wall collisions together with the d.d. interaction raises an apparent paradox. We saw that, in the case under study, the d.d. interaction is then dominant. On the other hand, in Rb-noble gas collisions the existence of the $\mathbf{S}\cdot\mathbf{N}$ interaction seems fairly well established, and in all cases (even when the noble gas has a nuclear spin and the d.d. interaction is present) it is found to be dominant.[21] This effect increases with the mass of the noble gas (some doubt exists for He).[21]

In both cases of surface and gas-phase relaxation, the spin **S** is acted upon by the disorienting process of correlation time τ_c at time intervals Θ for a duration τ_d ($\tau_d \ll \Theta$), where Θ is equal to τ_v for atom-wall collisions and to the inverse frequency collision for gas-phase collisions. Similarly τ_d equals τ_s or τ_k in the two cases above. One finds then, that *all* relaxation times are inversely proportional to the product $\tau_d\cdot\tau_c$ [see for instance Eq. (6) below]. In the *gas-phase collision*, τ_d and τ_c can both be taken equal to the length of time the collision lasts, τ_k. Taking typical cross-section values, τ_d and τ_c are both of the order of 10^{-12} sec for the two interactions ($\mathbf{S}\cdot\mathbf{N}$ and d.d.). Under those circumstances, as we have seen, the $\mathbf{S}\cdot\mathbf{N}$ interaction is predominant.

The problem is now to evaluate τ_d and τ_c for the d.d. and $\mathbf{S}\cdot\mathbf{N}$ interactions in the *atom-wall collision* case. As we saw, τ_d is equal to the dwell time τ_s for both interactions. On the other hand, the evaluation of τ_c requires a knowledge of the behavior of a Rb atom on a $(CH_2)_n$ surface.

Physical adsorption[22] is characterized by a small adsorption energy E_a. When the atom gets near the wall, its motion is determined by the van der Waals attractive forces and electrostatic repulsive forces; this determines τ_s. When the atom bounces elastically, τ_s is of the order of 10^{-12} sec. When it does not, it can reach thermal equilibrium with the surface, and one can show that

$$\tau_s = \tau_0 e^{E_a/kT}, \tag{1}$$

where τ_0 is the high-temperature limit of τ_s, i.e., an elastic bouncing time, typically 10^{-12} sec. E_a is the kinetic energy an atom must have to escape surface attraction. One sees that τ_s decreases(and accordingly the relaxation gets slower), when T increases. This is the fact we used to determine E_a ($E_a \approx 0.1$ eV) (see Fig. 2). E_a is not uniform over the surface, and varies on the atomic scale (there exist potential wells). If one calls ΔE_a the mean difference E_a takes between neighboring sites, one sees that the atom will migrate on the surface and jump from site to site whenever its kinetic energy is of the order of ΔE_a. The mean time an atom dwells on a given site is τ_s',

$$\tau_s' = \tau_0' e^{\Delta E_a/kT}. \tag{2}$$

τ_0' is again of the order of 10^{-12} sec, and τ_s' satisfies the inequality $\tau_s' \lesssim \tau_s$. At the same time, while an atom is on a given site it vibrates at random around its equilibrium position with a frequency typical of thermal waves, i.e., in times of the order of 10^{-12} sec.

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[19] J. H. Van Vleck, Rev. Mod. Phys. **23**, 213 (1951); C. H. Townes and A. L. Schawlow, *Microwave Spectroscopy* (McGraw-Hill Book Company, New York, 1955), pp. 17, 182.

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

[21] R. M. Herman, Phys. Rev. **137**, A1062 (1965).

[22] J. H. De Boer, *The Dynamical Character of Adsorption* (Oxford University Press, New York, 1963).

Figure 4 shows the fluctuations in time of $H_1^{(j)}(t)$ and $H_2^{(j)}(t)$, any one of the three components of the random fields seen by **S**, and produced by the d.d. and the $\mathbf{S}\cdot\mathbf{N}$ interactions. $\mathbf{H}_1(t)$ suffers large changes at time intervals τ_s', whenever **S** jumps from site to site, but it also suffers small fluctuations every 10^{-12} sec because of the vibrations at a given site. (This picture can be justified, because nuclear spins **K** have relaxation times long compared to H_s', and because they cannot be appreciably polarized by the very dilute spins **S**.)

$\mathbf{H}_2(t)$, on the other hand, will change sign at intervals of the order of 10^{-12} sec, because of vibrations, and average to zero after a few of these.

As a conclusion, one sees that, on the wall, τ_{c1} pertaining to the d.d. interaction is of the order of τ_s', whereas τ_{c2} (belonging to $\mathbf{S}\cdot\mathbf{N}$) is of the order of 10^{-12} sec, as in the gas phase collision. One can then expect the following: *The d.d. interaction should have a long correlation time, which can be interpreted as* τ_s', *dwell time in a given site*; *the* $\mathbf{S}\cdot\mathbf{N}$ *interaction on the other hand, independent of* **K**, *should have a correlation time* τ_{c2} *of the order of* 10^{-12} *sec.*

We will see that this picture fits in very well with experimental results (one finds $\tau_{c1}=\tau_s'=4\times10^{-10}$ sec, and $\tau_{c2}\approx10^{-12}$ sec): It is because of its much longer correlation time (400 times roughly) in atom-wall collisions that the d.d. interaction is predominant in that case. One can add, that the same picture explains also the greater relaxation efficiency of the $\mathbf{S}\cdot\mathbf{N}$ interaction in atom-wall collisions as compared to the gas-phase case (at equal collision frequency Θ^{-1}); in the first instance the interaction lasts τ_s, in the other, 10^{-12} sec. The proportion of atoms being relaxed at a given time, $\tau_d/(\tau_d+\Theta)\approx\tau_d/\Theta$ is much greater in the first case ($\tau_d=\tau_s$) than in the second ($\tau_d\sim10^{-12}$ sec).

As we shall see, the root-mean-square value of $H_2(t)$ one obtains from the data makes it plausible that the "second interaction" is indeed the "spin-orbit" interaction. But even though it appears likely, we do not consider this fact as established.

IV. THEORETICAL STUDY OF THE RELAXATION

We present now the theoretical results which will serve as a basis for an interpretation of our measurements. We have already defined all the microscopic parameters. The detailed calculation of the relaxation has been published elsewhere.[15] We will recall here only the formulas which are of importance in the present discussion. These are valid for any weak interaction of the magnetic type $\mathcal{H}_1(t)=\gamma_S\mathbf{S}\cdot\mathbf{H}(t)$, and it is not necessary to make any assumption concerning the physical origin of $\mathbf{H}(t)$.

The spin **S** is coupled to **I** by the hfs interaction $a\mathbf{I}\cdot\mathbf{S}$. As we shall see below, the results have been extended to the case when two uncorrelated interactions of the above type are simultaneously present.

All assumptions concerning $\mathcal{H}_1(t)$ are expressed in the following equations:

$$\langle|\mathcal{H}_1(t)|^2\rangle\tau_c^2\ll1\,, \tag{3a}$$

$$\langle\mathcal{H}_1(t)\rangle=0\,, \tag{3b}$$

$$\langle\mathcal{H}_1(t)\mathcal{H}_1(t-\tau)\rangle=\frac{\tau_s}{\tau_s+\tau_v}\langle\mathcal{H}_1(t)\mathcal{H}_1(t)\rangle_{\text{av}}e^{-\tau/\tau_c}, \tag{3c}$$

$$\langle H^i(t)H^j(t)\rangle=\tfrac{1}{3}h^2\delta_{ij}. \tag{3d}$$

The first average $\langle\ \rangle$ is taken over the fraction $\tau_s/(\tau_s+\tau_v)$ of atoms which are submitted to relaxation at a given time, whereas the second average $\langle\ \rangle_{\text{av}}$ is over all atoms. Equation (3a) means that the interaction is weak and obeys the motion-narrowing condition. Equation (3b) indicates that we have included in the static Hamiltonian all terms which might produce a shift. Equation (3c) defines the correlation function we chose for $\mathcal{H}_1(t)$; it is an exponential, and this defines τ_c. This assumption is not essential and it is enough to suppose that the correlation function is a rapidly decreasing function of τ. $\langle\mathcal{H}_1(t)\mathcal{H}_1(t)\rangle$ is independent of time: $\mathcal{H}_1(t)$ is a stationary random operator. Equation (3d) means that there is no correlation between two different components of $\mathbf{H}(t)$. It defines h the root-mean-square value of the amplitude of the field $\mathbf{H}(t)$.

The calculation of the evolution of different observables under the influence of $\mathcal{H}_1(t)$ goes along lines which are commonly used in the theory of relaxation of liquids and gases (see, for instance, Ref. 23).

We give now the results concerning the longitudinal relaxation times of $\langle S_z\rangle$ and $\langle\mathbf{S}\cdot\mathbf{I}\rangle$.

A. Case of an Isolated Spin S

We consider first the case of a spin **S** which is *not* coupled to **I**. The relaxation of $\langle S_z\rangle$ is of course exponential in this case. The time constant T_{S1} is given by

$$T_{S1}^{-1}=Cj(\omega_S)\,, \tag{4}$$

$$j(\omega_S)=(1+\omega_S^2\tau_c^2)^{-1}. \tag{5}$$

We have the following expression for C:

$$C=\tfrac{2}{3}[\tau_s/(\tau_s+\tau_v)]\gamma_S^2h^2\tau_c. \tag{6}$$

$j(\omega_S)$ is proportional to the Fourier transform of the correlation function at frequency $\omega_S/2\pi$. This factor in the expression of the reciprocal time constant is very familiar; it just means that **S** will flip only when it can find its eigenfrequency ω_S in the Fourier spectrum of $\mathbf{H}(t)$. One has $0\lesssim j(\omega_S)\lesssim1$. The time constant T_{S1} becomes very long at high-field values when $\omega_S\tau_c\gg1$. The relation giving T_{S1} is interesting; we will find in the general case, when **S** is coupled to **I**, that all lifetimes which appear in the relaxation are given by an ex-

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[23] A. Abragam, *Principles of Nuclear Magnetism* (Oxford University Press, New York, 1961), Chap. 8.

pression which has a similar structure: It is the product of C by a linear combination of $j(\omega_F)$ and $j(\Delta W)$ which are proportional to the Fourier transform at the eigenfrequencies, ω_F and ΔW (hfs interval) of the atom. We next discuss the formula [Eq. (6)] giving C.

The fraction $\tau_s/(\tau_s+\tau_v)$ shows that relaxation times are proportional to the dimension of the cell when $\tau_s \ll \tau_v$. This is what we called the "volume effect." C depends on the product $\tau_s \cdot \tau_c$, and not on τ_c alone. This is just because the number of atoms being relaxed at a given time is proportional to τ_s. Finally, the relaxation time depends on the "strength" h of the interaction and on the correlation time τ_c in the usual fashion (the motion-narrowing condition being obeyed).

When $\mathbf{H}(t)$ is produced by the d.d. interaction between $\mathbf{S}$ and $\mathbf{K}$, h^2 can be computed, and is found to be equal to C';

$$C' = k \frac{\gamma_S{}^2 K(K+1)\gamma_K{}^2 \hbar^2 \tau_s \tau_c}{(R)^6(\tau_s+\tau_v)}; \tag{7}$$

it is proportional to $\gamma_K{}^2 K(K+1)$, and this is the origin of the factor 16 we mentioned between the values of all d.d. relaxation times where one goes from $(CH_2)_n$ to $(CD_2)_n$ coatings (τ_s is the same for both types of coatings, bebecause it is determined by electrostatic forces). In Eq. (7) the value of the numerical factor k and the definition of the length R are not the same depending on which part of d.d. interaction is predominant, i.e., scalar (contact term) or tensorial. In this last case, $k = 16\pi/3$ and R is given by

$$R^{-6} = \langle |r_{SK}(t)|^{-6} \rangle, \tag{8}$$

$r_{SK}(t)$ being the distance at time t between interacting spins $\mathbf{S}$ and $\mathbf{K}$.

B. Case of a Spin S Coupled to I by the hfs Interaction *a*S·I

The results differ, depending on the relative magnitude of the Zeeman energy ω_S, and the hfs energy $\Delta W = (I+\frac{1}{2})a$.

Low-Field Case $\omega_S \ll a$

Relaxation of $\langle \mathbf{S} \cdot \mathbf{I} \rangle$. We consider first $\langle \mathbf{S} \cdot \mathbf{I} \rangle$ which depends linearly on the population difference of the two hfs levels and vanishes at the Boltzmann equilibrium. Theory shows[15] that the relaxation of $\langle \mathbf{S} \cdot \mathbf{I} \rangle$ is exponential with time constant T_H;

$$T_H{}^{-1} = C \cdot j(\Delta W), \tag{9}$$

which critically depends on the value of $\Delta W \cdot \tau_c$.

When two uncorrelated interactions are present the relaxation of $\langle \mathbf{S} \cdot \mathbf{I} \rangle$ is still exponential, and one gets

$$T_H{}^{-1} = C_1 j_1(\Delta W) + C_2 j_2(\Delta W). \tag{10}$$

As we shall see, this exponential character has been confirmed experimentally for the two isotopes ^{85}Rb and ^{87}Rb and on the two types of coatings $(CH_2)_n$ and $(CD_2)_n$. C_1 and C_2 are the values of C for the d.d. and for the "second interaction", respectively. One must then distinguish between $C_1{}^{\mathrm{H}}$ $(\tau_{c1}, h_1{}^{\mathrm{H}})$, $C_2{}^{\mathrm{H}}$ $(\tau_{c2}, h_2{}^{\mathrm{H}})$, $C_1{}^{\mathrm{D}}$ $(\tau_{c1}, h_1{}^{\mathrm{D}})$, and $C_2{}^{\mathrm{D}}$ $(\tau_{c2}, h_2{}^{\mathrm{D}})$. j_1 and j_2 are the Fourier transforms at ΔW for the two interactions with correlation times τ_{c1} and τ_{c2}. One has $h_1{}^{\mathrm{H}} = (\sqrt{12.8}) h_1{}^{\mathrm{D}}$. If the "spin-orbit" interaction is indeed interaction 2, its magnitude is essentially determined by what happens near a carbon atom of the coating because it is a rapidly increasing function of Z.[18,20] It is then the same for $(CH_2)_n$ and $(CD_2)_n$ coatings, i.e., $h_2{}^{\mathrm{H}} = h_2{}^{\mathrm{D}}$, and $C_2{}^{\mathrm{H}} = C_2{}^{\mathrm{D}}$. As we shall see, experimental results are compatible with this relation.

Because the C's are independent of I, T_H depends on the isotope through the $j(\Delta W)$'s only, i.e., through the values of $\Delta W \cdot \tau_{c1}$ and $\Delta W \cdot \tau_{c2}$. If an interaction with a very short correlation time is predominant, T_H is the same for the two isotopes.

Relaxation of $\langle S_z \rangle$. When one interaction only is present, one finds that *two* time constants T_e and T_n appear in the relaxation of $\langle S_z \rangle$[15]:

$$\langle S_z \rangle = \langle Q_e \rangle_0 e^{-t/T_e} + \frac{2}{(2I+1)^2 - 2} \langle I_z \rangle_0 e^{-t/T_n}, \tag{11}$$

$$T_e{}^{-1} = C \left\{ \frac{j(\omega_F) - j(\Delta W)}{(2I+1)^2} + j(\Delta W) \right\}, \tag{12a}$$

$$T_n{}^{-1} = \frac{C}{(2I+1)^2} \{ j(\omega_F) + j(\Delta W) \}. \tag{12b}$$

$\langle Q_e \rangle_0$ and $\langle I_z \rangle_0$ depend on the initial conditions from which the relaxation takes place.

On the other hand, the relaxation of $\langle I_z \rangle$, nuclear longitudinal polarization is exponential, with time constant T_n;

$$\langle I_z \rangle = \langle I_z \rangle_0 e^{-t/T_n}. \tag{13}$$

The evolutions of $\langle S_z \rangle$ and $\langle I_z \rangle$ are coupled;

$$\frac{d\langle S_z \rangle}{dt} = \frac{-C}{(2I+1)^2} \{ [j(\omega_F) + 4I(I+1) j(\Delta W)] \langle S_z \rangle - 2j(\Delta W) \langle I_z \rangle \},$$

so that observable $\langle Q_e \rangle$,

$$\langle Q_e \rangle = \langle S_z \rangle - \frac{2}{(2I+1)^2 - 2} \langle I_z \rangle, \tag{14}$$

relaxes exponentially with time constant T_e.

The above formulas call for the following comments. The ratio T_n/T_e takes very different values depending on τ_c.

(1) When the following relation holds: $(2I+1)^2 j(\Delta W) \ll j(\omega_F)$ (this corresponds to a rather long value of τ_c) then, $T_e = T_n = T'$:

$$T'^{-1} = \frac{C}{(2I+1)^2} j(\omega_F) \approx \frac{C}{(2I+1)^2}. \tag{15}$$

$\langle S_z \rangle$ relaxes with a single time constant (which is rather long). T' can be compared to T_{S1}, relaxation time for an uncoupled spin. One obtains

$$T' = (2I+1)^2 \mathrm{T}_{S1}. \tag{16}$$

T' is $(2I+1)^2$ longer than T_{S1}. This can be understood in a qualitative way: A single flip is necessary to destroy $\langle S_z \rangle$ for an isolated spin, whereas it takes a cascade of such processes through m_F levels to do it when **S** is coupled to **I**. Condition (1) is found to be satisfied for ^{87}Rb on $(CH_2)_n$ coatings, i.e., when the d.d. interaction is predominant. (This indicates that τ_{c1} is rather long.) On the other hand, it is not satisfied for ^{85}Rb on the same coatings. This can happen, of course, because I is greater and at the same time, ΔW is smaller for ^{85}Rb than for ^{87}Rb; the two factors $(2I+1)^2$ and $j(\Delta W)$ are larger then, and inequality (1) is not satisfied. As we shall see, those facts set a rather narrow range of possible values for τ_{c1}.

(2) When τ_c is very short ["extreme narrowing," $j(\omega_F) = j(\Delta W) = 1$], T_e and T_n are very different, T_n being longer by a factor $(2I+1)^2$ (32 in the case of Cs). There are two time constants which are easy to recognize in the relaxation curve of $\langle S_z \rangle$ if their weights are comparable.

This situation is met, for instance, in gas-phase collisions (when τ_c is equal to the duration of the collision, 10^{-12} sec) and for the $\mathbf{S}\cdot\mathbf{N}$ interaction on the wall.

(3) When $(2I+1)^2 j(\Delta W)$ is of the order of $j(\omega_F)$, the ratio T_n/T_e lies between 1 and $\frac{1}{2}(2I+1)^2$. It varies from isotope to isotope, depending on I and ΔW.

(4) When there is just one interaction present, the ratios of T_n, T_e, T_H for a given isotope are the same whatever the coating, $(CH_2)_n$ or $(CD_2)_n$, on which the relaxation takes place. The fact that these ratios change from one coating to the other is a clear indication that several interactions are indeed present. This is what is found experimentally in the present case.

When two uncorrelated interactions are present, one finds theoretically that $\langle I_z \rangle$ and $\langle Q_e \rangle$ still relax exponentially with time constants T_e and T_n given in Eqs. (12);

$$T_e^{-1} = 1C_1 \left\{ \frac{j_1(\omega_F) - j_1(\Delta W)}{(2I+1)^2} + j_1(\Delta W) \right\} + C_2 \left\{ \frac{j_2(\omega_F) - j_2(\Delta W)}{(2I+1)^2} + j_2(\Delta W) \right\}, \tag{17a}$$

$$T_n^{-1} = \frac{C_1}{(2I+1)^2} \{ j_1(\omega_F) + j_1(\Delta W) \} + \frac{C_2}{(2I+1)^2} \{ j_2(\omega_F) + j_2(\Delta W) \}. \tag{17b}$$

Two time constants appear again in the relaxation of $\langle S_z \rangle$ given by the above expressions. Experiment shows that two time constants indeed appear in the relaxation of $\langle S_z \rangle$, for ^{85}Rb on $(CH_2)_n$ and for both isotopes on $(CD_2)_n$.

As a result of the above analysis, one can say that, in the case under study, there are six unknown parameters C_1^{H}, C_1^{D}, C_2^{H}, C_2^{D}, τ_{c1}, and τ_{c2} which describe the "strength" of the two interactions present on both coatings, and their correlation times. Measurements on the relaxation of $\langle \mathbf{S}\cdot\mathbf{I} \rangle$, and $\langle S_z \rangle$ in weak fields, give three time constants, T_e, T_n, T_H for the two isotopes and the two coatings, i.e., 12 equations. All parameters can be determined in this way, and many checks are possible. The results so obtained will be described in detail later on.

High-Field Case $\omega_S \gg a$

One finds that the relaxation of $\langle S_z \rangle$ is exponential with time constant T_{S1}, characteristic of an uncoupled spin at the same frequency ω_S.

Intermediate Case $\omega_S \approx a$

This corresponds to field values of the order of 1000 G for ^{87}Rb and 300 G for ^{85}Rb. The relaxation of $\langle S_z \rangle$ is found to be very complex and involves a large number $(4I+1)$ of time constants. The way the relaxation curve can be computed, once initial conditions are known, is described in detail in Ref. 15. One finds that the values of the time constants do not depend on initial conditions, whereas their relative weight does. As a rule then, the shape of the relaxation curve depends on initial conditions (at a given field value). $(4I+1)$ parameters (e.g., populations of all sublevels at time $t=0$) are necessary to define initial conditions, and the mere knowledge of $\langle S_z \rangle_0$ is not sufficient in this case. When the polarization of the vapor is complete, $\langle S_z \rangle_0 = \frac{1}{2}$ for instance, all atoms are in the Zeeman level with m_F maximum. Initial conditions are particularly simple then. (The same kind of remark holds for $\langle S_z \rangle_0 = -\frac{1}{2}$). Numerical computations have been made for $\langle S_z \rangle_0 = \frac{1}{2}$ and $\langle S_z \rangle_0 = -\frac{1}{2}$ and measurements were carried out with the highest polarizations we could achieve.[24] This was done at all field values.

When drawn in semilog coordinates, the relaxation curve is then *not* a straight line. We define a "pseudo" time constant T_1, as the inverse of the slope of the tangent to this curve at the point where the ordinate is half-maximum. T_1 can be determined experimentally because the same convention can be used to analyze the data. From what we said, T_1 depends on initial conditions (and is not the same for instance for $\langle S_z \rangle_0 = \frac{1}{2}$ and $\langle S_z \rangle_0 = -\frac{1}{2}$). The theoretical variations of T_1^{-1} with the field H_0 are illustrated by Fig. 5, drawn for ^{87}Rb, when two interactions are present: one with a rather

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[24] J. Vidal-Couret, M. A. Bouchiat, J. Nasser, and J. Brossel, Compt. Rend. **260**, 1904 (1965).

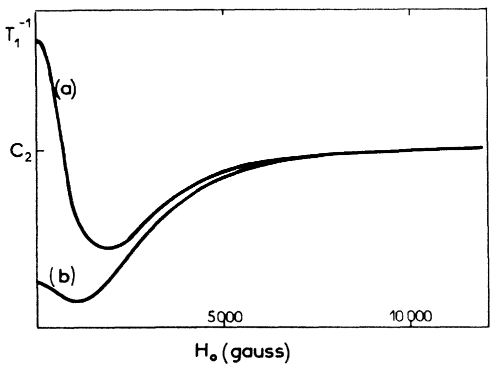

FIG. 5. Theoretical plot of T_1^{-1} versus H_0, corresponding to the field variations of "pseudo" time constant, T_1 characteristic of $\langle S_z\rangle$ decay for ^{87}Rb when two uncorrelated weak interactions of the magnetic type are present. The values chosen for the correlation times are $\tau_{c1}=3\times10^{-10}$ sec, $\tau_{c2}=10^{-12}$ sec, and for the relative strength C_1/C_2 of the interactions 16 for curve (a) and 1 for curve (b). C_2 is taken the same in both cases and determines T_1 in fields larger than 5000 G.

long correlation time $\tau_{c1}\approx3\times10^{-10}$ sec, the other with $\tau_{c2}\approx10^{-12}$ sec; their relative strength defined by the value of the ratio C_1/C_2 is taken equal to 16 for curve (a) and 1 for curve (b).

There are two main causes for the very large changes of T_1 with field. In all expressions of the decay constants there appear the Fourier transforms of the correlation function at the eigenfrequencies of the atom. (We have seen examples of this in formulas giving T_e, T_n, T_H.)

Let us suppose first that the dominant interaction has a long correlation time ($\Delta W\cdot\tau_c\gg1$). There exists (in low fields) a small range of values of ω_F which is enough to ensure the full variation of $j(\omega_F)$. T_1^{-1} is then continuously decreasing when H_0 increases. The curve T_1^{-1} versus H_0 is a typical bell-shape curve with a width of the order of τ_c^{-1} (Fig. 6, curve α). In this case, the variations of T_1 are due to changes in the atom eigenfrequencies.

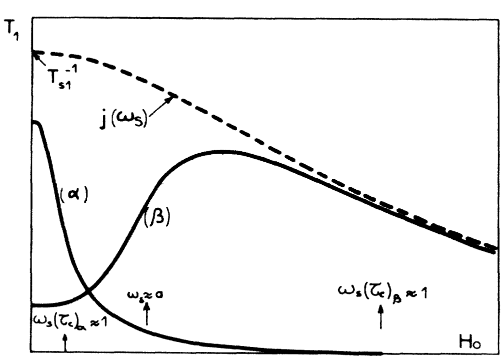

FIG. 6. Theoretical variations of T_1^{-1} due to the field variations of the "pseudo" time constant T_1 characteristic of $\langle S_z\rangle$ decay for ^{87}Rb when one interaction only is present (of the magnetic type). Curves (α) and (β) correspond to the case of a long ($\Delta W\cdot\tau_{c\alpha}\gg1$) and a short ($\Delta W\cdot\tau_{c\beta}\ll1$) correlation time, respectively. The dashed curve represents the field variations of T_{S1}^{-1} in the case of a spin S uncoupled to I.

On the other hand, if the dominant interaction has a correlation time τ_c very short ($\Delta W\cdot\tau_c\ll1$), there exists a range of field values (up to $\omega_S\approx a$) where all Fourier transforms are constant and equal to one. No variations of T_1 can be expected on their account: The eigenfrequencies of the atom do change but this does not affect T_1. In this same range though, the transition probabilities induced by the relaxation between Zeeman levels, do change because of the decoupling between **I** and **S**. The result can be inferred from what we have already said: In very low fields (**S** and **I** coupled), T_1^{-1} has a value intermediate between C and $2C/(2I+1)^2$, and in "high" fields (i.e., as soon as decoupling is complete), it is equal to $T_{S1}^{-1}=C$. In other words, T_1^{-1} increases in that region as shown on curve β, Fig. 6. At still higher field values, the usual $j(\omega_S)$ Lorentzian decrease takes over.

In Fig. 5, are shown the results when two interactions are present: τ_{c1} is long and τ_{c2} is very short. One sees that, in a *qualitative* way, the variations of T_1^{-1} with H_0 look, in this case, like the sum of the variations due to the two interactions acting independently. The decrease observed in low fields is due to the long τ_{c1}. One finds then a minimum and an increase due to the short τ_{c2}. The $j_2(\omega_S)$ decrease would take place well above 10^4 G and has not been drawn on the figure.

The study of the variations of T_1^{-1} as a function of field gives another method for obtaining information about physical adsorption. The curve giving T_1^{-1} versus H_0 can be computed, as we mentioned, and this has been done for sets of values of the different parameters τ_{c1}, τ_{c2}, C_1, C_2. On the other hand, as we describe later, it has been obtained experimentally up to 5000 G for the two isotopes and on the two types of coatings. The comparison between the two types of results leads to the numerical determination of τ_{c1}, τ_{c2}, etc. The agreement obtained with the method in low fields as described earlier, is found satisfactory.

V. EXPERIMENTAL RESULTS AND INTERPRETATION

In the present section, we give the results of our measurements on the relaxations of $\langle\mathbf{S}\cdot\mathbf{I}\rangle$ [25] and $\langle S_z\rangle$ by wall collisions on $(CH_2)_n$ and $(CD_2)_n$ coatings. The influence of electron exchange on these observables will be briefly examined first.

A. Influence of Exchange Collisions

The method of investigation has been described in Sec. II; θ_1 (wall temperature) is kept constant, and the number N of Rb atoms per cc in the cell is monitored by the temperature θ_2 of the reservoir. The results are as follows.

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[25] This observable is not the same, of course, as the population difference between states ($F=I+\frac{1}{2}$, $m_F=0$), and ($F=I-\frac{1}{2}$, $m_F=0$).

Relaxation of $\langle S_z \rangle$

We could not detect any influence of exchange collisions on the relaxation of $\langle S_z \rangle$, if the measurements are made on a pure isotope. This has been explained by the theory of electron exchange between identical atoms.[26]

On the other hand, when two isotopic species A and B are present, there is a very strong influence of B on the $\langle S_z \rangle$ relaxation of A.

Relaxation of $\langle \mathbf{S}\cdot\mathbf{I} \rangle$

In a pure isotope, there is a very strong influence of θ_2 on the relaxation of $\langle \mathbf{S}\cdot\mathbf{I} \rangle$.[14]

Theory shows that, when $\langle S_z \rangle_0$ is zero, no longitudinal polarization will appear because of exchange, and relaxation of $\langle \mathbf{S}\cdot\mathbf{I} \rangle$ due to exchange collisions is then exponential with time constant T_{eH}.

We have seen that theory shows that wall relaxation of $\langle \mathbf{S}\cdot\mathbf{I} \rangle$ is also exponential with time constant T_H (for interactions of the "magnetic type").

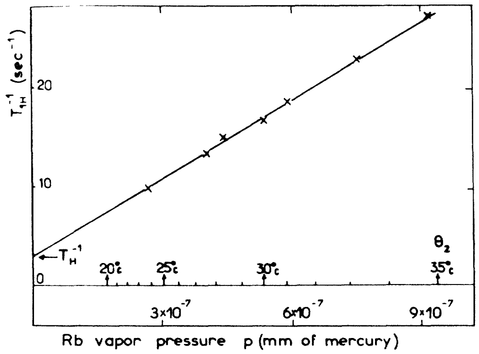

FIG. 7. Measured variation of $\langle \mathbf{S}\cdot\mathbf{I} \rangle$ relaxation time, T_{1H}, with Rb vapor pressure p in the cell (effect of exchange collisions): T_{1H}^{-1} is a linear function of p. The relaxation time T_H due to wall collisions is obtained by extrapolating at zero p values. The pressure scale makes use of values of p_S, saturated Rb vapor pressure, as given in Ref. 30. $p_S/p=\eta$ was found to be 1.2 as shown in Fig. 3 (case of ^{87}Rb on $(\mathrm{CH_2})_n$ coating).

In the presence of exchange and wall collisions, one expects then $\langle \mathbf{S}\cdot\mathbf{I} \rangle$ relaxation to be exponential with time constant T_{1H},

$$T_{1H}^{-1}=T_H^{-1}+T_{eH}^{-1}, \tag{18}$$

where T_{eH}^{-1} is proportional to N.

These conclusions are in excellent agreement with experimental results: We could never find any discrepancy between the relaxation curve and an exponential; moreover T_{1H}^{-1} is indeed a linear function of the vapor pressure p in the cell (Fig. 7). T_H due to $\langle \mathbf{S}\cdot\mathbf{I} \rangle$ relaxation on the wall, is determined by extrapolating at zero vapor pressure. One sees in Fig. 7 that even at fairly low temperatures *exchange is the dominant relaxation mechanism* of $\langle \mathbf{S}\cdot\mathbf{I} \rangle$. Figure 8 gives the results of the measurements for ^{85}Rb and ^{87}Rb in different cells (one gets parallel straight lines). This shows that ^{85}Rb–^{85}Rb and ^{87}Rb–^{87}Rb exchange cross sections are equal (they do not depend on I).

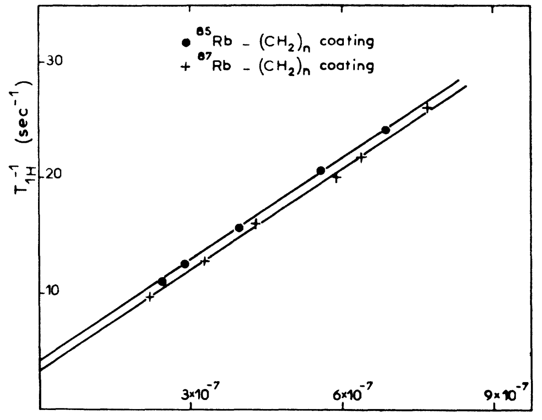

FIG. 8. Experimental results showing the variations of T_{1H}^{-1} versus Rb pressure, for ^{85}Rb and ^{87}Rb in two different cells on $(\mathrm{CH_2})_n$ coatings. Wall relaxation of $\langle \mathbf{S}\cdot\mathbf{I} \rangle$ is faster for ^{85}Rb and exchange cross sections ^{85}Rb–^{85}Rb and ^{87}Rb–^{87}Rb are equal.

$\langle \mathbf{S}\cdot\mathbf{I} \rangle$ relaxation can also be studied for the two isotopes *in an isotopic mixture* in a single cell (Fig. 9). Here again, theory shows that if $\langle S_z^A \rangle_0$ and $\langle S_z^B \rangle_0$ are zero, they remain zero in the presence of exchange, and relaxations of $\langle \mathbf{S}^A\cdot\mathbf{I}^A \rangle$ and $\langle \mathbf{S}^B\cdot\mathbf{I}^B \rangle$ are exponential, the time constant depending on the A-B exchange cross section.[27] These conclusions are confirmed experimentally and if one plots T_{1H}^{-1} (for one isotope) versus p (the total vapor pressure of the isotopic mixture) one finds a straight line with the same slope as before; the ^{85}Rb–^{87}Rb exchange cross section is equal to the other two. As a consequence of this, one can measure T_H (due to wall collisions) for the two isotopes in a single

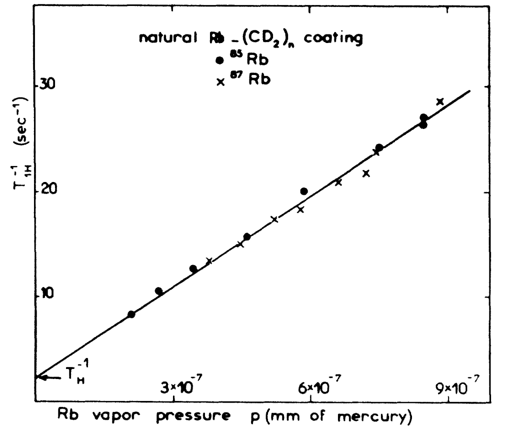

FIG. 9. Variations of T_{1H} with Rb total pressure as measured for ^{85}Rb and ^{87}Rb in a cell containing the natural mixture of isotopes: ^{85}Rb–^{87}Rb exchange cross section is the same as ^{85}Rb–^{85}Rb and ^{87}Rb–^{87}Rb. The coating was $(\mathrm{CD_2})_n$: Wall relaxation of $\langle \mathbf{S}\cdot\mathbf{I} \rangle$ is the same for both isotopes in this case.

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[26] F. Grossetête (private communication).

[27] F. Grossetête, J. Phys. Radium **25**, 383 (1964).

TABLE I. Comparison between experimental and theoretical results pertaining to wall relaxation of $\langle S_z\rangle$ and $\langle \mathbf{S}\cdot\mathbf{I}\rangle$ for the two Rb isotopes and the $(CH_2)_n$ and $(CD_2)_n$ coatings.[a]

	Measured values	Corrected values[b]	Theoretical values[c]
$(CD_2)_n$ coating			
^{87}Rb $1/T_n$	0.92	0.63	0.6
$1/T_e$	2.9	2.6	2.55
$1/T_H$ cell 1	2.6	2.3	2.2
$1/T_H$ cell 3	2.3	2	
^{85}Rb $1/T_n$	0.57	0.28	0.27
$1/T_e$	2.5	2.2	2.35
$1/T_H$ cell 2	2.5	2.2	2.2
$1/T_H$ cell 3	2.3	2	
$(CH_2)_n$ coating			
^{87}Rb $1/T_n$	5.5	5.2	4.1
$1/T_e$			6.5
$1/T_H$ cell 1	3.2	2.9	2.6
$1/T_H$ cell 3	2.9	2.6	
^{85}Rb $1/T_n$	1.9	1.6	1.8
$1/T_e$	6	5.7	5.1
$1/T_H$ cell 2	4	3.7	3.4
$1/T_H$ cell 3	3.7	3.4	

[a] All results are in sec^{-1}.
[b] The reservoir effect has been assumed to have a value $\bar{t}=3.5$ sec.
[c] The theoretical values have been computed with the following values: $\tau_{c1}=4\times10^{-10}$ sec, $\tau_{c2}<10^{-11}$ sec, $C_1^H=12.8\times4.8$ sec^{-1}, $C_1^D=5.5$ sec^{-1}, $C_2^H=2.4$ sec^{-1}, $C_2^D=2.2$ sec^{-1}.

cell containing the mixture; one has the same coating for the two isotopes and the large dispersion in the properties of coatings plays no role; the ratio of the T_H's of the two isotopes can be determined with much better precision than when a different cell is used for each isotope. It is quite certain, for instance, that, in spite of their small difference, hyperfine relaxation is faster for ^{85}Rb than for ^{87}Rb on $(CH_2)_n$, whereas it is practically the same on $(CD_2)_n$ (see Table I, and Fig. 9).

When the value of exchange cross section is wanted, the knowledge of N is necessary. We explained that we determined the ratio η^{-1} of N to N_S the number of atoms per cc in the vapor in equilibrium with the metal. We did not make measurements of N_S; but two values appear in the literature which differ by a factor 2.8.

We use the formula

$$\frac{1}{T_{eH}}=4N\pi\sigma^2\left(\frac{RT}{\pi M}\right)^{1/2}. \tag{19}$$

If N_S is computed from the vapor pressure given in Ref. 29, we find $\pi\sigma^2=6.2\times10^{-14}$ cm^2, whereas the vapor pressure in Ref. 30 leads to $\pi\sigma^2=2.2\times10^{-14}$ cm^2. Recent measurements[31] of $\pi\sigma^2$ are in excellent agreement with this last value, indicating that it is unwise to make use of Ref. 29.[32]

B. Wall Relaxation of $\langle \mathbf{S}\cdot\mathbf{I}\rangle$ and $\langle S_z\rangle$ in Weak Fields

The experimental results pertaining to wall relaxation of $\langle S_z\rangle$ and $\langle \mathbf{S}\cdot\mathbf{I}\rangle$ are given in Table I. Several cells have been used in every case: "Cell 1" contains ^{87}Rb; "cell 2," ^{85}Rb and "cell 3," the natural mixture. If the coatings are identical T_H should be the same in cells 1 and 3 for ^{87}Rb, and in cells 2 and 3 for ^{85}Rb; as seen in column 1, this is indeed the case. In column 2, the correction due to the "reservoir effect" ($\bar{t}=3.5$ sec) has been made.

Relaxation of $\langle \mathbf{S}\cdot\mathbf{I}\rangle$

As can be seen in column 2 of Table I, one finds for the reciprocal lifetime T_H^{-1} in sec^{-1}, 2.15 for ^{85}Rb, 2.10 for ^{87}Rb on $(CD_2)_n$ coating, 3.5 for ^{85}Rb, and 2.7 for ^{87}Rb on $(CH_2)_n$ coating. This calls for the following comments: In the case of ^{87}Rb, the ratio of the T_H's on (CD_2)n and $(CH_2)_n$ is $2.7/2.1\approx1.3$, whereas it is of the order of 5 for the ratio of the T_1's and should be 12.8 if the d.d. interaction alone were present. It is clear *that the d.d. interaction plays practically no role in the relaxation of* $\langle \mathbf{S}\cdot\mathbf{I}\rangle$ *for* $(CH_2)_n$ *and no role at all for* $(CD_2)_n$. In other words [see Eq. (10)], $C_1j_1(\Delta W)$ is negligiable in comparison with $C_2j_2(\Delta W)$. In particular, for $(CD_2)_n$ coatings, one may safely write

$$T_H^{-1}\approx C_2^Dj_2(\Delta W).$$

When one notices that T_H^{-1} is the same for both isotopes in this case (see Fig. 9), (2.15 and 2.10), it appears that $j_2(\Delta W_{85})=j_2(\Delta W_{87})=1$. This shows that $\Delta W\cdot\tau_{c2}\ll1$, i.e., that *the second interaction* (independent of spins K) *has a very short correlation time* $\tau_{c2}<10^{-11}$ sec. On the other hand, the value of T_H^{-1} on $(CD_2)_n$ coatings gives a precise measurement of the strength $C_2^D=C_2^H=2.2$ sec^{-1} of interaction 2.

If one goes now to the $(CH_2)_n$ case, one sees that the d.d. interaction gives a small contribution to T_H^{-1} equal to (3.5–2.1) sec^{-1} for ^{85}Rb and (2.7–2.1) sec^{-1} for ^{87}Rb. Relaxation is faster for ^{85}Rb. Such a dependence on the isotope can appear through $j_1(\Delta W)$ only; it goes in the correct direction because $\Delta W_{85}<\Delta W_{87}$.

Lastly, when one tries to understand why $C_1j_1(\Delta W)\ll C_2$, one can show, considering measurements of T_e in the $\langle S_z\rangle$ relaxation, that this is not due to the fact

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[28] See Ref. 9, p. 155.

[29] *Metals Reference Handbook*, edited by Colin J. Smithells (Butterworth Scientific Publications Ltd., London, 1962), 3rd ed., Vol. II, p. 655.

[30] T. J. Killian, Phys. Rev. **27**, 578 (1926).

[31] H. W. Sands and R. H. Moos, Phys. Rev. **135**, A591 (1964); Sand's definition of the exchange cross section is slightly different from the present one [Eq. (19)]. When using our definition and his data Sands's value obtained is 2.6×10^{-14} cm^2, for ^{87}Rb–^{87}Rb, and 2.4×10^{-14} cm^2 for ^{85}Rb–^{85}Rb.

[32] This is why we make use here of the values given in Ref. 30 to evaluate Rb vapor pressure (Figs. 3, 7, 8, and 9). In previous publications, we had used values of Ref. 29.

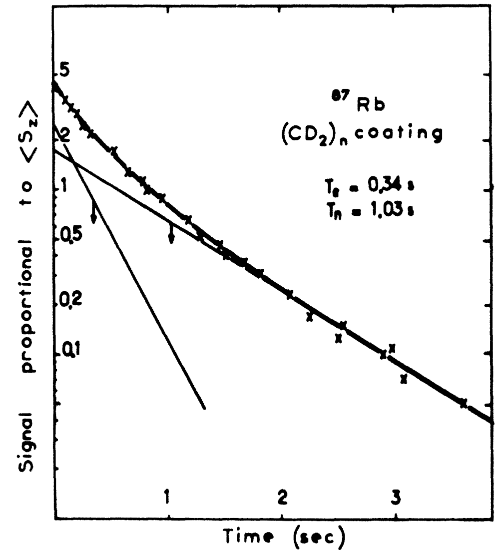

FIG. 10. Experimental relaxation curve for $\langle S_z\rangle$ in the case of ^{87}Rb on a $(CD_2)_n$ coating. In semilog representation two time constants T_e and T_n appear clearly: The relaxation curve is obtained by Franzen's sequence (relaxation in the dark).

that C_1 is unduly small, but because $j_1(\Delta W)\ll 1$,i.e., because *the correlation time* τ_{c1} *of the d.d. interaction is long*: $\Delta W\cdot\tau_{c1}\gg 1$. This point will be established clearly in the discussion of $\langle S_z\rangle$ relaxation below.

Relaxation of $\langle S_z\rangle$

As theory predicts, two time constants T_e and T_n are found experimentally in the relaxation of $\langle S_z\rangle$ (see Fig. 10.) Their values do not depend on initial conditions, whereas their relative weights do. As seen in Table I, there is again no proportionality between time constants in $(CH_2)_n$ and $(CD_2)_n$, which again shows the presence of two interactions with very different correlation times. One interesting feature appears in Table I.: T_e and T_n are easily identified in relaxation curves for ^{85}Rb and ^{87}Rb in $(CD_2)_n$, and for ^{85}Rb in $(CH_2)_n$, but only *one* time constant is found for ^{87}Rb in $(CH_2)_n$. This means that T_e and T_n are very close to each other and cannot be distinguished experimentally in this case. (In our experiment, the sum of two exponentials cannot be distinguished from a single exponential when the two time constants differ by a factor smaller than 2.)

Because the d.d. interaction is dominant, the condition $T_e=T_n$ means, as pointed out before, $(2I+1)^2\times j_1(\Delta W_{87})\ll 1$. A similar relation does not hold for ^{85}Rb. As a consequence of these facts one gets 0.9×10^{-10} sec$<\tau_{c1}<10^{-9}$ sec; thus the d.d. interaction has a correlation time τ_{c1} (which we interperted as the dwell time in a given site), which is much longer than an elastic bouncing time. The atom gets adsorbed and migrates on the surface.

Finally, one gets the best fit with experiment by taking

$$\tau_{c1}=4\times 10^{-10}\text{ sec},\quad C_1^H=12.8\times 4.8=62\text{ sec}^{-1},$$
$$\tau_{c2}<10^{-11}\text{ sec},\quad C_2^H=2.4\text{ sec}^{-1},$$
$$C_1^D=5.5\text{ sec}^{-1},\quad h_1^H=14\text{ G}.$$
$$C_2^D=2.2\text{ sec}^{-1},\quad h_2=51\text{ G}.$$

With these values one gets for the different time constants T_H, T_e, T_n, for the two isotopes and the two coatings the results listed in column 3. The agreement is satisfactory when one bears in mind the dispersion of the properties of coatings in different cells and the difficulty in evaluating $\bar{t}$.

When use is made of the numerical value of C_1^H above and of the formula [Eq. (7)], one obtains 2.2 Å for R. Because the interaction is stronger for shorter adsorption distances, those are favored by Eq. (7), so that R is smaller than the mean adsorption distance [Eq. (8)]. Since the atomic radius of Rb is 2.35 Å and that of H is 0.25 Å,[33] the value of R quoted above looks reasonable.

C. Influence of H_0 on the Relaxation of $\langle S_z\rangle$

We now give the results of the measurements of T_1, "pseudo" time constant pertaining to $\langle S_z\rangle$ at different field values (up to 5000 G).[24] The first difficulty is to start the relaxation with well-known initial conditions. We have indeed observed that the "pseudo" time constant T_1 depends qualitatively on initial conditions, in the sense predicted by theory. We chose $\langle S_z\rangle_0=\pm\frac{1}{2}$ to draw theoretical curves; experimentally, this situation can be met at all field values provided the intensity of the pumping light is high and its circular polarization good.

Figure 11 gives the results of the measurements for ^{87}Rb in $(CH_2)_n$ and $(CD_2)_n$, and ^{85}Rb in $(CH_2)_n$. The

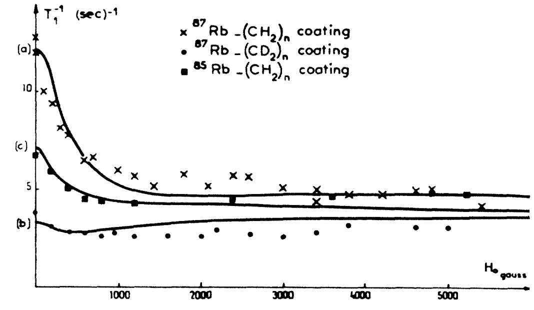

FIG. 11. The curves represent theoretical variations of T_1^{-1} versus magnetic field. T_1 being the "pseudo" time constant of $\langle S_z\rangle$. The values taken for the parameters are those obtained in the study of relaxation in low fields. Initial conditions are assumed to correspond to $\langle S_z\rangle_0=\frac{1}{2}$. The points give the results of the measurements: crosses (and curve a) correspond to ^{87}Rb on $(CH_2)_n$, closed circles (and curve b) to ^{87}Rb on $(CD_2)_n$, and squares (and curve c) to ^{85}Rb on $(CH_2)_n$.

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[33] J. C. Slater, J. Chem. Phys. 41, 3199 (1964).

cells were 30-mm diam instead of 60-mm used in previous measurements. Accordingly the dispersion of results is higher and the importance of the "reservoir effect" is enormously increased. Since it would have been the dominant factor in the relaxation of ^{85}Rb in $(CD_2)_n$ no results are reported in this case. The reservoir effect is still important for ^{87}Rb in $(CD_2)_n$. In small cells the dispersion of its values is rather large and this makes a quantitative check rather difficult.

The following features appear in Fig. 11:

(1) For ^{87}Rb and ^{85}Rb on $(CH_2)_n$ coatings (curves a and c), T_1^{-1} is a rapidly decreasing function of H_0 in the range of field values between zero and a few hundred gauss. This shows that an interaction with a long correlation time $\tau_{c1} > 10^{-10}$ sec is present.

(2) The above feature is hardly visible for ^{87}Rb in $(CD_2)_n$ (curve b). This proves that this interaction is much weaker in $(CD_2)_n$, namely, it is the d.d. interaction between **S** and spins **K** of the coating.

(3) In high fields (5000 G) on the other hand, T_1^{-1} is the same for cases a and c. It is not quite the same for case b, but between 1500 and 5000 G there is a small but regular increase in T_1^{-1} values. It seems reasonable to believe that at still higher values all three curves would merge within the precision of our measurements. Moreover, there appears in (b), around 600 G, a small and flat minimum, whose existence is real in our opinion.

All these facts show the existence of a second interaction with a very short correlation time $\tau_{c2} \approx 10^{-12}$ sec. This interaction does not depend on spins **K**.

It appears then that the influence of H_0 confirms in a very concrete way all the results obtained by the method of study in low fields. The curves which are drawn on Fig. 11 are not those giving a best fit with experimental data, but theoretical curves, assuming the values of parameters determined by the first method and listed above. The fit is better for curves (a) and (c) than for curves (b) because of the difficulties in choosing the value of the reservoir effect $\bar{t}$ in small cells. Moreover, small variations of parameters characteristic of physical adsorption are expected to occur from one coating to another. For all these reasons, we feel that the agreement between theoretical curves and experimental points is fairly good.

VI. CONCLUSIONS

In conclusion, one can say that optical pumping has proved a powerful tool to study the behavior of Rb atoms on paraffin-coated walls. We have arrived at a detailed picture of this behavior, and we are able to determine the parameters of physical adsorption in this case. We found for the adsorption energy a value 0.1 eV which is in good agreement with Brewer's result.[34] We have proved that two interactions are present in producing the disorientation of Rb atoms. One is the d.d. interaction between **S** and the nuclear spins **K** of H or D in the paraffin of the coatings; it has a correlation time $\tau_{c1} \approx 4 \times 10^{-10}$ sec which can be interpreted as the dwell time in a given site of the wall. The properties of the second interaction satisfy the predictions of the theory for relaxation by a random, weak interaction of the magnetic type. Its correlation time $\tau_{c2} \approx 10^{-12}$ sec is of the order of the period of thermal vibration. Its strength is determined by the root-mean-square value of the effective magnetic field seen by **S** on the wall, $h_2^{H} \approx h_2^{D} \approx 50$ G. There is reason to believe that it might be the spin-orbit, $\mathbf{S}\cdot\mathbf{N}$, interaction as determined essentially by carbon atoms in the paraffin.

All the above conclusions are compatible with experimental results on gas-phase relaxation of Rb on buffer gases. In that case the problem is to a large extent simpler because of the very small value of the collision time. The d.d. interaction should rapidly be overwhelmed by the $\mathbf{S}\cdot\mathbf{N}$ interaction (except perhaps in the case of helium). All formulas given here (with constant C_2 only) should apply in this case.

One may also compare the strength of the "second interaction" measured in the present work (i.e., 50 G) to the one, h, obtained in gas-phase relaxation of Rb on ethane.[35] Assuming a gas-phase collision time of 10^{-12} sec and a dwell time on the wall $\tau_s \approx \tau_{c1} = 4 \times 10^{-10}$ sec one obtains very reasonable agreement between h and h_2. This may be taken, perhaps, as an argument showing that the "second interaction" (found on the wall) and the one appearing in gas-phase collisions are very similar in nature. It may be that both are the $\mathbf{S}\cdot\mathbf{N}$ interaction.

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[34] R. G. Brewer, J. Chem. Phys. 38, 3015 (1963).

[35] R. J. McNeal, J. Chem. Phys. 37, 2726 (1962).