

Review

# Low Energy Atomic Photodesorption from Organic Coatings

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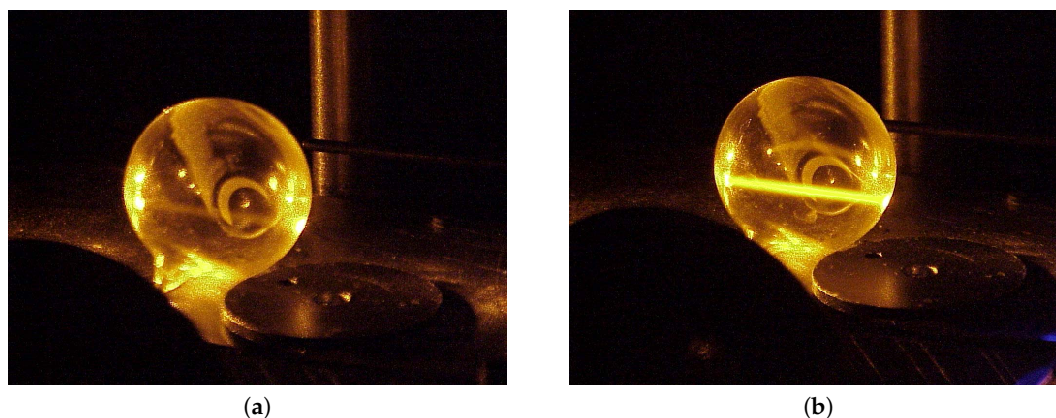
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**Abstract:** Organic coatings have been widely used in atomic physics during the last 50 years because of their mechanical properties, allowing preservation of atomic spins after collisions. Nevertheless, this did not produce detailed insight into the characteristics of the coatings and their dynamical interaction with atomic vapors. This has changed since the 1990s, when their adsorption and desorption properties triggered a renewed interest in organic coatings. In particular, a novel class of phenomena produced by non-destructive light-induced desorption of atoms embedded in the coating surface was observed and later applied in different fields. Nowadays, low energy non-resonant atomic photodesorption from organic coatings can be considered an almost standard technique whenever large densities of atomic vapors or fast modulation of their concentration are required. In this paper, we review the steps that led to this widespread diffusion, from the preliminary observations to some of the most recent applications in fundamental and applied physics.

**Keywords:** photon stimulated desorption; atomic desorption; antirelaxation coatings; polymers and organics

## 1. Introduction

Organic coatings have been widely used in atomic physics since the 1960s because of their anti-depolarization properties. However, the first evidence of ejection of atoms from an organic coating induced by the light was observed only in 1993 by Gozzini et al. [1]. During an optical-pumping experiment on sodium vapor in a polydimethylsiloxane (PDMS) coated pyrex cell, an intense yellow fluorescence induced by a dye laser tuned on the Na D lines was observed at room temperature, which usually is too low to have an atomic density sufficient to produce a fluorescence visible with the naked eye. The effect was further enhanced when an additional non resonant beam illuminated the cell, and the authors measured a vapor density corresponding to a temperature of 160 °C. This was immediately explained by a sudden release (desorption), triggered by the low intensity light of the Na atoms previously adsorbed by the organic coating. As an example of the fluorescence increase upon illumination in the case of sodium, in Figure 1, the pictures of a spherical cell coated with PDMS in the absence and in the presence of atom ejection are presented.



**Figure 1.** Sodium fluorescence at room temperature without (a) and with (b) atom ejection induced by 435 nm LED radiation. The photos are related to the experiment presented in [2].

The following year, the same effect was observed with non coherent and much weaker desorbing light by Meucci et al. [3]. In this experiment, photodesorption of Rb atoms from PDMS was measured as a function of the desorbing light intensity and frequency, and the acronym LIAD (Light Induced Atomic Desorption) was introduced [4]. In 1996, the photodesorption of Na and Na<sub>2</sub> from PDMS was demonstrated and suggested a tentative interpretation of LIAD at microscopic scale along with a first theoretical model [5]. After these pioneer works, LIAD has been extensively investigated with a growing interest both as a tool to obtain a deeper insight into surface/atom interaction and as a technique for numerous applications.

Besides PDMS [6–17], organic films investigated so far include octamethylcyclotetrasiloxane (OCT) [18], octadecyltrichlorosilane dry film (OTS) [19] and paraffin [20,21]. Details on the preparation of different coatings are reported in [1,4,19,20].

LIAD represents an efficient technique to produce large and controllable atomic densities, particularly appealing for miniaturized devices that can easily be completely illuminated by the desorbing light. The possibility to combine LIAD with coherent spectroscopy, high resolution magnetometry and metrology makes this technique very interesting in many applications that will be discussed in the following sections.

Several works have been produced on the photodesorption of different atoms from organic compounds named above or porous materials [22–29] in sealed glass cells, high-vacuum chambers or photonic bandgap fibers.

To date, low energy atomic photodesorption from organic coatings—or other dielectric surfaces—has become a common tool in many fields, from fundamental science to sensing, for obtaining relevant and fast increase of atomic density without the need of heating. This provides immediate and obvious advantages in terms of ease of use, response speed, and power consumption, not to mention that it benefits all those cases when high temperatures could be dangerous for equipment, including the coating itself, operators or sensors' targets. In addition, as discussed in the following, the investigation of the characteristics of the photodesorbed atoms allows assessment of the quality and the condition of the organic compound. It also represents a promising approach for shading new light on the mechanisms of adsorption, desorption and diffusion in the coating. Because of all of these reasons, LIAD and organic coatings are nowadays the object of a renewed multidisciplinary interest.

This review work is structured as follows: in Section 2, we present the main concepts related to the interaction between atomic vapor and organic coatings, as well as the definition of photodesorption from such coatings. In Section 3, we describe the phenomenology and the main results in alkali atoms in the case of organic coatings (Section 3.1) and (Section 3.2). In addition, for the sake of completeness in Section 3.3 a brief overview of light-induced desorption phenomena in other

dielectric media is given. In Section 4, we present the model describing the microscopic mechanisms, diffusion and charge transfer, involved in LIAD. In Section 5, we report on the investigations of the dynamics of photodesorption from organic coatings. In Section 6, some of the most recent applications of light-induced atomic desorption in fundamental and applied research will be briefly reviewed. The paper ends with Section 7 devoted to those problems still unsolved or widely debated, and Section 8, which provides conclusions and perspectives.

## 2. Adsorption and Photodesorption from Organic Coatings

In its broadest meaning, adsorption designates a large wealth of physical processes, leading an independent particle to be captured by a surface of a different physical phase. A general review of such complex and diverse phenomena is well beyond the length and the scope of the present work. Therefore, in the following, we will restrict the analysis to the case of atoms in the gas phase captured by a layer of an organic coating, which is of immediate interest for atomic physics and its applications.

In more detail, the adsorption process is mainly governed by the surface energy ([30] Chap. 4). As a consequence, two types or rather two regimes of surface interaction can be observed: (i) the high adsorption energy case, or chemisorption, when the adsorbed particles is bound to the surface by a covalent bonding or a pure Coulombian interaction, and (ii) the low adsorption energy case, or physisorption, where the adsorbed atom is bound by weak van der Waals forces. Whereas chemisorption leads to loss of the adsorbed particles, with physisorption, the atom retains partial diffusion capability and, therefore, the possibility to escape the surface after an average sticking time  $\tau_s$ , provided that suitable excitations are created.

In the case of physisorption from gas phase onto a dielectric substrate such as organic coatings,  $\tau_s$  depends on the local adsorption energy  $E_a$ , defined as the kinetic energy necessary for the atom to escape the surface van der Waals forces:

$$\tau_s = \tau_s^{(el)} \exp \left[ \frac{E_a}{k_B T} \right] \quad (1)$$

where  $k_B$  is the Boltzmann constant,  $T$  is the absolute temperature, and  $\tau_s^{(el)} \sim 10^{-12}$  s is the sticking time for a pure elastic collision, practically corresponding to the duration of the interaction between the atom and the coated surface. Typically, for atomic physisorption,  $10^{-3}$  eV  $\leq E_a \leq 1$  eV. A subtle aspect of this process is the thermalization of the adsorbed particles: upon physisorption from gas phase, the adsorbed atom quickly dissipates its kinetic energy, which becomes comparable or smaller than the difference in  $E_a$  of neighboring sites. Consequently, surface diffusion, although in principle favored by the low adsorption energy, is not efficient.

This can be dramatically changed by light with the LIAD effect, extensively treated in the following.

It is noteworthy that LIAD is one of the numerous photo-induced desorption processes, or photodesorptions. However, it has its own well-defined characteristics, which distinguish it from high-intensity photodesorption, such as in laser ablation [31], as well as from resonant light-induced evaporation, such as that induced by surface plasmons [25]. In this context, the first evidence of photo-stimulated effects—different from LIAD—from dielectric substrates were reported for Na atoms from sapphire substrate, with resonant and even large intensity radiation [32,33].

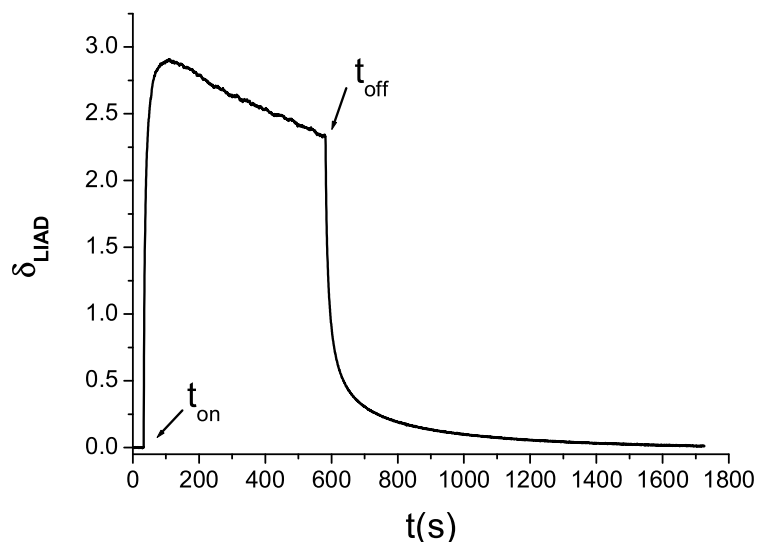
## 3. Phenomenology of LIAD from Organic Coatings

The overall characteristics of the effect are very similar, although the chemical compositions of the organics are rather different. We divide this section into three parts, one dedicated to silane compound coated vapor cells, the second to paraffin coated vapor cells due to their stability to temperature, chemical composition and different building techniques, and finally the third to other dielectric media.

### 3.1. LIAD in Silane Compounds

PDMS is a silicon based organic polymer with chemical formula  $\text{CH}_3[\text{Si}(\text{CH}_3)_2\text{O}]_n\text{Si}(\text{CH}_3)_3$ , where  $n$  is the number of repeating monomer units, and its structure is a linear chain. OCT is an organosilicon compound with the formula  $[(\text{CH}_3)_2\text{SiO}]_4$ , and its structure is a crown. OTS is a hydrocarbonic chain with chemical formula  $[\text{CH}_3(\text{CH}_2)_{17}\text{SiCl}_3]$ . The adsorption energy of alkali-metal atoms with this coated glass falls in the eV range so that the formation of atomic surface layers is prevented. When a coated alkali-metal vapor cell is illuminated with non resonant light (either incoherent or laser) in the  $\text{mW}/\text{cm}^2$  range, an increase of the vapor density is observed, even larger than one order of magnitude. The large desorption yield indicates that the desorbed atoms come not only from the film surface but also from its bulk [3]. Most of the experiments have been performed in closed cell systems with a quasi-equilibrium between atomic vapor phase, atomic density inside the coating and the solid alkali-metal reservoir, thus the maximum achieved density upon illumination decreases due to the progressive re-adsorption of atoms by the cell walls.

Typical LIAD temporal behavior is shown in Figure 2. The Rb relative density variation  $\delta_{\text{LIAD}}(t)$  starts to increase when the desorption light is turned on at time  $t_{\text{on}}$ , reaches a maximum, and then slowly decreases back to the equilibrium value. When the desorbing light is turned off at time  $t_{\text{off}}$ , a faster decay of the vapor density is observed.



**Figure 2.** Typical example of an LIAD (Light Induced Atomic Desorption) signal: Rb relative vapor density variation as a function of time in a polydimethylsiloxane (PDMS) coated cell.  $t_{\text{on}}$  and  $t_{\text{off}}$  indicate the time when the desorption light ( $I_L = 17 \text{ mW}/\text{cm}^2$  at 514 nm) is turned on and off.

Multiple illumination of the cell leads to the decrease of the maximum number of desorbed atoms and this difference becomes less pronounced by increasing the time delay between the light pulses [18]. This was 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 in more slowly in the dark, and patterned with both the desorption efficiency and the diffusion coefficient of the alkali atoms embedded in the dielectric film. All of these experiments were performed at room temperature. LIAD is a non-thermal effect, in fact the number of desorbed atoms does not increase exponentially with the desorbing light intensity and exhibits saturation at higher intensity [3]. For the maximum relative atomic density increase  $\Delta_{\text{max}}$  as a function of the desorbing light intensity  $I_L$ , a square root dependence was reported for Rb from PDMS [3,6], for Rb and Cs simultaneously desorbed from PDMS [13], for Rb from OCT [18], Rb from OTS [19], and K from PDMS [10]. For Na from PDMS, a linear dependence of the desorbed atoms has been found at low desorbing light intensity [1]. For Rb from PDMS and OCT [18], for Rb and Cs from PDMS [13] and Rb from OTS [19], the desorption

rate  $R = dn/dt$  at  $t = t_{on}$  at the beginning of the illumination as a function of the desorbing light intensity has been reported. This parameter has a smaller dependence on the cell geometry compared to  $\Delta_{max}$ . It is related to the atoms coming from the surface of the coating, not affected by diffusion processes, and increases linearly with  $I_L$ , the intensity of the desorbing light. No desorbing intensity threshold has been found so far from various polymers with alkali atoms. This leads to the conclusion that LIAD is independent from the chemical composition of the coating, while it depends more on physical parameters such as sticking and diffusion probability inside the organics. Various attempts of comparison of the LIAD efficiency for different atom+substrate systems were reported, in the case of Rb (see, for example [34,35]). Nevertheless, the high variability of the experimental details makes it difficult to compare the data. Simultaneous light-induced desorption of rubidium and cesium atoms has been observed in PDMS coated Pyrex cells at room temperature and at low light intensity [13]. In this work, the two alkali atoms show the same dynamics and the same dependence on the desorbing light frequency. No competition in the free sites occupancy was observed. A monotonic increase of the efficiency with the desorbing photon energy, independent from the atomic species and the coating, was reported [1,3,8,10,13,19]. The absorbance of PDMS, obtained by using a spectrophotometer, is reported for a sample thickness of 1 cm [13]. It shows huge absorption in the IR and UV regions, but it is transparent in the visible. All these facts rule out the possibility that LIAD may depend on a resonant process.

According to some experiments, a photon energy threshold can be extrapolated, specifically for the atomic species/substrate pair. Thresholds for Na and Na<sub>2</sub> from PDMS at 1.18 eV and 1.43 eV, respectively [7], 1.38 eV for Rb from PDMS [8], and 1.43 eV for K from PDMS [10], are reported. Photodesorption of non-alkali atoms such as Ca from PDMS, according to ref. [14], exhibits both an intensity and a frequency threshold. Some other experiments did not find any frequency threshold as Rb and Cs desorbed at the same time from PDMS [13], or Rb from OTS [19], in the limits of the explored frequency range. Moreover, in the case of both Rb and Cs from PDMS, a threshold at 1.38 eV could be extrapolated, but the authors claim that this result is contradicted by their observation of LIAD with longer wavelengths and by the data of [11], which provide evidence of the LIAD effect with excitation at 1.17 eV. In the last experiment, the dynamics of short pulsed laser-induced desorption of Na atoms from PDMS coated glass prism surfaces are investigated. Kinetic energies of desorbing sodium atoms of several hundred meV are found, increasing with increasing laser intensity. Evanescent wave measurements suggest that the desorbed atoms stem from a subsurface layer of the PDMS film, resulting in diffusive characteristics for the total yield of the desorption process. In the same experimental conditions, the diffusion coefficient for rubidium in PDMS thin films has been determined both via pulsed laser depletion and via continuous (CW) laser time-of-flight detection of desorbing atoms [12].

### 3.2. LIAD in Paraffin

Paraffin [C<sub>n</sub>H<sub>2n+2</sub>] consists of a mixture of hydrocarbon molecules containing between twenty and forty carbon atoms. Paraffin has been the most known and utilized organic coating in the past, since the pioneer work in which the relaxation of the spin of rubidium atoms was measured [36]. A disadvantage of this type of coating is its instability with temperature, which cannot be increased above about 50 °C; as a consequence, the use of paraffin coatings in the case of alkali atoms is limited only to Cs, Rb, and to a lesser extent K, which have sufficient vapor pressures for spectroscopic measurements at room temperature. For this reason, in view of an optical method for increasing the atomic density, LIAD opens new perspectives in atomic physics experiments using paraffin.

The first systematic study of LIAD from paraffin coating has been presented by Alexandrov et al. in 2002 [20]. In this work, the authors studied LIAD dynamics as a function of the desorbing light intensity and frequency in cells with different geometries and, consequently, different ratio between the enlightened area and the total cell surface; the cells are filled with Cs or Rb or with the two alkalis contained in two separate stems. Systematic studies in cells with the same geometry



and different alkalis or alkali combinations in different cells led to similar results, supporting the conclusion that LIAD is governed by the properties of the coating. Different cell geometries affect the ratio between the number of the desorbed and the initial number of atoms. As in the case of other organic compounds, the coating is emptied by the desorbing light, but, after a period of darkness, the adsorbate density is restored by atoms from the stem. The authors find a threshold in the photon energy of the desorbing light of about 1 eV, and a linear behavior of the rate of atom desorption from the coating in the cell volume as a function of the desorbing light intensity. The time evolution is on the order of tens of seconds. In a successive paper, the same authors studied LIAD from paraffin, paying much attention to the role of the cell stem. In the paper, the authors extended the experiment on potassium using UV desorbing light [37].

In 2008, a detailed analysis of LIAD from paraffin coating in Na has been reported [21]. In this experiment, faster dynamics have been observed than the ones reported in Rb and Cs described above (tenths of seconds). As a consequence, there is no need to keep the cell in the dark to re-establish the initial density of sodium embedded in paraffin. Data show that in this case desorption may be ascribed to atoms at the surface; in the experiment led at room temperature, a relative increase of the density up to  $\Delta n/n_0 = 25$  has been observed, which led to an equivalent temperature of about 75 °C. An interesting effect not present in other coatings like PDMS is that LIAD dynamics becomes slower at each measurement session, related to the effective time of use. This is consistent with the fact that paraffin is more sensitive to local heating due to photon energy of the desorbing light. Anyway, this does not prevent atoms from being desorbed, as the overall amplitude of LIAD is the same; this supports the fact that during the illumination, we have a rearrangement of dangling bonds in which alkali atom in which alkali atoms are trapped.

### 3.3. LIAD in Other Dielectric Media

Although not of immediate interest for the present review, for the sake of completeness, we recall here that low-intensity light-induced atomic desorption has been observed also in other contexts and configurations.

An important class of light-stimulated desorption is from porous dielectric materials. Evidence of LIAD was in fact found from porous glass, a chemically altered silica matrix, characterized by an interconnected network of pores of controlled diameter, usually in the range of 10–100 nm. LIAD effect from bare quartz [38] and from porous alumina with Rb atoms [26] was also demonstrated. In this context, as a consequence of the tight confinement of the desorbed atoms, light-assisted formation of metallic nanoparticles was observed in Rb, Cs and K from porous glass [22–25,28,29] and also from Vycor glass [27].

Cluster formation has been related to strong bindings. The clusters originate near the surface defects. Moreover, in very small pores, in the nanometer range as in mesoporous glasses, phase transition can be observed. Van der Waals forces keep atoms and molecules bound together, which then tend to accumulate. Upon further increase of the alkali concentration, they form a status similar to liquid. Montecarlo simulation [39] shed more light upon the quasi-equilibrium behavior defined by adsorption and diffusion processes inside the porous observed in presence of the LIAD effect. On the contrary, the presence of organic coatings inhibit the formation of atomic layers on the surface [40].

Furthermore, photoejection of Na atoms from amorphous porous silica mimicking the lunar surface was obtained in ultra-high vacuum conditions at 250 K with UV photons ( $\lambda < 300$  nm) [41]. This photo-ejection was later indicated as the main source for the Na and K traces detected in the tenuous atmosphere of the Moon and Mercury [42]. Effects attributed to LIAD were recently observed also in other porous or quasi-porous materials, such as opals loaded with Cs vapor [43].

LIAD was also observed from the core of hollow photonic fibers, as reported in [44–51], just to name a few.

#### 4. Microscopic Interpretations

The study of the LIAD phenomenon has been growing in interest year by year due to the many links among different branches of the material science, like Physical Chemistry, Atomic and Molecular Physics, and Solid State Physics. Historically, the solid/vacuum interfaces played important roles in the material science as well in electronics; therefore, the behavior of the atomic absorption and desorption from polymeric or porous interfaces is very intriguing as its comprehension could shine more knowledge in differently organized surface systems. Consequently, many research groups around the world tried to deeply understand the physics that stand beyond the LIAD effect itself, also with the aim of optimizing the possible practical applications, as it will be shown in a following section. From these works, applied mainly to alkali atomic species, the following has emerged.

The interaction of the light with the potential wells in the coatings, starting from the infrared, induces the atom to desorb; and the yield of the process improves with increasing the light frequency, showing a threshold. In particular, the alkali-carbon and alkali-oxygen interaction potentials in the coatings are affected by the desorbing light even if non resonant with the alkali atoms transitions [52]. Moreover, the more energetic blue e.m. excitation seems to rearrange the bonds in the hydrocarbon chains in a reversible way.

Most of the works show two different activation energies related to the thermal and the photon excitations, in the range of hundreds of meV and eV, respectively [7,10]. They depend very much on the coating materials and procedures.

If we define the dimensionless LIAD parameter in order to quantify the atom density variation:

$$\delta_{\text{LIAD}} = \frac{n - n_0}{n_0} = \frac{\Delta n}{n_0} \quad (2)$$

where  $n$  is the atom density under illumination and  $n_0$  is the density in the dark, in the thermal case, it follows the classical Boltzmann statistic, that is

$$\delta_{\text{LIAD}}(T) \propto e^{E_A/(k_B T)} \quad (3)$$

where  $E_A$  is the thermal activation energy and  $k_B$  is the Boltzmann constant. This implies that beyond a certain temperature, there is an atomic density saturation in the closed measurement cell anyway. Instead, the photon yield recalls what happens in amorphous materials for the radiation absorption by bands of localized states [53]:

$$\delta_{\text{LIAD}}(h\nu) \propto c(h\nu - h\nu_0)^2 \quad (4)$$

where  $c$  is a constant and  $h\nu_0$  is the photon energy threshold. In this case, it is analogous to the work function of the material.

The dynamic of the process has been experimentally observed to consist of both atomic emission and diffusion with different rates, giving an atomic density evolution equation under illumination with at least two time constants  $\tau_1$  and  $\tau_2$ , respectively [10]:

$$n(t) = n_0 + \Delta n_{\text{max}}(1 - e^{-t/\tau_1})e^{-t/\tau_2} \quad (5)$$

with usually  $\tau_2 \gg \tau_1$ .

By a “time-of-flight” experiment, Brewer et al. [9] found that the dynamic of photodesorption of alkali-metal atoms from a PDMS substrate is governed by the relative position of the energy level that is initially populated by photoexcitation. If this level lies below the crossing point between the excited term of the charge transfer complex and the term for physically adsorbed atoms, then desorption occurs after thermalization. The resulting desorption flux is Maxwellian with temperature determined by the resonant heating.

However, it must be emphasized that, in [13], an interpretation of the experimental results in terms of non-resonant light scattering from the PDMS is proposed. In this work, no experimental

evidence of resonant processes or frequency threshold for LIAD is observed for Rb and Cs desorbed from PDMS. The authors estimate a ratio of the dwelling times for atoms in the coating in the presence and in the absence of light on the order of  $10^2$ – $10^3$ , corresponding to a binding energy change  $\Delta E$  equal to a few kT. Such a small energy change supports the picture that light excites phonons inside the coatings with a transfer of energy to the most loosely bound atoms that are then desorbed.

#### 4.1. Diffusion

The alkali diffusion inside the paraffin coatings has been verified by using the X-ray photoelectron spectroscopy (XPS) technique [52]. The experiment validates the existence of a reservoir of adsorbed atoms in the coating bulk, as it is usually assumed in LIAD models.

Atutov et al. [6] take into consideration the current fluxes of the alkali atoms in and out of the coating (PDMS), the total flux being:

$$J = J^+ + J^- = \alpha N - \beta n \quad (6)$$

where  $J^+$  is the flux of atoms leaving the surface,  $J^-$  is the flux of adsorbed atoms,  $N$  is the atomic density in the coating,  $n$  is the atomic density in the vapor phase,  $\alpha$  the atom desorbing rate and  $\beta$  characterizes the adsorbing rate. In absence of desorbing light,  $J = 0$ . When the light is turned on, they identify two regimes: weak desorbing light intensity and high desorbing light intensity. In the former, the light intensity is assumed weak enough to induce a negligible change of  $N$  near the coating surface. Then, in the first short time interval,  $n$  increases linearly with time and it is related to a small fraction of the atoms confined within the surface. Then, the atom density diminishes and the diffusion from the bulk of the polymer plays a role. In the latter, namely high light intensity, the atoms in the region close to the surface are instantaneously desorbed into the cell volume, and then the vapor density decreases as  $1/\sqrt{t}$  and the variation of the atom density is limited by the diffusion coefficient of the atoms inside the coating. The alkali atom diffusion coefficient inside the polymer is proportional to the light intensity itself. With this assumption, they explain the experimentally verified nonlinear dependence of the LIAD yield on the light power ( $P_L$ ) in high light intensity conditions, that is:

$$\delta_{\text{LIAD}}(P_L) \propto \sqrt{P_L} \quad (7)$$

Instead, in a low desorbing light intensity regime,  $\delta_{\text{LIAD}}$  is directly proportional to the light intensity itself.

Nevertheless, the assumption of the diffusion inside the polymers as the principal cause of the long-lasting part of the process is questioned by Rebilas et al. [15]. They principally distinguish between the illuminated and non illuminated surface with the related fluxes  $J_i$  and  $J_d$  from these regions, respectively. The atoms that leave the irradiated region create a flux of desorbed atoms ( $J^*$ ), which is a consequence of very quick atomic diffusion in the direction normal to the surface. The following equations define the parameters:

$$J_i = J^* - \beta n, \quad J_d = \alpha_0 N_0 - \beta n \quad (8)$$

where again  $\beta$  is the coefficient characterizing the adsorption rate,  $\alpha_0$  is the desorption rate in the dark, and  $N_0$  is the atomic density inside the coating in the dark. Therefore, the lateral diffusion of atoms from the non-illuminated part of the siloxane coating to the illuminated one plays the main role in the slower part of the phenomenon. Here, the dependence of  $\delta_{\text{LIAD}}$  as  $\sqrt{P_L}$  is not expected, but a saturation behavior is guaranteed by an hyperbolic function resulting from the theory.

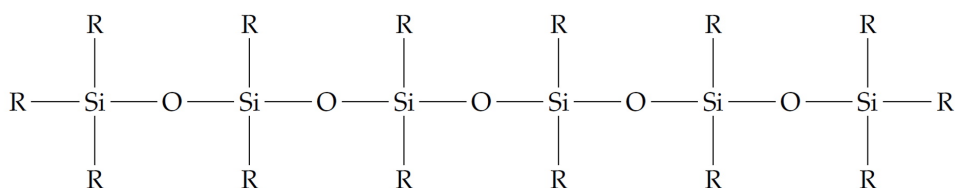
The role of the diffusion process on the polymer surface has been discussed also in [7]. The authors find the analogy with the desorption mechanism of particles on quartz surfaces related to the excitation of surface plasmons.



In a field effect experiment, a threshold behavior is evident with paraffin coated cells, which is not present in the uncoated ones [54]. This comforts the idea of the main role played by the interaction–potential wells within the coatings, even if it depends strongly on the coating procedure.

#### 4.2. Light-Induced Charge Transfer

A theory takes into account a chemical process (chemisorption) in order to explain the LIAD, at least for the silanes coatings [5,41]. In particular, Xu et al. [5] consider the adsorption process of Na from PDMS. They claim that the oxygen atoms in the PDMS backbone can serve to stabilize the  $\text{Na}^+$  by complexation. An energy stabilization can also come from the PDMS electronegativity, and this is significant if the electron from a neutral Na atom can be delocalized onto a number of Si atoms in the PDMS polymer (the low-lying empty silicon orbitals would form a basis for a highly degenerate set of levels that can accept the alkali-metal electrons) (Figure 3).



**Figure 3.** Silicon–oxygen backbone of silane polymers. R stands for a  $\text{CH}_3$  group.

Practically, if a neutral Na atom approaches the neutral PDMS surface, a van der Waals interaction should occur. However, if a  $\text{Na}^+$  cation approaches the negative charge of the  $\text{PDMS}^-$ , the potential energy curve would follow the Coulomb law. Therefore, neutral and ionic interactions are expected and an anticrossing of the two corresponding potentials, van der Waals and Coulomb, would result. The corresponding interaction potentials lie in the eV range. Photons of this energy, by interacting with the system, can free the adsorbed atoms and reverse the process.

However, even if this model is intriguing, it is not suitable for paraffin coatings, where LIAD is still observed. Certainly, the hydrocarbon chains and the outermost methyl groups, which are essentially the same as in paraffins, play the major role in the process of chemisorption.

Another theory, which takes into account the alkali physisorption process, has been proposed, but it can describe only the interaction between the bare non-polymeric materials and the atoms, where the equilibrium between the van der Waals attraction and the thermal desorption mechanisms plays the main role [55]. Here, the binding potentials are in the meV range.

At this point, however, the LIAD process remains not fully understood.

### 5. LIAD Dynamics in Organic Coatings

The time behavior of a typical system where LIAD is observed is the object of many investigations due to the importance of control of the fluxes from and towards the gas phase for practical applications of the LIAD effect. In general, a simplified system comprising free atomic vapor, adsorbed atoms with residual diffusion capability and organic coating in presence of desorbing light is taken into consideration.

The models are essentially phenomenological, and, therefore, while they are independent from the details of the photodesorption microscopic mechanisms, they are strictly dependent on the characteristics of the specific experimental conditions. For example, the time response can be dramatically different in a sealed vessel such as a spectroscopy vapor glass cell, or in an open environment, such as a continuously evacuated vacuum chamber. We limit the discussion to models developed for organic coatings in sealed cells, although phenomenological treatments of low-energy non-resonant photodesorption have been proposed for porous materials [26] and for metal layers in the context of cold atoms experiments [56].

These models, developed originally for PDMS [6] and paraffin [20], focus their attention on the complete system formed by the vapor phase and the coating, in order to model the complex interplay among adsorption and desorption fluxes in various conditions.

### 5.1. Light-Enhanced Diffusion at the Coating Surface

In [6], LIAD is directly related to the diffusion in the coating bulk. The system dynamics are modeled as a 1D diffusive process from the bulk to the surface of the coating, hence perpendicular with respect to the vapor/substrate interface.

The core of the model is the increase of the adsorbed atoms residual mobility upon exposure to the desorbing light. In detail, adsorbed atoms are assumed to be spread in the interstitial positions inside the coating, where they diffuse to the closest sites according the Arrhenius relation:

$$D_0 \propto e^{-E_{\text{act}}/kT} \quad (9)$$

where  $E_{\text{act}}$  is the activation energy of the diffusion process, and  $D_0$  is the diffusion coefficient in the dark.

The mobility of adsorbed atoms is enhanced during external illumination; consequently, the diffusion coefficient presents a term dependent on the light intensity:

$$D = D_0 + d(\lambda)I_L \quad (10)$$

where  $d(\lambda)$  quantifies the desorption efficiency of the light. The dependence of the light wavelength is thus incorporated into the phenomenological coefficient  $d(\lambda)$  and can thus be adapted to different experimental configurations.

Within this assumption, the dynamics of the LIAD effect during and after illumination are produced by the variation in the flux of atoms from ( $J^+$ , desorption) and to ( $J^-$ , adsorption) the coating (see also, for comparison, Equation (8) in the present review):

$$J^+ = \alpha N, \quad \alpha = \alpha_0 + k(\lambda)I_L \quad (11)$$

$$J^- = -\beta N \quad (12)$$

Here,  $N$  is the atomic density inside the coating,  $\alpha$  is the velocity of desorption, exhibiting a light-dependent term and a thermal term  $\alpha_0$ , which can be considered fixed in the typical experimental conditions.  $n$  is the atomic vapor density  $\beta$ , which characterizes the absorption rate unaffected by the light.

With some algebra [6], by imposing that at the equilibrium in the dark  $J^+(0) = J^-(0)$  and under the assumption of gas homogeneous density, one obtains the following evolution for the vapor density during LIAD:

$$\frac{dn}{dt} = \frac{J}{L} - \gamma(n - n_0) \quad (13)$$

where  $L = V/S$  is the volume/surface ratio of the cell, also referred to as the cell characteristic length, and  $J = J^+ + J^-$ .  $\tau = 1/\gamma$  is the macroscopic relaxation characteristic time of the system: it is the time necessary for the restoration of the equilibrium vapor density in the dark.

At the same time, a slower diffusion, because of the residual bonding at the surface, is produced between surface sites of the coating, hence *perpendicularly* to the fluxes  $J^{+, -}$ . By neglecting any bulk contribution, the atomic diffusion within the coating is described by:

$$\frac{\partial N}{\partial t} = D \frac{\partial^2 N}{\partial x^2} \quad (14)$$

According to this model, then, two regimes can be individuated:

- **Weak desorbing limit:** the vapor density variation initially grows linearly in time, reaches a maximum and then starts decreasing exponentially towards the equilibrium value.
- **Intense desorbing limit:** the vapor density variation initially grows as  $\sqrt{t}$ , reaches the maximum at  $t = 1/\gamma$  and then decreases towards the equilibrium value as  $1/\sqrt{t}$ .

It is worth recalling that the two regimes predicted here are observed also in other systems, such as K+PDMS with green desorbing light [10]. Moreover, the exponential decay in the low-desorption regime was clearly observed in PDMS with Na [2] and K [57] even with violet desorbing light. On the contrary, no evidence of the change of desorption regime is found instead in paraffin in the case of Na, even with more than 1 W of 514 nm radiation [21].

The enhancement of diffusion induced by light is studied also in [18], in which a relative increase of the parameter  $d(\lambda)/D_0$  of the order of  $10^2 \text{ cm}^2/\text{W}$  is reported for Rb atoms photodesorbed from PDMS and OCT.

### 5.2. Role of the Reservoir

In many experiments in sealed vapor cells, the atomic vapor is supplied by a solid sample of the metal under investigation, which produces, at the equilibrium, a given density in the gas phase because of thermal evaporation.

As explained in detail in [20], the presence of the so-called reservoir affects the LIAD dynamics, and, therefore, it has to be taken into account in the modelization. In particular, a virtually infinite source of atoms which tends to re-establish the initial conditions is included in the model. Under these assumptions, the system is divided into three parts with atomic densities of “free” atoms that are, respectively,  $n_s$ , assumed constant, in the case of the stem or reservoir,  $N_c(t)$  in the case of the coating and  $n(t)$  in the case of the vapor phase. The total number of atoms  $n_s + n(t) + N_c(t)$  remains constant at any time.

If  $\zeta$  indicates the flux of atoms between the vapor phase and the solid reservoir,  $n(t)\rho v_{\text{th}}A/4$ , where  $A$  is the illuminated area and  $\rho$  is the constant probability of capture, we obtain the following set of equations:

$$V \frac{d}{dt} n(t) = - \frac{\rho v_{\text{th}} A}{4} n(t) + \zeta [n_s - n(t)] + (\gamma + \gamma_d) N_c(t) + \Phi_c \quad (15)$$

$$\frac{d}{dt} N_c(t) = + \frac{\rho v_{\text{th}} A}{4} n(t) - \Gamma N_c(t) - (\gamma + \gamma_d) N_c(t) \quad (16)$$

where  $V$  is the cell free volume,  $\Gamma N_c(t)$  is the amount of atoms permanently lost in the coating and  $\gamma_d N_c(t)$  is the thermal flux coming out from the coating. Here, the flux of desorbed atoms coming from the coating  $\Phi(t)$  is given by:

$$\Phi(t) = \gamma N_c(t) + \Phi_c \quad (17)$$

where  $\Phi_c$  is a light-induced contribution which results in being time-independent and small compared to the term  $\gamma N_c(t)$ .

In summary, we note that this model is able to reproduce experimental dynamics based on six parameters which determine the density time evolution. This was further confirmed and somehow simplified in a later work [37].

### 5.3. Role of Diffusion from Non-Illuminated Sites and from the Coating Bulk

The previous models do not take into account diffusion in the bulk of the coating, *parallel* to the surface, which instead is a key feature of two more recent works, in the case of partial [15] and complete [16] illumination of the coating surface.

In these approaches, the intrinsic one-dimensional nature of the previous theories is challenged: a model comprising also lateral diffusion from non-illuminated regions and convection from the bulk is proposed.

In conclusion, although the dynamics of the process can be effectively reproduced in a large number of experimental configurations regardless of the details of the photodesorption mechanisms, the proposed models depend on numerous phenomenological parameters that prevent a generalization of the first principles' processes and calculations, or even a simple extension to different systems. It is, however, clear that diffusion and its enhancement upon illumination play a key role in determining the time evolution of systems in presence of LIAD, and that—in the case of sealed glass cells—the solid phase of the system drives the time evolution of the system during and after illumination.

## 6. Recent Applications of LIAD from Coatings

### 6.1. Stabilization of Atomic Density

LIAD has been proposed and successfully applied as a new technique to increase and stabilize vapor density in closed cells containing Rb with paraffin [37], and Na with PDMS [2]. In these experiments, the power of the desorbing light emitted by a blue diode array is modulated in order to achieve a controlled vapor density stabilized over several minutes within a range of a few percent. Another potentiality shown in [2] is that this technique can be applied to the precise vapor density modulation with a frequency of tenths of Hertz, controlling the LED intensity by means of a sinusoidal or sawtooth function. Therefore, the optical control of vapor density is a powerful method when heating techniques are not suitable; in addition, this technique can be helpful for building portable and compact devices, when the use of a conventional oven is not possible.

In a more recent work [57], optical stabilization has been applied to an experiment on Electromagnetically Induced Transparency (EIT) [58] on K in PDMS coated pyrex cells. The experiment has been performed in Hanle configuration, where a narrow magneto-optic resonance is observed with degenerate Zeeman sublevels at zero magnetic field, thus allowing for high resolution measurement of small magnetic fields. In this experiment, it is observed that atomic photodesorption reduces the depolarization rates by enhancing the antidepolarizing properties of the cell coating. Moreover, the performance of the coherent resonances obtained with the optical technique are comparable or even superior to those obtained with the heated sample, in terms of higher sensitivity with the same resolution. The work opens new perspectives in coherent spectroscopy and magnetometry performed outdoors in critical conditions.

### 6.2. LIAD in Photonic Bandgap Fibers

Photonic bandgap fibers (PBGF) are powerful devices that provide large densities of atoms confined in a region that can extend to meters of lengths of and a few microns in diameter, which can be completely illuminated and hence have several applications in nonlinear optics [59]. However, a severe limitation to the storage of alkali atoms in the fiber is their strong interaction with the silica walls both by physisorption and chemisorption. This limitation has been overcome by coating the fiber inner walls with *n*-octadecyl dimethyl methoxysilane (ODMS) [44]. In addition, LIAD has been successfully applied to release Rb atoms stored in the coating to produce an optical depth, defined as  $\kappa = nL\sigma$  (where  $n$  is the density of the atomic sample of length  $L$  and  $\sigma$  is the atomic absorption cross section) up to 2000. This is consistent with the fact that the density varies over two orders of magnitude. As a demonstration of the method, the authors observed EIT resonances in the probe–pump Lambda scheme, with up to 90% transparency and Full Width at Half Maximum, FWHM = 100 MHz by using a probe laser power as low as 10 nW. In a more recent paper [46], the same authors studied LIAD dynamics in PBGF both in a standard fiber and in an ODMS coated one with pulsed desorbing light and observed EIT resonances after switching off the desorbing light.

### 6.3. LIAD for Atomic Spectroscopy

The potentiality of LIAD was applied in 2004 to perform, for the first time, saturated absorption (SA) spectroscopy of K at room temperature [10]: in that case, the crossover splitting have been measured with precision. In a recent experiment [60] devoted to the study of the influence of coating on the spectral features of the SA D<sub>1</sub> line of K, significant modifications in the absorption profile have been observed in uncoated and PDMS coated cells. LIAD has been successfully applied to increase the signal without affecting the shape of the hyperfine transitions.

In 2005, the relaxation rate of atomic polarization in paraffin coated Cs vapor cells has been measured: the vapor is oriented by a circular pump beam, it is blocked, and after that, the “relaxation in the dark” has been measured by observing the optical rotation of a low intensity linearly polarized probe beam. The authors applied LIAD and observed no significant change in the spin relaxation rate beyond what was expected from the faster rate of the spin-exchange collisions due to the density growth [61].

In a recent paper, an experiment devoted to determining the role played by the desorbed atoms by LIAD on the atomic spin orientation [62] has been performed. There, it has been observed that without the LIAD effect, the Rb atoms contained in paraffin and PDMS coated glass undergo a strong hyperfine optical pumping; instead, this has been strongly reduced by the LIAD desorbed atoms that have been demonstrated to exhibit a random spin distribution.

### 6.4. LIAD from Organic Coatings for Cold Atoms

One of the most remarkable applications of LIAD is the efficient loading of Magneto-Optical Traps (MOTs) [63,64] and atom chips [65,66]. This technique gained a renewed attention after [2,37]: the possibility of controlling and quickly modulating the background vapor density, in fact, it permits obtaining large trapped populations during the loading phase, while maintaining good ultra-high vacuum conditions in the following stages, thus without compromising the lifetime of the cold atoms sample. This feature is of major importance in single-chamber setups. In fact, as demonstrated in [2], fast and periodic quenching of the vapor density can be achieved, thanks to the non-thermal nature of the LIAD effect, which eliminates thermal inertia and, at the same time, the need of chamber heating, which would be detrimental for the vacuum conditions.

Typically, in cold atom applications of LIAD, an incoherent photon source in the visible or UV, such as an LED or a halogen lamp, illuminates the coating during the trap loading, thus allowing the sudden release of adsorbed atoms. Accordingly, a controlled increase of the vapor density is detected. In this way, the MOT loading speeds up, taking advantage of the increased number of atoms in the vapor phase available for the capture by the laser beams. Once the desired MOT population is reached, in order to prevent reduction of the trap lifetime due to background collisions, the desorbing source is switched off and the vacuum system re-establishes the initial vacuum conditions.

Pulsed photo-desorption from PDMS coating deposited on the inner surface of a Pyrex vacuum chamber was applied to the loading of an <sup>85</sup>Rb MOT [64]. The abrupt burst of atoms released in the vapor phase allowed fast loading of the magneto-optical trap at a remarkable rate of  $2 \times 10^8 \text{ s}^{-1}$ , without relevant consequences on the vacuum conditions and hence on the lifetime of the MOT. It is noteworthy that the use of organic coating here produces a significant increase of the desorption efficiency, mainly because of the lower atom adsorption energy at the cell surface.

Regardless, the use of organic coatings for cold atom experiments may be limited by the de-gassing produced by the coating itself. Therefore, either the organic compound is optimized for minimum contamination of the residual background pressure, or the light-desorption effect is obtained from other surfaces, including the glass or metallic walls of the vacuum chamber or thin metal layers [56,65,67–70].

Organic coatings for the inner walls of the vacuum chamber are again appealing in the case of extreme conditions for laser cooling and trapping, such as in large-losses experiments with radioactive atoms. In this case, in fact, the high efficiency of the trapping system is a critical



parameter [71]. Therefore, in order to reduce the impact of adsorption at the chamber's surface, suitable organic coatings [72] are used, such as OTS [73,74], SC-77 (dimethyldichlorosilane and methyltrichlorosilane) [75] and PDMS [74]. To date, a direct demonstration of LIAD of radioactive isotopes from organic coatings has been only preliminary reported in a laser cooling experiment, with pulsed photodesorption of  $^{210}\text{Fr}$  from PDMS [76].

In summary, whenever the outgassing from the coating is not a critical issue, organic coatings allow more efficient loading of cold atomic samples, but a compromise has to be found if the residual pressure has to be on the order of  $10^{-10}$  mbar or lower.

## 7. Unsolved Problems and Open Questions

We summarize here the problems concerning low energy non resonant photodesorption from organic coatings still widely debated, as already briefly introduced in the previous sections.

The first only partially answered question is about terminology. Although it may sound otiose, the problem of what can be defined as "low energy, non resonant light induced desorption" is of major importance to highlight differences with respect to other classes of photodesorption. The solution is well beyond the scope of the present review. Therefore, we have followed a phenomenological approach, thus grouping together as "LIAD" all those photo-induced desorption processes exhibiting common features such as lack of direct excitation of atomic levels, negligible thermal effects, non-destructive and thus reversible nature and dielectric supporting substrates.

A major unsolved question, as widely described in Sections 4 and 5, is the lack of detailed insight in the microscopic mechanisms of low energy photodesorption and hence of a general and comprehensive model of LIAD, which takes into account a limited number of general parameters. Although attempts have been recently made in order to overcome this limitation, the large wealth of experimental realizations and the difficulty of bridging different disciplines have been so far preventing the extrapolation of general and possibly first-principles physical models.

A more technical issue, closely related the previous one, is the repeatability of the coating manufacturing and deposition. In fact, practical unknowns and parameters not under control during the coating procedure make the success rate of the procedure less than ideal. At the same time, the variability of the coatings' final characteristics is often larger than the typical experimental uncertainties. In other words, although coatings realized with the same procedure exhibit similar properties, some parameters, such as relaxation time or desorption efficiency, can significantly vary, leading to a wide range of experimental results.

## 8. Conclusions

Organic coatings, widely used in atomic physics for their spin-preserving properties, have gained a renewed interest in recent years thanks to the possibility of producing controlled released of adsorbed atoms by exposing the coating to weak, non-resonant and even incoherent light.

The advent of Light-Induced Atomic Desorption (LIAD) and related techniques in fact generated a large wealth of investigations and research, which progressively moved from a very specialized and hence limited audience to a broad community of experimental researchers. In fact, with the need of operating with large atomic vapor densities or in the case of strict requirements of background vacuum conditions, just to mention two examples, light-controlled desorption found applications in many areas, ranging from coherent spectroscopy to photonics in hollow core optical fibers.

In spite of this, the research on the fundamental mechanisms of the LIAD effect to date failed to find a general theory capable of accounting for all the experimental observations. This is certainly due to the complex details and interactions of the processes involved in the atomic photodesorption and to the diverse experimental configurations realized so far. Nevertheless, the major causes are the incomplete knowledge of the details of the processes at the coating surface and the large variability of the coating manufacturing processes.

This fact, on the one hand, points towards the need of a more comprehensive investigation of such phenomena, involving not only physics, but also other disciplines such as microscopy and chemistry. Nevertheless, on the other hand, one can imagine using LIAD and related effects to indirectly investigate the properties of organic coatings and their evolution in time. Ultimately, the possibility of directly addressing and increasing the mobility of adsorbed atoms at the coating surface by using lasers represents an alternative approach to macroscopic control of surface dynamics and transport by means of microscopic interactions, thus bridging several areas from fundamental science to technology. This allows one to envisage future interdisciplinary applications, for example, in the context of materials science and nanofabrication.

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