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A new class of photo-induced phenomena in siloxane films

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Abstract. The light induced atomic desorption effect, known as LIAD, is observed whenever Pyrex cells, coated with siloxane films and containing alkali atoms, are illuminated. LIAD is a non-thermal phenomenon and it can be observed even with very weak light intensities. We show that the simultaneous contribution to the photo-emission of atoms adsorbed both at the film surface and within the film must be taken into account in order to fit the experimental data. We demonstrate that both the desorption efficiency and the diffusion coefficient of the alkali atoms embedded in the dielectric film depend on the desorbing light intensity. These features characterize a new class of photo-induced phenomena whose analysis gives new insights in the comprehension of the atom-surface interaction and of the atom-bulk diffusion and opens interesting perspectives for applications.

PACS. 34.50.Dy Interactions of atoms, molecules, and their ions with surfaces; photon and electron emission; neutralization of ions – 79.20.La Photon- and electron-stimulated desorption

1 Introduction

A new class of phenomena involving alkali atoms, dielectric films and light has been recently observed by Gozzini *et al.* [1]. The effect, named by us LIAD (light induced atomic desorption [2]), consists of a huge emission of alkali atoms from siloxane films when they are illuminated by laser or ordinary light. We have tested two siloxane compounds with very different molecular structures: the poly-(dimethylsiloxane) (PDMS), that is a polymer, and the octamethylcyclotetrasiloxane (OCT) that is a crown molecule. Both of them show the desorption effect but with some differences that have to be related to the physical structure of the film. The effect has been observed with Na [1,3], K [1], Rb [2,4] and Cs [5]. Na_2 molecular desorption has been also reported [3]. Desorption efficiency is so high that an intense source of rubidium based on LIAD has been realized at room temperature [6]. These results were totally unexpected as the adsorption energy of alkali atoms on the surface of these films has been measured to be so small to make unlikely the presence of a large number of atoms on the cell internal surface [7].

Photo-desorption processes are currently observed, correlated with direct surface heating, photon absorption, surface plasmon excitation and other phenomena [8–10]. All these different mechanisms can be easily discriminated one from the other by looking at the dependence of the desorption rates as a function of the desorbing light intensity I_{L}. For example, pure photo-desorption shows a linear dependence on I_{L}, while thermal-desorption increases exponentially with I_{L}.

LIAD from siloxane surfaces shows instead a peculiar behavior that is different from the two others. Namely, the number of desorbed atoms increases as the square root of the desorbing light intensity I_{L}, whereas the desorption rate at the beginning of the illumination increases linearly with I_{L}. Moreover, it is worth noting that LIAD has been observed with light intensity weaker than one mW/cm^2. This value has to be compared, for example, with the few tens mW/cm^2 reported for photodesorption of sodium from sodium rough films [10] or with the 100 W/cm^2 for thermal desorption of sodium from sapphire [8].

We stress in this paper the physical nature of these differences and we demonstrate that the new features are due to the increased mobility of alkali atoms adsorbed within the film when light is present.

2 Experimental analysis and theoretical model

This new photo-desorption effect has been observed in Pyrex sealed cells having internal surface coated with either a PDMS or an OCT film. The coating preparation is quite simple and it has been described elsewhere (see for example [2]). Desorption light is delivered by different light sources which can be either continuous or pulsed. Argon ion laser, dye laser, LEDs, high pressure Hg lamp or flashes have been used to have access to extended frequency, intensity and time domain regimes. Desorption light can shine the whole cell or only a selected part of it.

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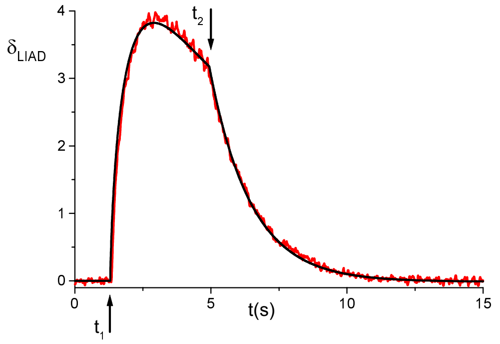

Fig. 1. Absorption signal as a function of time. Data are elaborated so to give directly the relative density variation $\delta_{\rm LIAD}$ induced by the desorbing light. The continuous curve is the least squares fit calculated according to our model. The desorbing light (Ar$^+$ laser @514 nm) is switched on at $t = t_1$ and off at $t = t_2$. The cell is coated by PDMS.

A diode laser monitors the rubidium vapor density *via* absorption spectroscopy, in such a way that LIAD is detected as a density change in the gas phase. The cell is connected, through a short capillary, to a reservoir containing a metal drop, that imposes, for a fixed temperature T, the equilibrium vapor density $n_0(T)$. The measurements reported here are made at room temperature, with cells coated by PDMS or OCT and containing Rb vapor, which were shined by an Ar$^+$ laser tuned to the 514 nm line.

When the cell is illuminated, the vapor density n increases, reaches its maximum $n_{\rm max}$, then slowly decreases back to the equilibrium value n_0. If the desorbing light is switched off, a faster decay is observed. In this case the density decay follows an exponential law with a characteristic time $\tau_{\rm D}$. A typical time dependent absorption signal is shown in Figure 1. The data are elaborated in order to show directly the relative density variation $\delta_{\rm LIAD}(t) = [n(t) - n_0]/n_0$ induced by the desorbing light. At the time $t = t_1$ the desorbing light is switched on and a fast increasing of the Rb density is detected. $\delta_{\rm LIAD}$ reaches a maximum then starts decreasing. At $t = t_2$ the desorbing light is switched off and the Rb density decreases much faster with a characteristic time constant $\tau_{\rm D}$ that is usually of the order of a few seconds (in this specific case, $\tau_{\rm D} \cong 1.6$ s). The continuous curve gives the best fit according to the diffusion model as described below and also in [4].

With this detection scheme, LIAD is well characterized by the parameter

$$\delta_{\rm LIAD}^{\rm max} = \frac{n_{\rm max} - n_0}{n_0} \tag{1}$$

that gives the maximum relative increase of the vapor density.

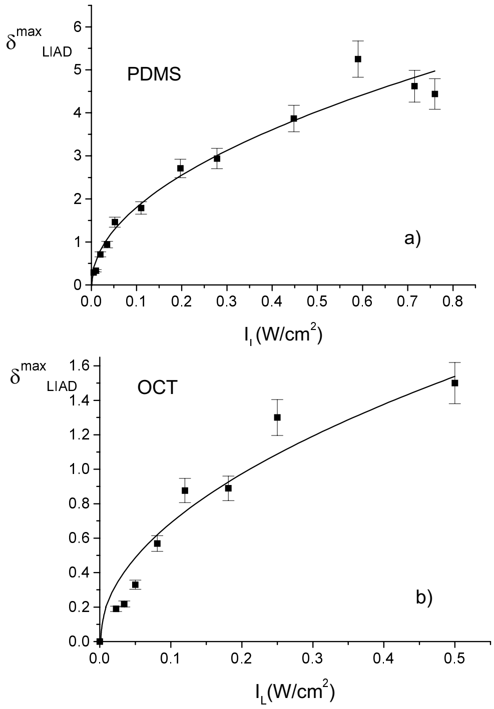

Fig. 2. Dependence of $\delta_{\rm LIAD}^{\rm max}$ as a function of the desorbing light intensity $I_{\rm L}$. (a) PDMS film; (b) OCT film. The solid curves are least squares fits.

Careful measurements of $\delta_{\rm LIAD}^{\rm max}$ as a function of the desorbing light intensity $I_{\rm L}$ are reported in Figure 2. Figures 2a and 2b show the results for the PDMS and OCT films respectively. The least squares fit of the data shows that at large $I_{\rm L}$ intensities $\delta_{\rm LIAD}^{\rm max}$ is proportional to the square root of $I_{\rm L}$ for both coatings, *i.e.*

$$\delta_{\rm LIAD}^{\rm max} \propto \sqrt{I_{\rm L}}\,. \tag{2}$$

We observe that the PDMS film desorbs, upon the same conditions, about 3 times more atoms than OCT.

The main experimental feature of the LIAD effect is that $\delta_{\rm LIAD}^{\rm max}$ does not show a linear dependence on the desorbing light intensity $I_{\rm L}$, as it should be for a pure photo emission process, but it increases according to equation (2). It is also important to remark that this square root dependence is clearly observable starting from intensities as low as few tens mW/cm^2, while photodesorption of sodium from metallic sodium particles remains linear up to 160 W/cm^2 [9]. For sodium adsorbed on sapphire, the linear dependence on the desorbing light intensity is observed up to 10^5 W/cm^2 [8].

In order to extract information about surface emission properties, we define a second parameter

$$R = \frac{1}{n_0}\left(\frac{{\rm d}n}{{\rm d}t}\right)_{t=0}. \tag{3}$$

R is the relative increasing rate of the vapor density that immediately follows the light switching on at $t = 0$.

R can be extracted from the absorption signals like the one shown in Figure 1. In Figure 3 R is reported as a function of $I_{\rm L}$ for the PDMS film (Fig. 3a) and for the OCT film (Fig. 3b), respectively. R shows a linear dependence on $I_{\rm L}$ for both coatings, *i.e.*

$$R = k\,I_{\rm L}. \tag{4}$$

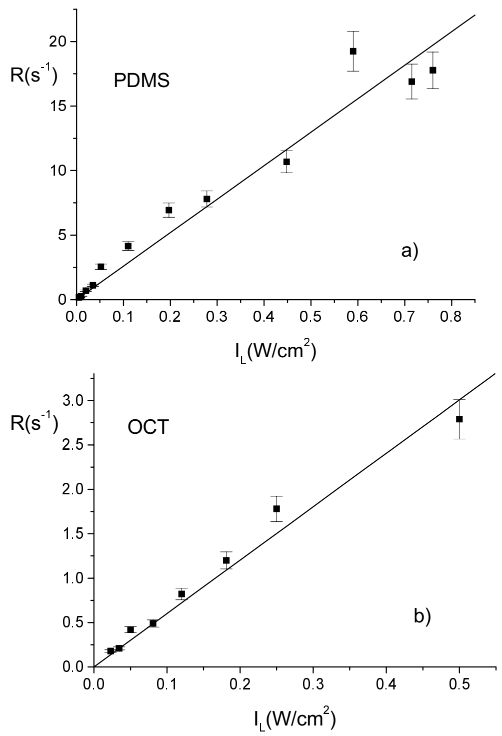

Fig. 3. The rate R as a function of desorbing light intensity. (a) PDMS film; (b) OCT film. The solid curves are least squares fits.

k gives the normalized vapor density increase per unit area and desorbing light energy. The parameter k depends, as well as R, on the cell geometry. In particular, in our 1D model it results proportional to the inverse of the characteristic cell length L, defined as the ratio between the cell volume and the illuminated surface portion.

From the experiment, we get $k(\mathrm{PDMS}) = (26 \pm 1)\ \mathrm{cm}^2/\mathrm{J}$ and $k(\mathrm{OCT}) = (6.0 \pm 0.2)\ \mathrm{cm}^2/\mathrm{J}$. From these values we can finally evaluate the desorption atomic rates per unit power at $t = 0$

$$\eta = kn_0L. \tag{5}$$

η gives the effective number of desorbed atoms per Joule. From the measurements $\eta(\mathrm{PDMS}) \cong 3.9 \times 10^{10}$ atoms/J and $\eta(\mathrm{OCT}) \cong 1.1 \times 10^{10}$ atoms/J are obtained. These two rates are orders of magnitude larger than those measured in thermal desorption [8] and comparable with those measured in surface-plasmon excitation experiments [9,10].

We want to stress here that the different dependencies of $\delta_{\mathrm{LIAD}}^{\max}$ and of R on I_L do not produce any internal contradiction and, on the contrary, give important insights. In fact, the two parameters give different information about the effect and have different meanings. R is related to desorption of the atoms laying on the surface, *i.e.* at the coating/gas-phase boundary. If LIAD would be only a surface effect, not only R, but also the total number of desorbed atoms, and hence $\delta_{\mathrm{LIAD}}^{\max}$, should be proportional to the light intensity I_L. In fact, as a general feature for a pure surface effect we would have simply first order linear differential equations (rate equations) and a linear response of the system to all the main parameters. The experimental results force us instead to the conclusion that the desorbed atoms do not come only from the coating surface but they also emerge from the coating bulk. In other words, LIAD is a combination of two processes: direct photo-desorption from the surface and diffusion within the siloxane layer. The photo-desorbed atoms are replaced by fresh atoms diffusing to the surface. Moreover, from the experimental data it comes out that the atomic diffusion and hence the diffusion coefficient D_c increases with the light intensity. To our knowledge this is the first time that such an effect is clearly observed, measured and discussed: LIAD represents a new class of photo-effect characterized by two simultaneous phenomena due to the light: surface desorption and fastened bulk diffusion.

In reference [4] we have developed a theoretical model which explains both qualitatively and quantitatively the dependencies of R and $\delta_{\mathrm{LIAD}}^{\max}$ on the light intensity I_L. This model is here summarized and specialized to the discussed experimental results.

$N(x,t)$ and $n(t)$ are the densities present inside the coating and the cell volume respectively. At the equilibrium and with the cell in the dark, we have a homogeneous density in the coating $N(x,t) = N_0$ and in the gas $n(t) = n_0$. Upon this condition, the flux J^+ of desorbed atoms must be opposite to the flux J^- of adsorbed atoms, *i.e.*

$$J^+ + J^- = \alpha_0 N_0 - \beta n_0 = 0. \tag{6}$$

α_0 is proportional to the probability for an atom arriving on the coating surface to be desorbed in the dark; in the same way β is proportional to the probability for an atom in the gas phase to be adsorbed when hitting the wall. When the desorbing light is switched on, the equilibrium is broken and a net flux of desorbed atoms into the cell volume appears. According to our model, light modifies the desorption coefficient as

$$\alpha = \alpha_0 + \alpha_1(I_\mathrm{L}, \lambda) \cong \alpha_0 + a(\lambda) I_\mathrm{L} \tag{7}$$

where $a(\lambda)$ is a coefficient depending only on the light wavelength. In fact, the experimental results show a linear dependence of R on the light intensity, then α must be a linear function of I_L. As a result of this modification, the vapor density changes according to

$$\frac{\mathrm{d}n}{\mathrm{d}t} = \frac{\alpha}{L} N - \frac{\beta}{L} n - \gamma(n - n_0). \tag{8}$$

The last term of equation (8) describes the relaxation of the vapor density to its equilibrium value controlled by the reservoir. The characteristic time of this relaxation process is $\tau_\mathrm{D} = L/(L\gamma + \beta)$ (in our case $\gamma \gg \beta/L$, so that $\tau_\mathrm{D} \cong 1/\gamma$). From equations (6–8), it follows that

$$R = \frac{1}{n_0} \left(\frac{\mathrm{d}n}{\mathrm{d}t} \right)_{t=0} = \frac{a(\lambda) N_0 I_\mathrm{L}}{L n_0} \tag{9}$$

and according to (4)

$$k = a(\lambda)\, N_0/(L n_0). \tag{10}$$

Equation (9) shows that the photo-desorption rate is proportional to the intensity of the desorbing light. Atoms that are desorbed from the coating surface are replaced by others emerging from the coating bulk. These latter follow the 1D diffusion equation

$$\frac{\partial N}{\partial t} = D_{\mathrm{c}} \frac{\partial^2 N}{\partial x^2} \tag{11}$$

where x is the coordinate inside the coating. The boundary condition

$$-D_{\mathrm{c}} \left(\frac{\partial N}{\partial x} \right)_{x=0} = \alpha N - \beta n \tag{12}$$

has to be satisfied at the gas-coating interface. It reflects the fact that the atomic diffusion flux near the surface must be equal to the net flux of desorbing and adsorbing atoms on the surface. In fact, as it shall discussed in Section 3, it is not possible to fit experimental curves without assuming a dependence of D_{c} on I_{L}. Because of the experimentally inferred linear dependence of R on I_{L}, it is reasonable to assume that other kinetic coefficients, and in particular D_{c}, have a linear dependence on I_{L}, so that D_{c} can be written as

$$D_{\mathrm{c}} = D_0 + D_1(I_{\mathrm{L}}, \lambda) \cong D_0 + d_1(\lambda) I_{\mathrm{L}}. \tag{13}$$

When the vapor density reaches its maximum $n_{\max}$, it must be $\mathrm{d}n/\mathrm{d}t = 0$. From equation (8) it follows

$$\frac{\alpha}{L} N_1 - \frac{\beta}{L} n_{\max} = \gamma (n_{\max} - n_0) \tag{14}$$

where N_1 is the atomic density in the coating close to the surface at this given time. The atoms participating to the desorption process are then only those confined in a coating layer of thickness h, the order of magnitude of h being

$$h = (D_{\mathrm{c}}/\gamma)^{1/2}. \tag{15}$$

Therefore the diffusion flux to the coating surface is of the order of

$$\frac{D_{\mathrm{c}}(N_0 - N_1)}{h} = \sqrt{D_{\mathrm{c}} \gamma}\,(N_0 - N_1) \tag{16}$$

that must equal the net flux of atoms across the surface

$$\sqrt{D_{\mathrm{c}} \gamma}\,(N_0 - N_1) = \alpha N_1 - \beta n_{\max}. \tag{17}$$

From the experiments we have typically that $\beta \ll \gamma L$ and $\alpha_1 \gg \alpha_0$ (see also [4]). Applying these conditions and combining equations (14, 17, 7, 6) we find

$$\delta_{\mathrm{LIAD}}^{\max} = \frac{n_{\max} - n_0}{n_0} \approx \frac{a(\lambda) I_{\mathrm{L}}}{L\gamma} \frac{\sqrt{D_{\mathrm{c}}\gamma}}{\sqrt{D_{\mathrm{c}}\gamma} + \alpha} \frac{N_0}{n_0}\,. \tag{18}$$

In the weak intensity limit the condition $\alpha \ll (D_{\mathrm{c}}\gamma)^{1/2}$ holds and equation (18) becomes

$$\delta_{\mathrm{LIAD}}^{\max} \approx \frac{a(\lambda) I_{\mathrm{L}}}{L\gamma} \frac{N_0}{n_0} \propto I_{\mathrm{L}}. \tag{19}$$

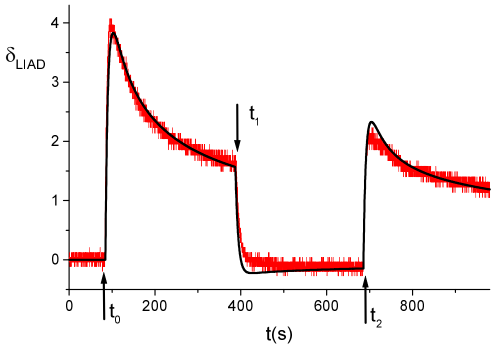

Fig. 4. Double illumination measurements: absorption signal as a function of time. Data are converted so to give directly the δ_{LIAD} value. Desorbing light (Ar$^+$ laser @514 nm) is switched on at t_0, is off at t_1, and back on at t_2. The continuous curve is the signal computer simulation obtained after our model. The cell is coated by PDMS.

In the high intensity regime the condition $\alpha \gg (D_{\mathrm{c}}\gamma)^{1/2}$ is valid [4] and moreover equation (13) gives $D_{\mathrm{c}} \propto I_{\mathrm{L}}$: equation (18) becomes

$$\delta_{\mathrm{LIAD}}^{\max} \cong \frac{1}{L} \sqrt{\frac{D_{\mathrm{c}}}{\gamma} \frac{N_0}{n_0}} \propto \sqrt{I_{\mathrm{L}}}\,. \tag{20}$$

These equations give the observed dependence of the effect on I_{L} as shown in Figure 2, where a very good agreement is obtained between the experimental data and the best fitting curve.

3 Discussion and conclusions

The LIAD features are well described by our 1D model that predicts on one side a linear dependence on the light intensity of both the diffusion coefficient and the desorption rate and, on the other side, a square root dependence on I_{L} of the maximum relative density variation.

A qualitative but impressive check of it is obtained by exposing two consecutive times the same cell to the desorbing light, as shown in Figure 4. The first illumination gives a $\delta_{\mathrm{LIAD}}^{\max}(\mathrm{I})$ that is much larger than $\delta_{\mathrm{LIAD}}^{\max}(\mathrm{II})$ obtained with the second illumination. The difference between the two $\delta_{\mathrm{LIAD}}^{\max}$ values decreases by increasing the time delay between the two light pulses. But the difference does not go to zero even for delays as long as many hours. This can be explained by assuming that a fast depletion of the coating region close to the surface is induced when the cell is illuminated, while this same part is filled back more slowly in the dark. Therefore, we have to wait a much longer time before getting the same atomic emission from the surface. A computer evaluation of the experiment made by solving equations (8, 11, 12) allows us to fit the double illumination signal, provided the diffusion coefficient and the desorption rate are assumed to be dependent on I_{L} as specified. When the dependence of the diffusion coefficient on the light intensity was neglected, no fit was obtained.

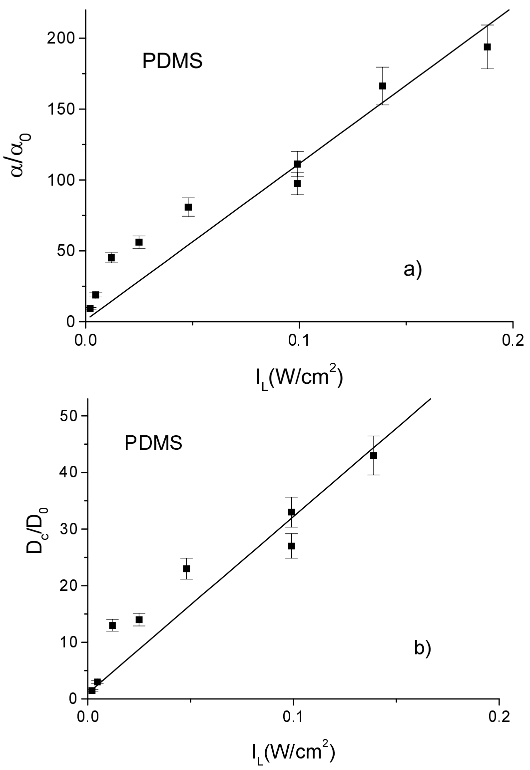

Fig. 5. The ratios α/α_0 (a) and D_c/D_0 (b) as functions of the desorbing light intensity. The cell is coated by PDMS.

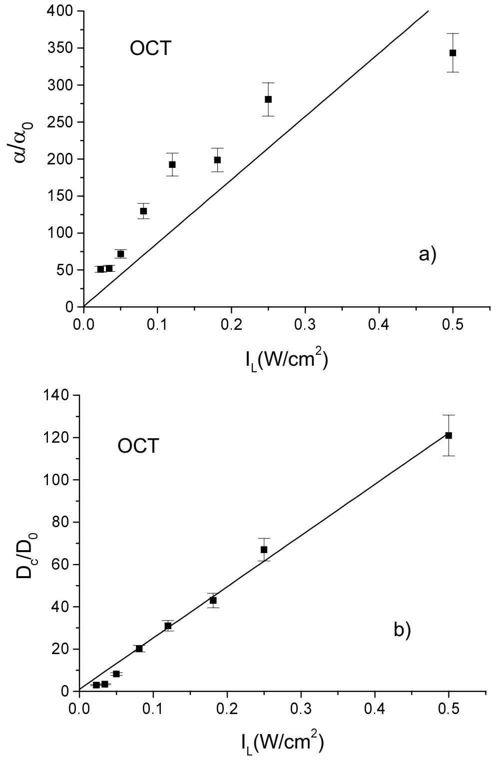

Fig. 6. The ratios α/α_0 (a) and D_c/D_0 (b) as functions of the desorbing light intensity. The cell is coated by OCT.

By a least squares fitting of the experimental data for the two coatings and upon different illumination conditions it is possible to obtain the dependence of both D_c/D_0 and α/α_0 on I_L. The final results are shown in Figure 5 for PDMS coating and in Figure 6 for OCT coating respectively.

The best fit curves reported in Figures 5 and 6 correspond to values

$$a(\lambda)/\alpha_0 = (1.1 \pm 0.1) \times 10^3 \text{ cm}^2/\text{W}$$

$$\text{and } d_1(\lambda)/D_0 = (3.1 \pm 0.2) \times 10^2 \text{ cm}^2/\text{W}$$

in PDMS and

$$a(\lambda)/\alpha_0 = (9 \pm 1) \times 10^2 \text{ cm}^2/\text{W}$$

$$\text{and } d_1(\lambda)/D_0 = (2.4 \pm 0.1) \times 10^2 \text{ cm}^2/\text{W}$$

in OCT, respectively.

As a first approximation the dependencies on the light intensity of both D and α for the PDMS and OCT coatings are about the same. A systematic analysis of these parameters as a function of the desorbing wavelength is under way, in order to get more detailed information about the LIAD effect and the interaction between alkali atoms and the two studied coatings.

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