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# Spectroscopy of cesium atoms adsorbing and desorbing at a dielectric surface

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**ABSTRACT** We use evanescent waves in a counterpropagating beams configuration to study the adsorption/desorption processes at a Cs vapor/dielectric interface in a sealed cell. Atoms close to the surface are velocity-selectively spin-polarized before adsorption by an amplitude-modulated pump beam. We subsequently observe the contribution of the desorbed atoms to the probe-beam absorption by way of phase-sensitive detection. We measure the number of desorbing polarized Cs atoms as a function of the surface temperature. The analysis of results is done through a simple thermodynamical model for the atomic desorption and we discuss its validity to infer the adsorption energy of the cesium atoms on a fused-quartz surface.

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## 1 Introduction

Among the motivations to study the fundamental processes of interaction between an atomic gas and a dielectric cell window we point out that, whereas in most techniques for transmission spectroscopy the atomic interactions with the reservoir walls may be neglected due to the usual integration of the atomic response over the probed volume, in many experiments these interactions with the cell walls indirectly affect the process to be studied, through optical de-excitation or thermalization of the hyperfine-levels population of the atoms at the surface. Therefore the atom–wall interactions turn out to be of great importance. This is the case, for instance, in experiments of light-induced drift [1] or in magneto-optical traps for neutral atoms in some particular experimental conditions [2]. Due to surface processes, glass cells exposed to dry cesium vapor become electrically conductive, prohibiting their use for experiments requiring the application of an external electric field [3]. The surface also strongly influences the shape of the optical resonance lines of reflection spectroscopy [4–7]. The atom–surface interactions may also play a decisive role in transmission spectroscopy through thin cells [8]. Thus it is of interest to have a good knowledge of the fundamental processes occurring to the atoms at the surface, specifically

the adsorption time and energy, in order to take into account the vapor interaction with the cell walls in these kinds of experiments. As a matter of fact, there are few studies of the microscopic kinetics of the adsorption–desorption processes involving alkali atoms and dielectric surfaces, contrasting with the numerous experiments with light atoms and metallic or dielectric surfaces [9]. Also, surface experiments are frequently carried out in clean, or at least coverage-controlled, conditions, which permits an easier, although still complex, theoretical interpretation [9, 10]. Nevertheless, a lot of atomic physics experiments where the surface effects are relevant have to be carried out in conditions where there is not such good control of surface parameters such as coverage, surface structure and orientation, contamination, swelling, etc. Measurements of the adsorption time and adsorption energy for interfaces between alkali atoms and dielectric surfaces have been reported [1, 3, 11–15], but more detailed data are necessary for a better understanding of the mechanisms involved and, specifically, there are no systematic studies of the adsorption/desorption of alkali atoms as a function of the surface temperature. In this paper we present our measurements of the evolution of spin-polarized cesium atoms on a quartz window of a cell, using a spectroscopic technique in the usual conditions employed for atomic spectroscopy.

## 2 Adsorption of atoms on solid surfaces

In the adsorption process atoms move toward a surface and are trapped in the surface well with a certain sticking probability. As a result, the particles stick or diffuse on the surface during a mean time  $\tau$  and are finally desorbed back into the gas phase. In a microscopic analysis, two physical origins may be distinguished for the adsorption of neutral particles on surfaces, according to the range of the adsorption energy,  $E_a$ , they involve: the physisorption, essentially originating in the long-range van der Waals dipolar interaction scaling as  $z^{-3}$  ( $z$  being the distance to the surface); and the chemisorption, binding the atoms more strongly to the surface through chemical forces. Actually, the frontier between these two regimes of adsorption is not well defined [16], but is usually considered to lie around  $E_a = 0.5$  eV for an alkali atom–glass wall system.

For a regular clean surface the adsorption of an atom occurs at definite energies, which may be calculated from the

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Schrödinger equation for the surface potential [17]. We are particularly interested in a surface potential well, arising from the combination of a repulsive (Coulomb) and an attractive (van der Waals) potential, in the sense that it constitutes a bidimensional wave guide for neutral adsorbed atoms [18]. One motivation of this work is to determine the mean energy of the adsorption potential in view of experiments that put in evidence the quantum nature of the interaction for atoms slightly bound to a dielectric surface. The signature of such quantum states for the atomic center-of-mass was only indirectly observed in experiments of light atoms scattering on crystalline surfaces [9], permitting the empirical determination of the potential parameters through the observed selective adsorption resonances [19, 20]. An optical technique to prepare such quantum states for cesium atoms and a dielectric surface system was recently proposed [21], but no experimental observation has been reported. In fact, dynamical aspects of the adsorption and desorption processes are usually described by phenomenological thermodynamic and kinetic models.

In this description, the desorption rate of the trapped atoms is assumed to have a classic Arrhenius expression:

$$\nu = \nu_0(\theta) \exp\left(-\frac{E_a(\theta)}{k_B T_S}\right) \theta^n, \quad (1)$$

where  $\theta$  is the coverage,  $\nu_0$  the pre-exponential factor, and  $E_a$  the adsorption energy, i.e. the energy the adsorbed atom has to acquire in order to escape from the surface well.  $k_B$  is the Boltzmann constant,  $T_S$  the surface temperature, and  $n$  the desorption order [22]. The mean time of adsorption for an atom on the surface takes the form:

$$\tau = \tau_0(\theta) \exp\left(\frac{E_a(\theta)}{k_B T_S}\right). \quad (2)$$

The characteristic time  $\tau_0 = 1/\nu_0$  is predicted to lie between  $10^{-13}$  and  $10^{-12}$  s [23], but may deviate from these values by many orders of magnitude, as often observed on metallic or semiconductor surfaces [24].

From (2) we see that, at a given coverage  $\theta$ , a measurement of the adsorption time as a function of the surface temperature would allow one to determine the adsorption energy and the pre-exponential factor, through the expressions:

$$E_a(\theta) = -k_B T_S^2 \frac{d(\ln \tau(\theta, T_S))}{dT_S}, \quad (3)$$

$$\tau_0(\theta) = \tau(\theta, T_S) \exp\left(-\frac{E_a(\theta)}{k_B T_S}\right). \quad (4)$$

The aim of this work is to obtain information on the residence time of atoms of a low-density cesium vapor on a dielectric window.

### 3 Sub-Doppler spectroscopy with evanescent waves

The idea of the optical technique used in this work [11] is to prepare atoms going toward the surface in a particular state and to probe them when they are desorbed back into the gas phase after having spent a certain time adsorbed on the surface. A laser field, the pump beam, must therefore induce in the atoms a change of state that should survive (at least partially) to the collision with the surface. In the

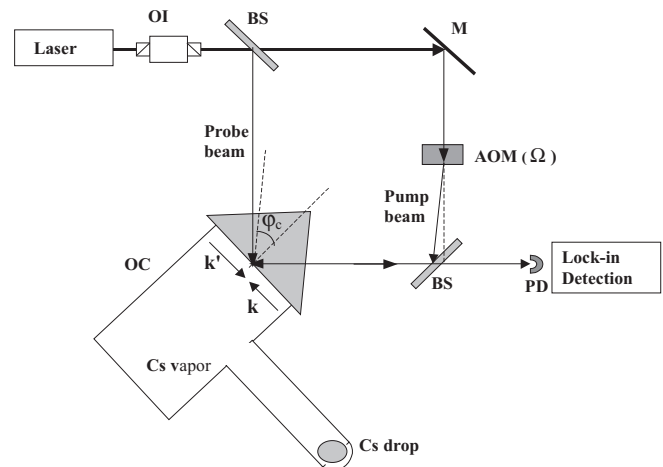
case of alkali atoms adsorbed on glass surfaces, the optical excitation is destroyed at the surface, but the hyperfine polarization is only partially thermalized during the atom/surface interaction, with a degree of depolarization depending of the type of surface [25, 26]. This study is therefore performed with a sample of Cs atoms, spin-polarized through velocity-selective optical pumping by the pump-laser beam.

The separation between the  $F = 3$  and  $F = 4$  hyperfine sublevels of the cesium  $6S_{1/2}$  ground state is 9.2 GHz, so that their thermal populations at room temperature are in the ratio of their respective degeneracies. An out-of-equilibrium sample can be obtained by way of a laser beam, resonant with a transition between ground and excited sublevels, which will transfer the population to the non-resonant ground sublevel through spontaneous de-excitation. This optical pumping of the population is velocity-selective in the direction of the laser-beam wave vector  $\mathbf{k}$ , so that the contribution of the pumped atoms to the absorption of a resonant counterpropagating probe beam yields a sub-Doppler line shape. This sub-Doppler feature is lost if a velocity-changing process occurs before the pumped atoms are probed. This is the case for the atoms probed as they leave the surface with a velocity distribution which depends essentially on the surface temperature. As there is no noticeable specular reflection [27], there is no memory of the incident velocity.

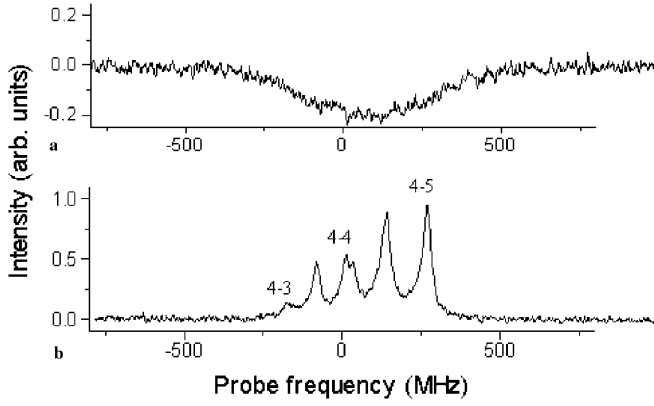
In the experiment described here, atoms close to the surface are pumped and probed by confined electromagnetic fields obtained by total internal reflection of two counterpropagating resonant laser beams at a prism/vapor interface. The evanescent waves in the vapor side of the interface propagate along the surface with wave vectors  $\mathbf{k}$  and  $\mathbf{k}'$  (see Fig. 1) and their amplitudes decrease exponentially along the normal to the surface, with a decay length

$$\Lambda = \frac{\lambda}{2\pi \sqrt{n_p^2 \sin^2 \varphi - 1}}, \quad (5)$$

where  $\lambda$  is the radiation wavelength,  $n_p$  the refractive index of the dielectric prism, and  $\varphi$  the incidence angle at the prism/vapor interface. This short decay length, of the order



**FIGURE 1** Experimental set-up for the saturated absorption with evanescent waves. OC, optical cell; AOM, acousto-optic modulator; PD, photodetector; M, mirror; BS, beam splitter; OI, optical isolator



**FIGURE 2** Optical spectra of the  $D_2$  line of Cs: **a** quadrature detection of the probe laser showing the thermalized background of the desorbing atoms and **b** comparison with the Doppler-free in-phase signal, where the main hyperfine transitions are indicated

of  $\lambda$ , strongly depends on the incident angle, which is a parameter to be carefully adjusted to obtain good signal-to-noise ratio and resolution. The transit time of the atoms with a velocity component normal to the surface  $v_z$  may result in a spectral broadening [28] that becomes important when the transit time in the evanescent fields  $t = \Lambda/v_z$  approaches the limiting value  $1/\Gamma$ , where  $\Gamma$  is the natural line width of the resonant transition. As a result the resolution of the sub-Doppler signal diminishes with increased incidence angle for total internal reflection.

Pumped atoms spend on the surface a mean adsorption time,  $\tau$ , much longer than a typical time of free flight in the evanescent-wave region. Due to the short extent of the evanescent fields, this time of free flight is of the order of a few nanoseconds only. Hence, *assuming* that their spin polarization outlives this process, a time-resolved pump-probe technique is suitable to evaluate the mean adsorption time of Cs atoms at the surface. Studying the temporal decay of the probe absorption after the pump beam has been turned off, in a time-resolved pump-probe technique, is equivalent to studying the phase-shifted probe response when a c.w. pump is amplitude-modulated (AM). As discussed above, the optically pumped atoms probed after spending a mean adsorption time  $\tau$  on the surface yield a Doppler-broadened signal, easily discriminated from the ‘instantaneous’, sub-Doppler, atomic response (Fig. 2b) in a phase-shift measurement. The sticking probability is assumed to be unity [27], so that the dephased signal (Fig. 2a) appears as Doppler-broadened, free of any sub-Doppler structure that would correspond to the response of atoms that did not interact with the surface.

#### 4 Experimental results

The experimental set-up is schematized in Fig. 1. The cesium vapor is contained in a sealed cell, consisting of two parts: one is the cesium reservoir; the other is the body of the cell, with a quartz prism at one extremity. Each part can be separately heated, permitting independent control of the vapor pressure and of the window temperature. The temperatures of the reservoir and of the prism/vapor interface are measured by Chromel–Alumel thermocouples and an overheating of the

body is assured in order to avoid the condensation of the cesium on the windows.

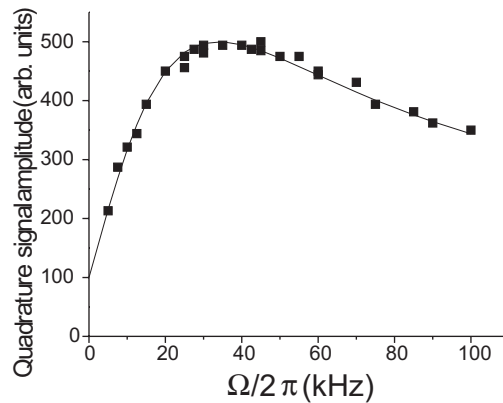
The pump and the probe beams are issued from the same diode laser, tuned around the frequency of the  $D_2$  line of Cs ( $\lambda = 852$  nm). The pump, with its amplitude modulated at the angular frequency  $\Omega$  by an acousto-optic modulator, is directed onto the prism so that the angle of incidence at the prism–vapor interface,  $\varphi$ , is slightly larger than the critical angle  $\varphi_c$  for total internal reflection,  $\Delta\varphi = \varphi - \varphi_c \approx 0.5^\circ$  ( $\varphi_c = 43.5^\circ$ , with the index of refraction of the fused-quartz prism  $n_p = 1.45$ ). The probe beam is aligned counterpropagating with the pump. The powers of the probe and pump beams are  $65 \mu\text{W}$  and  $2.5$  mW, respectively, both with a diameter of 2 mm. The absorption of the probe beam by the Cs atoms in the vapor cell is detected by a photodetector and treated by a lock-in amplifier. The modulation had a sinusoidal shape but we did not notice any difference in the results obtained using a square modulation. The in-phase and the quadrature signals appear as shown in Fig. 2. In fact, the assumption that the interaction between the vapor atoms and the modulated pump is instantaneous neglects possible dephasing effects due to the atomic response time at high frequency, for example, or in the presence of saturation and optical pumping. The phase of the ‘quadrature signal’ is therefore slightly adjusted to eliminate sub-Doppler contributions corresponding to atoms still not velocity-thermalized by the surface, i.e. detected before being adsorbed on the surface.

A series of measurements was carried out at fixed surface temperatures, and we obtained the relative number of desorbed atoms as a function of the rate of the pump amplitude modulation. The temperature  $T_R$  of the reservoir, i.e. the vapor density, was maintained constant throughout the various measurements. A typical result is shown in Fig. 3 for a surface temperature of 372 K. The curve shows a dispersive behavior of the signal amplitude as a function of the AM rate.

The dispersive curve is satisfactorily described in the frame of a simple, first-order desorption law:

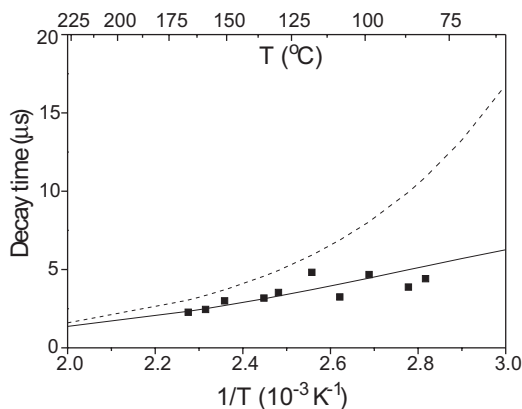
$$\frac{dN}{dt} = -\gamma N + A(1 + \cos \Omega t), \quad (6)$$

where  $N$  is the number of optically pumped adsorbed atoms,  $\gamma$  a decay time constant, and the last term a pumping term



**FIGURE 3** Number of desorbed atoms as a function of the pump modulation frequency, for  $T_S = 372$  K and  $T_R = 344$  K. *Squares*: experimental measurements; *full line*: theoretical fit (see text)

at the frequency of the modulation. The best fitting however requires that we allow for a constant background, corresponding to a non-negligible number of atoms spin-polarized by the pump beam, but desorbing at times independent of the modulation phase. We interpret this contribution as being due to the spin exchange [29] between Cs atoms at the surface, where atoms are polarized via this exchange process and leave the surface at times decorrelated from the pump-modulation phase. We also observed that for some experimental conditions, the time-dependent part of the curves could be fitted by two dispersive curves, the fast contribution probably coming from the atoms of the vapor excited far from the surface by spurious laser pump beam reflections [30]. The existence of this fast contribution could be visualized through a broad contribution in the signal of the in-phase detection, and could be avoided or minimized by a careful alignment of the beams and a judicious placement at the prism internal face. The delayed response of atoms not having interacted with the surface may be detected by the probe beam, especially at the ‘high-frequency’ modulations. This contribution is minimized by decreasing the interaction length in the vapor, i.e. by increasing the incidence angle of the probe beam. On the other hand, the ‘low-frequency’ signal may be overestimated due to the contribution of atoms having collided with a lateral wall of the cell and flown back into the evanescent-wave volume. The cell is a cylinder with an internal diameter of 18 mm and a length of 50 mm, and the laser beams are aimed at the center of the circular illuminated entrance window, so that the shortest distance the vapor atoms have to travel to meet a cell wall out of the evanescent-wave volume is approximately 10 mm. Assuming a desorption rate proportional to the cosine of the angle of desorption, we can neglect the contribution of atoms moving slowly almost parallel to the surface that could collide with the illuminated window at distances less than 10 mm. At the highest temperature at which we worked (440 K), the thermal velocity of the Cs atoms is 286 m/s and it takes them  $\approx 70 \mu\text{s}$  to travel this distance and return into the evanescent-wave volume. These atoms will therefore contribute to the quadrature probe absorption curve at a corresponding modulation frequency  $\leq 2.3 \text{ kHz}$ . However, as could be verified on the spectra, the number of these atoms is small.



**FIGURE 4** Decay time of the polarized adsorbed atoms,  $1/\gamma$ , as a function of the inverse of the surface temperature (*solid squares*: experimental measurements; *solid line*: best fit with  $T_d = 10^5 \text{ s}$ , see text). The *dashed line* represents the adsorption time,  $\tau$ , as deduced from this best fit

A maximum in the quadrature (delayed) signal is obtained for a modulation frequency corresponding to the decay rate  $\gamma$  (see (6)) of the polarized atoms adsorbed on the surface. This decay rate is the sum of the decay rates  $\tau^{-1}$  and  $T_d^{-1}$  corresponding to the processes of desorption and of surface depolarization, respectively:

$$\gamma = \frac{1}{\tau} + \frac{1}{T_d}. \quad (7)$$

Our measurements of  $\gamma$  were carried out for different values of the surface temperature, ranging between 355 and 440 K. The results are shown in Fig. 4.

We observe on this curve that the decay time of polarized adsorbed atoms increases very smoothly with decreasing temperature, being almost constant in the range of temperatures explored.

## 5 Discussion

### 5.1 Wall relaxation of the hyperfine polarization

The interpretation of Fig. 4 requires a preliminary discussion on the depolarization process on the surface. During the time the atom is adsorbed on the surface, interactions with fluctuating magnetic fields thermalize its hyperfine polarization, at a mean rate that essentially depends on the magnitude and on the correlation time of the depolarizing interaction. In a given cell, the relaxation rate has the form [31]:

$$T_1^{-1} = \frac{\tau}{\tau + \tau_v} \left( \frac{2\gamma_g^2}{3} \frac{h^2 \tau_c}{1 + (\tau_c W)^2} \right), \quad (8)$$

where  $\gamma_g$  is the gyromagnetic ratio of the electronic angular momentum,  $\tau$  the adsorption time,  $\tau_v$  the mean time of flight between alkali–surface collisions,  $h$  and  $\tau_c$  the magnetic field amplitude and the correlation time of the depolarizing interaction at the surface, and  $W$  the ground-state hyperfine splitting of the Cs atom. The experimental determinations of the surface relaxation rates then usually depend on the adsorption time, and there are few data available on the fundamental relaxation parameters at the surface [32–34], although it seems that the depolarization properties of surfaces may be much more reproducible than their adsorption properties [33].

In the limiting case of a weakly depolarizing surface ( $T_d \gg \tau$ ),  $\gamma$  would be the desorption rate. However, spin relaxation always occurs in real systems. In the literature, two surface relaxation regimes have so far received attention: on the one hand, the necessity to produce large numbers of spin-polarized atoms for nuclear or atomic physics applications [36] has led to the study of special coated walls that only depolarize after hundreds or thousands of wall collisions [34]. On the other hand, very few data on relaxation at uncoated glass surfaces are available, and the assumption usually made is that a unique collision with the wall is sufficient to completely thermalize the ground hyperfine levels on this kind of surface [35]. However, Grafström and Suter [26] measured the depolarization probability per wall collision for Na atoms on a bare Pyrex-glass surface and found a value of approximately 0.5.

The experimental technique we used does not permit the deconvolution of the two decay processes of desorption and

depolarization, so that we have to estimate the surface depolarization time  $T_d$  (the time it would take to thermalize the hyperfine levels on the surface if the adsorption time were sufficient, i.e. in the case  $\tau \gg T_d$ ). The surface depolarizing rate  $T_d^{-1}$  would then correspond to the term in brackets in (8), which depends on the depolarizing interaction independently of the adsorption time. The factor preceding this term is simply the probability of finding an atom at the surface rather than in the volume of the cell. In our measurements, the surface depolarizing time is longer than the adsorption time. On the contrary, there would be a significant signal only at the highest modulation rates used. However, the surface depolarizing time is not much longer than the adsorption time, as indicated by the value of  $\approx 0.5$  for the depolarization probability per wall collision [26] and by our own measurements of the relaxation time  $T_1$  in glass cells (see the Appendix). In other words,  $T_d$  and  $\tau$  are of the same order of magnitude. As  $T_d$  is longer than  $\gamma^{-1}$  (see (7)), which, in the temperature range we explored, is at most equal to  $5 \times 10^{-6}$  s, it seems reasonable to assume that the surface depolarization time  $T_d$  is of the order of  $10^{-5}$  s.

The correlation time  $\tau_c$  probably diminishes with increasing temperature but not so strongly as  $\tau$  does. In the range of temperatures we explored, we neglect this temperature dependence and take for  $T_d$  in (7) the value  $10^{-5}$  s, with the adsorption time  $\tau$  obtained through (2). In this case, the parameters  $\tau_0$  and  $E_a$  that better fit the experimental measurements of  $\gamma^{-1}$  (solid line in Fig. 4) are  $1.4 \times 10^8$  s and 0.2 eV, respectively. The dashed line in Fig. 4 represents the temperature variation of the adsorption time  $\tau$  for these parameters.

## 5.2 Adsorption parameters

To further discuss the results presented above, we first need to evaluate the coverage of adsorbed Cs atoms on the cell window during our measurements. The surface density of adsorbed atoms is given by [23],

$$\bar{n} = \frac{1}{4} N(T_R) \bar{v}(T_S) \tau(T_S), \quad (9)$$

where  $N$  and  $\bar{v} = \sqrt{8k_B T_S / \pi m}$  are the density and the mean velocity of the Cs atoms in the vapor and  $m$  is their mass. For each series of measurements  $\bar{n}$  is calculated by substituting in (9) the adsorption time  $\tau$  by its value evaluated as explained in Sect. 5.1, and the coverage  $\theta$  is obtained from the ratio  $\theta = \bar{n}/n_0$ , where  $n_0$  is the Cs surface density for a complete monolayer:  $n_0 = 2 \times 10^{14}$  atoms  $\text{cm}^{-2}$  [3]. We obtain values of  $\theta$  of the order of a few  $10^{-4}$ , i.e. corresponding to very low coverages, at which the adsorbed Cs atoms may be considered as isolated and their mutual interactions neglected. In this case, considering the coverage as constant, we can try to evaluate the parameters  $E_a$  and  $\tau_0$  using (3) and (4), respectively. We find  $E_a/T_S^2 \approx 13 \times 10^{-7}$  eV/K<sup>2</sup>. As  $T_S$  is increased, the value of  $E_a$  increases from  $\sim 0.16$  to  $\sim 0.25$  meV in the temperature range examined, while  $\tau_0$  decreases from  $\sim 4 \times 10^{-8}$  to  $\sim 4 \times 10^{-9}$  s. First of all we note that these values for  $E_a$  are rather different from the ones obtained by other authors, around 0.50 eV [12, 14]. However, the value of  $10^{-12}$  s for  $\tau_0$  [12, 13, 23] has been shown to be mistaken many times [24]. Secondly, we find that  $E_a$  and  $\tau_0$  vary with

the surface temperature. This may signify that, at least in the frame of this interpretation, we cannot consider the coverage as constant: at a fixed reservoir temperature, the coverage decreases as  $\sqrt{T_S} \exp(E_a/k_B T_S)$  for increasing wall temperature  $T_S$ , so that the increasing of  $E_a$  with  $T_S$  seems to suggest, even in this low-coverage regime, a repulsive interaction between adsorbed atoms [37]. Finally, it may be stressed that, in agreement with all the reported measurements of the desorption parameters [24],  $E_a$  and  $1/\tau_0$  move in the same direction as a function of the surface temperature. From this analysis it follows that, even by taking into account a favorable value of the surface depolarization time  $T_d$  (a longer value of  $T_d$  would decrease the importance of the depolarization rate in (7) and so lead to a shortest value of  $E_a$ ), we can not fit our experimental results by an adsorption time of the form (2) with  $\tau_0$  and  $E_a$  with values around  $10^{-12}$  s and 0.5 eV, respectively.

As a matter of fact, we do not know what is the real state of the surface of the cell used in our experiments. It certainly is not a clean quartz–Cs vapor interface. We calculated the coverage  $\theta$  as a reversible function of the temperatures  $T_R$  and  $T_S$ , but the nature of the surface also depends on the ‘history’ of the cell. Indeed, the preparation of that kind of sealed cell for general spectroscopic purposes is such that its walls are ‘saturated’ with alkali atoms, probably in a thickness, into the solid, of a few atomic diameters. A typical evolution happens with new cells, when exposed for the first time to a dry (no condensation on the walls) alkali atomic vapor: in spite of a constant supply of atoms through heating of the reservoir, the vapor density in the body of the cell (monitored e.g. by light-induced fluorescence) may take a very long time (tens to hundreds of hours at room temperature [38]) to stabilize and, in particular, to be spatially uniform and to attain a stationary regime where the vapor density in the cell body is determined essentially by the temperature of the reservoir. This suggests a complex evolution of the cell window internal surfaces involving bulk contamination [39]. The experiments related here were carried out in this condition of Cs-‘saturated’ walls, in contrast to the majority of surface studies where the surfaces are cleaned (through etching, sputtering, annealing, etc.) prior to each measurement. Doubts remain therefore about the real state of the surface where, in addition, thermionic emission at glass–hot alkali vapor interfaces may take place, leading to the creation of an electron gas at the surface [3], and where stray electric [3] and magnetic [40] fields may be present, modifying the dielectric nature of our surface, for which the simple model assumed above (see (1)–(4), (6)) may no longer be valid.

The influence of the contamination feature was demonstrated in a series of experiments (see the Appendix) we carried out to measure the temporal decay of the ground-state hyperfine population in evacuated sealed cells containing cesium vapor at low density, where the relaxation mechanism was essentially the atom–surface interaction. Bouchiat and Brossel [31] have observed that contaminated walls alter the relaxation time of optically oriented alkali atoms on paraffin-coated walls. We verified the existence of the same phenomenon on bare glass surfaces, similar to the internal walls of our cell with a prismatic window. In the short (1-cm long), ‘clean’ cell (see the Appendix), the measured depolarization time  $T_1$  was 58  $\mu\text{s}$ , and the calculated time of flight  $\tau_v$  46  $\mu\text{s}$ .

In the 2-cm-long cells the time of flight was 61  $\mu\text{s}$ . We measured a depolarization time of 46  $\mu\text{s}$  in the less contaminated one and of 40  $\mu\text{s}$  in the most contaminated one. The depolarization time  $T_1$  is proportional to  $(\tau + \tau_v)/\tau$  [31], where  $\tau$  is the adsorption time and  $\tau_v$  the time of flight, so that  $T_1$  increases with the linear dimensions of the cell, for constant surface conditions (same  $\tau$ ). A ‘clean’ 2-cm-long cell should then lead to a depolarization time longer than in the clean 1-cm-long cell, while we measured shorter times. This behavior obviously confirms that the wall contamination alters the adsorption time:  $\tau$  increases with the degree of contamination, as shown by the comparisons between the depolarization times for the three cells with different degrees of Cs contamination. This result may be understood by considering that the body of the contaminated cells contains sources of Cs atoms in the surfaces and that the polarized Cs atoms colliding with the metal drops are replaced in the gas phase by atoms from these sources. These results corroborate the suggestion that the measurements with evanescent fields described above were carried out in conditions rather comparable with these contaminated cells.

## 6 Conclusion

In conclusion, we used a reflection spectroscopic technique to measure the temporal decay of interaction processes, namely the hyperfine relaxation and the adsorption of cesium atoms and a saturated fused-quartz surface. From experimental data, we estimated the adsorption time and found it to exhibit a very weak temperature dependence in the explored range of wall temperature. The interpretation of this behavior through a classic Arrhenius description leads to values of the adsorption energy  $E_a$  and of the time pre-exponential factor  $\tau_0$  of the order of 0.2 eV and  $10^{-8}$  s, respectively. These values vary slightly with the surface temperature in the low-coverage regime studied. These results raise new questions about the surface that we actually study and about the adequacy of the theoretical model usually employed to describe the interaction between alkali atoms and dielectric surfaces. The spectroscopic technique that we used in this paper appears adapted for further study of the dynamics of atom–surface interactions, as well as the processes of spin exchange and spin relaxation on surfaces.

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## Appendix

### Measurement of the decay time of the ground-state hyperfine population

A series of experiments was carried out to measure the relaxation time of the optically pumped hyperfine populations, on different optical cells. A large laser beam (2.0-cm diameter, 3.0 mW/cm<sup>2</sup>) changes the relative population of the Cs-atom sublevels ( $F = 3$  and  $F = 4$ ) by way of the optical pumping mechanism. A small-section, low-intensity laser beam (2-mm diameter, 0.13 mW/cm<sup>2</sup>) probes the population of the

pumped ground sublevel, whose temporal evolution, after the pump has been turned off, is then observed on a digital oscilloscope screen. Both lasers are of 3-MHz line width and tuned in the transition  $6S_{1/2} \rightarrow 6P_{3/2}$  ( $F = 4$ ).

We first used a carefully prepared cell, containing in its cylindrical body (2.0-cm diameter and 1.0-cm length) only dry atomic vapor, supplied by a drop of metallic cesium in the cell reservoir. The decay time is almost independent of the laser frequency in the Doppler-absorption curve and we measured 58  $\mu\text{s}$  for the population of the  $F = 4$  hyperfine sublevel to return to the equilibrium after the pumping beam is turned off. With a second, longer cylindrical cell (2.0-cm diameter and 2.0-cm length), with no special preparation, i.e. with walls possibly ‘contaminated’ by the alkali atoms, the observed decay time was 46  $\mu\text{s}$ . We also studied a third cell (also 2.0-cm diameter and 2.0-cm length) where we had let a liquid cesium drop fall into the cell body: in these conditions we measured a shorter decay time, of 40  $\mu\text{s}$ .

We analyze these results by considering that the only mechanism changing the electronic spin of Cs atoms is the interaction on the cell surface. The clear dependence of the relaxation time with the condition of the walls of the cells corroborates the idea that the interaction, and so the spin relaxation, depends on the state of the surface, due to the contamination by alkali atoms. In order to compare the measurements we should first calculate the time of flight of the atoms into the body of the cells [41]: from the kinetic theory [42], this time is given by

$$\tau_v = 4 \frac{V}{\bar{v}S} \quad (\text{A.1})$$

for a cell with a volume  $V$  and an internal surface  $S$ .  $\bar{v} = \sqrt{8k_B T_S / \pi m}$  is the thermal velocity at the vapor temperature  $T_S$ ,  $k_B$  is the Boltzmann constant, and  $m$  is the mass of the atoms. For our ‘clean’ cell (cylindrical, 1.0-cm long) the time of flight is 46  $\mu\text{s}$ . For the two other cells (2.0-cm long) it is 61  $\mu\text{s}$ . Notice then that the polarization decay time in the ‘clean’ cell (58  $\mu\text{s}$ ) is longer than the time of flight, meaning that the collisions with the wall are not 100% depolarizing [26]. On the other hand, with the ‘contaminated’ cells we measured depolarization times shorter than the time of flight, indicating more depolarizing collisions, with either strongly Cs-saturated walls or small drops of metallic Cs. Anyway, these measurements point out that the depolarizing time at the surface is of the order of a few  $10^{-5}$  s.

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