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Pulsed light desorption of molecular nitrogen from a glass surface



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ABSTRACT

Experimental results on the pulsed light desorption (PLD) of molecular Nitrogen from the surface of C-52 and Pyrex glasses are presented. The aim of the study was to determine the experimental conditions to obtain the maximum manifestation of the PLD effect of molecular gases. These studies were conducted in vacuum glass cells of different sizes and shapes filled by Nitrogen, whose inner surface was illuminated by the light of a powerful flash lamp. The variation in the density of the desorbed gas in the cell caused by PLD was studied using both a mass spectrometer and a vacuum gauge attached to the illuminated cells. The experimental results are in qualitative agreement with the theoretical model developed. We demonstrate that PLD can drastically increase a peak density of desorbed Nitrogen in a cell and the maximal Nitrogen density can be achieved in a small diameter long cell of cylindrical form. We believe that the results of this experiment can be applied to the loading of some gases inside a hollow-core, photonic band-gap fiber to generate a large optical depth for an experiment in low-light-level nonlinear optics.

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1. Introduction

The photodesorption of such particles as atoms or molecules from a solid surface is a process in which the atoms or molecules are desorbed from a solid surface in a variety of ways by illuminating the surface with either visible or UV light (see, for example, Refs. [1,2] – atomic desorption, Ref. [3] – molecular desorption, and the references therein). The effect occurs in a system which is in a state of sorption equilibrium between a gas phase and an adsorbing surface. Photodesorption can be a thermal process, caused by the direct heating of the surface by an incident light, or as the result of various non-thermal processes. Photodesorption is characterized by a yield of desorbed particles from the surface. By and large, the yield is proportional to the amount of adsorbed particles on the surface and is subject to the frequency and intensity of incident light, temperature, the surface energy of the particles, the presence of some coating on it, its surface purity or porosity and etcetera.

Apart from its purely academic interest, the photodesorption effect also has a significant number of applications. It can be used for loading some gases into the fiber core from the inner walls of the fiber made of different types of glass [4]. This application has particular relevance to the generation and control of quantum states of light using atomic vapors, including the realization of on-demand single photon sources [5], the manipulation of photonic

states [6] and the storage and retrieval of these states with high fidelity [7,8]. The study is interesting as it realizes a practical quantum network [9].

Photodesorption has been successfully used in the development of light-driven pulse sources of atoms and molecules [10–15].

Note that the effect of the increasing of the density of the particles caused by pulse light desorption (PLD) can be potentially very big. In fact, if with the help of PLD only one monolayer of particles with a size of 1 angstrom from a surface area of 1 cm² (i.e. 10¹⁶ particles) in an evacuated volume of 1 cm³ is released as the result of the burst of the desorbed gas, the density of the particles will increase from 0 up to 10¹⁶ cm⁻³ i.e. by 16 orders of magnitudes.

A sensor can be inserted inside the volume. This allows the sensitivity of the various sensors which can be used to detect trace gases in the air to be detected, which has many very interesting applications in medicine, environmental protection, criminality, geology and etcetera [16].

The paper presents the results of a study of the PLD of molecular Nitrogen from the surface of either molybdenum C-52 or Pyrex glass. The aim of the study is to determine the experimental conditions which will produce the maximum manifestation of this phenomenon. These studies were conducted in vacuum glass cells of differing sizes and shapes filled with Nitrogen, whose inner surface was illuminated by a light- powerful flash lamp. The variation in the density of the desorbed Nitrogen in the cells caused by PLD was studied using a mass spectrometer and a vacuum ionic gauge. Below, these experimental studies are preceded by a discussion of the model of the desorption process and by the definition of

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the relevant quantities. We also present a qualitative comparison of the model with the experimental results obtained.

2. Theoretical model

Let us consider a spherical glass vacuum cell with a radius R_s , which is connected to a turbo-pump by a pumping tube whose length is L and radius r . We assume that $R_s \gg r$, the detector, is placed inside the cell, and that it has a negligible dimensions compared to all the characteristic dimensions of the cell system. After switching on the flash light, photodesorbed molecules begin to fill the volume of the cell. The evolution of the number of the desorbed molecules in the detection volume of N is described in the following differential equation:

$$\frac{dN}{dt} = I - \tau^{-1}N, \quad (1)$$

where I is a flux of the desorbed molecules, τ^{-1} – the inverse lifetime of the molecules or the rate of loss of the molecules caused by their leakage from the cell towards the turbo-pump and re-adsorption back into the walls of the cell. According to the results published in [17], the inverse lifetime can be written in the form:

$$\tau^{-1} = \left(\frac{1}{\tau_{esc\ s}} + \frac{1}{\tau_{read\ s}} \right), \quad (2)$$

where $\tau_{esc\ s}$ is the leakage time, i.e. the time the molecules take to escape from the cell to the turbo-pump, $\tau_{read\ s}$ – the time taken for the molecules to be re-absorbed into the cell walls. In a spherical cell with a pumping tube in a Knudsen regime, these times can be written in the following form equations

$$\tau_{esc\ s} = \frac{2L R_s^3}{\bar{v} r^3}, \quad (3)$$

$$\tau_{read\ s} = \frac{4R_s\chi}{3\bar{v}}. \quad (4)$$

Here the parameter χ is interpreted as the average number of bounces that it takes to re-adsorb molecules back on to the surface of the walls. $\bar{v} = \sqrt{8kT/\pi m}$ is the average atomic thermal velocity at the temperature T and m is the mass of the atom.

The solution to the Eq. (1) which satisfies the following initial condition $N=0$ at $t=0$, can be expressed as:

$$N = I\tau[1 - \exp(-t/\tau)]. \quad (5)$$

The maximal value of the density of the desorbed molecules is obtained at the end of the light pulse which we assume has a rectangular form. It can be written as:

$$N = I\tau[1 - \exp(-\tau_{des}/\tau)], \quad (6)$$

where τ_{des} is the duration of the light pulse. It is obvious that, after the light is switched off $I=0$, the solution of the Eq. (1) will be:

$$N = N_{peak}\exp(-t/\tau), \quad (7)$$

which describes an exponential decay in the number of the desorbed molecules with the characteristic time τ . Note that the time in the expression (7) is counted from the moment at which the light is switched off.

When short light pulses and large-volume cells are used in the experiment, the ratio τ_{des}/τ can be considered to be much smaller than unity, so the peak number of desorbed molecules can be written:

$$N_{peak} = I\tau_{des}. \quad (8)$$

and the peak density of the desorbed molecules n_{peak} can be expressed as:

$$n_{peak} = \frac{I\tau_{des}}{V_s} \quad (9)$$

where $V_s = 4/3\pi R_s^3$ is the volume of the spherical cell.

We assume that only a small quantity of the absorbed molecules can be released by one light pulse. If this is correct, the flux of the desorbed molecules I will be proportional to a power of light at its maximum, multiplied by the total number of molecules accumulated on the inner surface of the cell. In turn, the total number of molecules on this surface will be proportional to the volume density of molecules of interest, n_0 , multiplied by an accumulation time T and also multiplied by an area $S_s = 4\pi R_s^2$, the inner surface of the walls of the spherical cell. Therefore, the peak density of molecules released at n_{peak} can be written

$$n_{peak} = \alpha P\tau_{des}n_0T\frac{S_s}{V_s}, \quad (10)$$

where P is the light intensity on the surface of the cell, n_0T – the surface density of the molecules, α – a constant, which is usually a function of the wave length of the light used, the binding energy of the molecules on the surface, temperature and etcetera. We assume that for very small n_0 , the surface density of the adsorbed molecules will be proportional to the accumulation of time T . This allows us to write the peak density of released molecules in the following form:

$$n_{peak} = 3\alpha n_0T\frac{W}{R_s}, \quad (11)$$

where $W = P\tau_{des}$ is the total energy of the light pulse. From expression (11) it can be concluded that the peak density of the desorbed molecules, n_{peak} , is increased according to the length of the accumulation time T and the total energy of the light pulse W and the decreasing of the radius of the cell. As can be seen the peak density and detected signal are scaled as $1/R_s$. This is because the total number of molecules released is proportional to the area of the inner walls of the cell (i.e. R_s^2) but the density is inverse in proportion to the volume of the cell (i.e. to R_s^{-3}).

It should be noted that the size of the illuminated spherical cell cannot be too small in comparison with a size of the light source used—were this to be so, it would be impossible to focus all the light from a flash lamp on the cell using any optical system. The optimal condition to attain maximal illumination, and thus the PLD effect, is to choose a spherical cell with a wall area that is equal to the area of the spherical light source used. Of course, this is what happens when a sizeable light source like a lamp is used. When pulsed laser light sources are used, the size of the cell can be very small.

When using a cylindrical form cell with an internal radius R_l and length l , the peak density of the desorbed molecules n_{peak} can be written as:

$$n_{peak\ l} = 2\alpha n_0TW\frac{(R_l+l)}{R_l l}. \quad (12)$$

When a cell has $R_l \ll l$, the expression (12) becomes:

$$n_{peak\ l} = 2\alpha n_0T\frac{W}{R_l}, \quad (13)$$

which actually has the same structure as (11). However, in contrast to what has been said above about the spherical cell, in order to maximize the peak density of the released molecules $n_{peak\ l}$, the radius of the cylindrical cell R_l can be small. The requirement of the equality of cell wall area to the area of the light source used can be achieved by using a cell whose length is adequate, so that its length equals the length of the cylindrical light source used.

When a laser light source which can be tightly focused on the end of the glass cell used is exploited, the diameter of the cell chosen can be extremely small. This interesting fact opens up the possibility of using PLD for the generation of the controlled gas densities in the photonic-band-gap fibers and this will provide a long interaction length while a small light mode area is still maintained. In fact, when a Gaussian laser beam is used, the interaction length is limited by the waist length of the focused beam (hundreds of micrometers), whereas inside a low-loss waveguide the interaction length of the focused beam can be quite long (tens of centimeters). This is of significant interest when performing experiments on low-light-level optical nonlinearities [4].

In experiments, we have evaluated the PLD effect by parameter γ which describes the relative increase in the molecular density at a light pulse maximum against the initial density of detectable molecules. This equals the ratio n_{peak}/n_0 .

3. Experiment and discussion

The experimental setup shown in Fig. 1 consists of a spherical Pyrex glass cell 1 with an inner radius $R_s=60$ mm and a pumping pipe (tube radius $r=7$ mm, length $l=200$ mm).

The cell was evacuated through the vacuum valve 3 using a turbo-molecular pump 2 (Drytel 1025). Filling the gas into the vacuum system was carried out by fitting a valve 4. The density of the molecular Nitrogen in the cell was measured using a mass spectrometer 5 (Pfeiffer vacuum Prisma Plus QMG 220) connected to the system by the vacuum valve and tube 6. The length of this tube was 300 mm size; its inner radius 7 mm. The external position of the mass spectrometer was determined by too much size of the spectrometer's input device. The residual pressure in the system was controlled by gauge 7 (PDR 900 Series vacuum controller RS232/RS485) in combination with an ionic gauge (PMT, controller VIT-2). This allowed us to measure the vacuum from one atmosphere to pressures of the order of 10^{-7} Torr. A standard commercial photographic lamp 8 was used as the pulsed light source. The maximum energy of the light pulse was approximately 20 J. The energy density of the flash light on the surface of the cell was varied by changing the distance between the lamp and the cell over the range of 0.01–0.2 J/cm².

To test the assumptions at the basis of the theoretical model, we carried out a measurement of the duration of the light pulse and the lifetime of the Nitrogen molecules in the cell.

Fig. 2 shows a light pulse from the lamp used. As can be seen from the figure, the duration of the light pulse τ_{des} was of the order of 3 ms.

To measure the lifetime of the Nitrogen molecules in the cell, the vacuum system was first evacuated to a residual pressure of about 10^{-6} Torr. Thereafter, valve 3 was closed and the cell was filled with Nitrogen to a pressure of 10^{-5} Torr via valve 4. Then at

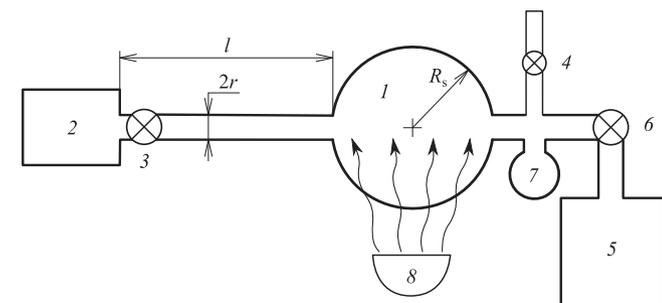


Fig. 1. Schematic diagram of the apparatus: 1—Pyrex glass cell, 2—turbo-molecular pump, 3, 4, 6—vacuum valves, 5—mass spectrometer, 7—gauge, 8—photographic flash lamp.

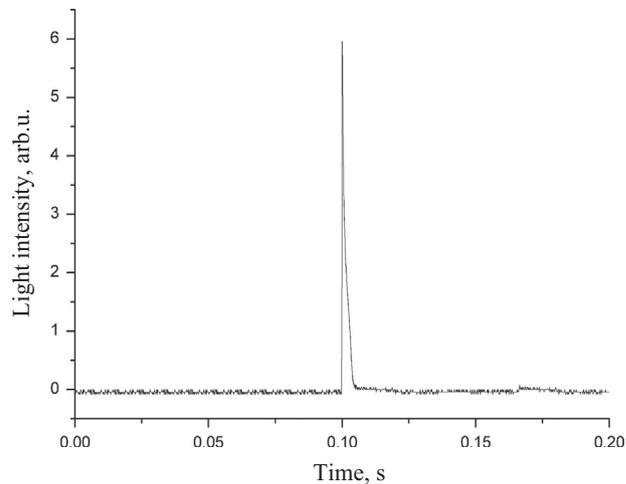


Fig. 2. Light pulse form of the lamp used.

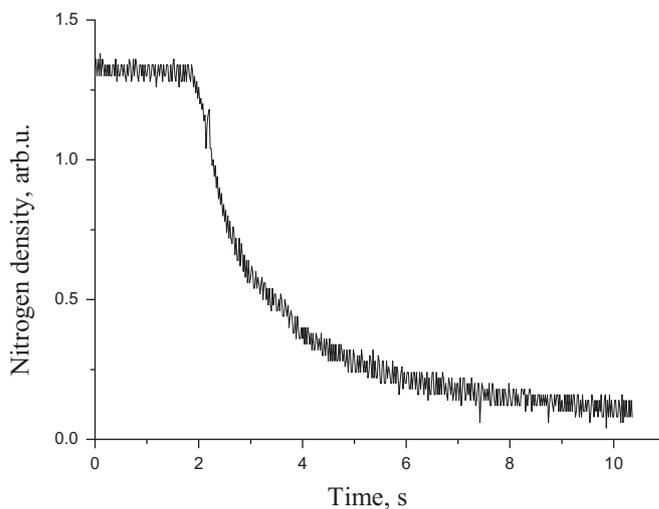


Fig. 3. Density of nitrogen gas in the cell. At $t=0$ valve 3 was opened.

time 0 valve 3 was abruptly opened and the signal proportional to the density of Nitrogen which was pumped away from the cell was recorded by the mass spectrometer. The signal is shown in Fig. 3. The signal decays within the characteristic time of $\tau=1.3$ s. Both these measurements allow us to conclude that the ratio of the duration of the light pulse τ_{des} to the lifetime of the Nitrogen molecules in cell τ was much smaller than unity, which corresponds to the basic assumption of the model.

The measurement of the photodesorption of Nitrogen was performed as follows. At the beginning of each measurement, we cleaned the rest gas molecules from the inner surface of the cell. This was done by heating of the cell and illuminating it with a 300 W lamp, continuing the long-term pumping of the rest gas through valve 3. After that the rest gas had attained a working pressure of the mass spectrometer of 10^{-7} Torr, we opened valve 4 slightly and set up a controllable flux of Nitrogen through the cell. Once the cell had attained a stabilized Nitrogen pressure, we irradiated it with the flash lamp.

Fig. 4 shows an example of a signal taken by the mass spectrometer from the photodesorbed Nitrogen in the Pyrex cell. The figure shows that the density of Nitrogen in the cell increases very quickly and, after reaching a maximum, decreases with a characteristic time of 1.2 s. This time coincides with the time value obtained in the previous measurement. The plot also shows that the density after the flash falls to a level which differed from

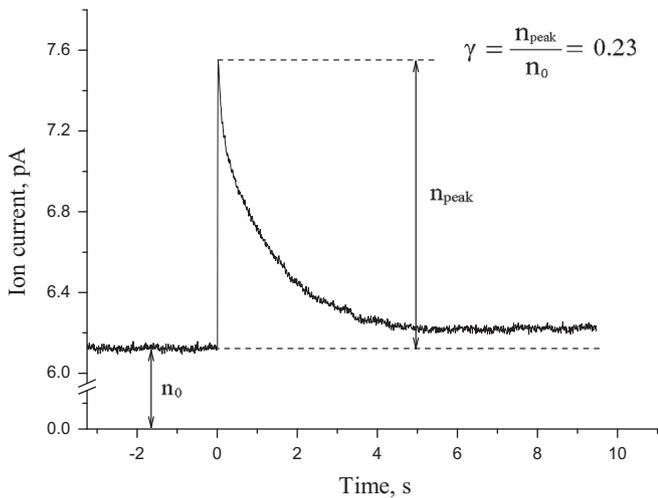


Fig. 4. The dependence of the density of nitrogen in the spherical cell versus of time.

the equilibrium density level of the Nitrogen before the flash. Obviously this was because of the heating of the wall by the flash light. In this measurement, we found that $\gamma=0.23$.

It was found that about 10 flashes are enough to clear the inner surface of the cell completely of the adsorbed Nitrogen. Taking into the account the sum of peak densities of the desorbed Nitrogen during the 10 flashes, we evaluated the total number of molecules in the volume of the cell, and, in turn, knowing the area of the inner walls, we calculated the coverage C ($0 \leq C \leq 1$) of the surface by the Nitrogen molecules. This was done for eleven different Nitrogen equilibrium densities n_0 . Fig. 5 shows the coverage of the coating C versus the Nitrogen densities.

It can be seen that initially the plot appears to increase linearly with the equilibrium density n_0 of Nitrogen in the cell, then at high concentrations approaches a saturation level at $C_0=0.2$. This plot is described by the following equation, known as the Langmuir's adsorption isotherm:

$$C = C_0 \frac{n_0}{n_0 + b}, \quad (14)$$

where the constant $b=0.045$ is the ratio of the rate of adsorption to the rate of desorption of the Nitrogen on the surface of the glass. Note that because no special efforts were taken to clean the inner surface of the cell of the different kinds of pollution, only 1/5 part of the glass surface area was covered with a monolayer of adsorbed Nitrogen. This small wall coverage substantially limited the value of the peak density obtained in the experiment. Furthermore, the small PLD effect observed in the last experiment can be explained by the fact that the cell used had neither an optimal shape nor an optimal size and because of the external positions of the detector and the external position of the light source relative to the cell. The external position of the detector led to the large effective volume of the vacuum system that in turn lowered the density of the desorbed Nitrogen molecules and decreased the peak signal. The external detector location of the flash lamp made it completely impossible to concentrate all the light from the lamp on the cell. A single passage of light through the cell, when only a small fraction of the light was absorbed by the glass surface, triggered the photodesorption of only a small number of molecules.

In order to enhance the PLD signal and increase γ , we constructed the second system, in which a cylindrical cell was used instead of the spherical one. The second experimental setup is shown in Fig. 6. It consists of a cylindrical glass cell 1 of molybdenum glass (C-52) with an inner radius of $R_1=14$ mm and

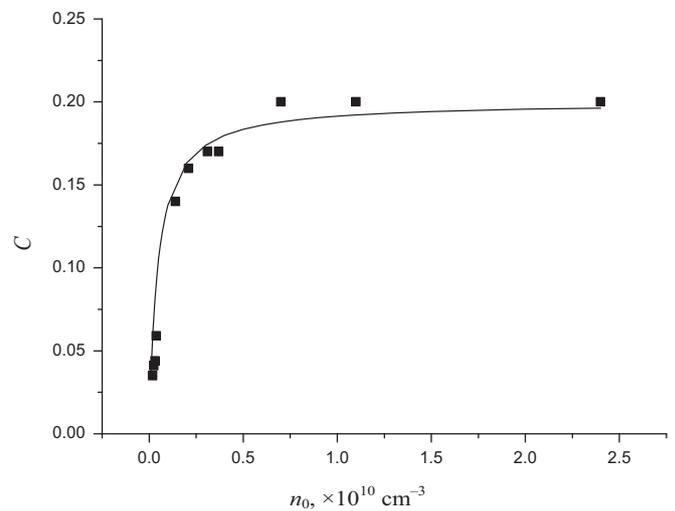


Fig. 5. The dependence of coverage C of the inner surface of the cell's walls by nitrogen molecules as a function of the equilibrium density n_0 .

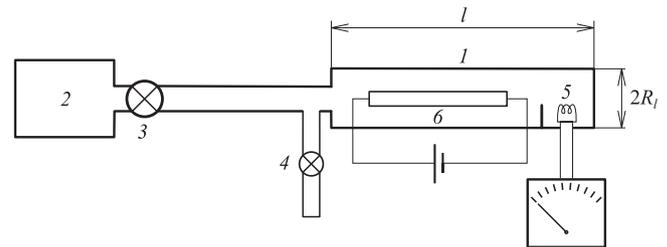


Fig. 6. The experimental setup with a cylindrical cell: 1—cylindrical cell made of molybdenum glass, 2—turbo, 3, 4—vacuum valves, 5—ionic gauge, 6—linear flash lamp.

length $l=100$ mm; turbo pump 2, which is connected to the cylindrical cell via the vacuum valve 3. Filling the cell with Nitrogen was done via valve 4. The inner surface of the cell was carefully cleaned by heating the cell, by illuminating it with a halogen 300 W lamp and by long-term protracted pumping. The density of the desorbed Nitrogen was measured using the compact ionic gauge 5, which was placed directly into the cell.

In order to enhance the intensity of illumination significantly, a linear flash lamp 6 was placed inside the cell and the outer surfaces of the walls of the cell were made to reflect the light. To avoid any interference from the photoelectric effect which occurs because of the ionization of the filament of gauge 5 when subjected to the pulsed light used, a screen was placed between the flash light source and the gauge, and the cell wall near the filament was deprived of the mirror coating. The absence of the photoelectric effect was verified by the direct illumination of the gauge filament by a light emitted from an additional pulsed light source. The verification was made at a low vacuum level when the photodesorbed signal from the released Nitrogen had dropped close to zero.

Fig. 7 shows an example of the signal received from the photodesorbed Nitrogen in the cylindrical cell.

The figure shows that the density of Nitrogen in the cell increased very quickly and, after reaching a maximum, decreased within a time of about 1 s. The graph also shows that the Nitrogen density fell after the flash to a level which differed from the density level of the Nitrogen before the flash. This effect can be attributed to the heating of the wall by the pulsed light. In this experiment, we found that the γ is equal to 300. This means that, under these conditions, the PLD effect could increase the

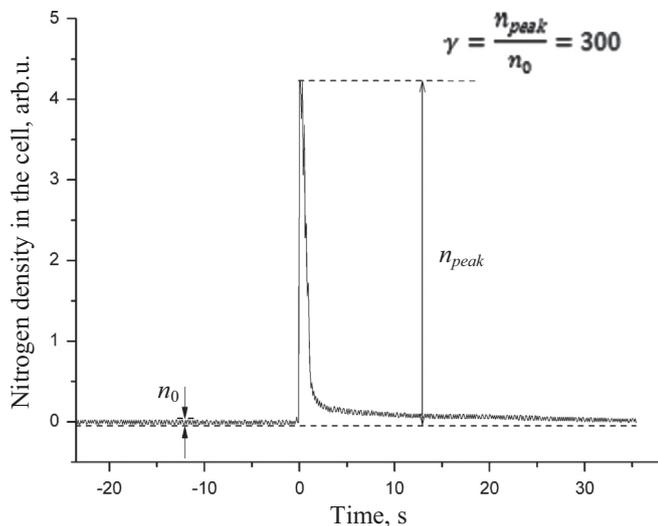


Fig. 7. The dependence of the density of nitrogen in the cylindrical cell versus of time. Equilibrium density $n_0=0.25 \times 10^{10} \text{ cm}^{-3}$.

concentration of the molecules of interest by nearly three orders of magnitude.

4. Conclusion

We have presented the results of experiments on the pulsed light desorption of molecular Nitrogen from a glass surface. The experimental results are in qualitative agreement with the model developed which describes the photodesorption processes in cells of different shapes and sizes. We have shown that the maximal peak density of the desorbed gas is attainable in a cylindrical cell with reflecting walls, with a pulse light source placed inside of the cell used. Moreover, it is very important to clean the inner surfaces of the walls which are used for accumulation of the molecules detected from any pollutants. When a laser light source which can

be tightly focused on the end of glass cylindrical cell is used, the diameter of the chosen cell can be extremely small. This fact opens up the possibility of the use of PLD for the generation of controlled high density gases in photonic-band-gap fibers, which provide a long interaction while maintaining a small light mode area. This is of significant interest in performing experiments on low-light-level optical nonlinearities.

Acknowledgments

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