Photoextraction of Molecular Gases from an Organic Polymer Film

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Photoextraction of various molecular gases from a polydimethylsiloxane (PDMS) polymer film has been studied. Change in the density of molecular gases has been measured as a function of the illumination duration, intensity and wavelength of light, and temperature of the coating. A linear dependence of the rate of photoextraction on the intensity of the incident light has been established. Similar to the photoelectric effect, photoextraction is absent in the long-wavelength spectral range down to 550 nm. The effect increases sharply in the short-wavelength spectral range below a threshold of about 550 nm. Photoextraction is absent at temperatures below the glass-transition temperature of PDMS ($-125°C$), at which, as is known, the bulk diffusion of molecular gases in the film is strongly suppressed. At long-term irradiation of the film, the number of photoextracted molecules decreases exponentially with time. This increase is accompanied by a long tail of a diffusion form. The results indicate that photoextraction has a nonthermal nature and demonstrate the important role of bulk diffusion in the process of light-induced extraction of molecules from the surface.

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It is well known that atoms and molecules can be adsorbed from a gas phase on the surface of solids. A phenomenon inverse to adsorption is manifested as the extraction of adsorbed particles from the surface of a solid to the gas phase through desorption. Desorption can be initiated by electron and ion irradiation of the surface of solids, heating of the surface, acoustic action on the surface, vibration, etc. In addition, desorption can be induced by irradiation of the surface by light in the visible or ultraviolet range. In this case, this phenomenon is often called photodesorption of particles from the surface of solids. Another phenomenon is absorption of particles when they are captured not on the surface but in the bulk of an absorber. A bright example of absorption is the absorption of poisonous gases by activated carbon. It is surprising that the possibility of light-induced extraction of particles from the bulk of an absorber, which can be treated as a phenomenon inverse to absorption, has not been considered until recently. Even a term for this phenomenon is absent. It is noteworthy that the so-called extraction of organic molecules from the bulk of an absorber heated by microwave radiation was studied in numerous works (see, e.g., [1]). As will be shown below, photoextraction of atoms and molecules from the bulk of an absorber is not attributed to the trivial heating of the medium and has a more complex and interesting nature.

In this work, photoextraction of various molecules from the bulk of a polydimethylsiloxane (PDMS) organic film is studied with the use of a spherical Pyrex cell whose inner surface was coated by the PDMS film. In order to avoid the effect of chemically active gases such as oxygen and water vapor, as well as other substances adsorbed on the surface of the film, the film was passivated through treatment with rubidium vapor [2], which was obtained by heating a source of atomic vapor in the cell. This source contained metallic rubidium. Passivation lasted for several days. The pressure of Rb vapor was established at a level of 10^{-7} mbar. The concentration of vapor was estimated through the temperature of rubidium in the source [3].

Photoextraction of molecules from the film was performed at continuous pumping of the cell at a pressure of the residual gas of 10^{-8} mbar by irradiation of light from a flash lamp. The evolution of the density of photoextracted molecules was recorded with a QME 220 (Pfeiffer Vacuum GmbH) quadrupole mass spectrometer.

Figure 1 shows the mass spectrum of residual gases in the cell. It contains about 100 peaks, which are in three groups in the ranges 12–19, 29–35, and 35–45 amu. Furthermore, mass peaks are located in the range from 62 to 100 amu. Analysis of the spectrum shows that the observed peaks correspond to atmospheric gases (nitrogen, oxygen, and carbon dioxide), which were adsorbed by the surface. Numerous peaks correspond to the fragments of PDMS molecules. These fragments are products of the chemical interaction between rubidium atoms and coating molecules
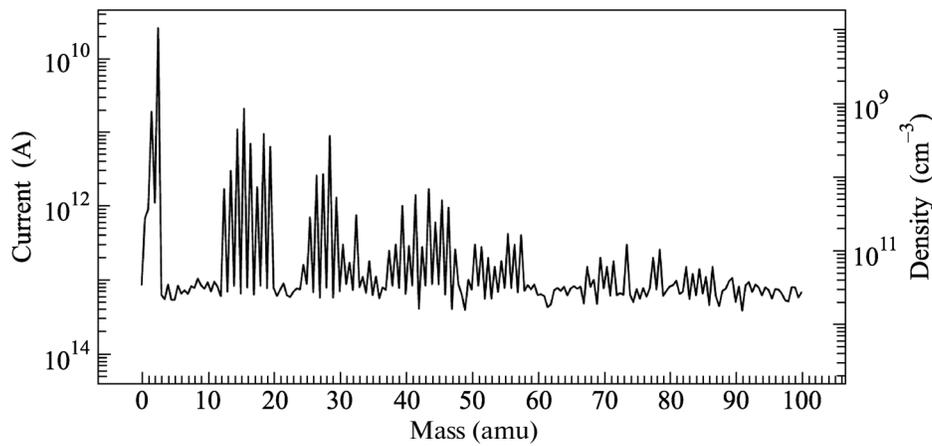
Fig. 1. Mass spectrum of residual gases in the cell after action of Rb vapor.

[4−6]. Apparently for this reason, peaks associated with $^{85-87}$Rb isotopes are absent in the mass spectra.

Figure 2 shows a signal of photoextraction of ethane gas (C_2H_6). It can be seen that the concentration of ethane before a flash is constant and corresponds to the partial pressure of the gas in the absence of irradiation. At the time instant $t = 18$ s corresponding to the flash of light, the concentration of ethane increases sharply. After end of irradiation, it decreases to the initial value because of the evacuation of this gas by a turbopump and because of reabsorption of molecules by the walls of the cell. The characteristic time of a decrease in the concentration after irradiation is 0.3 s. Since the initial and final concentrations are equal to each other, the temperatures before and after the flash are the same. Consequently, the observed photoextraction of molecules is not attributed to the direct heating of the walls of the cell. According to the direct experiment, in order to reach such an increase in the concentration of ethane, it is necessary to heat the walls of the cell to a temperature of about 75°C. We measured the effect in terms of a relative increase γ in the concentration as a result of photoextraction.
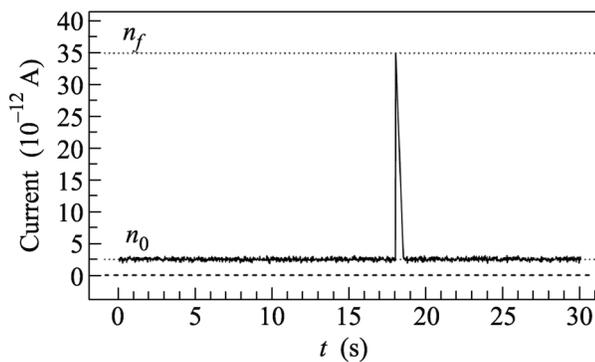
This quantity is equal to the ratio of the peak concentration n_f to the initial concentration n_0. In this case, $\gamma = n_f/n_0 = 12$.

The table presents the results of photoextraction of 22 different fragments and gases. The table contains their masses, chemical formulas, and relative concentration increase γ. It can be seen that the relative concentration increase γ depends on the gas and varies from 1.2 for N_2 to 35 for CO_2 and 37 for C_3H_7. This allows the conclusion that the observed molecular fragments of the PDMS film were independently extracted from its bulk, rather than appearing in the dissociation of large PDMS molecules on the hot filament of the mass spectrometer. Moreover, several elements with mass peaks at 25, 50, and 52 amu were not identified.

The dependence of the effect of photoextraction on the intensity of the light flash is shown in Fig. 3 for acetylene (C_2H_2). It is clearly seen that the ratio $\gamma = n_f/n_0$ increases linearly with the intensity of the incident light. This behavior again indicates that the nature of photoextraction of molecules from the
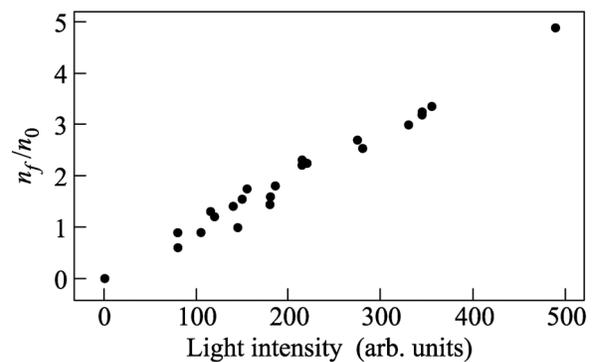

Fig. 2. Signal of photoextraction of ethane (C_2H_6).

Fig. 3. Relative change in the density of acetylene (C_2H_2) versus the intensity of light.

organic film is not thermal, because its magnitude in the case of heating should exponentially depend on the intensity of light. Furthermore, the direct measurement shows that the temperature of the walls of the cell before and after the flash of light does not change. Consequently, the effect of heating of the surface on the magnitude of the effect is excluded.

It was found experimentally that the ratio $\gamma = n_f/n_0$ depends on the wavelength of light. This dependence for propene (C_3H_6) is shown in Fig. 4. These data were obtained at the maximum energy density of the flash of about 0.1 J/cm². Photoextraction is absent in the long-wavelength spectral range down to 550 nm. The effect increases sharply below a threshold of about 550 nm in the short-wavelength spectral range from 550 to 200 nm. The presence of the threshold together with the linear dependence of the effect on the power of radiation implies a certain analogy of the observed photoextraction of molecular gases to the photoelectric effect.

Figure 5 shows the result of the experiment on photoextraction of molecular gases at low temperatures for ethane C_2H_6. In this experiment, the cell was cooled by liquid nitrogen to a temperature of −196°C. After that, the parameter γ was measured in the process of natural heating of the cell by ambient air when the temperature of the cell varied from −196°C to room temperature (25°C). Figure 5 was obtained at the maximum intensity of pulsed light (0.1 J/cm²). It is clearly seen that the effect is absent up to a temperature of −150°C. Then, it increases linearly and is saturated. This plot is well described by the Arrhenius formula $\gamma = \gamma_0 \exp(-T_a/T)$, where T_a is the photoextraction activation temperature and γ_0 is a constant at $T = \infty$. The approximation of the plot by the Arrhenius formula gives $T_a = -135$°C.

Such a temperature behavior of the parameter γ can be explained as follows. Surface molecules in the organic film irradiated by light can be desorbed from

Masses, chemical formulas, and relative change in the density of extracted fragments of molecules (x marks unidentified molecular ions)

Mass	Fragment	γ	Mass	Fragment	γ
2	C	2.8	38	C_3H_2	6.6
13	CH	1.7	39	C_3H_3	2.3
14	N	1.2	40	C_3H_4	5.8
15	CH_3	3.8	41	C_3H_5	10
16	O	2.5	42	C_3H_6	9.5
25	x	1.8	43	C_3H_7	37
26	C_2H_2	5.1	44	CO_2	35
27	C_2H_3	6.8	45	SiOH	7.1
28	CO	9	50	x	5.3
29	C_2H_5	9.3	52	x	1.9
30	C_2H_6	12	55	C_4H_7	2

the film to a gas phase. As a result, the density of such molecules in the surface layer vanishes. This results in the intense diffusion of molecules from the bulk of the film to the surface, where they can also be desorbed. Molecular diffusion is insignificant at a low temperature and is quite large at a high temperature. The diffusion activation temperature is determined by the glass-transition temperature. We measured the glass-transition temperature of PDMS by the differential scanning calorimetry method (DSC 200 F3 Maia, Netzch). This temperature was −125°C, which is close to the temperature $T_a = -135$°C. This fact indicates that the bulk diffusion is important in the process of extraction of molecules.

The effect of bulk diffusion in the process of extraction of molecules was observed at photoextraction of molecular gases at long-term irradiation of the cell (see Fig. 6). In the process of these measurements, the cell was in the continuous pumping regime for 25 days. After that, its surface was irradiated by light of a halo-
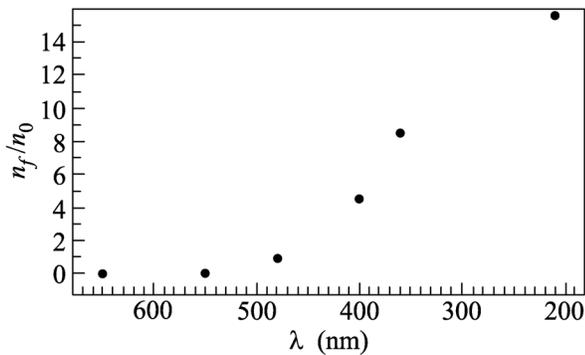
Fig. 4. Relative change in the density of propene (C_3H_6) versus the wavelength of light.
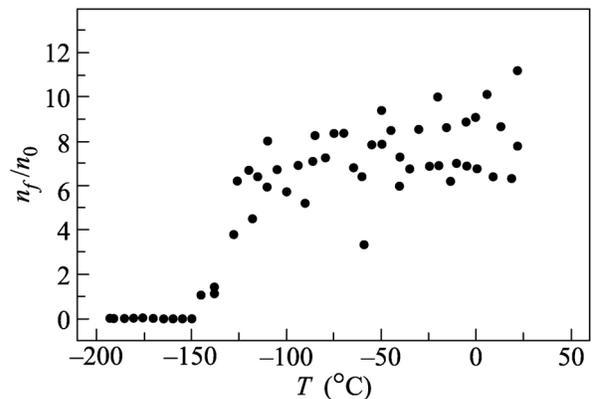
Fig. 5. Temperature dependence of relative change in the density of ethane (C_2H_6).
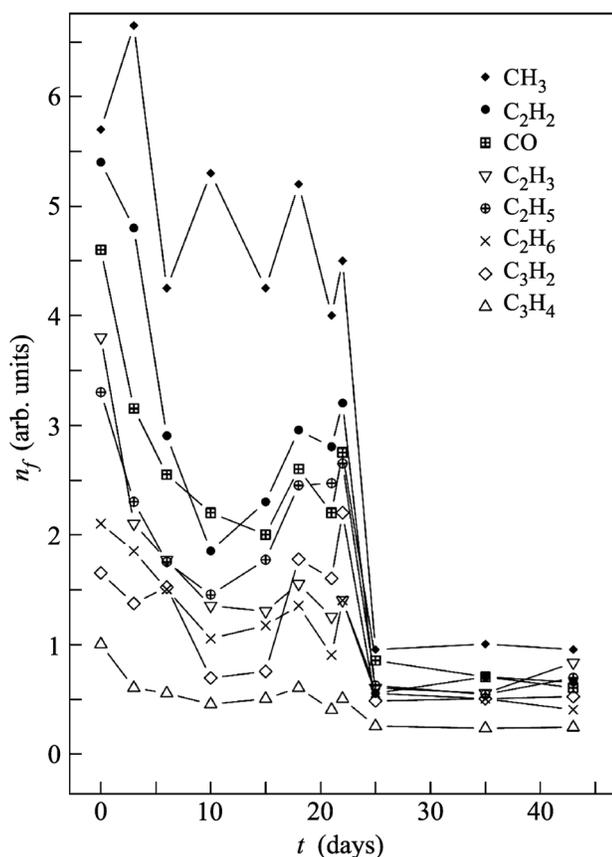
Fig. 6. Time dependence of the density of molecular gases.

To summarize, we have observed change in the density of molecules of the gas caused by photoextraction in the gas cell as a function of the duration, intensity, and wavelength of radiation and the temperature of the coating. The yield of extracted molecules decreases rapidly with a decrease in the temperature, because diffusion in the polymer in the glassy state decreases. We have measured the activation temperature of photoextraction of PDMS molecules and have found that it coincides with its glass-transition temperature. Photoextraction of molecules from the cell continuously illuminated by the halogen lamp decreases rapidly and, then, exhibits a long tail owing to diffusion of molecules in the bulk of the film. The results presented above clearly indicate that bulk diffusion plays an important role in the observed photoextraction of molecules. The interesting possibility opens for using the photoextraction effect as the method for studying the dynamics of transitions in a glass in supercooled liquids.

gen lamp. The densities of various gases for which photoextraction is most pronounced were measured. The time instant $t_0 = 25$ d in Fig. 6 corresponds to the beginning of the experiment. The observed sharp decrease in the number of desorbed molecules is due to a radiation-induced decrease in the number of molecules in the surface layer. It is clearly seen that this decrease is accompanied by a smooth weakening of the effect. We attribute this weakening to the slow diffusion of molecules from the bulk of the film to its surface.

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