# ACCURATE MEASUREMENT OF THE STICKING TIME AND STICKING PROBABILITY OF Rb ATOMS ON A POLYDIMETHYLSILOXANE COATING

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We present the results of a systematic study of Knudsen's flow of Rb atoms in cylindrical capillary cells coated with a polydimethylsiloxane (PDMS) compound. The purpose of the investigation is to determine the characterization of the coating in terms of the sticking probability and sticking time of Rb on the two types of coating of high and medium viscosities. We report the measurement of the sticking probability of an Rb atom to the coating equal to  $4.3 \cdot 10^{-5}$ , which corresponds to the number of bounces  $2.3 \cdot 10^4$  at room temperature. These parameters are the same for the two kinds of PDMS used. We find that at room temperature, the respective sticking times for high-viscosity and medium-viscosity PDMS are  $22 \pm 3 \ \mu$ s and  $49 \pm 6 \ \mu$ s. These sticking times are about million times larger than the sticking time derived from the surface Rb atom adsorption energy and temperature of the coating. A tentative explanation of this surprising result is proposed based on the bulk diffusion of the atoms that collide with the surface and penetrate inside the coating. The results can be important in many resonance cell experiments, such as the efficient magneto-optical trapping of rare elements or radioactive isotopes and in experiments on the light-induced drift effect.

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## 1. INTRODUCTION

The major technical difficulty in many resonance cell experiments, such as cooling and trapping shortlived radioactive isotopes using a magneto-optical trap (MOT) [1–10] or experiments on light-induced drift (LID) [11–19], lies in the atomic vapor interaction with the inner wall of the resonance cell.

Since short-lived radioactive isotopes are available only in limited quantities, an efficient optical trapping process is of great importance to the possibility to create large samples of these elements. In this kind of experiment, atoms that are injected into the cell stick to the wall of the cell due to physical adsorption for a period of a characteristic sticking (dwell) time and return to the vapor. Obviously, to ensure efficient trapping of these short-lived radioactive isotopes, the sticking time of the atoms to the cell wall must be shorter than their radioactive lifetime. Low trapping efficiency can also be attributed to a large loss through high chemical sorption, when the atoms react chemically with the wall and are irreversibly removed from the vapor.

The interaction of the vapor with a cell wall is also a serious problem in experiments on the LID effect. In this kind of experiment, resonance atoms can be pushed or pulled either inside or outside a capillary cell by light. When the atoms inside the capillary are pushed by light, they stick to the wall as soon they arrive. When the dwell time is long, the fraction of the incoming atoms absorbed to the wall is much higher than in the vapor phase. As a result, it takes far too long time to saturate the wall with a relatively weak flux of incoming atoms that are pushed by light. The opposite is also true: when the atoms are pulled out of the saturated capillary by light, it takes a rather long time to clean the adsorbed atoms off the wall by pulling them out of the capillary using LID. Thus, the long sticking time leads to long time to achieve a steadystate distribution of atoms in the cell. This masks the manifestation of the LID effect to a considerable extent.

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| Surface materials   | E,  eV          | $	au_s,{ m s}$                  | Reference |
|---|-----------------|---------------------------------|-----------|
| Paraffin coated pyrex   | 0.1             | $4 \cdot 10^{-10}$              | [22]      |
| Paraffin coated pyrex   | —               | $(1.8 \pm 0.2) \cdot 10^{-6}$   | [26]      |
| Tetracontane coated glass   | 0.06            | $10^{-11}$                      | [23]      |
| Tetracontane coated pyrex   | 0.062           | $10^{-11}$                      | [24]      |
| Octadecyltrichlorosilane<br>coated pyrex $(T = 103 ^{\circ}\text{C})$ | $0.19 \pm 0.03$ | $(0.53 \pm 0.03) \cdot 10^{-6}$ | [25]      |
| Octadecyltrichlorosilane<br>coated pyrex $(T = 72 ^{\circ}\text{C})$  | _               | $(0.9 \pm 0.1) \cdot 10^{-6}$   | [26]      |

Table 1. The results of the measurements of the adsorption energy and sticking time for Rb

It is known that as atoms collide with the surface, they undergo an attractive potential whose range depends on the electronic and atomic structures of both the surface and the atoms. Therefore, a fraction of the atoms is physadsorbed in the attractive potential well at the surface. It is generally assumed that physical adsorption is characterized by an adsorption energy Ethat determines the sticking time

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

where  $\tau_0 \sim 10^{-12}$  s is the period of vibration of the adsorbed atom in the wall potential, k is the Boltzmann constant, and T is the absolute temperature [20].

Presently, many publications are dealing with studies of different sorts of nonstick coatings with a view to minimize the sticking time. Wieman et al. performed the first direct measurement of the sticking time of Cs with a dry-film coating on Pyrex to make an efficient atom collection in vapor cell magneto-optical traps. In the experiment, adsorption energy of  $(0.40 \pm 0.03 \text{ eV})$ and sticking time with the upper limit of 35  $\mu$ s were measured [21]. The results of the measurements of the adsorption energy and sticking time for Rb achieved by other authors are summarized in Table 1.

The work described in this article is focused on measuring the sticking probability and sticking time of Rb atoms on a film made of a polydimethylsiloxane (PDMS) compound. We measured these quantities using Knudsen's flow of Rb atoms in capillary cells. We demonstrate in what follows that the proposed method is simple and allows accurately measuring both the sticking probability and the sticking time. We use cells with a capillary coated with two different types of PDMS coatings of different viscosities. The experimental studies are preceded by a discussion of a model of atoms in Knudsen's flow in a capillary and by a definition of the relevant parameters. We note that the developed method can be effectively used for the study of many others atoms and molecules on a wide class of coatings.

### 2. EXPERIMENTAL SETUP

A sketch of the setup is shown in Fig. 1.

The Rb vapor density was measured through the detection of the intensity of atomic fluorescence by a fast, movable photodiode connected to a data acquisition (DAQ) system. The fluorescence was excited by a free-running diode laser with the frequency tuned to an Rb atom resonant transition of 780 nm. The fluorescent signals were processed by a digital oscilloscope connected to a computer. The DAQ system allows collecting data with a 0.1 ms resolution in time as well as measuring the variation in the Rb vapor over a wide range. The temperature of the cell walls was measured by a digital thermometer. The absolute Rb vapor density at the origin of the capillary and the Rb source is estimated from the temperature of the of Rb metal drop [27].

In the experiment, we used two groups of three glass capillaries with diameters of 16 mm, 5 mm, and 2 mm in each group. The inner surface of the cell area close to the Rb source and one group of three capillaries were covered by a nonstick coating prepared from a 3 % solution of commercial polydimethylsiloxane (PDMS,  $M_w.92.400, 11000 \text{ mm}^{-2} \cdot \text{s}^{-1}$  viscosity) in ether. Three more capillaries were coated with a different compound (PDMS,  $M_w.182.600, 410000 \text{ mm}^{-2} \cdot \text{s}^{-1}$  viscosity). We call the first type of PDMS with a medium viscosity, the mvPDMS, and the second type with a higher viscosity, the hvPDMS. Both types of PDMS were bought from



**Fig. 1.** Experimental setup: 1 — laser; 2 — turbo pump; 3 — cell; 4 — source of Rb vapor; 5 — glass capillary; 6 — photodiode; 7 — data acquisition system (DAQ); 8, 9 — gauges; 10 — photographic flash lamp; 11 — source of Na vapor

the Aldrich Chemical Company Inc. The cell preparation is described, for example, in Ref. [28]. The chosen capillary is held inside the cell by two aluminum perforated disks, which allow the whole cell to be easily pumped but, because of the absence of the coating between these disks, prevent any penetration of the desorbed atoms around the capillary.

The turbo pump provides a vacuum of up to  $10^{-7}$  mbar in the cell. The rest gas pressure is measured by two vacuum gauges: one attached to the cell area close to the Rb source and the vacuum pump, and the other attached to the entrance of the cell where the probe laser beam enters the cell. We assume that a steady-state vacuum is obtained when both gauge readings are stable and the gauge that is kept away from the pump shows a bit less vacuum than that near the Rb source and the vacuum pump. The steady-state level of the vacuum in a cell with any capillaries inside is usually reached after one week of continuous pumping. This was verified by an RF discharge switched on inside the capillary. The RF voltage is then applied to two gauges that are disconnected from their monitors. The indicator that the steady-state vacuum is achieved is that the discharge luminescence is weak, stable, and uniform along the length of the capillary.

# 3. THEORETICAL CONSIDERATIONS

We consider the diffusion of atoms in the evacuated capillary in detail and assume that the atoms collide with the wall only. These atoms move from the initial position along the distance

$$z(t) = \sum z_i \tag{2}$$

(a one-dimensional shift along the capillary axis). The mean quadratic shift is

$$\langle z^2 \rangle = \left(\sum z_i\right)^2 = N \langle z_i^2 \rangle = \frac{t}{\tau} a^2,$$
 (3)

where t is time, and  $a^2$  and  $\tau$  are the mean quadratic elementary shift and the mean elementary time between two collisions. On the other hand, we know that

$$\langle z^2 \rangle = 2Dt, \tag{4}$$

where D is the diffusion coefficient, and we can write

$$D = \frac{a^2}{2\tau}.$$
 (5)

The time  $\tau$  between two collisions consists of the time needed by the atoms to fly between the walls (the mean pass time  $\tau_f$ ) and the sticking time  $\tau_s$ :

$$\tau = \tau_f + \tau_s. \tag{6}$$

Therefore, the diffusion coefficient D can be written as

$$D = \frac{\tau_f D_0}{\tau_f + \tau_s},\tag{7}$$

where  $D_0$  is the diffusion coefficient in the case  $\tau_s = 0$ . In Knudsen's flow in a cylindrical tube with a diameter d [29],

$$D_0 = \frac{d\overline{v}}{3} \tag{8}$$

and

$$\tau_f = \frac{d}{\overline{v}} \,, \tag{9}$$

where  $\overline{v} = \sqrt{8kT/\pi m}$  is the average atomic thermal velocity at a temperature *T*, and *m* is the mass of the atom. For the natural Rb average mass  $85.493 \cdot 10^{-27}$  kg and room temperature 298 K, we have  $\overline{v} \approx 2.7 \cdot 10^4$  cm/s. For the three capillaries used, with diameters of 16 mm, 5 mm, and 2 mm, the respective mean pass times  $\tau_f$  are 59  $\mu$ s, 18.5  $\mu$ s, and 7.4  $\mu$ s.

The diffusion flow of Rb atoms in a capillary without a buffer gas is governed by the one-dimension diffusion equation

$$\frac{\partial n}{\partial t} = D \frac{\partial^2 n}{\partial x^2} - \frac{n}{\tau_N} \,, \tag{10}$$

where n is the density of the atomic vapor and D is the diffusion coefficient of the atomic flow in the capillary,

$$\tau_N = N(\tau_f + \tau_s) \tag{11}$$

is the lifetime of the atoms before they are absorbed into the inner surface of the capillary by chemical adsorption, and N is the number of bounces (collisions) of the Rb atoms in the capillary before their chemical reaction to the PDMS coating commences. The sticking probability of an Rb atom to the coating is a 1/N. It ranges from zero to one.

The steady-state solution  $(\partial n/\partial t = 0$ , no flash light) can be written in the simple form

$$n(x) = n_0 e^{-x/l},$$
 (12)

where  $n_0$  is the vapor density at the origin of the capillary (x = 0) and

$$l = \sqrt{D\tau_N} \tag{13}$$

is the characteristic length of the decay in density along the capillary. Using Eqs. (3), (4), and (11) we can write

$$N = \frac{3l^2}{2d^2}.$$
 (14)

Then, given the characteristic length l measured in the experiment and the diameter d, we can calculate the number of bounces (collisions) experienced by an Rb atom in the capillary before its adsorption by the PDMS coating and the sticking probability of the Rb atom to the PDMS coating.

To obtain the sticking time  $\tau_s$ , we have to solve nonsteady-state equation (10) with the initial condition

$$n_{t=0} = \delta(0) \tag{15}$$

and the boundary condition

$$n \to 0 \quad \text{as} \quad x \to \infty,$$
 (16)

where  $\delta(x)$  is the delta function which describes a burst of photodesorbed atoms by the photographic flash at the capillary origin x = 0. By using a trivial solution, we find a solution n = n(x, t) that satisfies both the initial and the boundary conditions:

$$n(x,t) = \frac{A}{2\sqrt{\pi Dt}} \exp\left(-\frac{x^2}{4Dt}\right),\qquad(17)$$

where A is some constant. There are two ways to find the sticking time  $\tau_s$ . Using Eq. (17), it is possible to find  $t_m$  when the density n of the atomic vapor approaches its maximum,

$$t_m = \frac{x^2}{2D} \,. \tag{18}$$

Then we can write

$$\tau_s = \tau_f \left(\frac{D_0}{D} - 1\right),\tag{19}$$

where D can be found from Eq. (18) using the experimental values of  $t_m$  and  $D_0$  given in Eq. (8). Another way to obtain the sticking time  $\tau_s$  is to measure the delay time  $t_d$  — the time at the flex point, i. e., where the second derivative of the fluorescence curve is equal to zero. Using Eq. (17), we can evaluate D as

$$D = 0.0459 \frac{x^2}{t_d},$$
 (20)

and using the experimental value of  $t_d$  and x and Eqs. (8) and (19), we obtain the sticking time  $\tau_s$ . In the measurements and calculations of the sticking time in what follows, we use the second possibility only. We note that in these calculations we ignore the term  $n/\tau_N$ in Eq. (10). This omission is possible because the lifetime  $\tau_N$  of Rb atoms in the cell is much longer than either  $t_m$  or  $t_d$ .

## 4. RESULTS

We found that a freshly coated cell did not show any fluorescence from the Rb atoms, meaning that the lifetime and the number of bounces of the atoms in the cell were both very small. This can be attributed to the fact that the fresh coating in the cell has a chemically active surface and volume, probably because of traces of a gas like oxygen or of water adsorbed and mixed with the molecules in the coating. To minimize the residual chemical activity of the coating, we carried out a curing (or passivation) procedure [3, 30, 31]. Maintaining continuous pumping of the cell, we heated the source of the Rb atoms such that the pressure of the alkaline vapor in the cell was about  $10^{-7}$  mbar. After a few days of this curing, fluorescence appeared; first near the source and the origin, then slowly spreading as far as the entrance of the capillary. After one week of the curing process at a higher temperature, the pressure of the Rb vapor was reduced by keeping the source at room temperature. After the curing, the fluorescence became more or less uniform along the length of the cell. The steady-state distribution of the Rb vapor along the capillary could be typically achieved after one or two weeks of exposure to the Rb vapor, but it never reached a uniform distribution along the capillary. We believe that the observed decay in the Rb vapor density in the completely passivized capillary is determined both by the irreversible chemical reaction of the atoms with the PDMS coating and by the slow diffusion of the Rb atoms into the coating toward the glass substrate. We found that cleaning molecular impurities from the area close to the Rb source and the origin of the capillary by the illumination of this area by a powerful halogen lamp can improve the vacuum and the reproducibility of fluorescence dynamics [32].

Because we measure the density of Rb atoms by the detection of the atomic fluorescence intensity, an optical pumping through the hyperfine atomic levels of the atoms can deform the fluorescence signal and hence distort the dynamics of the photodesorbed atoms. To avoid the influence of the optical pumping before any experiment begins, we reflect a small amount of laser radiation back to the laser. In reaction to this feedback, the laser starts to generate a spectrum consisting of a large central peak with two small sidebands separated by about 3 GHz from the central peak. This spectrum is generated by the so-called "oscillation relaxation effect" in diode lasers (additional information can be found in [33]). Then we tune the central peak to the maximum of the  $5S_{1/2}, F = 3 \rightarrow 5P_{3/2}, F' = 4$  $^{85}$ Rb transition, while one of the side bands automatically tunes to the  $5S_{1/2}$ ,  $F = 2 \rightarrow 5P_{3/2}$ , F' = 3<sup>85</sup>Rb repumping transition. This simple method allows illuminating the optical pumping effect in our experiment completely without having to use a repumping laser. It was verified that the signal produced by suddenly opening the laser beam demonstrates a perfectly rectangular form.

The measurement of the number N of collisions is as follows: keeping the cell pumped at a constant temperature, we heat the Rb vapor source to a temperature



Fig. 2. Steady-state fluorescence intensity of Rb atoms as a function of the distance from the capillary origin. The graph has been derived from a capillary 2 mm in diameter coated with hvPDMS

of 30 °C. This creates the density  $1.6 \cdot 10^{10}$  cm<sup>-3</sup> in the Rb vapor, which is high enough to allow a clear detection of a steady-state distribution of the vapor along the capillary, but low enough not to cause the deterioration of the vacuum in the cell. Then we detect the distribution of the Rb density along the capillary and measure the characteristic length l. A typical result of the steady-state fluorescence intensity as a function of the distance x is shown in Fig. 2. The plot is taken from a 2-mm diameter capillary coated with hvPDMS after two months of pumping.

In Fig. 2, we see that the density of the Rb vapor reaches the 1/e level at the distance l from the capillary origin equal to 25 cm. From Eq. (13) and with l = 25 cm and d = 2 mm, it is possible to calculate N. It was found that it takes  $2.3 \cdot 10^4$  collisions (sticking probability  $4.3 \cdot 10^{-5}$ ) for the Rb atoms to be irreversibly absorbed into the hvPDMS coating. This result is consistent with the values published in the literature for various alkalis, preponderantly Na on paraffin passivized by Na atoms [11] and Rb on PDMS passivized by either Na or Rb atoms [31]. Results of the measurements of N as a function of the pumping time are reported in Table 2 for capillaries 2 mm in diameter coated with hvPDMS.

In principle, the fairly long vapor distribution and large number of bounces observed can be attributed to the collision of the Rb atoms with the film surface at the detection point that are released by sputtering of other Rb atoms previously stored at this point. This

Table 2.Number N of collisions as a function ofpumping time for 2 mm in diameter capillaries coatedwith hvPDMS

| Pumping time         | N               |
|----------------------|-----------------|
| 1 week               | $\sim 10^4$     |
| 1 month              | $2\cdot 10^4$   |
| $2  \mathrm{months}$ | $2.3\cdot 10^4$ |



Fig. 3. Sticking probability 1/N for the adhesion of Rb atoms to hvPDMS as a function of the PDMS film temperature

exchange process was found by Guckert et al. [34] to be important for radioactive atoms, whereas it is not observed in stable atom experiments. We checked the negligibility of this possible systematic effect by curing the capillary using Na atoms that cannot be detected by the probe laser light used. We found that the fluorescence behavior and the number of bounces were exactly the same as for an Rb passivized cell.

We perform the measurement of the sticking probability as a function of the PDMS film temperature. To do this, we cool the part of the cell containing the capillary using liquid nitrogen and then leave the cell to heat itself until room temperature is reached, then measure l and calculate the sticking probability. To take measurements above room temperature, we heat the same cell area with the capillary using a heater. Measurements of the sticking probability P of the Rb atoms to hvPDMS as a function of temperature are presented in Fig. 3, taken after 2 months of pumping. It is evident that in the temperature range from -100to  $160 \,^{\circ}$ C, the sticking probability does not change to



Fig. 4. Fluorescence intensity of Rb atoms as a function of the time triggered by a flash of light in the 2 mm capillary cell coated with mvPDMS. The time scale is 10 ms/div, and the intensity scale is 5 mV/div

any great extent, but it does sharply increase at a temperature lower than -100 °C. This temperature corresponds to the surface adsorption energy E = 0.026 eV, which, according to Eq. (1), implies the sticking time  $\tau_s = 2 \cdot 10^{-11}$  s.

To measure the sticking time of Rb atoms to the PDMS film directly, we cool the Rb vapor source to below the steady-state density of the vapor. Then we illuminate the area of the cell (as shown in Fig. 1.) close to the Rb source and the origin of the capillary by a photographic flash lamp. Next, we detect the dynamics of the fluorescence signal of the burst of desorbed atoms and measure the delay in the arrival of the atoms at the detection point. We measure the delay time as a function of the distance between the detector and the origin. Under this ultra-high vacuum condition, the delay in the arrival of the atoms at the detection point is principally attributable to the many collisions of the atoms with the capillary wall, and this delay can be increased by a nonzero stick time in every collision. Because the mean path time in a narrow capillary is relatively small, even a very short sticking time would have a significant effect on the delay.

Figure 4 shows a typical example of a recording of the Rb fluorescence intensity as a function of the time taken in a cell with a capillary of 2 mm coated with mvPDMS compound. This curve was taken at a distance of 20 cm from the origin. It can be seen that



Fig. 5. Fluorescence intensity of Rb atoms as a function of time triggered by flash light. In curve A, the capillary diameter is 16 mm, while in curve B the capillary diameter is 2 mm. In both cases the coating is hvPDMS and the signals are taken at a 23 cm distance from the capillary origin

the intensity of the fluorescence of the Rb atoms as a function of the time immediately after the flash (sharp peak at t = 0) is close to the low steady-state intensity at a selected distance of the detector from the capillary origin. After some delay, it increases and then, after approaching a maximum, the intensity slowly declines. We note that the form of this curve is in complete accordance with the prediction of Eq. (17).

Figure 5 shows two fluorescence curves taken at a distance of 23 cm from the origin of two capillaries: one 16 mm (curve A) and the other 2 mm (curve B) in diameter. In both cases, the coating is hvPDMS. It can be seen that the ratio of  $t_d^B/t_d^A$  and  $t_m^B/t_m^A$  is also near 8, in accordance with Eqs. (18) and (20), which predict a dependence on the capillary diameter d. This result can be considered a check on the agreement between the theory and the experiment.

Measurements of  $t_d$  as a function of the distance xare reported in Fig. 6 for capillaries 5 mm in diameter coated with two sorts of PDMS. For hvPDMS, the data were collected in three periods: one week after installation, after one month, and after two months of pumping. The data for mvPDMS were taken after two months of pumping. The theoretical curve for  $\tau_s = 0$ calculated above for the Rb atoms is also shown. It can be seen from these measurements that  $t_d$  is proportional to  $x^2$ , as predicted by Eq. (20).



**Fig.6.** Measurements of the delay  $t_d$  as a function of the distance x between the capillary origin and the detector. The capillary diameter is 5 mm. Data for mvPDMS after two months of pumping ( $\times$ ) and for hvPDMS at different times (one week after installation ( $\Box$ ), one month ( $\triangle$ ), and two months ( $\circ$ ) of pumping). The solid line is the theoretical curve for  $\tau_s = 0$ . Error bars are omitted for clarity

Table 3.Sticking time and its uncertainty calculatedby fitting the data in Fig. 6 according to the theoreticalmodel

| Coating                     | $\tau_s, \ \mu s$ | $\delta \tau_s, \ \mu s$ |
|-----------------------------|-------------------|--------------------------|
| hvPDMS                      | 111               | 10                       |
| hvPDMS (1 month)            | 38                | 4                        |
| hvPDMS $(2 \text{ months})$ | 22                | 3                        |
| mvPDMS (2 months)           | 49                | 6                        |

To calculate the sticking time  $\tau_s$ , we derived our data from Eq. (20). We evaluated the uncertainty  $\delta \tau_s$  using the standard deviation given by the fit for the values of D. The calculated sticking times are reported in Table 3.

It can be seen that the experimental results tend to approach the theoretical ones only after a long-term pumping of the coated cell. For example, the results shown in Fig. 6 demonstrate that the deviation between the experimental and the theoretical  $t_d$  decreases if the sort of coating is changed from mvPDMS to hvPDMS and/or if the cell is pumped for a longer time. For example, after two months of pumping, the difference between the experimental and theoretical curves for hvPDMS grows smaller, and this is important, but is not zero.

We note that the measured times for both types of PDMS are about million times larger than the sticking time  $2 \cdot 10^{-11}$  s derived above from the surface adsorption energy of Rb atom and temperature of the coating. These times are consistent with those measured in [21] for Cs atom on a dry-film coating on Pyrex (less than 35 ms), and are larger than in [25, 26] for Rb atom for octadecyltrichlorosilane and paraffin-coated surfaces.

It is clear that this surprisingly large difference between the sticking time estimated from Eq. (1) and the sticking time measured directly in the nonsteady-state experiment cannot be attributed to a slowing-down of the Rb atoms as a result of their collisions with the rest gas molecules. At a working vacuum pressure of  $10^{-7}$ -10<sup>-6</sup> mbar, n is of the order of  $10^{9}$ -10<sup>10</sup> cm<sup>-3</sup>. With this estimated n and the typical cross section for a collision of the order of  $10^{-15}$  cm<sup>2</sup>, we find that the mean free path  $l_{path}$  is of the order of  $10^5-10^6$  cm. Hence, the estimated mean free path of the Rb atoms in the cell is much larger than the diameters and lengths of all the capillaries used in our experiments. Therefore, the influence of the collision of Rb atoms with the rest gas molecules on the results of the measurements is surely negligible.

A possible interpretation of the difference can be as follows. When an atom collides with a surface it can be linked there for some period of time because of the van der Waals attractive force. We believe that once trapped, the atom can diffuse inside a PDMS film, then diffuse back to the surface, and then in turn be desorbed back to the vapor. Hence, a long sticking time has to depend on how deep the atoms can diffuse inside the coating. This is suggested by the fact that the sticking time for mvPDMS that has a higher diffusion rate has a longer sticking time than hvPDMS, in which the diffusion is less pronounced. It is known that PDMS films exhibit slow decreasing permeability and diffusion rate with a long aging time [35]. This can explain the slow decrease in the sticking time during two months that was observed in the experiment. We note that the adsorbed atoms can be attracted inside the film by the coating convective flow. Choosing a surface that has a low diffusion rate (or, in other words, has a high viscosity) would make it less likely that the atoms would remain inside the coating for a too long period of time. We believe that Eq. (1) is valid for particle collisions with a solid surface only.

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## 5. CONCLUSIONS

We present the results of a systematic study of Knudsen's flow of Rb atoms in cylindrical cells (tubes and capillaries) coated with two types of PDMS compounds of different viscosities. We have developed a one-dimensional model that agrees with our observations of the diffusion flow of Rb atoms in a capillary. Our model includes the decay of the density of the Rb vapor along a capillary because of the chemical adsorption of atoms into the PDMS film surface, and the dependence of the delay of the desorbed atoms at the detection point on both the mean free path time and the sticking time. We have shown that because of the many collisions of the Rb atoms with the capillary under ultra-high vacuum conditions, it is possible to accurately estimate both the sticking probability and the sticking time. We have described the results of the measurements of these parameters for two types of PDMS of different viscosities and as a function of the physical aging of the organic film. We observed a fairly long sticking time and proposed a tentative explanation for this surprising result.

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