Light-induced atomic desorption from PDMS films and porous glass: application and fundamental issues

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Abstract. Light-induced desorption and diffusion of alkali atoms embedded in dielectric substrates are experimentally and theoretically investigated. The goal is to realize atomic dispensers fully controlled by light, to study the atom-dielectric interaction and to make spectroscopy of atoms confined in micro-nano structures. Very interesting results have been obtained with Rb and Cs in PDMS films and porous glasses.

1. Introduction

In atomic physics the analysis of interaction between atoms and surfaces is one main issue. The atom-surface interaction is in general very complex as atoms may elastically or quasi-elastically collide with the walls, may stick on it or even diffuse inside it. Complexity increases in presence of light. Light in fact may play an important role and trigger new phenomena. In particular, adsorption-desorption processes in presence of light are important for application and fundamental aspects. Alkali atoms interacting with dielectrics are interesting subjects to be studied, as their interaction potential with dielectric surfaces can range from few meV (physisorption) to few eV (chemisorption) and the outcome of the experiment can deeply change depending on this value. The alkali atom-glass or silica interaction potentials fall in the eV range [1]. This value gives, at thermal equilibrium and according with the Langmuir equation [2], a surface density $\sigma$ of adsorbed atoms

$$\sigma = \frac{n}{4} \frac{E_a}{v_T \tau_0 e^{kT}}$$

that corresponds to a Rb or Cs monolayer at room temperature. In equation (1), $n$ is the atomic density, $v_T$ is the mean thermal velocity, $\tau_0$ is the shortest possible collision time and its value is about $10^{-12}$ s, $E_a$ is the adsorption energy and $kT$ is the thermal energy.

The presence of the alkali atom monolayer has been a problem in the past, for example, in optical pumping experiments where the electronic spin orientation is quenched by the depolarizing atom-glass collisions [3]. The high $\sigma$ value is a problem also in the “light-induced drift” experiments [4]. In that case the presence of huge amount of adsorbed atoms is a severe drawback for getting high drift velocities. For the same reason it is very difficult to put in evidence radiation pressure in a gas. A very efficient solution was found by coating the cells with paraffin or siloxane compounds, namely polydimethyl-siloxane (PDMS) or octamethylcyclotetra-siloxane (OCT). PDMS coated cells allowed...
for very high drift velocities [5] and for observation of light pressure in sodium vapor [6]. These results demonstrate that the coatings inhibit the monolayer formation and that the interaction potential is in the meV range.

For many years these coatings have been used without apparent problems. Few years ago Gozzini et al. [7] and Meucci et al. [8] found that PDMS film could release huge amount of sodium and rubidium atoms respectively upon weak illumination of the cell. The effect was named, after ref. [7], light-induced atomic desorption (LIAD). In ref. [7] the desorbing light was the resonant dye laser itself. In ref. [8], instead, the desorbing light was delivered by a pocket lamp. Such weak light is enough to increase the Rb vapor density by one order of magnitude at room temperature. Since then many LIAD experiments have been made with Na [7, 9], K [10], Rb [8, 11, 12] and Cs [13]. In figure 1, Rb and Cs fluorescence spectra with and without cell illumination are reported to show the relative absorption signal increase.

![Figure 1](image.png)

**Figure 1.** Absorption spectra of Rb (figure 1a) and Cs (figure 1b) with desorbing light off and on. The spectra are obtained at room temperature in PDMS coated cells. The desorbing light is a filament lamp for rubidium and a high pressure mercury lamp for cesium.

Similar results have been obtained with OCT [12] and paraffin [14]. LIAD effect has been used to make a Rb atomic source at room temperature controlled by light [15]. LIAD has been employed to load magneto-optic traps (MOT) [16,17]. Very recently LIAD has been used to load a Bose-Einstein Condensate (BEC) in a microelectronic chip [18].

LIAD is a non thermal effect and has no relation with those desorption phenomena driven by intense laser pulses that produce sudden local heating of the substrate and surface ablation. Moreover the adsorption energy is so weak that the formation of a metallic monolayer or of clusters on the surface is not possible as already discussed. Therefore the desorbed atoms cannot be only from the coating surface but also from inside it. This means that atoms diffuse inside the coating in the dark and at room temperature. For this reason, LIAD from PDMS needs, in order to be explained, not only to accept an increasing of the desorption rate at the surface induced by light, but also a faster diffusion in the coating bulk. LIAD, in this case, can be considered as a manifestation of a light-induced enhancement of atomic mobility.

Detailed experimental analysis of LIAD effect has been made in the last few years both measuring the vapor density changes in sealed cells and the atomic velocity distribution with the Time of Flight (TOF) technique in special vacuum chambers [19]. Measurements have been done as a function of the film temperature, the desorbing light intensity and frequency, the illumination time [4,5]. Experiments clearly confirm that the atomic bulk diffusion, both with and without cell illumination, plays a major role in the effect that is not a simple surface effect.

Recently we have measured the LIAD effect for Rb and Cs both embedded in the same film in order to put in evidence possible differences between the two atoms due to their atomic level structure or specific properties. We have found for the two atoms the same dependences on frequency and intensity of desorbing light as well as exactly the same desorption dynamics.
Recently light induced desorption from porous glasses, previously loaded with rubidium and/or caesium has been observed [20]. Due to the huge effective surface of these glasses a large number of atoms are desorbed even upon weak illumination. The general features and the differences between the two different substrates (PDMS and porous glasses) are discussed in following paragraphs. The increased vapor diffusion in presence of light is demonstrated in both cases.

It is important to remark that the similar macroscopic behaviour of PDMS and porous glass, observed in the experiments, originates from quite different microscopic processes. The two substrates show in fact different morphology and properties. The adsorption energies, for example, differ by about one order of magnitude. In PDMS film, the atoms drift “inside” the coating that can be sketched as a continuous medium (figure 2a). In Porous glass the atoms leave the glass surface and fly free from one point to the other inside the tiny pores that can be sketched as nano-tubes (figure 2b). In both cases the net result consists in a huge light-induced atomic desorption that makes quite promising the realization of alkali atom dispensers controlled by light as sketched in figure 3.

The increased atomic mobility induced by light has been measured in PDMS, and measurements are in progress for porous glass. Moreover new features are observed which open new interesting scenarios.

2. LIAD with PDMS
A detailed experimental analysis of the LIAD effect has been made as a function of few parameters: the desorbing light intensity and frequency, the cell temperature, the buffer gas pressure, the illumination time interval. A model has been then developed that is able to fit the experimental data and to derive information about the desorption efficiency, the atomic mobility etc. The relative density variation induced by the desorbing light is introduced.
\[ \delta_{LIAD}(t) = \frac{n(t) - n_0}{n_0} \]  

where \( n_0 \) is the vapor density at thermal equilibrium when the cell is not illuminated. In figure 4 \( \delta_{LIAD}(t) \) as a function of time is shown. A double illumination of the cell is made. When desorbing light is on, a vapor density increasing is recorded. The first illumination time produces the most intense peak, while the following peaks are weaker. This is clearly shown in fig. 4, where the second peak is weaker than the first one. This behaviour is due to the slower diffusion of atoms in the dark as compared with that in presence of light. It is a direct evidence that light increases the atomic mobility inside the coating. The slow decrease during each illumination time is correlated with the depletion of substrate layer close to the surface. The solid curve is the best fit of the data according to our model [12].

\[ \delta_{max}^{LIAD} \sim \sqrt{I_L} \]  

\[ R = \frac{1}{n_0} \left( \frac{d n}{d t} \right)_{t=0} \sim I_L \]  

to conveniently characterize the effect. \( \delta_{max}^{LIAD} \), according with our model, is proportional to the square root of the light intensity, while \( R \) is proportional to it. The experimental results are shown in figure 5 and confirm the predicted behaviour.

LIAD effect depends on the desorption light frequency as shown in figure 6 for both rubidium and caesium embedded in PDMS. The two alkali atoms show the same dependence and do not show resonances. In order to better investigate this point, and also to get more information about possible
differences connected to specific atomic characteristics, we have prepared coated cells containing a mixture of Rb and Cs. In this way the two atomic species interact with the same film and differences concerning possible impurities or defects are eliminated. The interesting result is that not only the dependence on the frequency is the same but also the dynamics.

We interpret this result as a clear evidence that LIAD is due to non resonant light scattering (Brillouin and Raman) and not to resonant excitation between ground and excited bound molecular states crossing with a repulsive one, as proposed by Bernheim et al. [9] for sodium. According to their model, sodium atoms are solvated in the siloxane compound and the Na+PDMS- complex is formed. Light excitation makes the atoms to make backward the same pathway. This approach supports their experimental results about the presence of a threshold in the desorbing light frequency, but, on one side, confines the effect to the surface neglecting the atomic diffusion inside the coating and, on the other side, makes the effect strongly dependent on the molecular level structure that contradicts our last observation with Rb-Cs cells.

A similar analysis has been recently adopted also by Rubahn et al. [19, 21] to explain the outcome of their desorption experiments. In this case pulsed lasers are used to allow one to make velocity distribution measurement of desorbed atoms with time of flight method. They find that desorbed atoms have quite high temperatures. A resonant process is supposed to bring atoms from the deep potential well, where they are confined, to a repulsive state from where the excess energy is transformed into kinetic energy. They make the experiment with the 1064 nm and 532 nm wavelengths from a Nd-Yag laser and get similar temperatures with both wavelengths [21]. Therefore
a double resonance condition is supposed that qualitatively explains the results but it makes stronger the correlation between the effect and the level structure of the alkali atom.

We believe that the apparent contradiction is due to the fact that the adsorbed atoms experience potential wells having different deep and shape. Atoms occupy permanently the deepest ones, while they may move around drifting from one potential well to the next one. This process is possible even without illumination and at room temperature. When the cell is illuminated the mobility is increased and also the atoms trapped in deepest potential wells are involved. If the light is very intense other excitation processes become possible as discussed by Rubahn [21].

3. LIAD from porous silica
When an uncoated glass cell, containing alkali atom vapor, is illuminated by weak light, no LIAD effect is observed. But if a small sample of porous glass is placed inside the cell, then LIAD is observed. We have tested porous glass by putting a sample of it inside a cell containing Rb or Cs and by sealing it under vacuum. After some time, needed to passivate the cell and to “fill up” the glass, a stable vapor pressure is obtained and LIAD effect is observed. The apparatus is sketched in figure 7.

Porous materials have huge internal surfaces where particles can be stored. We have tested porous silica samples having an internal surface area of 250 m²/g, and porous diameters of 7 and 17 nm. Porous glass is prepared from a quaternary glass mixture of typical composition 62.7% SiO₂, 26.9% B₂O₃, 6.6% Na₂O, 3.5% Al₂O₃. This glass is melted and formed into the desired shape, and then held at a temperature above the annealing point but below that would cause deformation. The material phase-separates on a microscopic scale into two continuous phases, one rich on silica, the other in borosilicate and alkali. It is then treated with a hot dilute acid solution that dissolves away the borate leaving some small colloidal silica particles inside the pores of the other phase. The finished glass is 96% silica.

When the porous glass sample, previously loaded with the alkali atoms, is illuminated, desorption takes place and an increase of the vapor density is detected. The signal dynamics is shown in figure 8. The measurement is similar to the one reported in figure 4 that is made with PDMS coating. Also in this case the second peak is weaker than the first one, but the dynamics is now slower. It is interesting
to remark that the second peak height depends on the exposition time. Longer is this time deeper is the 
evacuated fraction of the glass and longer is the time needed by the atoms to fill back the pores.

4. Conclusion
We have demonstrated that it is possible to store alkali atoms inside organic polymer films, like 
PDMS, and inside the pores of specially prepared glasses. Even if the adsorption energies in the two 
cases are quite different, nevertheless LIAD effect is observed in both cases and the main features look 
similar for both substrates. The possibility to realize atomic dispenser driven by light has been 
demonstrated and a model has been developed for PDMS.

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Figure 8. Relative vapor density changes as a function of time. The 
cell is exposed twice to the desorbing light, starting at t = t1 and t = 
t2. The desorbing light is delivered by Ar+ tuned to the 514 nm. Laser 
intensity is 13 mW/cm².
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