Dwell Time Measurement of Wall Collisions of Spin Polarized Rb Atoms on Antirelaxation Coatings

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Abstract. Methods commonly used in surface science have difficulties in studying surface interaction between spin polarized atoms and anti-relaxation coatings in sealed atomic vapour cells. The average dwell time of atom-wall collisions can provide important information for understanding the atom surface interaction. Here we present a simple method for directly measuring the average dwell time of spin polarized rubidium atoms on coated glass surfaces. The method relies on evanescent-wave induced light shift of the Zeeman resonance of Rb atomic spins, and does not depend on the microscopic details of surface interactions. This is the only reliable method currently available for measuring surface dwell time of spin polarized atoms sealed in vapor cells.

1. Introduction

Spin polarized alkali-metal atoms contained in vapour cells are of great importance in many areas of physics such as precision tests of fundamental symmetry[1], atomic clocks[2], ultra-sensitive atomic magnetometers[3] and quantum information[4]. Also they can, through spin exchange collisions, polarize nuclear spins of noble gas isotopes, which are very useful in neutron physics[5] and nuclear magnetic resonance imaging[6]. Long-lived atomic spin coherence is a core requirement in the above applications. The most damaging depolarization mechanisms taking place in a vapor cell are spin-exchange relaxation caused by collisions between atoms[7, 8] and wall relaxation by collisions between atoms and inner walls of the cell[7, 9]. The latter is even worse for miniature atomic devices where the surface to volume ratio is much greater[10].

Wall relaxation is due to the fluctuating microscopic magnetic fields experienced by the spin of the alkali atom while it is adsorbed on the surface. Antirelaxation coatings of long chain organic molecules such as paraffin and Octadecyltrichlorosilane(OTS) have been used to mitigate the wall relaxation[11] for many years. The saturated hydrocarbon coatings have small adsorption energy and almost no unpaired electrons than bare glass surfaces. Thus, comparing to the bare glass surfaces, on which a single collision will depolarize the atomic spin, coated surfaces allow an atom to have several hundred (for OTS) or several thousand (for paraffin) of wall collisions before its spin coherence is destroyed. Therefore, coatings have very important application in many fields of atomic physics, such as atomic frequency standard[12], atomic magnetometer[13, 14] and quantum memory[15, 16].

In spite of the great success of anti-relaxation coatings, details of surface interaction between coatings and spin polarized atoms are still not well understood, and this leads to poorly guided
searches for better coatings. Cells coated by same protocol often yield very different results \cite{17}. The most influential study by Bouchiat \cite{11} showed that there are two kinds of processes contributing to the spin relaxation of rubidium atoms on paraffin coatings. One is the dipole-dipole interaction between the spin of a Rb atom and the nuclear spin of hydrogen ion on the paraffin. The other is the spin-orbit interaction caused by the relative thermal vibrational motion between the Rb atoms and the carbon atoms of the coating.

One of the most important characteristics of surface interactions is the average time of interaction between the surface and a spin-polarized atom. Two time scales are of interest: the surface coherent interaction time \( \tau_c \) and the average dwell time \( \tau_s \) that a polarized atom stays on the surface for each collision. One deduces the coherent surface interaction time \( \tau_c \) by studying magnetic decoupling of wall relaxation rate. Previous studies found that \( \tau_c \) of Rb on paraffin coatings is on the order of one tenth of nanosecond, which sets the lower limit of \( \tau_s \) \cite{11, 18}. The only experimental measurement on \( \tau_s \) before our research is given by Stephens \cite{19}, which only gives an upper limit of 35 \( \mu s \). The range of the value of \( \tau_s \) was so large that one can hardly deduce from it any useful information about the surface interaction. Here we present a method for accurately measuring the average dwell time of spin-polarized \(^{87}\)Rb atoms on anti-relaxation coatings and then apply it to the two mostly used coatings, paraffin and OTS.

2. Experimental methods and results

2.1. Preparation of the cells

Cells are made of Pyrex glass, and have a cylindrical shape of one inch in diameter and one inch in length. A moveable glass prism is sealed inside the cell to act as the adjustable back wall of the cell, so that the effective cell length (L) can be varied from 60 to 700 \( \mu m \) by tapping the stage to which the cell is fixed during the experiment.

The coating procedure of paraffin is similar to that in Ref. [20, 21]. The cell was first sealed onto the manifold of a vacuum system which already contained paraffin and rubidium in separate side arms. The paraffin was evaporated at 300 \(^\circ\)C in vacuum and allowed to condense on the inner walls of the cell. The paraffin used in the present experiment was pentacontane (\( \text{CH}_3(\text{CH}_2)_{48}\text{CH}_3 \)) with a purity of 97\% and a melting point of 93 \(^\circ\)C. After coating, rubidium was distilled into the stem of the cell, followed by the filling of inert buffer gas. Finally, the cell was pulled off the manifold, and then annealed in an oven at about 60 \(^\circ\)C for three days. The coating procedure of OTS is the same as that in Ref. [22]. After standard cleaning, the cell was treated in freshly prepared Piranha acid (one part H2O2 35\%, three parts H2SO4 98\%) for 30 min to prepare an OH surface termination. It was then rinsed in turn with distilled water, methanol, and distilled water a second time. The cell was blown dry. A solution of 2 mM OTS was prepared in a mixture of 25\% chloroform and 75\% hexane. The inner surfaces of the cell were immersed in OTS solution for 2 minutes. The cell was then rinsed three times with chloroform and then sealed on to the vacuum manifold to be baked up to 200 \(^\circ\)C for 10 hours in vacuum (~10-8 Torr). After baking, rubidium was distilled into the stem of the cell. Finally the cells were filled with various pressures of N2 gas at 250\(^\circ\)C before they were pulled off the manifold. Cells were then cured at about 70 \(^\circ\)C for two days. In our experiment, both types of cells contain isotopically enriched Rb (98.3 at. \% \(^{87}\)Rb).

2.2. Experimental procedure

Experiments are carried out inside a two-layer magnetics shielding [Figure 1]. Three orthogonal pairs of Helmholtz coils inside the shielding cancel the residual field and provide a uniform magnetic field along the positive x direction. A He-Ne laser is used to measure the cell thickness by retro-reflection with an accuracy of 20 \( \mu m \) \cite{23}. Measurements are done at a cell temperature of 72 \(^\circ\)C in order to have enough vapor density and also be sufficiently far away from the melting point of paraffin. The temperature is stabilized to within 0.5 \(^\circ\)C throughout the experiment. The
A glass cell is held inside a peek oven. The cell is heated by hot air such that the stem, where the Rb metal is, is kept at a temperature a few degrees lower than the cell body so as to prevent Rb condensation on the coatings.

![Figure 1](image1.png)

**Figure 1.** (Color online) Experimental setup. The pump laser B is circularly polarized after passing through a linear polarizer (LP) and a quarter-wave plate (λ/4). The probe laser A is s-polarized by a linear polarizer (LP). Inset: a Rb cell of variable thickness. Reprinted with permission from Ref. [24]. Copyright (2011) by American Institute of Physics.

Two diode lasers, A and B, are used to provide probe and pump beams respectively. The linewidth of the lasers is 45 MHz. The probe beam A is s-polarized and the pump beam B is circularly polarized. Both beams are incident on the same spot of the cell window with slightly different incidence angles, and undergo total internal reflection at the front surface of the cell, with penetration depths of 1.16 μm and 0.82 μm for the pump and probe beams, respectively.

![Figure 2](image2.png)

**Figure 2.** (Color online) A simple level scheme of $^{87}$Rb using the direction of field as quantization axis. The pump beam is $\sigma^+$ polarized, and the probe beam is linear polarized which can be decomposed into a coherent superposition of $\sigma^+$ and $\sigma^-$ polarization. When the vapor is polarized, the refractive indices for the two circular polarized light are different, causing a rotation of the polarization axis of the probe when it exits the vapor.

Shown in Figure 2 is the simple level scheme of our experiment. The pump beam, whose frequency is tuned to the F=1→F'=1,2 transitions of the $^{87}$Rb D1 line, creates a spin polarization in the Zeeman multiplets of the F=2 hyperfine level. The spin polarization is monitored by the rotation of the polarization plane (Faraday rotation) of the probe beam, the frequency of which is...
tuned slightly above the $F=2 \rightarrow F'=1,2$ resonance to maximize the signal. The Faraday rotation is measured by a polarization analyzer which is composed of a half wave plate, a Wollaston prism and a balanced photo detector. An amplitude-modulated radio frequency (rf) field is applied along the $y$ axis. The scan of the frequency of the oscillating magnetic field across the Larmor frequency of the $^{87}\text{Rb}$ Zeeman transitions yields a magnetic resonance line in the Faraday rotation of the probe beam. One can also use a circularly polarized probe and measure its reflection directly as was done in Ref. [25].

One notices that the evanescent pump beam not only creates the spin polarization but also causes a frequency shift for the probed Zeeman transitions as if it introduces an effective magnetic field in the direction opposite to its photon spins[26]. To ensure the stability of this effective field, a spectrum analyzer is used to monitor the frequency of the pump beam so that its frequency does not drift by more than 40 MHz.

The observed Larmor frequency of the Rb atoms can be interpreted as the ensemble average of the average Larmor frequencies of Rb atoms as shown in Figure 3 and is given by[25]

$$\omega^{(+)} = \omega_0 + \delta \phi_0 + \delta \phi_e^{(+)} \tau_s + \tau_b,$$

where “+” and “-” superscript denote two light polarizations, $\omega_0$ is the Larmor frequency of Rb atoms in the bulk which is determined solely by $B_0$, $\delta \phi_0$ is the average phase shift of a Rb atom during its dwell time $\tau_s$ on the coating surface, $\delta \phi_e^{(+)}$ is the average phase shift of the atomic spin precession caused by the effective field due to the interaction between the evanescent pump beam and the Rb atom, and $\tau_b$ is the average time the atom spends in the bulk of the cell between two consecutive wall collisions. Defining $\delta = \omega^{(-)} - \omega^{(+)}$, we have from (1)

$$\delta = \frac{\delta \phi_e^{(-)} - \delta \phi_e^{(+)} \tau_s + \tau_b}{\tau_s + \tau_b} = \frac{\delta \phi_e^{(-)} - \delta \phi_e^{(+)} \tau_s + L / \langle v_z \rangle}{\tau_s + L / \langle v_z \rangle}.$$  

Figure 3. (Color online) A representative segment of the diffusion path of a Rb atom between two consecutive wall collisions. $B_0$ is the uniform holding magnetic field along the $x$ direction, and $B_e$ is the effective magnetic field due to the light shift of the pump beam. The figure is not drawn to scale.

2.3. Data analysis

The observed Larmor frequency of the Rb atoms can be interpreted as the ensemble average of the average Larmor frequencies of Rb atoms as shown in Figure 3 and is given by[25]
Figure 4. (Color online) Two representative magnetic resonance signals curves corresponding to $\sigma^+$ and $\sigma^-$ pump and probe beams are shown in the same figure in order to display the frequency shift more clearly. Adapted and reprinted with permission from Ref. [25]. Copyright (2009) by American Physical Society.

Rearranging Equation (2) one finds a linear relationship between the cell length and $1/\delta$,

$$\frac{L}{\langle v_e \rangle} = \left( \frac{\delta \phi_e^{(+)} - \delta \phi_e^{(-)}}{\delta} \right) \frac{1}{\mu} - \tau_s$$  \hspace{1cm} (0)

We measure $\delta$ for a number of cell lengths $L$, and plot $L/\langle v_e \rangle$ against $1/\delta$. The absolute value of the y-intercept is equal to the negative of the average dwell time $\tau_s$. Shown in Figure 5 are the representative data demonstrating this linear relationship between $L/\langle v_e \rangle$ and $1/\delta$ for OTS- and paraffin-coated cells respectively. Averaging over all the experimental data, we find that at a cell temperature of 72 °C the dwell time for OTS-coated cells is $\tau_s = 0.9 \pm 0.1 \mu$s and that for paraffin-coated cells is $\tau_s = 1.8 \pm 0.2 \mu$s [24].

Figure 5. Two representative plots of cell length $L$ versus $1/\delta$ for cells coated with OTS (left figure) and paraffin (right figure) respectively. Reprinted with permission from Ref. [24]. Copyright (2011) by American Institute of Physics.

3. Discussion
Adsorption energy $E_a$ of rubidium atoms on OTS and paraffin coatings were measured to be on the order of 0.1 ev [11, 18, 25], from which one can deduce the dwell time on each adsorption site to be on the order of one tenth of a nanosecond. Our measurement indicates that during each wall collision, a rubidium atom has to visit thousands of sites before leaving the coating.

The difference of dwell times for OTS and paraffin coatings also merits some discussion. The dwell time for OTS is shorter than that for paraffin whereas the relaxation probability for OTS is larger than that for paraffin by about one order of magnitude. This implies that the superior antirelaxation property of paraffin is not because of an extremely short dwell time of spin polarized Rb atoms in paraffin, but because the average strength of the interactions experienced by them while they are inside paraffin is much weaker than while they are inside OTS. Paraffin coating is done using vapor and tends to be thick. However chemically self-assembled OTS coating consists only one or two layers of molecules and is only several nanometers thick [18]. Thus, for wall collisions of longer dwell time, spin polarized Rb atoms may diffuse to the sites near the interface between the glass surface and OTS and become depolarized. These Rb atoms, upon leaving the OTS coating, cannot be depolarized by the rf again, and do not contribute to the rf resonance signal. Thus the long dwell time tail of the dwell time distribution of Rb atoms is truncated, resulting in a shorter average dwell time. It was reported that due to packing defects, the OTS coating does not completely cover the glass surface [27]. Thus Rb atoms can occasionally collide with these bare glass patches and become depolarized, which explain the larger relaxation probability of Rb atoms on OTS coating.

A recently discovered coating of single compound alkene shows improvement of a factor of 100 over paraffin [28]. It should be very interesting to measure the dwell time on this new coating.

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