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Reexamination of the theory of light-induced atomic desorption

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The commonly accepted theory of light-induced atomic desorption (LIAD) [S. N. Atutov *et al.*, Phys. Rev. A **60**, 4693 (1999)] explains the dynamics of this effect by referring to a light-enhanced diffusion process proceeding in the absorbing medium. On the other hand, recently performed measurements show that in siloxane films which are used in LIAD experiments, the characteristic time of diffusion is extremely short (a fraction of 1 s) compared to the duration of the LIAD effect (hundreds of seconds). This is in contradiction to the conceptual basis of the theory of Atutov *et al.* that requires the characteristic diffusion time to be sufficiently long. What is more, the theory of Atutov *et al.* relies on an unjustified assumption about the dependence of the diffusion coefficient on the light intensity. In consequence, the theoretical results of Atutov *et al.* yield unsatisfactory predictions and do not fit well with experimental data. In this paper, we consider a partially illuminated siloxane-coated cell and propose an alternative theory of LIAD dynamics based on an assumption about lateral diffusion proceeding in the siloxane coating. Our theory provides a unique solution for the desorbed atoms' density regardless of the power of the laser light, explains the lengthy duration of LIAD, and accurately reproduces experimental results. A reasoning which explains how the boundary condition at the siloxane surface is established by the incident light gives us a proper relation between the desorbed atoms' density and the intensity of the desorbing light.

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I. INTRODUCTION

Light-induced atomic desorption (LIAD) [1] is an effect that consists in a huge emission of alkali atoms from siloxane films when they are illuminated by laser or ordinary light. LIAD was observed and experimentally investigated with Na [2], Rb [1], and Cs [3,4] atoms previously solvated in the inner coating of a Pyrex glass cell. The coating film was made either of (poly)-dimethylsiloxane (PDMS) or octamethylcyclotetrasiloxane (OCT). Recent experiments have been performed also with porous glass [5], paraffin [6,7], sapphire [8], and stainless steel [9]. Evidence of LIAD from porous silica [10,11] and from Vycor has been reported in ultrahigh vacuum cells [12]. Recently, light-induced formation and evaporation of Rb clusters in porous silica has been observed [13].

Desorption efficiency of LIAD is so high that the effect can be recorded even at room temperature. LIAD is then effectively employed to load magneto-optic traps [9,14] or a Bose-Einstein condensate in microelectronic chips [15].

As the adsorption energy of alkali atoms on the surface of siloxane has been measured to be very small, the cell's inner surface cannot be the sole source of the desorbed atoms, but definitely it is mostly a bulk effect in which diffusion plays a major role. Based on this remark, a theory explaining LIAD dynamics was proposed by Atutov *et al.* [16]. Its main ideas are also referred to in [17]. According to [16], LIAD is caused by light-enhanced diffusion of alkali atoms contained in the siloxane film. Formally, it is represented in the theory by the assumption that the diffusion coefficient is proportional to the desorbing light intensity. Additionally, it is assumed that during irradiation the density of atoms near the surface is very small (close to zero). This leads to an intense transport of atoms from the inside toward the surface of the siloxane coating where, finally, the desorption from the coating to the vapor phase is accomplished.

Meanwhile, Kasprowicz *et al.* [18] investigated the process of dark lateral diffusion in a PDMS film caused by the atomic concentration gradient produced by previously applied local irradiation. The authors report that the diffusion coefficient D_0 in PDMS in the absence of light is of the order of 10^{-5} cm^2/s. Taking into account that the thickness of a typical coating is about $H \cong 10^{-4}$, we find that the characteristic diffusion time for the direction perpendicular to the film surface is very short and equal to $\tau_d = H^2/D_0 \cong 10^{-3}$ s. According to [16], the diffusion coefficient D_c for illuminated atoms is greater than D_0 so that the time τ_d according to [16] should be even shorter. If the diffusion from the inside part of the coating to its surface is to be treated as a source of the desorbed alkali atoms [16], the very short time of this diffusion is in manifest contradiction to the fact that the LIAD effect may last hundreds of seconds. Let us note that Eq. (24) in [16] is an incorrect solution for the flux of atoms with the boundary conditions assumed in [16]. The correct one is [19]

$$J = N_0 \sqrt{\frac{D_c}{\pi t}} \sum_{n=-\infty}^{n=\infty} (-1)^n \left[\exp\left(-\frac{n^2 H^2}{D_c t} \right) - \frac{1}{2} \exp\left(\frac{(2n-1)^2 H^2}{4 D_c t} \right) - \frac{1}{2} \exp\left(\frac{(2n+1)^2 H^2}{4 D_c t} \right) \right], \quad (1)$$

which even for $D_c = D_0 \approx 10^{-5}$ cm^2/s approaches zero within fractions of 1 s. This formally proves that no LIAD effect could be observed according to the model proposed in [16].

The assumption that the diffusion coefficient is proportional to the light intensity is declared to be indispensable for fitting theoretical curves to experimental data [17]. No other justification for this statement is provided. As we know, the diffusion coefficient characterizes the environment in which diffusion proceeds. But there are no reports that the absorbing medium is changed due to irradiation. Another factor

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determining the diffusion coefficient is temperature. One could then attempt to associate the increase in the diffusion coefficient with an increase in temperature caused by the incident light. However all experiments with LIAD are performed with monitored temperature of the cell. Even if an uncontrolled local heating of atoms proceeded inside the coating, it would have to lead to a change in temperature of 1 order of magnitude to make the theory [16] correctly reproduce experimental results. No such great increase in temperature can be expected for the thermostated environment. We conclude then that the discussed assumption that is used in [16] has no reasonable explanation.

The fits obtained on the basis of [16] are not satisfactory (see Fig. 4 in [5] or Fig. 4 in [17]): the relaxation curve that accounts for the vapor density change after the light is switched off does not fit well to the experimental data. The reason is that the proper fit of the curve describing LIAD signal requires a different value of the relaxation time than it actually is. We have encountered the same difficulty while trying to fit our experimental data to the Atutov model.

According to [16], a parameter $\delta_{\mathrm{LIAD}}^{\max}$ characterizing LIAD (defined below) is proportional to the light intensity for small laser power and proportional to the square root of the light intensity for high power of the laser light. Evidently, the dependence for small power of the light is not consistent with the high power dependence. What is more, one should expect a kind of saturation effect at the high power of light (i.e., asymptotically *constant* maximum number of desorbed atoms for increasing light intensity). This evidently cannot be reproduced by the dependence as the square root of light intensity. In effect, the theoretical predictions of [16] as concerns $\delta_{\mathrm{LIAD}}^{\max}$ do not fit well to the experimental data. The same applies to another LIAD parameter R_{LIAD}, characterizing the initial atomic desorption rate.

The aim of this work is to provide an alternative description of LIAD dynamics in which all the mentioned difficulties are overcome. The fundamental assumption of the Atutov theory [16] that LIAD is a combination of two processes—photodesorption of atoms and diffusion within the siloxane layer—is correct. However, since the diffusion in the direction perpendicular to the siloxane coating surface is very fast, the long-lasting time of the LIAD effect is ensured by a lateral diffusion from the dark area of the siloxane film to the illuminated region. The lateral diffusion of atoms was experimentally confirmed by [18]. Our theory leads to a unique analytical solution for the number of atoms in the vapor phase regardless of the intensity of desorbing light (in [16], only the opposite cases of low and high light intensity limits are considered, giving different analytical solutions). The theory explains the specifics for the LIAD dependence of the maximum number of desorbed atoms (or equivalently $\delta_{\mathrm{LIAD}}^{\max}$) on the light intensity I_L. So far, it has been incorrectly believed to increase proportionally to $\sqrt{I_L}$. In addition, our model accounts for a deviation from the linear dependence of the initial desorption rate, R_{LIAD}, on I_L. So far, it has been regarded as strictly linear [16] despite the experiments' clear indication that this is not true.

Predictions of our theory are compared to experimental data. The experimental setup (Fig. 1) consisted of a cylindrical glass cell with a natural mixture of Rb atoms. Inner walls of the cell were coated with a thin PDMS film. The cell preparation is described, for example, in [1]. A diode laser (TEC 100 Litrow laser system: LYNX, Sacher Lasrtechnik Group) tuned to Rb D_1 at 794.5 nm corresponding to Doppler broadened hyperfine transitions $F=3 \rightarrow F'=2$ and $F=3 \rightarrow F'=2$ was used to probe the vapor density. The laser frequency was scanned in the range of Doppler profile at the rate 60 Hz to avoid optical pumping. The beam diameter was approximately 5 mm. The diode laser power was attenuated down to a few W to further reduce optical pumping. To improve the signal-to-noise ratio, a lock-in detection was used. The amplitude of the laser beam was modulated by a chopper. The evolution of the vapor density was obtained by measuring the fraction of the probe diode laser light transmitted through the cell. Two different desorption lasers were used during the experiment. The argon ion laser (Carl Zeiss Jena, ILA120) was working at 514 nm. The beam diameter of this laser was approximately 5 mm and power density was 1.2 W/cm^2. To illuminate the cell with red light, the femtosecond laser *Tsunami* (Spectra Physics Laser Inc.) was used. The working wavelength was around 780 nm. The diameter and power density were similar to the argon ion laser.

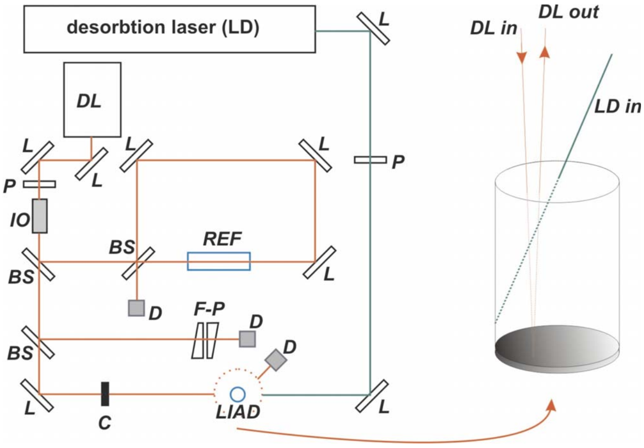

FIG. 1. (Color online) Experimental setup for LIAD dynamics measurements. DL-detection laser, L-mirrors, P-polarizer, IO-optic isolator, BS-beam splitter, C-chopper, REF-reference cell, D-detector, and F-P-Fabry-Pérot interferometer.

II. THEORY

When the desorbing light is switched on, the vapor dynamics of atoms contained in the cell can be described by the following equation [16]:

$$\frac{dn}{dt} = \frac{S^i}{V}J^i + \frac{S^d}{V}J^d - \gamma(n - n_0), \qquad (2)$$

where n is the atomic density in the vapor phase, n_0 is the equilibrium density, S^i and S^d are the surfaces illuminated and not illuminated, respectively, and V is the volume of the cell. In turn, J^i and J^d are, respectively, fluxes from the illuminated and nonilluminated surface of the cell and γ^{-1} is the relaxation time characterizing the vapor's approach to the equilibrium state after the light is turned off. The fluxes can be expressed as

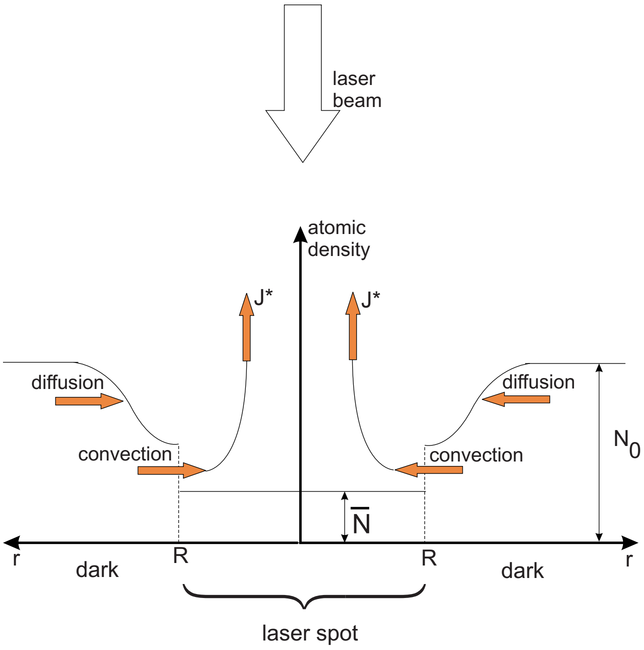

FIG. 2. (Color online) In the illuminated part of the siloxane, the atomic density is $\bar{N}$. $\bar{N}$ establishes the boundary condition determining the influx of atoms diffusing from the dark area toward the illuminated region. All the incoming atoms leave the irradiated region as a flux of desorbed atoms (J^*). The flux J^* is a consequence of very quick atomic diffusion in the direction normal to the surface (not indicated in the figure). Existence of this rapid diffusion constituting the flux J^* justifies the assumption about the convection-like boundary condition at $r=R$.

$$J^i = J^* - \beta n, \quad J^d = \alpha_0 N_0 - \beta n, \tag{3}$$

where J^* is the flux of the atoms leaving the illuminated surface, β is a coefficient characterizing the adsorption rate, α_0 is the desorption rate in the dark, and N_0 is the atomic density inside the coating in the absence of light. After some rearrangements Eq. (2) becomes

$$\frac{dn}{dt} = \frac{J^*}{L^i} - \left(\frac{\beta}{L} + \gamma\right)(n - n_0), \tag{4}$$

where $L^i = V/S^i$ and $L = V/(S^i + S^d)$ are the characteristic lengths of the cell. Since S^i is relatively small compared to S^d, the term $S^i \beta n/V$ is neglected in Eq. (4).

The main difference with respect to [16] is that we assume a lateral diffusion of atoms from the dark part of the siloxane coating to the illuminated one. The arriving atoms feed the illuminated region and due to the quick diffusion in the direction normal to the coating surface, they are almost at once thrown into the gas phase in the form of the flux J^* (Fig. 2). The lateral diffusion ensures then that the LIAD effect is such a long-lasting process.

To avoid misunderstanding, let us emphasize that we do *not* assume different values of the diffusion coefficient for illuminated and dark regions of siloxane film. We say that the diffusion in the direction perpendicular to the surface of the coating is fast because the coating is very thin in this direction. In effect, all the atoms travel from the inside to the surface of the absorbing medium in the direction normal to the surface within a very short time. Without the supplemental inflow of atoms from the neighboring nonilluminated region, the flux of atoms from the illuminated surface would finish within fractions of 1 s. Certainly the lateral diffusion with the same diffusion coefficient lasts much longer because of the relatively much greater size of the medium in the direction parallel to the surface.

Contrary to [16], in our model the flux J^* cannot be expressed simply as $J^* = \alpha \bar{N}$, where $\bar{N}$ is the atomic density in the illuminated part of the coating. The reason is that the number of atoms in the illuminated region is supplemented by the lateral diffusion. The number of atoms $\bar{N}$ in the illuminated region does not contribute directly to the flux J^*. Rather, the atomic density $\bar{N}$ controls the intensity of atomic diffusion from the dark region to the illuminated one. The fewer the atoms $\bar{N}$ in the illuminated region, the more intense is the lateral diffusion, and then the greater is the flux J^* consisting of these atoms.

Our first task is to show how the flux J^* is determined by $\bar{N}$. Certainly, the atomic density $\bar{N}$ in the illuminated region must somehow depend on the light intensity I_L. In this way the light intensity, by influencing the atomic density $\bar{N}$, determines indirectly the desorption flux J^*. Our next objective will be then to derive a relation between $\bar{N}$ and I_L.

The lateral movement of atoms in the nonilluminated region of siloxane is governed by the diffusion equation,

$$\frac{\partial N}{\partial t} = D_0\left(\frac{\partial^2 N}{\partial r^2} + \frac{1}{r}\frac{\partial N}{\partial r}\right), \tag{5}$$

where N is the atomic density in the nonilluminated part of the coating (in the vicinity of the illuminated region) and r denotes the distance from the center of the laser spot. We will look for a solution in the region $r \geq R$, where R is the radius of the desorbing laser spot.

The absolute value of the flux of atoms coming from the dark region, and feeding the illuminated region (this is just the flux that later is changed into the flux J^*) is defined at the illuminated/dark region boundary as

$$J^* = D_0 \frac{\partial N}{\partial r}_{r=R}. \tag{6}$$

We solve the diffusion equation [Eq. (5)] at the initial condition $N(t=0) = N_0$ and at the Newtonian boundary condition:

$$\partial N/\partial r - kN = g \quad \text{at} \quad r = R, \tag{7}$$

which means that we assume a convection process at the illuminated/nonilluminated boundary region ($r=R$) in the form

$$J^* = \kappa[N(R) - \bar{N}], \tag{8}$$

where κ is a convection constant multiplied by the surface of the cross section of the coating, $N(R)$ is the atomic density at $r=R$ *outside* the laser spot, and $\bar{N}$ is the atomic density inside the illuminated siloxane film (Fig. 2). The boundary condition in form (7) is justified by the fact that the diffusion process in the illuminated region proceeding perpendicularly to the lateral diffusion is relatively quick, which is a typical situation for convectionlike transport. Inserting Eq. (7) into Eq. (6) and comparing to Eq. (8) we get $D_0 g + D_0 k N(R) = \kappa N(R) - \kappa \bar{N}$. It follows that

$$k = \frac{\kappa}{D_0}, \tag{9}$$

$$g = -\frac{k\bar{N}}{D_0}. \tag{10}$$

Solving Eq. (5) at boundary condition (7) we find [19]

$$J^* = kN_0 D_0 \left[\int_R^\infty d\xi \int_0^\infty du e^{-D_0 u^2 t} F(R,u) F(\xi,u) \xi u - gR \int_0^\infty \frac{1}{u} F^2(R,u)(1 - e^{-D_0 u^2 t}) du \right] + g D_0, \tag{11}$$

where

$$F(r,u) = \frac{J_0(ur)[uY_1(ur) + kY_0(uR)] - Y_0(ur)[uJ_1(uR) + kJ_0(uR)]}{\sqrt{[uJ_1(uR) + kJ_0(uR)]^2 + [uY_1(ur) + kY_0(uR)]^2}} \tag{12}$$

and J and Y denote the Bessel functions of the first and the second kind, respectively.

Finally, solving Eq. (4) we get

$$n(t) - n_0 = \frac{e^{-(\beta/L+\gamma)t}}{L^i} \int_0^t e^{(\beta/L+\gamma)t'} J^*(t') dt', \tag{13}$$

which can be fitted to the experimental results. Before the fit is accomplished, first one has to determine the relaxation time $(\beta/L+\gamma)^{-1}$. It can be obtained from the exponential decay of $n(t) - n_0$ after the desorbing light is switched off [this exponential decay follows from Eq. (4) with $J^* = 0$]. Next, using the established $(\beta/L+\gamma)^{-1}$ we can fit Eq. (13) to the LIAD data by choosing appropriate values of the constants k and g.

As can be seen from Fig. 3 the function given in Eq. (13) fits well with the experimental results and our model does not suffer from the problem of unsuitable relaxation time. The value of the diffusion coefficient substituted to Eq. (11) is $D_0 = 1.2 \times 10^{-5}$ cm^2/s, in accordance with [18].

There remains to discuss the dependence of LIAD dynamics on the light intensity. The constant k is the convection constant divided by the diffusion coefficient D_0 in the dark, so it does not depend on the light intensity I_L. In turn, the constant g is proportional to the atomic density $\bar{N}$ inside the illuminated part of the siloxane film which certainly depends on the power of the incident light (detailed description below). Because the atomic density $\bar{N}$ determines the intensity of the lateral diffusion (and the flux J^*), the dependence of LIAD dynamics on the light intensity enters our theory through constant g.

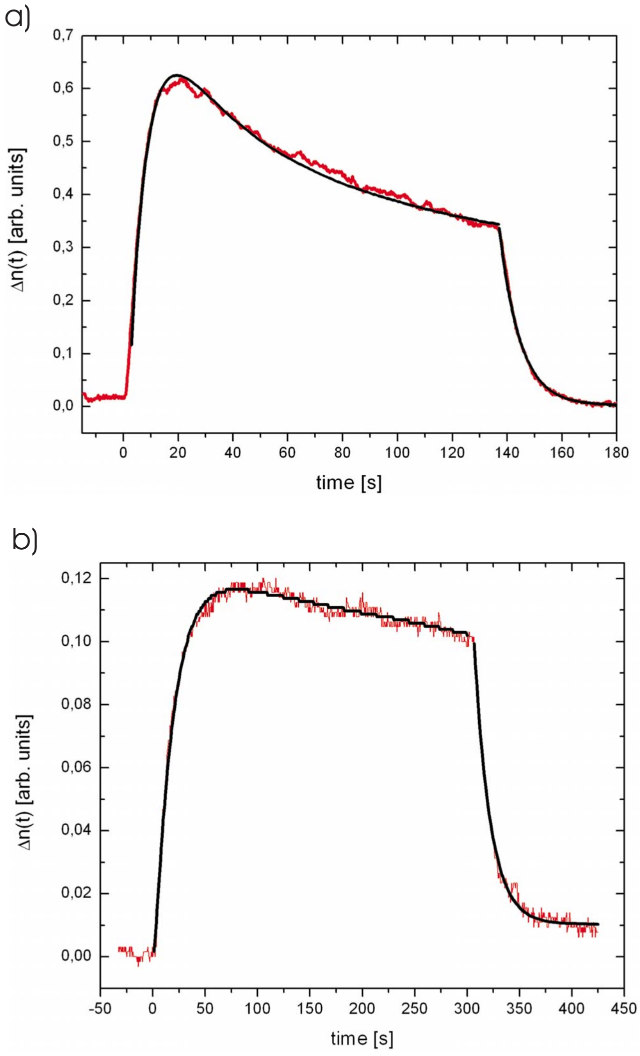

FIG. 3. (Color online) Increase in atomic density $\Delta n \equiv n(t) - n_0$ in the vapor phase as a function of time: (a) Ar$^+$ laser at 514 nm and (b) Ti-sapphire laser at 785 nm. The theoretical curves plotted according to Eq. (13).

To find how g depends on the light intensity I_L, we have to know how the atomic density inside the illuminated siloxane $\bar{N}$ is governed by the laser power. But due to the rapid diffusion in the direction normal to the surface, at any given moment the approximate equality $\bar{N} \cong N_s$ is valid, where N_s is the atomic density in the siloxane film near its illuminated surface. It follows that, to know $\bar{N}$, we have to consider how N_s depends on the light intensity. Let us emphasize that our reasoning will refer only to the very beginning of the LIAD effect when the boundary condition is being formed within a short period of time. The expression derived above for the desorption flux J^* is valid only for the established boundary condition. Now, for the initial phase of LIAD, the desorption flux must be characterized in a different manner.

Just after the light is switched on, we can distinguish two processes proceeding at the surface layer of siloxane film (Fig. 4).

Due to the incident light, there is a flux of atoms desorbed from the surface, which we assume is proportional to the

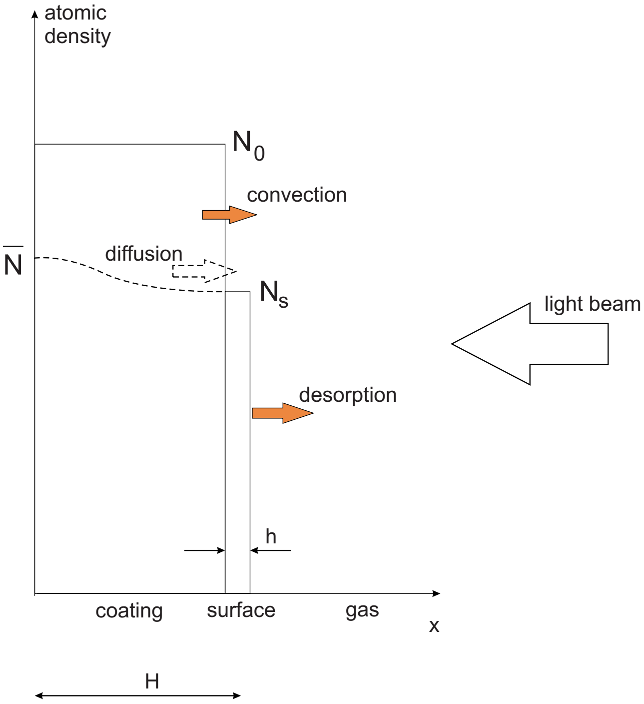

FIG. 4. (Color online) Sketch representing formation of the boundary condition just after the light is switched on. The incident light desorbs atoms from the surface to the gas phase and initially there is an abrupt change in atomic density between the inside (N_0) and the surface (N_s), which produces a convection flux of atoms to the surface layer. Later on, when an equilibrium is reached ($N_s = \text{const}$), the convection flux is replaced by a diffusion process (dashed line) with the atomic density in the inside of the coating $\bar{N}$ approximately equal to the atomic density in the surface layer N_s. This diffusion process is sustained by the lateral diffusion feeding the illuminated area with new atoms from the neighboring dark region.

actual atomic density in the surface layer and the intensity of light, i.e.,

$$J_{\text{des}} = a(\lambda) I_L N_s, \tag{14}$$

where $a(\lambda)$ is a coefficient depending only on the light length. As the process of desorption is very quick, initially (i.e., within the short time period considered while the boundary condition is being established) the inside atomic density remains unchanged and is equal to N_0. Therefore, there exists an abrupt change in the atomic density $N_0 - N_s$ between the inside part of siloxane and its surface. This causes a convectionlike flux from the inside part of siloxane to its surface equal to

$$J_{\text{conv}} = \kappa (N_0 - N_s) \tag{15}$$

(here κ is the convection constant multiplied by the surface of the laser spot). The atomic density N_s can then be described by the following equation:

$$\frac{dN_s}{dt} = \frac{\kappa}{h}(N_0 - N_s) - \frac{a(\lambda)}{h} I_L N_s, \tag{16}$$

where h is the thickness of the surface layer. In Eq. (16) we have omitted the contribution of atoms adsorbed from the vapor phase as negligibly small compared to the role of the light-induced desorption and the convection from the inside of the coating. Within a very short time, roughly of the order of $h/[a(\lambda)I_L + \kappa]$, an equilibrium is reached, i.e., $dN_s/dt = 0$ and the boundary condition is established:

$$N_s = \frac{N_0}{1 + \dfrac{a(\lambda) I_L}{\kappa}}. \tag{17}$$

Later, during the LIAD process proper, the convection flux J_{conv} will be replaced by the diffusion flux of atoms from the inside to the surface, proceeding at the boundary condition given by Eq. (17), and this diffusion flux will be maintained thanks to the lateral diffusion from which the flux J^* originates, as described above. (We assume that the initially reached boundary value of N_s is kept constant throughout the whole further LIAD process.)

As argued above, the atomic density inside the illuminated part of the siloxane coating $\bar{N}$ is equal to its boundary value N_s, so we get from Eqs. (10) and (17) that

$$g = -\frac{kN_0}{D_0\left(1 + \dfrac{a(\lambda) I_L}{\kappa}\right)}, \tag{18}$$

which together with Eqs. (11) and (13) represents the dependence of LIAD dynamics on the light intensity I_L. From Eq. (18) it follows that the maximum value of g approaches zero for great laser light intensity [in this case according to Eq. (10) the illuminated region is completely depleted of atoms, $\bar{N} \approx 0$]. On the basis of Eqs. (8) and (10), we find that for $g \to 0$ J^* approaches its maximum value as expected. In turn, for $I_L \to 0$ g has its minimum value $-kN_0/D_0$ (which is equivalent to $\bar{N} \approx N_0$) and in this case $J^* \to 0$.

To compare our result [Eq. (18)] to experimental data, let us introduce an experimentally measurable parameter characterizing LIAD:

$$\delta_{\text{LIAD}}^{\max} = \frac{n_{\max} - n_0}{n_0}. \tag{19}$$

It represents the maximum relative increase in vapor density in the cell. So far, it has been believed that $\delta_{\text{LIAD}}^{\max} \cong \sqrt{I_L}$ [16], and this result follows from the unjustified assumption that the diffusion coefficient is proportional to I_L. According to Eqs. (11) and (13) $n(t) - n_0$ has the form $n(t) - n_0 = f_1(t) + g f_2(t)$, where f_1 and f_2 are functions independent of the light intensity I_L (it can be verified by direct calculations that $f_1 > 0$ and $f_2 > 0$). If so, also $n_{\max} - n_0$ as a function of I_L can be presented in the same form. Recalling expression (18), for g we get

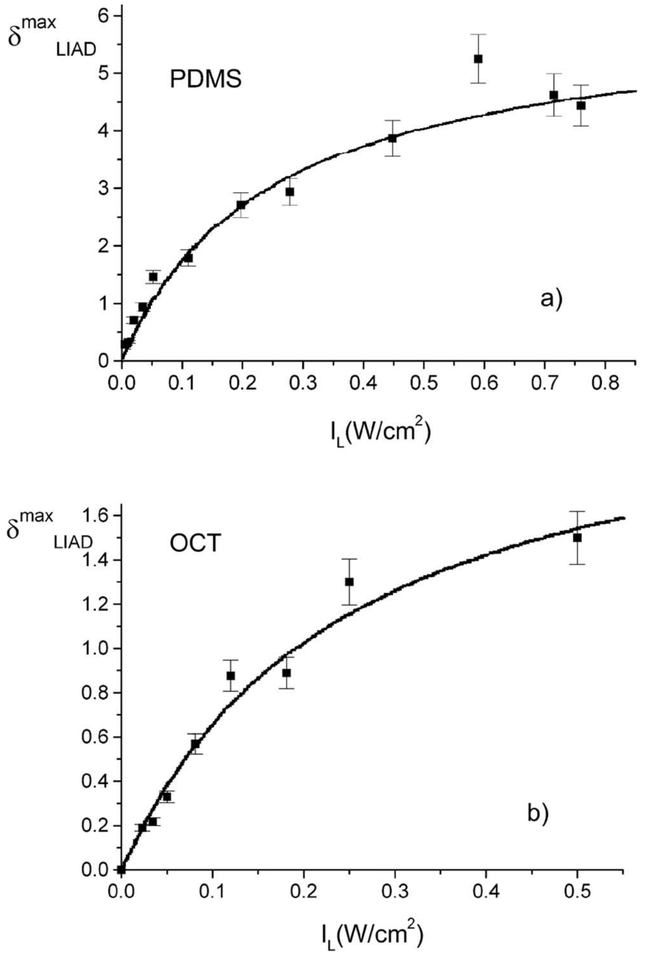

FIG. 5. Dependence of $\delta_{\text{LIAD}}^{\max}$ as a function of the desorbing light intensity I_L for PDMS and OCT films. The solid curves represent Eq. (20).

$$\delta_{\text{LIAD}}^{\max}(I_L) \propto \text{ const } (I_L) - \frac{kN_0}{D_0\left(1 + \dfrac{a(\lambda)I_L}{\kappa}\right)}. \qquad (20)$$

To test this result, we have fitted it to the data presented in [17] in Fig. 2. It is evident that our curves (see Fig. 5), especially for OCT coating, fit much better to the experimental outcomes than the curves of the Atutov theory. Especially the tangent to our curve at $I_L=0$ is not perpendicular to the I_L axis, which is evidently required by the experimental data. Certainly this condition is not fulfilled by the function proportional to $\sqrt{I_L}$ proposed in [16]. Moreover, one should expect a kind of saturation effect for a high intensity of light so that $\delta_{\text{LIAD}}^{\max}$ ought to become asymptotically constant for the increasing light power. No such effect follows from the dependence as $\sqrt{I_L}$ but is guaranteed by the hyperbolic function [Eq. (20)] yielded by our theory.

Another parameter characterizing LIAD is

$$R_{\text{LIAD}} = \frac{1}{n_0}\left(\frac{dn}{dt}\right)_{t=0}, \qquad (21)$$

which is the relative increase rate of the vapor density that immediately follows the light switching on at $t=0$. According to the Atutov theory $R_{\text{LIAD}} \propto I_L$, which seems to agree with the experiment fairly well. However, a closer inspection of the experimental data (see Fig. 3 in [17]) shows that the experimental points have a constant tendency to deviate from linear dependence toward the I_L axis. This effect can be explained on the basis of our concept of how the boundary condition is achieved.

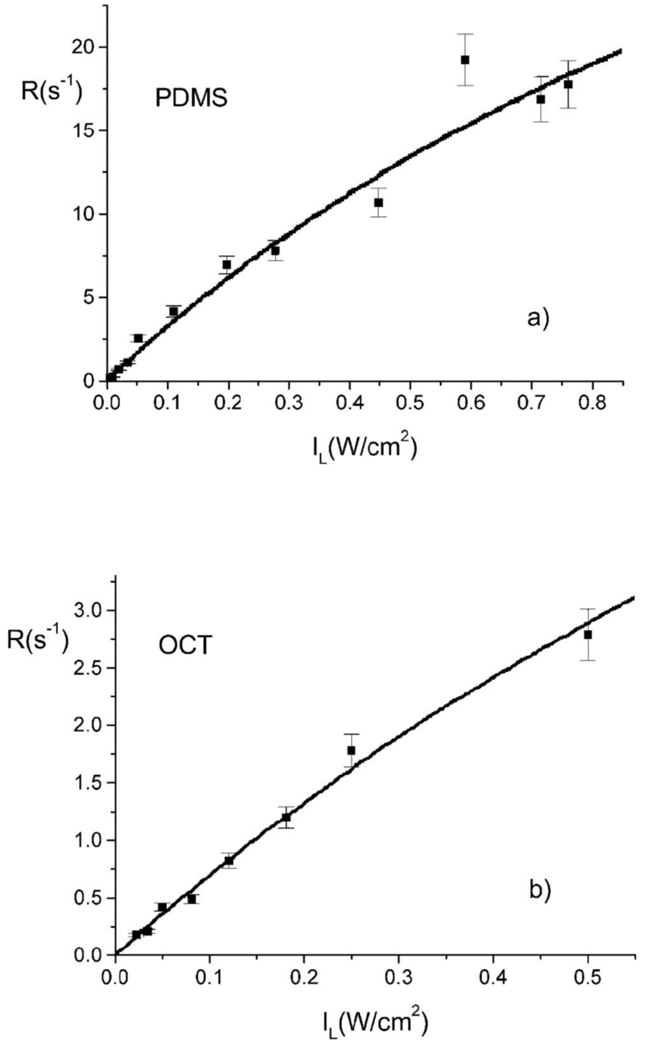

FIG. 6. The rate R as a function of desorbing light intensity for PDMS and OCT films. The solid curves are plotted according to Eq. (27).

At first approximation one can assume that just after the light is switched on, no convection from the inner part of siloxane toward the surface happens ($N_s \approx N_0$). Therefore, according to Eq. (16), the flux of atoms desorbed from the surface is equal to $J_{\text{des}}=a(\lambda)I_L N_0$. Thus, for the initial phase of LIAD process, we have

$$\left(\frac{dn}{dt}\right)_{t=0} = \frac{J_{\text{des}}}{L^i} = \frac{a(\lambda)I_L N_0}{L^i}. \qquad (22)$$

In effect, we get a linear dependence between R_{LIAD} and I_L. However, the more precise description indicates that the boundary condition initially is not stationary. The atomic density at the illuminated surface decreases in time in accordance with Eq. (16), i.e.,

$$N_s(t) = N_0\left[\left(1 - \frac{1}{1+\frac{a(\lambda)I_L}{\kappa}}\right)e^{-[a(\lambda)I_L+\kappa]t/h} + \frac{1}{1+\frac{a(\lambda)I_L}{\kappa}}\right]. \tag{23}$$

Initially, N_s changes very quickly (h is very small). If we take into account that measurements of R_{LIAD} require some finite time to be performed, it means that in experiments we always deal with time-averaged values of J_{des} contributing to the measured R_{LIAD}. From Eq. (14), it follows that to estimate the actually measured J_{des}, one should operate with the time-averaged value of N_s calculated within the short characteristic time $h/[a(\lambda)I_L+\kappa]$. That is, for the initial phase of LIAD we have

$$J_{\mathrm{des}} = a(\lambda)I_L\langle N_s\rangle \tag{24}$$

and

$$\left(\frac{dn}{dt}\right)_{t=0} = \frac{a(\lambda)I_L\langle N_s\rangle}{L^i}. \tag{25}$$

Averaging Eq. (23) we find

$$\langle N_s\rangle = \frac{\int_0^{h/[a(\lambda)I_L+\kappa]} N_s(t)dt}{h/[a(\lambda)I_L+\kappa]} = \left[1 + \frac{1}{e}\left(\frac{1}{1+\frac{a(\lambda)I_L}{\kappa}} - 1\right)\right]. \tag{26}$$

Therefore on the basis of the equality $R_{\mathrm{LIAD}} = a(\lambda)I_L\langle N_s\rangle/(n_0L^i)$ we obtain

$$R_{\mathrm{LIAD}} \propto I_L\left[1 + \frac{1}{e}\left(\frac{1}{1+\frac{a(\lambda)I_L}{\kappa}} - 1\right)\right]. \tag{27}$$

Linear dependence on I_L is then modified by the additional factor that deviates the curve toward the I_L axis as expected. Equation (27) is fitted to the experimental data reported in Fig. 3 in [17], which is presented in Fig. 6.

III. CONCLUSIONS

The approach to LIAD dynamics presented in this paper solves all the problems of the Atutov theory. It explains why LIAD is such an efficient and long-lasting process despite the fact that the characteristic diffusion time in siloxane is so short [20]. It reproduces well the experimental outcomes for the time dependence of vapor density (with no problems regarding the relaxation time parameter) and the dependence of $\delta_{\mathrm{LIAD}}^{\max}$ and R_{LIAD} on the light intensity together with the saturation effect expected for the high power laser light. As the LIAD effect is, in essence, similar for different kinds of atoms and coatings, it means that it is governed mainly by general aspects of atomic dynamics and not by the particular features of materials used in experiments. Thus, the LIAD dynamics theory has a fundamental significance for understanding this phenomenon and may help to improve experiments in which LIAD is employed.

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[20] A theory explaining LIAD in the case of an entirely illuminated cell is essentially different from the one presented in this paper because it does not hinge on the lateral diffusion. An approach to a completely illuminated cell will be provided in a separate paper.