

# Light-induced potassium desorption from polydimethylsiloxane film

S. Gozzini and A. Lucchesini<sup>a</sup>

Istituto per i Processi Chimico-Fisici del Consiglio Nazionale delle Ricerche, Area della Ricerca, Via G. Moruzzi 1, 56124 Pisa, Italy

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**Abstract.** Potassium photoejection from polydimethylsiloxane surfaces has been observed and analyzed in detail. By diode laser absorption spectroscopy the K concentration in a sealed measurement cell without buffer gas has been monitored as a function of the environment variables, like temperature, flooding light wavelength and power. The dynamic evolution of the process has been measured too, showing differences compared to previous measurements with different alkali-metal atoms. Saturation spectroscopy on the K D<sub>1</sub> line has been performed at room temperature by taking advantage of this phenomenon.

**PACS.** 34.50.Dy Interactions of atoms and molecules with surfaces; photon and electron emission; neutralization of ions – 42.50.Ct Quantum description of interaction of light and matter; related experiments – 68.43.Tj Photon stimulated desorption

## 1 Introduction

The photodesorption effect called LIAD, from Light Induced Atom Desorption, has been observed for the first time ten years ago in measurement cells coated with polydimethylsiloxane (PDMS) [1], a polymer with a chemically intermediate behavior between organic and inorganic materials and a good stability after dehydration. For this reason it has been used to coat the inner walls of measurement cells in order to reduce the spin-relaxation in the wall-atoms collisions. At that time a huge increase of the fluorescence of alkali atoms like Na, K and Rb was observed when illuminating the glass cell by nonresonant and nonmonochromatic radiation (room light). Later on this effect has been deeply studied with Rb [2] in PDMS and Cs [3] in octamethyl-cyclotetrasiloxane (OCT) and also in paraffin [4], taking into account the mobility of the atoms on the surface and inside the coating in order to explain the time evolution of the desorption process. Closed cells containing inert buffer gas have been used in almost all these cases. In the experiments reported so far it is evident the nonthermal characteristic of the phenomenon and its dependence on the wavelength of the incident radiation. This effect has been also utilized to improve the loading of Rb atoms in a magneto-optical trap [5].

In this work we describe the observation of the LIAD effect in closed measurement cells coated by PDMS and containing potassium, without any buffer gas. A huge effect is observed still caused by nonresonant visible light.

This effect has been detected in two different class of measurements: (a) low incident radiation power ( $w \leq 0.5 \text{ W/cm}^2$ ); (b) high incident radiation power ( $w > 0.5 \text{ W/cm}^2$ ) giving two different time responses, according to the diffusion theory inside the coating polymer [6].

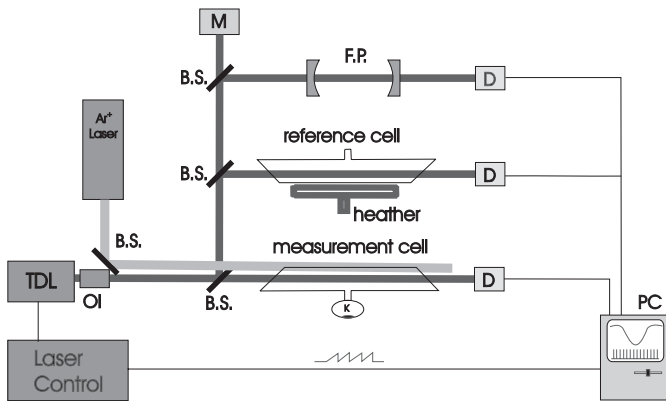
## 2 Experimental apparatus

The experimental apparatus adopted is shown in Figure 1.

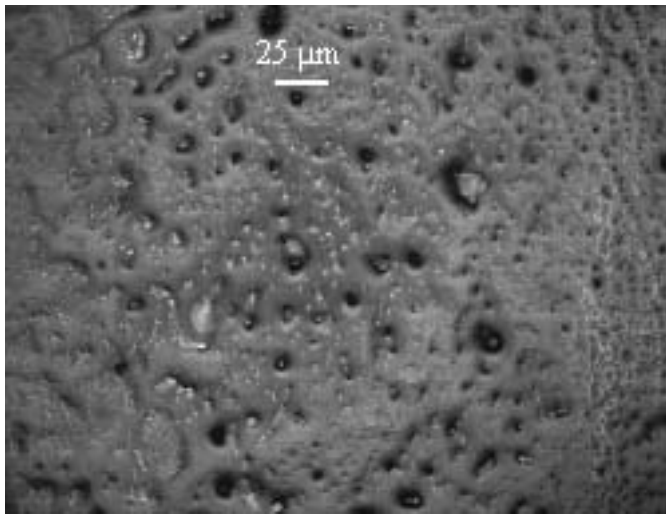
Most of the reported data are obtained from a special capillary cell consisting of a Pyrex cylindrical tube of 300 mm length, 8 mm external and 5 mm internal diameters: in this way we obtained a large surface/volume ratio and really we observed an increased LIAD effect and a good absorption signal from the potassium vapor that let us monitor the atomic concentration with low error. The cell is closed by two Brewster angle glass windows to minimize reflection losses and to avoid any radiation feedback. Other measurements have been carried on cells with “standard” dimensions in our laboratory, that is 5 cm long and 2 cm diameter. In this case the surface/volume ratio value was less favorable to the surface and this influenced the time constants of the process too.

After a careful cleaning, rinsing and pre-backing, the cell was internally coated by PDMS and baked for 4 hours at 490–500 K. Then the cell was evacuated down to  $10^{-5}$  Torr by a clean vacuum system. The cell was connected to a potassium reservoir where the alkali was distilled; after that the cell was pumped by a ionic pump down to  $6\text{--}8 \times 10^{-8}$  Torr and finally sealed. A Scanning

<sup>a</sup> e-mail: lucchesini@ipcf.cnr.it



**Fig. 1.** Outline of the experimental apparatus for saturated absorption spectroscopy. TDL: tunable diode laser; B.S.: beam splitter; D: photodiode; F.P.: Fabry-Perot interferometer; OI: optical insulator; M: monochromator; PC: desk-top computer.



**Fig. 2.** Optical microscope image of the PDMS surface.

Electron Microscope (SEM) observation [7] of the PDMS polymer surface showed a porous structure with holes of roughly  $1\ \mu\text{m}$  diameter, and our inspection via an optical microscope as shown in Figure 2 confirms the presence of a porous surface with holes that have different sizes from  $1$  to  $20\ \mu\text{m}$ . This qualitatively explains the big dimension of this “surface effect”.

As said previously, to monitor the potassium concentration the optical absorption from the  $D_1$  resonance at  $12985.17\ \text{cm}^{-1}$  ( $\lambda = 769.902\ \text{nm}$  at  $294\ \text{K}$ ) has been measured in the same measurement cell by the aid of a tunable diode laser (TDL). In addition, to localize the  $D_1$  resonance, we used a reference cell containing potassium, warmed up to  $330$ – $340\ \text{K}$  but without any coating.

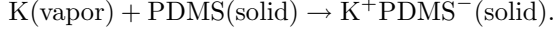
Initially a Toptica FIDL-20S-770C tunable diode laser (TDL) has been used in *free running* mode of operation by using the wavelength modulation spectroscopy (WMS) with the second harmonic detection technique [8]. Its nominal emission characteristic is  $20\ \text{mW}$  cw power at  $774\ \text{nm}$ . Its injection current was driven by a stabilized low-noise

current generator, which permitted also a fine scan of the emission wavelength ( $\sim 10\ \text{GHz}$ ) by mixing to the driving current an attenuated low frequency ( $\sim 1\ \text{Hz}$ ) sawtooth signal. The current dependence for small current variations can be considered linear, with a slope  $\sim 0.01\ \text{nm}/\text{mA}$ . The TDL was temperature controlled within  $0.001\ \text{K}$  by a high-stability temperature controller as the temperature dependence of the diode lasers emission wavelength is critical ( $\sim 0.2\ \text{nm}/\text{K}$ ). In this case the signal to noise ratio (S/N) was quite good ( $\geq 100$ ). But the TDL had to be cooled down to  $271\ \text{K}$  to reach the  $K\ D_1$  resonance, and the TDL current must be kept high, almost to its maximum operational limit ( $\sim 130\ \text{mA}$ ), in order to maintain a monomodal emission characteristic. For all these reasons the TDL emission stability was limited to a few minutes. Later on, a new Toptica DL 100 system was used, consisting of the LD-0765-0030 diode laser locked to an external cavity. It emits  $10\ \text{mW}$  cw at  $770\ \text{nm}$ . Coupling the diode laser to an external grating has the aim to force the laser to emit the requested wavelength and to reduce the mode hops, increasing the frequency tuning range. In this case the direct absorption (DA) technique gave a S/N ratio high enough to be used for the potassium concentration measurements without any modulation and in-phase detection. A confocal  $5\ \text{cm}$  Fabry-Perot interferometer was adopted to verify the linearity of the diode laser emission frequency scan and to check the laser mode. A  $0.35\ \text{m}$  monochromator was employed for the rough wavelength check. The transmission signal was collected by a silicon photodiode and sent to a digital oscilloscope. Once stabilized, a good S/N has then been achieved; this ratio typically varied from  $10$  in the worst to  $50$  in the best condition. In order to obtain a quantitative measurement of the atom concentration the signal was fitted to a Voigt profile and the line parameters extracted. An optical insulator was put at the exit of the TDL system to avoid any feedback from the several windows that could greatly increase the noise. An Innova 200  $\text{Ar}^+$  laser was used to illuminate the cell at the different wavelengths of its main emission lines ( $457.9$ ,  $476.5$ ,  $488.0$ ,  $496.5$ ,  $514.5\ \text{nm}$ ) with the same power density. For this purpose the laser emission power has been measured by using a Coherent Field Master power meter. Also a Coherent dye laser Mod. 490 has been used to add three more lines at  $574$ ,  $588$  and  $591\ \text{nm}$  in order to cover a broader spectrum.

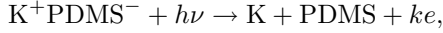
### 3 Experimental results and discussion

The photodesorption effect shows to be bound to two phenomena: one related to the diffusion inside the polymer [6] and the other strictly related to the atom emission from the polymer surface [9]. The total effect in some cases is huge and dependent on the light wavelength with the best efficiency on the blue part of the visible spectrum. Probably the roughness of the polymer surface enhances the effect in the way the dangling bonds of the methyl groups that form the top of the PDMS coating act as

charge transfer sites for the K 4s electrons giving:



This solid solution can then be perturbed by photons with enough energy to be absorbed by the related energy band system, and it could also explain the quadratic dependence of the LIAD on the photon energy that will be shown later. Then in presence of light, the reverse process occurs:



in the balance  $ke$  represents the kinetic energy that permits the atoms to leave the polymer surface.

To quantify the effect let us define the dimensionless parameter, which well characterizes the atom density variation:

$$\delta_{\text{LIAD}} = \frac{n - n_0}{n_0} = \frac{\Delta n}{n_0}, \quad (1)$$

where  $n$  is the atom density over illumination and  $n_0$  is the density in the dark.

We calculated the “dark” atom density inside the measurement cell by comparing the transmitted potassium absorption signal to the one obtained from an identical reference cell containing potassium but without any polymer coating. The reference cell had to be warmed up to 318 K in order to obtain the same potassium absorption signal of the measurement cell: the potassium vapor pressure at this temperature [10] gives a concentration of  $n_0 = 3.5 \times 10^9$  atoms/cm<sup>3</sup>. By illuminating with 110 mW cw (0.55 W/cm<sup>2</sup>) Ar<sup>+</sup> laser at 458 nm a sector that was about half the measurement cell inner surface ( $\simeq 20$  cm<sup>2</sup>), we measured roughly ten times higher concentration of potassium:  $\Delta n = 3.3 \times 10^{10}$  atoms/cm<sup>3</sup>. In comparison, a sealed and evacuated glass cell without coating where the K vapor pressure counts  $n = 5.5 \times 10^8$  atoms/cm<sup>3</sup>, that is almost two order of magnitude lower.

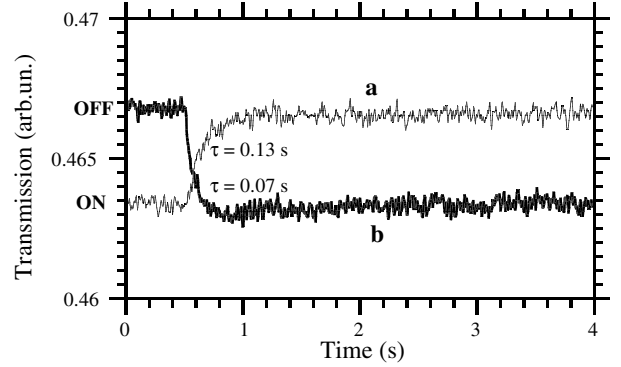
A simple model of the light-induced desorption assumes a “weak desorbing light regime”, that is the light shining onto the polymer induces a negligible variation on the potassium concentration in the polymer near the surface [6]. In this regime the K vapor density dynamics can be described by:

$$\frac{dn}{dt} = \frac{\alpha N_0}{L} + \gamma n_0 - \left( \gamma + \frac{\beta}{L} \right) n, \quad (2)$$

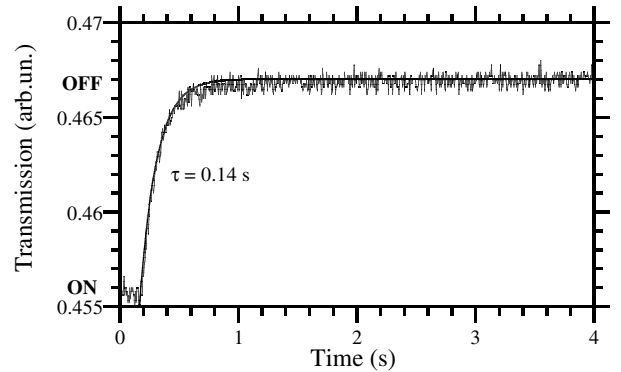
where  $N_0$  is the atomic concentration in the coating,  $L$  is the cell length,  $\alpha$  and  $\beta$  are the atomic desorption and adsorption rates respectively, and  $\gamma^{-1}$  is the relaxation time controlled by the K source. Its solution is:

$$n(t) = n_0 + \Delta n_{\text{max}}(1 - e^{-t/\tau}). \quad (3)$$

Here  $\Delta n_{\text{max}} = \alpha N_0 / (\beta + \gamma L)$  is the maximum density change and  $\tau^{-1} = \gamma + (\beta/L)$ . In this case the diffusion of the atoms inside the PDMS acts as a dynamic reservoir for the surface regime. But when the desorption light intensity increases, the surface thermal equilibrium expressed by equation (3) is broken and after an initial exponential



**Fig. 3.** Time evolution of the LIAD effect at RT under low light intensity regime ( $w_{\text{laser}} \simeq 0.5$  W/cm<sup>2</sup>) under all the Ar<sup>+</sup> laser lines: **a** switching the laser off, **b** switching the laser on.

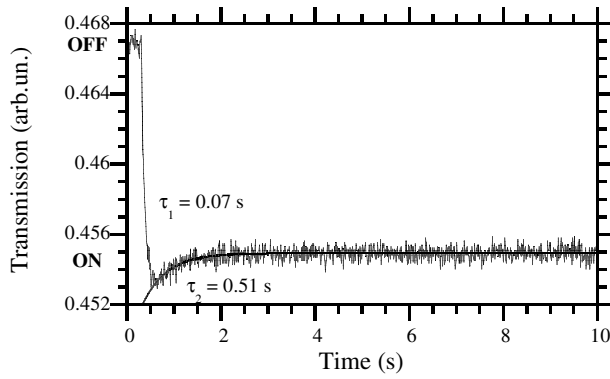


**Fig. 4.** Time evolution of the LIAD effect at RT, under high light intensity regime ( $w_{\text{laser}} = 2.5$  W/cm<sup>2</sup>) under all the Ar<sup>+</sup> laser lines, when switching the laser off. The continuous line is the exponential best fit.

increase, there is another exponential decrease toward an equilibrium. The time constants of the two processes differ by almost an order of magnitude. The final equilibrium is established by the K reservoir bulb with the evaporation and condensation processes of the potassium there contained.

All the measurements on the coated cell have been performed at room temperature (RT). The dynamic behavior of the K LIAD effect is faster than the others reported in the literature, probably not only because here a different atom is studied, but also because no buffer gas is added in the measurement cell. In particular we noted and distinguished two different regimes: low flooding light intensity ( $w \leq 0.5$  W/cm<sup>2</sup>), and high flooding light intensity ( $w > 0.5$  W/cm<sup>2</sup>). The work of Alexandrov [4] well explains how the light influences the atom desorption from the coating (paraffin in that case) to the cell and how the coating itself is replenished by atoms evaporated from the reservoir.

In our measurements the time constants of the LIAD extinguishing process when switching the flooding light off are almost the same in the two conditions, namely  $\tau_{\text{on} \rightarrow \text{off}} = 0.13\text{--}0.14$  s as shown in Figures 3a and 4 respectively. Instead, when turning the light on two different time evolutions come out.



**Fig. 5.** Time evolution of the LIAD effect at RT under high light intensity regime ( $w_{\text{laser}} = 2.5 \text{ W/cm}^2$ ) under all the  $\text{Ar}^+$  laser lines, when switching the laser on. The continuous line is the exponential best fit.

In Figure 3b the low light intensity induces an “integrating” behavior of the transmission, that is the atom density, as a function of time, showing a time constant of some tens of milliseconds.

In Figure 5 instead, the high light intensity regime shows a “derivative” behavior, where the rise time is still of the order of some tens milliseconds followed by a settling time of some hundred milliseconds. This can be understood by considering that in the high intensity regime the light induces a quick and complete removal of the K atoms from the surface and then the K diffusion process from the bulk to the surface of the polymer takes place with its own times. In this case equation (3) by itself does not describe the entire process any more, but an evolution equation with two different evolution rates is needed:

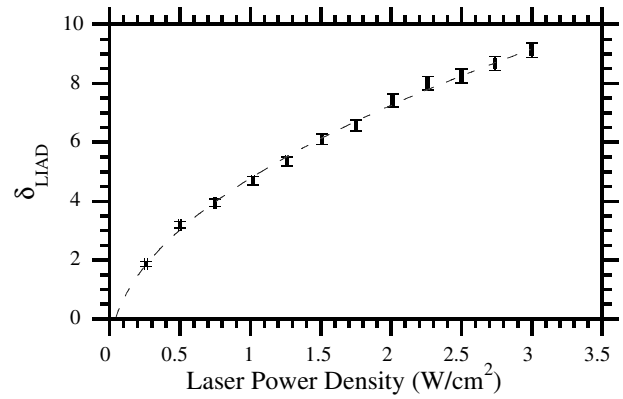
$$n(t) = n_0 + \Delta n_{\text{max}}(1 - e^{-t/\tau_1})e^{-t/\tau_2}, \quad (4)$$

with  $\tau_2 \gg \tau_1$ . Here  $\tau_2$  is directly correlated to the alkali atoms diffusion in the polymer, whose coefficient value under illumination ( $D$ ) can be estimated by putting  $D = h^2/\tau_2$ , where  $h$  is the polymer thickness. We measured the thickness of our PDMS coating by a Leika confocal optical microscope and it results  $10 \mu\text{m}$  in average, this gives  $D \simeq 2 \times 10^{-6} \text{ cm}^2/\text{s}$ .

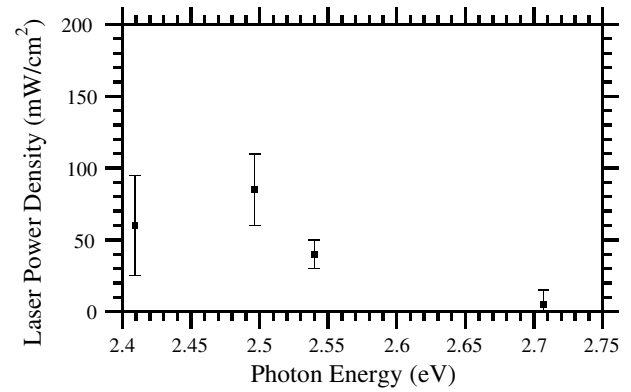
Within our measurement errors the respective time constant values did not vary when the luminous density was varied from  $0.5$  to  $3.5 \text{ W/cm}^2$  under all the  $\text{Ar}^+$  laser lines.

Instead an evident proportionality of  $\delta_{\text{LIAD}}$  parameter to the square root of  $w$  has been noted. This is shown in Figure 6, where the  $488.0 \text{ nm}$  line is used. In reference [11] this “square root” behavior is attributed to the linear dependence of  $D$  on the laser light intensity; certainly  $D$  deeply influences the time evolution of the adsorption process.

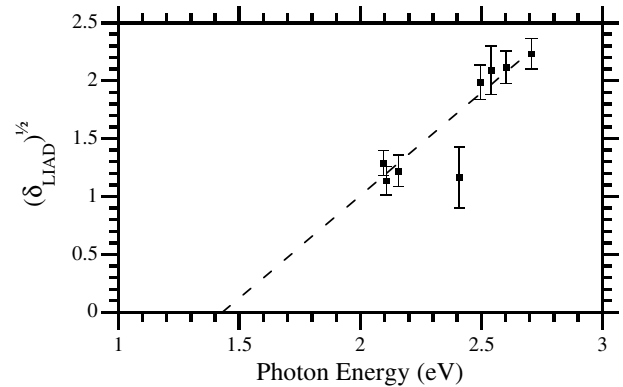
In all our experiments we observed a threshold for a minimum light power necessary to perform the LIAD effect: every time some tens of  $\text{mW/cm}^2$  were necessary to start the effect. For instance in Figure 6 the best square root fit gives a threshold of  $40 \text{ mW/cm}^2$  for the power density at  $\lambda = 488.0 \text{ nm}$ .



**Fig. 6.** Variation of the LIAD effect as a function of the laser power emission at  $488.0 \text{ nm}$ .



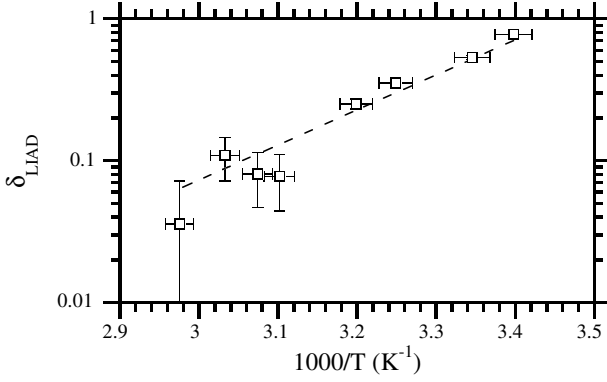
**Fig. 7.** Minimum laser power required for the LIAD effect as function of the photon energy.



**Fig. 8.** Square root of the LIAD effect vs. laser photon energy at RT along with the best linear fit weighted to the errors, giving a threshold  $h\nu_0 = 1.43 \text{ eV}$ .

In Figure 7 the variation of this threshold as a function of the photon energy is shown; within the errors there is an appreciable dependence on the wavelength.

The  $\delta_{\text{LIAD}}$  dependence on the photon energy is shown in Figure 8. The points with their errors are related to the  $\text{Ar}^+$  and dye laser lines of the same power:  $70 \text{ mW}$ , which means  $350 \text{ mW/cm}^2$  in our measurement conditions. If we consider a quantum approach to the phenomenon such as the one used for the photoemission effect [9], we could



**Fig. 9.** LIAD behavior when varying the temperature. The shown best fit gives an activation energy  $E_A = 0.49$  eV.

consider a dependence of  $\delta_{\text{LIAD}}$  as the square the photon energy starting from the threshold, that is:

$$\delta_{\text{LIAD}} = A(h\nu - h\nu_0)^2. \quad (5)$$

Remembering what said before on the solid solution system, this behavior recalls what happens to amorphous silicon and germanium photon absorption by bands of localized states [12]. This behavior is worthy to be investigated thoroughly by a future specific work.

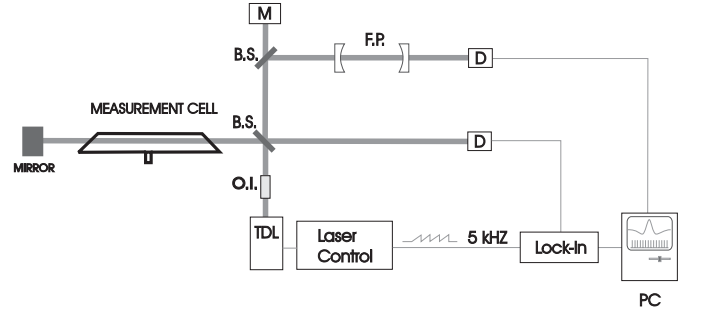
On measurements with different PDMS coated cells the best fit gives  $h\nu_0 = (1.4 \pm 0.1)$  eV. This is higher than the one reported for Na atoms (1.18 eV) in the work of reference [13] and also higher than the threshold (1.09 eV) attainable from the data related to Rb coming from reference [2]. The reason could be due to the different treatments and baking procedures used for the cells once coated.

The analysis of the temperature dependence of the LIAD effect gives the thermal activation energy ( $E_A$ ) of such phenomenon. The light used to induce the effect was the 514 nm  $\text{Ar}^+$  laser line and the temperature was varied from RT to about 330 K, where the absorption signal finally saturates. Figure 9 shows the LIAD signal vs.  $1000/T$  in a semilogarithmic scale, and on the basis of a desorption yield behavior:

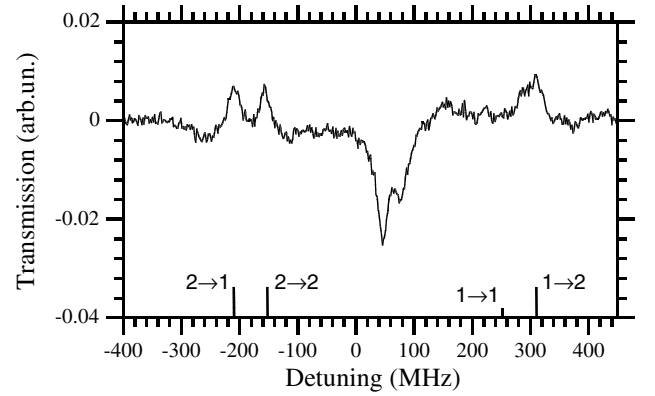
$$\delta_{\text{LIAD}} \propto \exp(E_A/k_B T), \quad (6)$$

where  $k_B$  is the Boltzmann constant, the activation energy can be deduced. In our case  $E_A = (0.49 \pm 0.02)$  eV, a value that is again higher than what obtained for Na (0.36 eV) in PDMS [9], but lower than the observed photon energy threshold  $h\nu_0$  and the surface binding energies like for instance the one between potassium and graphite (1.5 eV) [14].

An application of the LIAD properties to the fine spectroscopy has been attempted by using our diode laser system. In particular, saturated absorption measurements of the  $^{39}\text{K}$   $D_1$  hyperfine levels at RT have been performed under the apparatus configuration shown in Figure 10. The source is still the Toptica DL 100 system tuned to K resonance, but the main setup characteristic is the mirror at the end of the measurement cell that sends back



**Fig. 10.** Outline of the experimental apparatus. TDL: tunable diode laser; B.S.: beam splitter; D: photodiode; F.P.: Fabry-Perot interferometer; O.I.: optical insulator; M: monochromator; PC: desk-top computer.



**Fig. 11.** Saturation spectrum of the  $^{39}\text{K}$   $D_1$  line with the relative hyperfine transition positions and oscillator strengths.

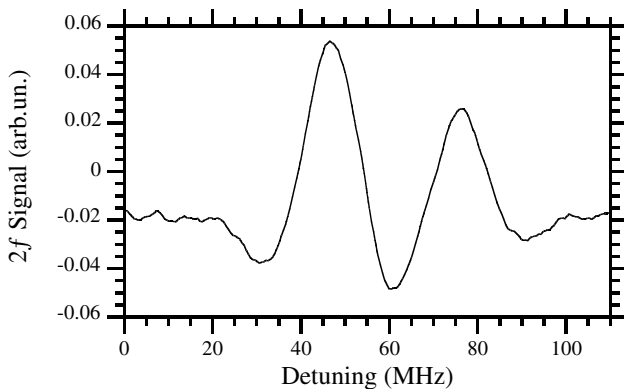
the TDL radiation through the very same path. In this way it saturates the absorption of the  $v = 0$  class atoms and eliminates the Doppler broadening. Compatibly to the laser mode width and noise, it permits to observe very fine structures like the hyperfine level transitions.

The saturated transmission of Figure 11 has been obtained by DA (no frequency modulation) under room light at  $T \simeq 300$  K to be compared to what obtained by Hänsch and coll. in 1971 on  $D_1$  hyperfine transitions of Na vapor at 383 K [15].

In our case to obtain the same K atom density in the measurement cell without any coating it should have been warmed up to at least 330 K. Going further, by the aid of the WMS with low modulation index we could measure the splitting of the crossover resonance in the center of Figure 11. The result is shown in Figure 12, where the 2nd harmonic signal gives:  $\delta\nu = (28.7 \pm 0.3)$  MHz to be compared to precise level position measurements which give  $\delta\nu = 28.85$  MHz [16].

## 4 Conclusion

In this paper we present the first systematic study of non-resonant and nonthermal light-induced atomic desorption (LIAD) of potassium in polydimethylsiloxane (PDMS)



**Fig. 12.** 2nd derivative of the crossover feature of the saturation spectrum of the K D<sub>1</sub> line. The Lock-in time constant was 12.5 ms.

observed by the aid of diode laser absorption spectroscopy. For this purpose a specially tailored cell was used in order to increase the S/N ratio. By working without any buffer gas in the measurement cell we observed relaxation time constants an order of magnitude lower than those reported in literature. We observed also that a minimum light intensity is required to start the process, depending on the photon energy, which suggests a quantum origin of the LIAD. Further measurements are in progress in order to clarify this aspect.

It has been demonstrated that even at room temperature with measurement cells coated by PDMS it is possible to have enough potassium vapor pressure to perform fine spectroscopy by illuminating the cells with a moderate non resonant (room) light.

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