

# Laser control of permeability of a molecular screen

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A considerable variation of the permeability of a monodisperse porous filter that is transparent to laser radiation is observed experimentally for resonance-excited bromine molecules diffusing through the filter.

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Recently, considerable interest is being generated concerning the possibility of controlling heterogeneous processes with the aid of lasers.<sup>1</sup> Among such processes is the diffusion of gases through porous screens. Earlier reports<sup>2</sup> have dealt with the laser-induced isotope separation for vibrationally excited molecules which diffuse through a porous filter that is transparent to IR-laser radiation. Moreover, a possibility was mentioned of the existence of a distinction in the permeability of porous structures for electron-excited and unexcited atoms and molecules.

In this paper we report on the first observation of a control effect for the permeability of a porous structure of the molecular screen type with the resonant laser excitation of the electron terms of the gas molecules diffusing through the screen.

The experiment was carried out for porous membranes consisting of 95% quartz

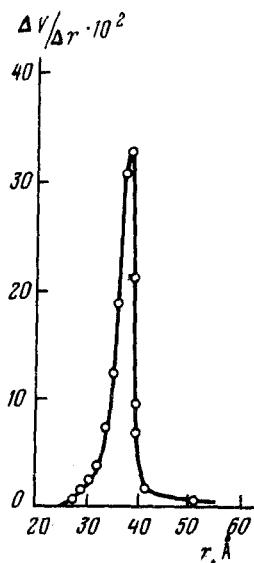


FIG. 1. Pore size distribution.

and featuring monodispersive porous structure with a narrow size distribution of pores. The distribution maximum corresponds to 40 Å (Fig. 1). A membrane is glued across a quartz cell whose input section receives a portion of the subject gas at the pressure of several torr. The output section is directly connected to the ionization chamber of a quadrupole mass-spectrometer (pressure  $10^{-5} - 10^{-6}$  torr, evacuation by an ion titanium pump at the rate 100 l/sec). Under these conditions the mean free path of gas molecules considerably exceeds the screen pore size and a free molecular gas flow occurs (Knudsen diffusion or effusion). The gas flowing through the membrane is illuminated with an argon-ion laser (Spectra Physics 171, wavelength 5145 Å, power 5 W). The membrane absorbs practically none of the laser radiation which penetrates the pore volume (easily and without scattering).

We studied the effect of laser irradiation on a membrane permeability for the molecular bromine  $\text{Br}_2$  in either pure form or in a mixture with  $\text{HBr}$ ,  $\text{SF}_6$  or Ar. Figure 2 shows time variation of the partial  $\text{Br}_2$  pressure behind the membrane for consecutive on and off switching of the laser. The partial pressure is recorded by a mass-spectrometer. A similar variation of membrane permeability for bromine was observed in all the mixtures under test at concentrations from 9 to 90%. In the course of this, changes in the permeability of solvent gases  $\text{HBr}$ ,  $\text{SF}_6$  and Ar were not observed. Changes in the direction of illumination (with or against gas flow) fail to alter the nature and magnitude of the effect. Membrane heating, including heating by laser, increases its permeability for all mixture components passing through. In the course of prolonged illumination, the laser-specific decrease in the permeability for  $\text{Br}_2$  and an increase in the same due to laser heating closely compete with each other.

Thus, the observed effect of laser-controlled permeability of a fine-pore membrane is of a selective nature and cannot be explained by the thermal effect of laser radiation (Fig. 3).

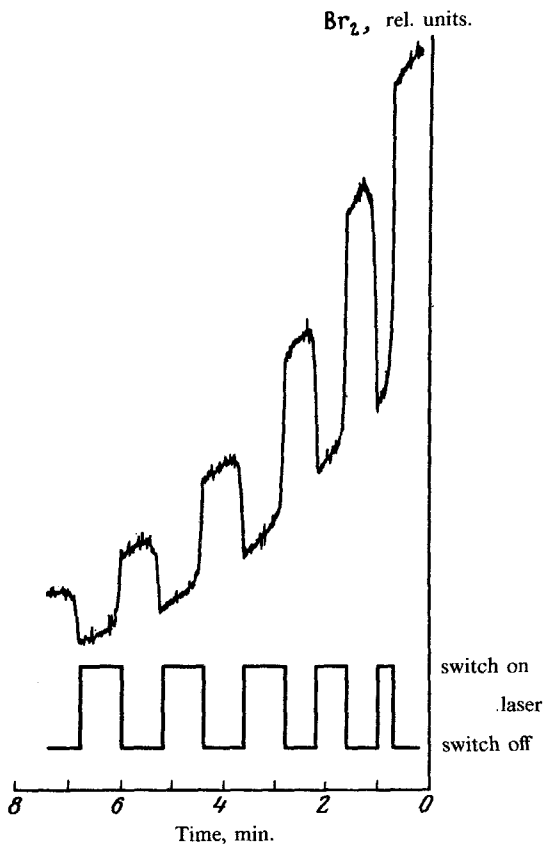


FIG. 2. Time-dependent variation of  $\text{Br}_2$  concentration at membrane exit under 4-W illumination.

As is well known, radiation from an argon-ion laser is resonance-absorbed by molecular bromine, which at a wavelength of  $5145 \text{ \AA}$  ( $^1\Sigma_{0g}^+ \rightarrow B^3\Pi_{0u}^+$  transition) falls into a predissociation region. The dissociation range of the term  $^3\Pi_{0u}^+$  exceeds the photon energy at  $5145 \text{ \AA}$   $150 \text{ cm}^{-1}$ . The excited molecules  $\text{Br}_2^*(^3\Pi_{0u}^+)$ , therefore, easily undergo collisional dissociation and the predissociation is accompanied by direct dissociation.<sup>3</sup> The radiative lifetime of  $\text{Br}_2^*$  is  $10^{-6} - 10^{-5}$  sec, the rate of spontaneous dissociation— $10^6 - 10^7 \text{ sec}^{-1}$ , and the cross section of collisional dissociation— $10^{-14} \text{ cm}^{-2}$  exceeds the gas-kinetic cross section.<sup>4</sup> The experimental data<sup>5</sup> permit the calculation of the absorption cross section of  $\text{Br}_2$  at  $5145 \text{ \AA}$ , which is  $2 \times 10^{-18} \text{ cm}^{-2}$ . In this case a fraction of the molecules excited by the laser radiation during their passage through one pore in a time  $\tau = 2 \times 10^{-11}$  sec, is  $l\sigma\tau/h\nu = 10^{-10}$ .

We shall assume that all the excited molecules dissociate upon collision with the wall and the atoms produced as a result of this are adsorbed by the latter. The probability of adsorption for a single molecule in a single act of wandering over the porous structure of the molecular screen is  $10^{-10}$ . The total number of wandering events that are required for penetration of a membrane with thickness  $z$  is  $(z - \delta)^2$ , where  $\delta$  is the mean value of the elementary wandering act, i.e., mean pore size. At  $z = 4 \text{ mm}$  and

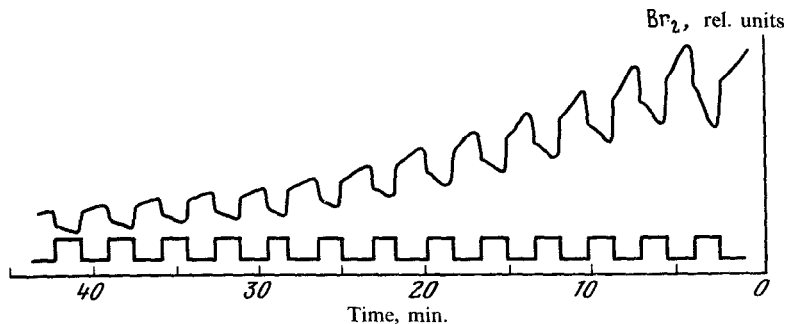


FIG. 3. Time-dependent variation of  $\text{Br}_2$  concentration at membrane exit under 13-W illumination.

$\delta = 40 \text{ \AA}$  this number attains  $10^{12}$  and, therefore, the resultant probability of adsorption may be high.

Evaluation within the framework of the subject model may be made by means of rate equations that are similar to those used in Ref. 6 for the analysis of the effectiveness of laser isotope separation by way of selective photoionization of atoms in a molecular beam

$$\frac{\partial}{\partial t} n_1(x) = (n_2 - n_1) \frac{l\sigma}{h\nu} - V_\partial \frac{\partial n_1}{\partial x} \quad (1)$$

$$\frac{\partial}{\partial t} n_2(x) = (n_1 - n_2) \frac{l\sigma}{h\nu} - \frac{n_2}{\tau} - V_\partial \frac{\partial n_2}{\partial x}$$

where  $n_1(x)$  and  $n_2(x)$  are molecule densities in the  $^1\Sigma$  and  $^3\Pi$  states, respectively,  $x$  is a coordinate along a normal to membrane plane,  $V_\partial$  is the diffusion rate along this direction, and  $\tau$  is time spent in a single wandering, i.e., time of flight through a single pore. Since the time of diffusion through a membrane with a thickness  $z$  is  $t = \tau z^2 / \delta^2$ , the mean diffusion rate may be expressed as  $V_\partial = z/t = V_T \delta / z$ , where  $V_T$  is the mean thermal velocity  $\delta/z$ . Strong retardation of directional motions along the concentration gradient in the case of diffusion through a fine-pore membrane sharply increases the effectiveness of laser coupling. Actually, the solution of Eq. (1) by standard methods under stationary conditions and for the boundary conditions  $n_1(0) = n$ ,  $\partial n(0)/\partial x = 0$  yields the following highly-accurate result

$$n_1(z) = n_0 \exp \left[ - \frac{z^2}{\delta^2} \frac{l\sigma\tau}{h\nu} \right] \quad (2)$$

At  $z^2/\delta^2 = 10^{12}$  and  $l\sigma\tau/h\nu = 10^{-10}$ , Eq. (2) results in a negligibly small molecule density at the membrane output.

The fact that our calculations, regardless of being approximate, correctly describe the order-of-magnitude changes in the membrane permeability speaks in favor of the assumption concerning the resonant excitation of molecules, their surface dissociation

and adsorption of the dissociation products as a possible mechanism of the observed effect of a resonant laser control of permeability of a molecular screen. We should note that this effect may be used for the separation of materials and, clearly, isotopes.

The current lasers operating in the optical and *UV* regions (excimer and dye lasers) lend themselves sufficiently well to application of the effect of controlling the permeability of a molecular screen.

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