# Accelerated Diffusion of Molecular Hydrogen in Optical Fibers Loaded at 150-170 MPa

**S.A.Vasiliev[1], V.G.Plotnichenko[1], A.O.Rybaltovskii[2], V.V.Koltashev[1], V.O.Sokolov[1], O.I.Medvedkov[1], E.M.Dianov[1]**

[1] *Fiber Optics Research Center at the A.M.Prokhorov General Physics Institute RAS, Moscow, Russia, Phone: +7(095) 1328306, Fax: +7(095) 1358139, sav@fo.gpi.ru*
[2] *Nuclear Physics Institute of the Moscow State University, Moscow, Russia*

## Abstract

Barodiffusion has been considered to be the main reason of the accelerated outlet of molecular hydrogen from optical fibers loaded at pressures 150 - 170 MPa. Increased solubility of hydrogen in UV-irradiated germanosilicate glass has been observed.

**Introduction.** Steady interest for the last two decades to the study of spectral characteristics of molecular hydrogen and its interaction with the network of high-purity silica and germanosilicate (GS) glasses is kept basically by the following reasons. Firstly, the penetration of $H_2$ molecules into optical fibers results in optical loss growth at the telecommunication wavelengths [1]. Secondly, the presence of dissolved hydrogen strongly enhances photosensitivity of fibers [2].

To clarify both the limiting value of hydrogen solubility in silica glass and the concentration dependences of thermo- and photochemical reactions with participation of $H_2$ molecules, the study of the properties of molecular hydrogen dissolved in the glass network at loading pressures exceeding 100 MPa is of much interest. Only a few papers [3, 4] are known to discuss some aspects of spectroscopic properties of $H_2$ molecules in the network of pure silica and GS glasses loaded at such pressures.

The aim of this paper is to investigate the spectral peculiarities of molecular hydrogen dissolved in germanosilicate glass network at a high loading pressure (150 - 170 MPa) by different spectroscopic methods. To obtain the information about the state, concentration and interaction of molecular hydrogen with the glass network during $H_2$ outlet from the fiber, we monitored Raman bands and 1.24 μm absorption band belonging to $H_2$ molecules. A change of $H_2$ concentration in the fiber core was also detected by measuring the shift of the resonance wavelength of Bragg gratings preliminary written in the investigated fibers.

**Experimental techniques and samples for investigation.** The main objects of our studies were single-mode optical fibers with external diameter of 125 μm. Fiber cores were doped with different germanium concentration. The fibers were $H_2$-loaded at the pressure of 150 - 170 MPa (100°C) during 24 hours. Before $H_2$ loading 5-mm long Bragg gratings were written in some fibers using the second harmonic of Ar-ion laser (λ = 244 nm) in the scheme with a Lloyd interferometer. Gratings of both type I and type IIa were fabricated for tests. All spectral measurements were carried out at room temperature. Other experimental details can be found in [5]

**Experimental results and discussion.** Assuming that hydrogen concentration is proportional to the 1.24 μm band intensity and using the results of paper [1] obtained for the loading pressure of about 0.1 MPa, we estimated the approximate concentration of $H_2$ molecules in fibers after our treatment to be about 10 mol.% $H_2$. It is remarkable that even at high pressures the absorption band intensity remains practically proportional to the hydrogen pressure in the $H_2$ loading chamber. This agrees well with the data obtained in [4], where similar measurements were carried out up to the pressure of 150 - 200 MPa.

At high loading pressures we have revealed a change in the time dynamics of molecular hydrogen outdiffusion from the fiber, which is characterized by the presence of a faster initial stage. To illustrate this fact Fig. 1 presents time dependences of intensity of the 1.24-μm absorption after hydrogen loading measured for optical fiber at 150 MPa and 12.5 MPa. The dependence measured at low pressures is multiplied by the factor of 5.3 in order to provide the best fit for the sections of curves at time intervals longer than 50 hours. The main difference between the curves, clearly seen in the figure, is the behavior of absorption in the initial time interval (less than 50 hours).
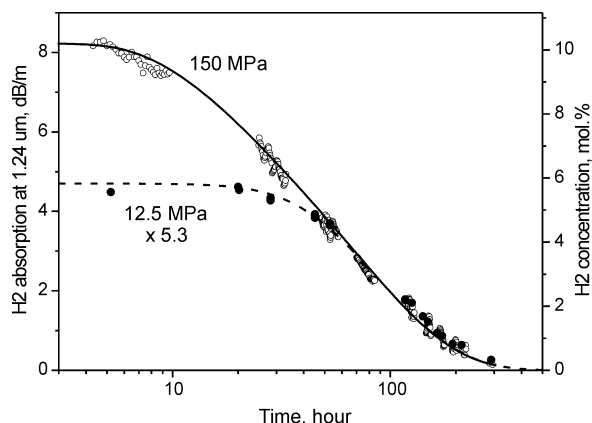
Fig. 1. Time dependence of the 1.24 μm band intensity during hydrogen outlet from fiber laded at: 150 MPa (open circles), 12.5 MPa (full circles). Solid and dashed curves represent the results of calculations (see explanations in the text)

Besides, the dotted curve in Fig. 1 shows the $H_2$ concentration at the fiber axis calculated by the solution of non-stationary diffusion equation with a constant diffusion coefficient $D_{H2}(25°C) = 2.5 \times 10^{-11}$ cm$^2$/sec [1]. It is seen that the theoretical curve agrees well with the measurements carried out at low loading pressures. At the initial stage (first 20 - 30 hours) the molecular hydrogen leaves fiber cladding, and only some time later, depending on the core diameter and temperature, hydrogen concentration in the fiber core region begins to reduce. Remarkably, that at high loading pressures the duration of the initial stage is just 3 - 5 hours.

The wavelength of resonance reflection $\lambda_{Br}$ of the Bragg grating written in the fiber core depends on the concentration of molecular hydrogen at the fiber axis [6], being at the same time unrelated directly to its vibrational spectra. Dissolution of molecular hydrogen in the fiber increases the effective refractive index of the fundamental mode and thus leads to a resonance wavelength shift to longer wavelengths. The spectra of two gratings written in optical fiber doped with 24 mol.% $GeO_2$ are presented in Fig. 2. According to the writing dynamics, the first grating (Gr1) is of type I, while the second grating (Gr2) is written to a state, when type I grating disappears, type IIa grating is still absent. The initial spectrum of these two gratings, as well as the two spectra measured 5 and 25 hours after the hydrogen loading (for clarity the spectra are shifted with respect to each other along the vertical axis), are shown in Fig. 2.

It is remarkable that the presence of dissolved hydrogen essentially affects not only the average induced index (Bragg wavelength shift), but also results in reversible changes in the amplitude of index modulation. As far as we know, this effect is observed for the first time. After hydrogen outlet from the fiber, practically full recovery of the grating spectrum to the initial state has been observed. We suppose that hydrogen-induced changes of the grating strength are related to a greater solubility of hydrogen in irradiated fiber regions as compared to non-irradiated ones. We estimated that in our experiments the solubility in irradiated regions increased approximately by 5% in comparison with that not exposed to UV-radiation.
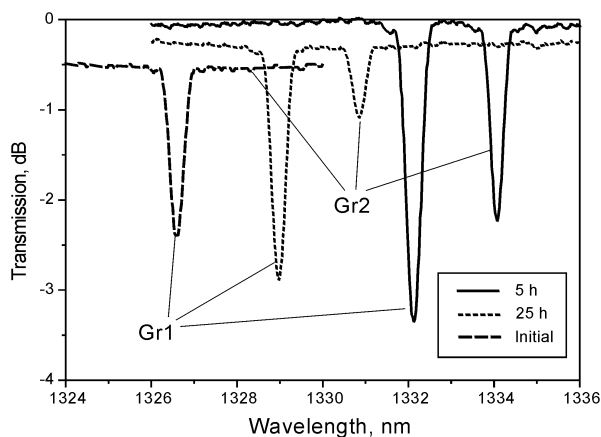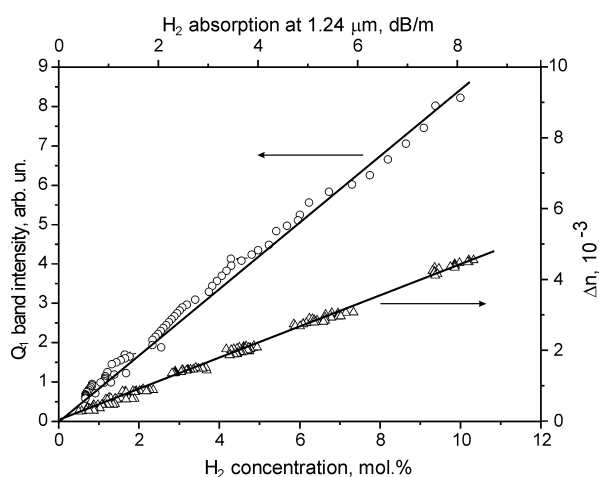


Fig. 2. Transmission spectra of Bragg gratings measured before hydrogen loading, as well as 5 and 25 hours after the loading was over.



Fig. 3. Dependence of integral intensity of Raman $Q_1$-band and hydrogen-induced mean index change on hydrogen concentration in the glass network.

As it is known, under the action of UV light the network of GS glass is rearranged, being accompanied by bond breaking and formation of rings of a lower order [7]. Such rearrangement, apparently, occurs owing to stretching or breaking of weak bonds at the boundaries of clusters in the glass network. In our opinion, this could lead to a reduction of the cluster size and a simultaneous increase in size of less dense regions between the clusters. The latter circumstance can be the main reason for enhancing the solubility of hydrogen in GS glass exposed to UV radiation.

Fig. 3. shows the dependences of the intensity of $Q_1$-band measured in Raman spectra as well as the Bragg wavelength on hydrogen concentration measured in the process of hydrogen outdiffusion. Note a good linearity of these dependencies testifying that there is no strong interaction between dissolved molecules up to concentrations of 10 mol.%.

To explain the accelerated decrease of hydrogen concentration in the fiber core we considered the contribution of the so-called barodiffusion mechanism [8] caused by a radial gradient of hydrogen pressure $P_{H2}$ in the fiber. In the presence of pressure gradient, the density $J$ of a flow of diffusing particles can be expressed by the following relation:

$$J = -D\left[grad(C_{H2}) + \alpha_P\,grad(\ln P_{H2})\right] \qquad (1)$$

where $D$ is the $H_2$ diffusion coefficient, $C_{H2}$ is the concentration of the $H_2$ molecules, $\alpha_P$ is the barodiffusion ratio.

At low concentrations hydrogen molecules collide mainly with the glass network atoms. Therefore, gradients of hydrogen pressure do not affect the total mass transfer (the first term in (1) prevails). This is the case, when the average number of molecules in the network interstitials is well below unity. According to our estimations at 150 MPa loading the average number of $H_2$ molecules in the network interstitials becomes comparable to unity, though not exceeding it. At such a high concentration the frequency of intermolecular collisions matches the frequency of collisions with the network atoms, and the presence of pressure gradient in any preferential direction results in the appearance of a flow of molecules in the direction opposite to this gradient (this flow is described by the second term in (1)).

The best fit of calculated and experimental curves of hydrogen outdiffusion (solid curve in Fig. 1) was obtained if $\alpha_P$ is expressed as a power function $\alpha_P = AC_{H2}^B$, where $A = 3.5 \pm 0.5$ and $B = 4 \pm 0.5$. For the calculation we supposed that $P_{H2}$ in any point of the fiber is proportional to $C_{H2}$ in this point.

It should be noted that we knowingly used the term "pressure" for description of barodiffusion in spite of the fact that the pressure of gas dissolved in solids is not widespread. This was done in order to emphasize the community of this phenomenon in gases and solids. Moreover, it is helpful for description of such phenomena as the alteration of the internal stress distribution [9] or the detectable increase of the external diameter observed in $H_2$ loaded fibers.

**Conclusions.** Raman and absorption bands of $H_2$ molecules in single-mode germanosilicate fibers have been investigated after their $H_2$ loading at 150 - 170 MPa. The accelerated initial stage in the dynamics of absorption and Raman scattering of $H_2$ molecules, as well as the characteristics of fiber Bragg gratings in the process of hydrogen diffusion from the fiber have been established. This phenomenon has been explained by the contribution of the barodiffusion of hydrogen in the glass network. Higher solubility of molecular hydrogen in the fiber regions subjected to UV-irradiation has been engaged to explain the change in the Bragg grating strength.

**References**

[1] P.J. Lemaire, *Optical Engineering,* **30**, p.780 (1991).
[2] P.J. Lemaire *et al.*, *Electronics Letters*, **29**, p.1191 (1993).
[3] K. Faerch *et al.*, *Proc. of Conf. BGPP'2003,* TuA2 (2003).
[4] C.M. Hartwig, *J. Appl. Phys.*, **47**, 956 (1976).
[5] V.G. Plotnichenko *et al.*, submitted to *J. of Non-Cryst. Solids.*
[6] B. Malo *et al.*, *Electronics Letters*, **30**, p.442 (1994).
[7] E.M. Dianov *et al.*, *Optics Letters*, **22**, p.1754 (1997).
[8] L.D. Landau, E.M. Lifshitz, Hydrodynamics, (Nauka, Moscow, 1988).
[9] N.H. Ky *et al.*, Applied Physics Letters, **74**, p.516 (1999).