

# Quenching of erbium and ytterbium luminescence by the random walk of H<sub>2</sub> and D<sub>2</sub> molecules in the silica glass of active optical fibers



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## ABSTRACT

Photoluminescence of Er<sup>3+</sup> (transition <sup>4</sup>I<sub>13/2</sub> → <sup>4</sup>I<sub>15/2</sub>, emission wavelength λ<sub>e</sub> ~ 1550 nm) and Yb<sup>3+</sup> (<sup>2</sup>F<sub>5/2</sub> → <sup>2</sup>F<sub>7/2</sub>, λ<sub>e</sub> ~ 1040 nm) ions incorporated in the silica of optical fibers immersed in a H<sub>2</sub> and/or D<sub>2</sub> environment at a pressure of up to 120 bar at temperatures of 80–873 K is investigated. The spectra and decay kinetics of the steady state luminescence excited by a 975-nm laser diode are recorded. It is shown that the thermal motion of interstitial H<sub>2</sub> and/or D<sub>2</sub> molecules quickens the decay kinetics and decreases the luminescence intensity. The effect becomes noticeable at temperatures greater than ~200 K and significantly increases with a further temperature increase in H<sub>2</sub> and/or D<sub>2</sub> environments. The luminescence decay curves increasingly differ from single exponents with the increase of temperature and become best fitted by stretched exponential dependencies. This effect is reversible at temperatures of up to 800 K. We explain the revealed quenching effect of excited f-electron in terms of the rare earth ions due to the appearance of an additional relaxation channel involved in the excitation of vibrational degrees of freedom of diatomic molecules experiencing random walks inside the glass network. This study found that the closer the electron excitation energy of a rare earth ion to an energy gap in the vibration spectrum of a molecule, the greater the deactivation effect. The quenching rate significantly decreases when the molecules' rotational degrees of freedom are frozen out.

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## 1. Introduction

Currently, hydrogen loading of optical fibers is applied to increase fiber photosensitivity in the Bragg grating writing process [1,2] and/or to increase fiber resistance to ionizing radiation [3]. In both cases, interstitial H<sub>2</sub> enters into a chemical reaction with excited defects and partially incorporates in the silica network to form OH-groups. This reaction is irreversible.

In the present article, however, we shall focus on another effect associated with the presence of interstitial hydrogen and deuterium molecules in the glass. The effect belongs to a phenomenon known as the collisional quenching of electronic excitations by acceptors via random walking in solutions. Many comprehensive studies were made to address this phenomenon, mainly from the theoretical standpoint (see reviews [4,5]). Optical fiber saturated with hydrogen molecules experiencing Brownian motion inside the glass network of amorphous silicon dioxide is a rather new and experimentally friendly object to study this phenomenon. The essence of this effect is as follows: randomly walking diatomic molecules are able to act as energy acceptors for electronic excitations, thus introducing an additional channel for the non-radiative transfer of energy from the excited species to the glass network vibrations.

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Luminescence quenching of excited intrinsic defects in the silica glass of an optical fiber caused by randomly walking interstitial hydrogen was first described in refs. [6,7]. The excited donors in those experiments were germanium oxygen deficient centers, with an excitation energy of approximately 5 eV.

The experiments of ref. [8] demonstrated the deactivation of excited Er<sup>3+</sup> and Yb<sup>3+</sup> ions and bismuth clusters incorporated in the optical fiber core caused by the Brownian motion of interstitial H<sub>2</sub> molecules. The excitation energy of these donors did not exceed 1.3 eV, making the deactivation process fully reversible. As a result, the subsequent outcome of hydrogen molecules from the glass network returned the spectral and kinetic characteristics of luminescence to their initial values.

This impact of dissolved hydrogen on the luminescent properties of active fibers presents a special case of the fundamental chemical kinetics problem of the diffusion-controlled bimolecular reaction. This problem appeared in the beginning of the last century. A variety of mathematical approaches have been developed and many experiments have been performed to tackle this problem [9]. The essence of the problem is as follows. A passive medium contains two types of particles that can enter into a chemical reaction. The motion of the particles is a random walk (Brownian type). The reaction between a pair of particles becomes possible when they approach one another at a certain distance (the effective reaction radius). This behavior explains the importance of the dependence of the rate of such a reaction on the properties of the medium and the particles, the interaction type between particles, and

so on. A common approach is to handle the problem in a framework of the so-called encounter theory, which is described in detail in refs. [10, 11].

As applied to the focal point of this study, there are particles of an activator located in the solid medium of silica. These particles are the ions of rare earth elements, which substitute for silicon and are chemically built into the silica network and thus have no chance to any travel at the temperatures under consideration. The other types of particles are interstitial H<sub>2</sub> and/or D<sub>2</sub> molecules. At relatively moderate (less than 473 K) temperatures, hydrogen and deuterium dissolve into silica physically, i.e., they are present in the form of molecules and do not enter into any chemical reactions with glass. It was shown [12] that molecules undergoing Brownian motion inside a glass network retain most of the degrees of freedom that they have when moving in free space. When approaching the excited active centers, these molecules can deactivate electronic excitation, accepting energy via the excitation of the vibrational degrees of freedom. Thus, the interaction process occurs in the following manner: one type of the particles due to Brownian motion encounters fixed particles of the other type.

The above-described process explains why encounter theory may be applied to describe the luminescence quenching induced by the Brownian motion of diatomic molecules dissolved in the glass of the fiber core in activated silica fibers. A similar case is described in ref. [13] from the theoretical standpoint. Our case differs from the ones considered in earlier works only in the point that one type of particle (H<sub>2</sub> or D<sub>2</sub> molecules) is unbounded and hence is able to freely travel, while particles of the other type (Er<sup>3+</sup> and/or Yb<sup>3+</sup> ions) remain fixed.

In the present work, we demonstrate and discuss the results of our newly conducted experiments on the deactivation of excited Er<sup>3+</sup> and Yb<sup>3+</sup> ions located in silica optical fibers. The experiments are targeted to reveal the feature of the motion of diatomic molecules inside the silica network responsible for the luminescence quenching effect discovered in our previous work [8]. To do so, we obtained and compared quenching parameters for H<sub>2</sub> and D<sub>2</sub> molecules, which are known to have different energy gaps in their vibration spectra.

## 2. Samples and measurement technique

In the experiments, we used multimode silica fibers with Er- or Yb-doped cores specially fabricated for this purpose. The fibers have 125 micron and 20 micron outer and core diameters, respectively. The measured refractive index profile of the fibers is presented in Fig. 1. The light-guiding structure consists of a core surrounded by a light reflecting cladding made from a fluorine-doped silica layer of decreased refractive index. Both fibers are coated with polymer protecting claddings and are drawn from preforms fabricated by SPCVD [14].

The key parameters of the active fibers are summarized in Table 1. Note that no dopants, except the rare earth elements, are present in the core glass, with the concentrations being sufficiently small to

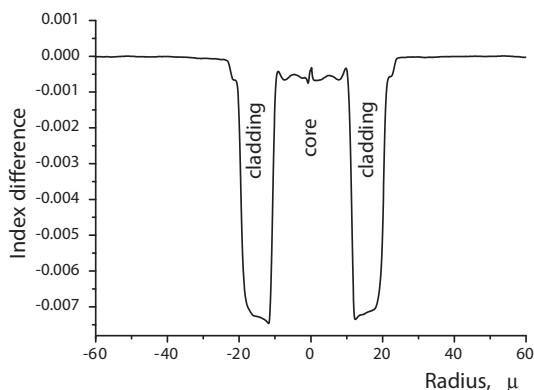


Fig. 1. Refractive index profile of the fibers under study.

prevent the possible clustering of the rare earth oxides due to their poor solubility in pure silica. Pure silica is used as a host for the rare earth ions to eliminate the possible influence of glass network modifiers, such as Al and P, on the random walk of H<sub>2</sub> and D<sub>2</sub> molecules inside the glass. The impact of these additives on the peculiarities of H<sub>2</sub> and D<sub>2</sub> random walking in silica will not be considered in this article because it is the topic of a separate study.

An approximately tenfold difference in the Er and Yb concentrations is set to provide a similar absorption coefficient of the fibers at the selected pump wavelength. Note that this difference is of no significance for the subsequent data analysis because the concentration of walking acceptors (H<sub>2</sub> or D<sub>2</sub> molecules) can solely influence the luminescence quenching phenomenon considered.

The absorption and luminescence spectra measured in the fibers at room temperature in air environment are depicted in Fig. 2.

Because an important part of our experiments constitutes measurements at different temperatures, reference luminescence decay curves are recorded in the fibers prior to their exposure to H<sub>2</sub> or D<sub>2</sub>. The results of these measurements are partly presented in Fig. 3.

The luminescence decay curves for Er<sup>3+</sup> ions and the decay time constants for Er<sup>3+</sup> and Yb<sup>3+</sup> luminescence are shown at various temperatures. The luminescence decay is observed to follow single exponential dependence at any temperature.

Fig. 4 illustrates the measurement scheme used for the photoluminescence study in the fiber samples exposed to hydrogen or deuterium loading.

A piece of an active fiber that is 5–20 cm in length is spliced with delivery fiber pigtailed to form a single fiber line. Pure-silica-core/fluorine-doped silica cladding fibers with a refractive index profile matching the active fibers are used as the pigtailed. The fiber line section with a piece of the active fiber is sealed in a chamber with a gas under the pressure of up to 100 bar for hydrogen and 125 bar for deuterium. The temperature in the chamber is set in the range of 473 to 873 K and is controlled by an external heater to an accuracy of 0.3 K. Photoluminescence is excited through a fiber pigtail by a laser diode operating in pulse-periodic regime (30 ms meander) at a wavelength of 975 nm. The average pump power launched into the fiber does not exceed 1 mW.

The pump source is connected to the delivery fiber through the port (a) of the 50% wideband directional coupler. The output port (c) of the coupler terminated by an oblique cut is immersed in a bath with an index-matching fluid for the more complete suppression of the backscattered pump light. The luminescence light is extracted through the port (b) of the coupler and, after passing the notch filter preventing back-scattered pump light, is delivered to the InGaAs photodiode connected to the Tektronix DPO3012 oscilloscope. The response time of the pump modulation system and the photodiode is less than 50 μs. To characterize the spectra, a luminescence light is delivered to the input of the Agilent 86142A fiber spectrometer, with the pump modulation switched off.

The experiment is composed of three stages. Shortly after filling the chamber with hydrogen or deuterium, photoluminescence decay kinetics are recorded at preset time intervals while gas molecules diffuse into the glass of the core containing active ions. At this stage, the temperature in the chamber is kept at 403 K to speed up in-diffusion; at this temperature, the chemical interaction of molecular hydrogen/deuterium with the silica network does not occur.

We estimate the concentration of the molecules reaching the axis of the fiber at a given time point using the macroscopic diffusion model described in detail in [15–17]. The diffusion coefficient is expressed by Arrhenius relation:

$$D(T) = D_0 \exp\left(-\frac{E_a}{k_B T}\right), \quad (1)$$

where  $D_0$  is a constant, which does not depend on temperature;  $k_B =$

**Table 1**

Characteristics of fiber samples. The Er and Yb concentrations are estimated according to the absorption spectra.

Activator	Pump wavelength, nm	Luminescence wavelength, nm	Initial lifetime, ms	Absorption at pump wavelength, dB/mm	Sample length, mm	Activator concentration, $\text{cm}^{-3} * 10^{20}$
Er <sup>3+</sup>	975	1532	11.92 ± 0.05	0.020 ± 0.001	200	1.56 ± 0.02
Yb <sup>3+</sup>		1040	0.65 ± 0.05	0.026 ± 0.001	200	0.17 ± 0.02

$8.62 \left( \frac{\text{eV}}{\text{K}} \right)$  – Boltzmann constant;  $E_a$  – activation energy; and  $T$  – temperature (K). For silica, typical values are:  $D_0 = 5.65 * 10^{-4} \frac{\text{cm}^2}{\text{s}}$ , and  $E_a = 0.450$  eV for hydrogen molecules and  $D_0 = 5.00 * 10^{-4} \frac{\text{cm}^2}{\text{s}}$  and  $E_a = 0.454$  eV for deuterium molecules [17].

Full saturation of the fiber core at 403 K takes 5 h, as per the calculations. For erbium-doped fiber, a comparison study on saturation at 20, 40, 60, 80 and 100 bar hydrogen pressures in the chamber is performed.

At the second stage of the experiment, the luminescence decay kinetics of the fibers saturated with gases is recorded at elevated temperatures. To do that, a chamber filled with H<sub>2</sub> or D<sub>2</sub> and containing a fiber is heated stepwise from 403 to 873 K. Luminescence decay curves are recorded in the process of heating every 50 °C. The buffer volume of the chamber (Fig. 4) enables the experiment with saturated fiber heating to be considered as a practically constant pressure process. However, the concentration of dissolved molecules in the core region varied with temperature because of changing solubility [18]. The transition speed to a new equilibrium value of concentration is determined by the diffusion coefficient, which in turn depends on the temperature as well. It takes approximately 20 min to raise the temperature of the sample by 50 K and to fix it at a new level. Estimations indicate that during this temperature increase process, at temperatures lower than ~423 K, the concentration of H<sub>2</sub> or D<sub>2</sub> molecules dissolved in the glass of the fiber core does not undergo significant changes. For this reason, measurements in the temperature range of 300 to 423 K are performed shortly after a new temperature value is reached, and the concentration of the dissolved gas molecules is considered to be unchanged. At temperatures greater than ~473 K, the changes in the concentration in the core region become noticeable within the time necessary for a jump to a new value of temperature. For this reason, after stabilizing the temperature at a new level, the sample is aged at this temperature for the time interval sufficient to achieve a new equilibrium value of concentration (~1 h for 473 K, ~30 min for 573 K, etc.).

At the third stage of the experiment, the measurements are performed in the process of cooling the H<sub>2</sub> or D<sub>2</sub> loaded fibers to the temperature of liquid nitrogen. After a full 5 h of saturation at 403 K, the heater is switched off, and then, the chamber is cooled down to room temperature within approximately 10 min. No significant change in the concentration in the fiber core region of the dissolved-in glass molecules can occur during this period of time. Subsequently, the fibers are

removed from the chamber, and a section of the fiber with the active core is mounted onto a rod, which is subsequently inserted in the inlet of a Dewar tank with liquid nitrogen. The speed of cooling in the nitrogen gas flow is constant and amounts to ~10 K/min. Note that the fibers prepared for this part of the experiment were not heated to temperatures greater than 403 K.

### 3. Results

Fig. 5 illustrates the changes of the luminescence spectrum of the Er<sup>3+</sup> ions, the integral intensity of the Er<sup>3+</sup> ions (inset), and the decay curves reflecting the increasing concentration of hydrogen molecules in the fiber core at room temperature. The inset in Fig. 5 shows the dependence of the luminescence integral intensity on the hydrogen concentration in the fiber core estimated in the manner described in Section 2.

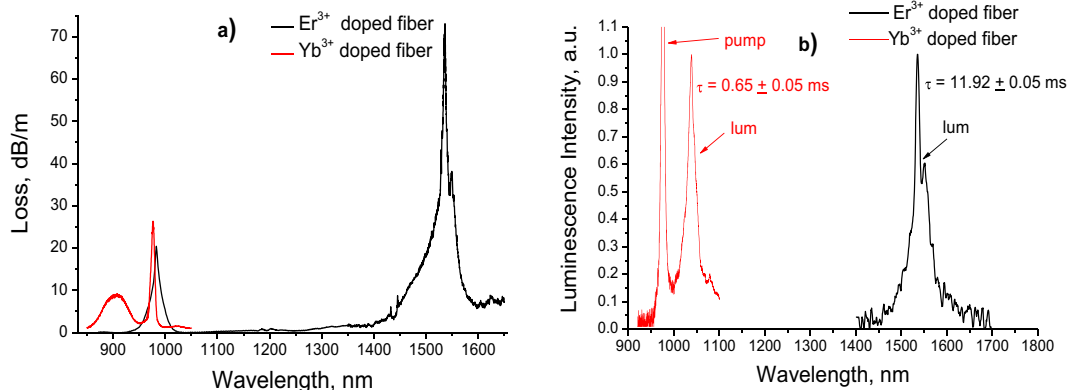
The H<sub>2</sub> molecules are observed to shorten the luminescence lifetime, and the kinetics decay curves no longer appear as single exponential curves. More accurate fitting was found to yield the stretched exponential (Kohlrausch) dependence [19]:

$$I(t) = I_0 * \exp\left(\left(-\frac{t}{\tau}\right)^\beta\right). \quad (2)$$

The origin of the stretched exponential dependence in our case will be discussed below. Here, two key settings are to be noted:  $\tau$ , which has the dimension of time, and  $\beta < 1$  – a dimensionless factor characterizing the deviation of the decay curve from a single exponential curve. The case  $\beta = 1$  clearly corresponds to the single exponential decay curve. For convenience, we shall name  $\tau$  the decay time constant.

Fig. 6 shows the dependences of  $\tau$  and  $\beta$  on the concentration of hydrogen molecules in the glass. The fibers loaded at different pressures exhibit no significant difference in the dependencies of the decay time constant on the concentration of hydrogen molecules in the fiber core (Fig. 6a). This result indicates that, under the pressures considered, the glass is still able to accumulate more hydrogen molecules and consequently is far from complete saturation.

Fig. 6b shows that the deviation of the single exponential decay induced by dissolved hydrogen is greater for the Er-doped fiber; the



**Fig. 2.** Absorption (a) and luminescence (b) spectra of the activated silica-core fibers under study.

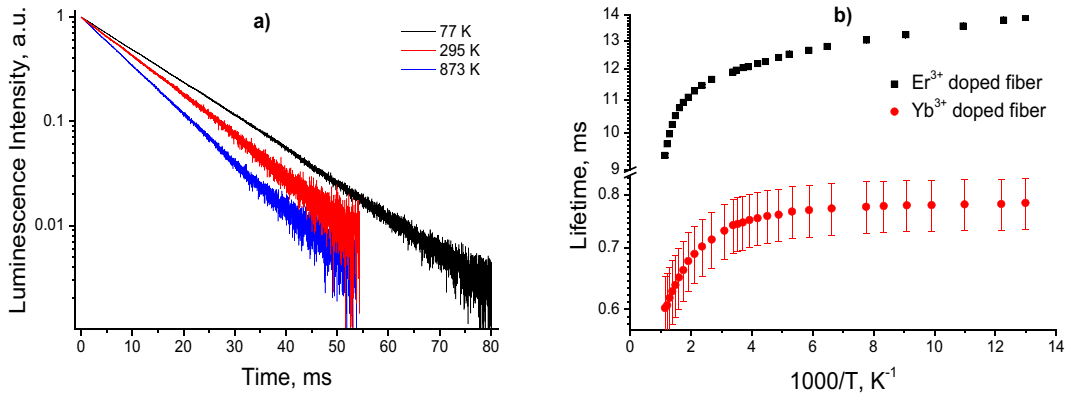


Fig. 3. Luminescence decay kinetics for Er<sup>3+</sup> ions (a) and dependencies of the lifetime on temperature (b) measured in the fibers prior to H<sub>2</sub>/D<sub>2</sub> loading.

relative decrease of the luminescence decay time constant caused by hydrogen penetration is greater for this fiber as well.

Fig. 7(a) and (b) shows the temperature dependences of the luminescence decay time constants in fibers saturated with hydrogen and with deuterium having Er and Yb doped core, respectively. Within the temperature range of 800 to 200 K, the dependences  $\tau(T)$  are of activation character. Similar dependences on temperature for the  $\beta$  factor are shown in Fig. 8.

According to Fig. 7, there is no considerable difference of the impact of hydrogen and deuterium molecules on the luminescence kinetics of Er<sup>3+</sup> ions. For Yb<sup>3+</sup> ions, this difference becomes significant at high temperatures. However, deviation from single exponential behavior in the luminescence decay for Er<sup>3+</sup> ions is greater. Note that in the case of Yb<sup>3+</sup> ions, the luminescence decay curves appear as single exponential decays at any temperature (Fig. 8). We attribute a small dip in the  $\beta(T)$  curve to a known ambiguity of the data approximation by the Kohlrausch function (the so called ill problem, see, e.g., ref. [20] for more details).

Note that saturation with monatomic helium under a pressure of 130 bar does not cause changes either in the spectrum or in the kinetics of the observed photoluminescence. To identify the contribution of randomly walking diatomic molecules in the process of non-radiative decay of the excited ions, it is more convenient to use the notion of a “rate of quenching” instead of a “decay time constant”:

$$\text{Rate} = \frac{1}{\tau} \quad (3)$$

According to the reasoning of ref. [8], the quenching rate can be expressed as:

$$\text{Rate} = \tau_{\text{rad}}^{-1} + k(T) * n_{\text{gas}}, \quad (4)$$

where  $n_{\text{gas}}$  – the concentration of diatomic molecules,  $k$  – probability of collisional deactivation per unit time per one molecule in a unit volume,  $\tau_{\text{rad}}$  – luminescence decay time constant in the absence of diatomic

molecules, and  $T$  – temperature. Whereas solubility variation does not allow the concentration of molecules dissolved in the fiber to remain invariable at temperatures greater than ~420 K, it is feasible to follow up the behavior of quenching rate normalized by the equilibrium concentration of the dissolved molecules in the glass gas at a given temperature:

$$k(T) = \frac{\text{Rate} - \tau_{\text{rad}}^{-1}}{n_{\text{gas}}} \quad (5)$$

The dependences  $k(T)$  for Er<sup>3+</sup> and Yb<sup>3+</sup> ions are calculated using the data depicted in Figs. 7 and 3. Fig. 9 summarizes the results.

#### 4. Discussion

Obviously, an additional channel for the deactivation of excited f-electron terms in Er<sup>3+</sup> and Yb<sup>3+</sup> ions located in silica impregnated by hydrogen and/or deuterium is the energy transfer to the vibrational degrees of freedom of diatomic molecules migrating over glass, with the consequent dissipation of the accumulated energy via vibrations of the glass network. Fig. 10 schematically shows the energy diagram of such a process.

In the figure, the horizontal arrows with legends denote the pump and luminescence light. The vertical arrows correspond to the energy transitions between the steady states of the active ions, with straight directed downward arrows corresponding to the relaxation with a photon emission and wavy arrows denoting non-radiative transitions or energy transfer from the excited ion to the acceptor (H<sub>2</sub> or D<sub>2</sub>). In the diagram, only the two lowest vibrational levels of the H<sub>2</sub> molecule with a gap of ~0.5 eV are indicated. Note, however, that the energy diagram of hydrogen and deuterium molecules in silica may turn more complicated because of interference of the molecular vibrational modes with those of the glass network [17].

In our experiments, both Er<sup>3+</sup> and Yb<sup>3+</sup> ions are excited by 1.27 eV photons. However, the energies of the luminescent photons are

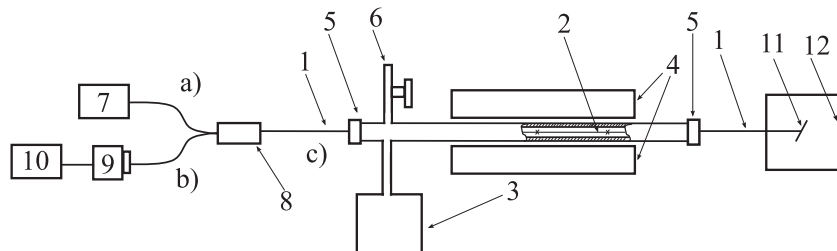
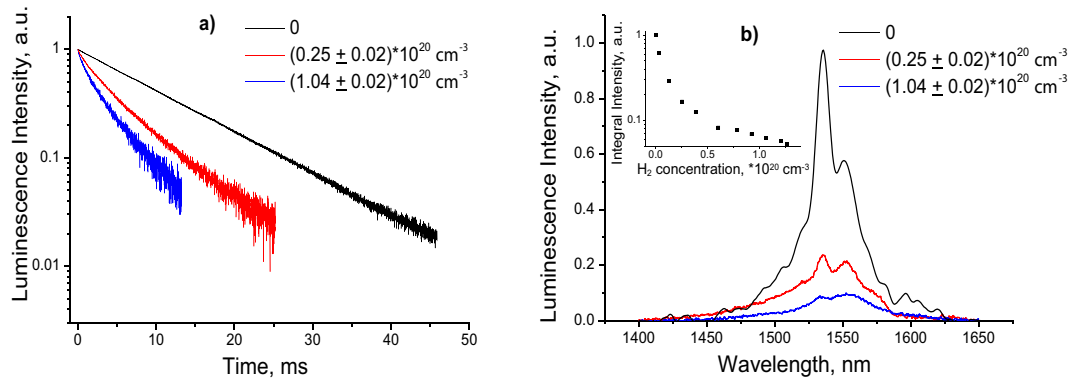


Fig. 4. Measurement scheme. 1 – delivery fiber, 2 – active fiber, 3 – buffer volume, 4 – heater, 5 – air tight seals, 6 – gas input/output valve, 7 – pump diode laser, 8 – directional coupler, 9 – photodiode with notch filter, 10 – oscilloscope, 11 – oblique cut, 12 – bath with index-matched liquid.



**Fig. 5.** Changes of the luminescence decay curves (a) and the spectra (b) when hydrogen molecules are entering the Er-doped silica fiber core. Inset – change of the luminescence integral intensity.

approximately 1.19 eV for  $\text{Yb}^{3+}$ , but only 0.81 eV for  $\text{Er}^{3+}$ . Therefore, an ytterbium ion is able to excite a hydrogen molecule on the second vibrational level while dissipating only a small portion ( $\sim 0.19$  eV) of the energy mismatch by oscillations of the glass network, while the similar process for an erbium ion would require accumulating approximately the same portion of energy. One could concede the transfer of an excitation energy of 1.27 eV to the  $\text{H}_2$  molecule directly from the upper  $^4\text{I}_{11/2}$  state, but this transfer is hardly probable due to the small ( $\sim 1$   $\mu\text{s}$ ) lifetime of  $\text{Er}^{3+}$  ion in this state. This lifetime is much shorter than the average time necessary for quenching of an excited ion by a hydrogen molecule ( $k^{-1}$  value in our terms, see relation (4)). Therefore, the most probable means to quench an excited erbium ion by a hydrogen molecule is deactivation of the metastable  $^4\text{I}_{13/2}$  level with the transfer of the 0.5 eV energy portion to the first excited vibrational level of the molecule. The energy mismatch for such energy transfer, which is to be dissipated by the glass network vibrations, amounts to 0.31 eV, which considerably exceeds the mismatch in the case of ytterbium. Consequently, luminescence quenching by hydrogen molecules is more probable for ytterbium ions, as reflected in our observations presented in Fig. 9.

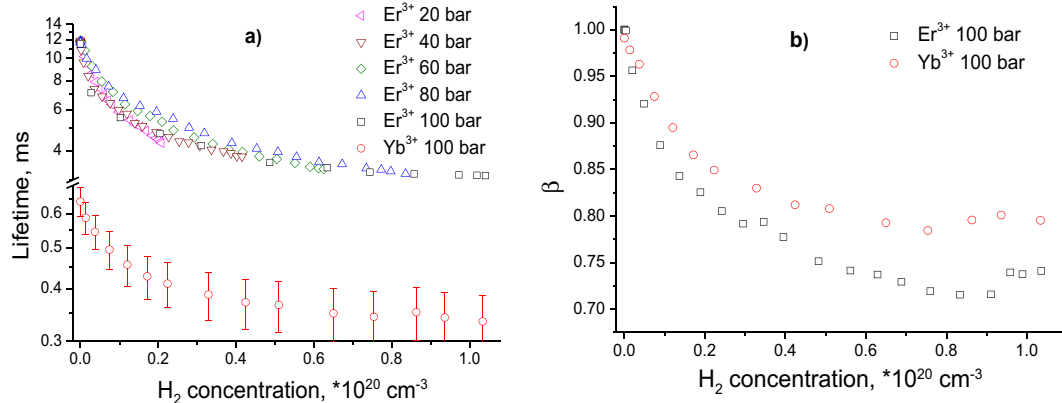
For deuterium molecules, the situation is different (Fig. 10b). The first excited vibrational level of a  $\text{D}_2$  molecule amounts to 0.72 eV. For this reason, deactivation of either the  $^2\text{F}_{5/2}$  term of  $\text{Yb}^{3+}$  or  $^4\text{I}_{13/2}$  term of  $\text{Er}^{3+}$  with the energy transfer to the fundamental vibration modes of a deuterium molecule is allowed in the context of the conservation energy law. The energy mismatch for this process is approximately 0.47 eV for  $\text{Yb}^{3+}$  and only 0.09 eV for  $\text{Er}^{3+}$ . As a result, luminescence quenching of erbium ions by deuterium molecules is more effective compared to the quenching of ytterbium ions, as is clearly shown in

Fig. 9. This result also explains why hydrogen is a more effective quencher for  $\text{Yb}^{3+}$  luminescence and deuterium for  $\text{Er}^{3+}$  luminescence.

Visually, the temperature dependences of the  $\text{Er}^{3+}$  luminescence quenching rates for hydrogen and deuterium appear similar in shape, regardless of the fact that mismatch in the energy transfer to deuterium is significantly smaller than the one to hydrogen (0.09 eV against 0.31 eV). To explain this feature, note that the dependences on temperature of the quenching rate in the high temperature region are of an activation nature. At temperatures greater than  $\sim 200$  K, one can approximate these curves by Arrhenius formula (1). Determined activation energies are as high as 0.25 eV for the system  $\text{Er}^{3+}-\text{H}_2$  and 0.16 eV for  $\text{Er}^{3+}-\text{D}_2$ . Hence, we see that deuterium quenches erbium luminescence more effectively than hydrogen, in agreement with the diagram of Fig. 10.

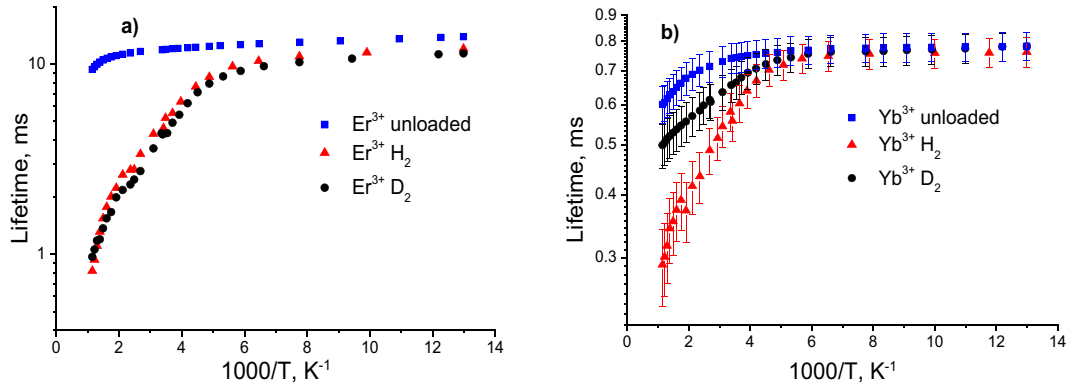
In the case of ytterbium luminescence quenching, the activation energies amount to 0.15 eV for hydrogen and 0.08 eV for deuterium, which are different than the diagram of Fig. 10. We attribute this difference to the fact that hydrogen more effectively deactivates luminescence of the excited centers due to its greater mobility. First, the diffusion coefficient of hydrogen molecules in silica slightly exceeds that of deuterium. Hence, during the lifetime of an excited ion, a hydrogen molecule is able to walk at a larger distance than a deuterium molecule; consequently, a hydrogen molecule has more chances to encounter an activated center. Moreover, thermally excited at a finite temperature, the rotational degrees of freedom of  $\text{H}_2$  and  $\text{D}_2$  molecules appear to play an important role in the collisional interaction mechanism between an interstitial molecule and an excited center.

From Fig. 7, the interstitial hydrogen molecules dissolved in silica start to noticeably influence the luminescence kinetics at temperatures



**Fig. 6.** Luminescence lifetime (a) and deviation of the decay curves from a single exponential curve (b) as functions of the hydrogen content in the fiber core. The Yb-doped fibers are saturated at a pressure of 100 bar, while the Er-doped fibers are saturated at five different pressures from 20 to 100 bar.

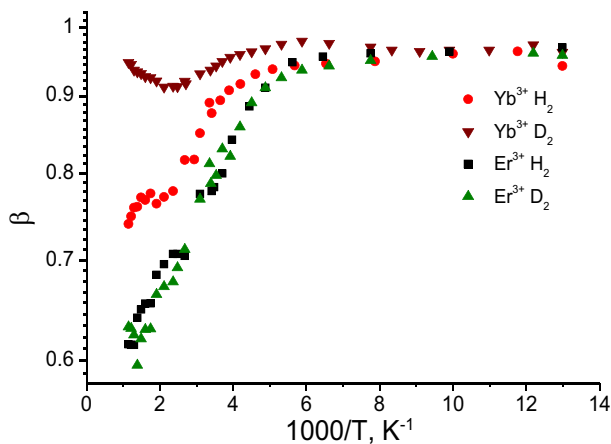




**Fig. 7.** Luminescence decay time constant as the function of temperature for H<sub>2</sub> and D<sub>2</sub> loaded Er (a) and Yb (b) doped fibers. Data for the unloaded fibers extracted from Fig. 3(b) are shown for comparison.

greater than 80–120 K, which coincide with the excitation temperature of the rotational degrees of freedom of free H<sub>2</sub> molecule. This result allows one to conclude that the interaction between an excited active center and a hydrogen molecule becomes possible only in the case when the molecule starts to exhibit non-zero rotations. Also supporting this hypothesis is the fact that the energy of rotation quantum for H<sub>2</sub> molecules is ~0.07 eV, which is close to the experimentally determined activation energies of luminescence quenching for hydrogen and deuterium. Whereas an atom of deuterium is heavier than the one of hydrogen, the energy and the “rotational” frequency of collisions with a nearest ion for the D<sub>2</sub> molecule is smaller than that for the H<sub>2</sub> molecule. This difference could be the reason why deuterium is a weaker quencher of luminescence compared to hydrogen.

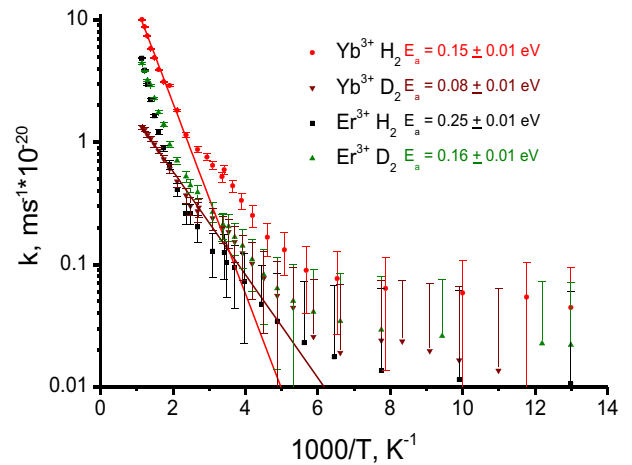
Let us consider the possible sources of deviation of luminescence decay kinetics from the single exponential law. In our experiments, these sources are obviously associated with the Brownian motion of interstitial H<sub>2</sub> and D<sub>2</sub> molecules inside the glass network. The general concepts for relaxation processes described by the stretched exponential behavior can be found in ref. [21]. As a rule, such a form of the decay curve arises in the case when the relaxation process is accompanied by a migration of excitation through a non-uniformly relaxing medium. In our case, the concentration of active ions is small, so there is practically no migration of excitations between separated active ions, which is testified by the exponential luminescence decay observed in the pristine active fiber samples. Consequently, the appearance of the luminescence decay in the form of Kohlrausch curves is foremost associated with diffusion-limited deactivation of excitations by migrating H<sub>2</sub> and D<sub>2</sub> molecules.



**Fig. 8.** Temperature dependence of  $\beta$  (deviation from the single exponent decay) in H<sub>2</sub> and D<sub>2</sub> loaded fibers.

The kinetics of the diffusion-limited reactions are usually considered using the “black sphere” concept [11]. In our case, the “black sphere” is the space in the vicinity of an active ion; hydrogen or deuterium molecules entering the “black sphere” are able to quench the excitation. Obviously, there are active ions having H<sub>2</sub> or D<sub>2</sub> molecules already present inside their “black spheres”, which can enter into the energy transfer reaction and thus be deactivated from their excited states. It is also clear that the excitation deactivation rate at that time reaches its maximum. Only in the subsequent course of time can farther H<sub>2</sub> or D<sub>2</sub> molecules, which must cover increasing distances to the nearest “black sphere” in the vicinity of an excited ion, quench the luminescence, which slows down the deactivation rate. This process corresponds to a non-Markovian process, for which the luminescence quenching rate at each time becomes dependent on the process prehistory. As a consequence, luminescence decay is no longer exponential.

According to Fig. 6b, deviation from the single exponential decay increases with the increase of the content of hydrogen molecules in the core of the fiber for both activators. In this case, in the Er-doped fiber, the  $\beta$  factor decreases from 1 to 0.7, and in the Yb-doped fiber,  $\beta$  changes from 1 to ~0.8. This difference between the activators is associated primarily with a tenfold greater luminescence lifetime in silica for Er<sup>3+</sup> compared to Yb<sup>3+</sup>. Considering the diameters of the “black spheres” for Er<sup>3+</sup> and Yb<sup>3+</sup> ions being equal, one should conclude that the probability for H<sub>2</sub> and/or D<sub>2</sub> to encounter an excited long living erbium ion is greater, due to a longer distance that the dimer molecule



**Fig. 9.** Temperature dependences of the contribution of hydrogen and deuterium molecules to the luminescence quenching rate. The symbols correspond to experimental data; the lines reflect the Arrhenius approximation with an activation energy corresponding to a process.

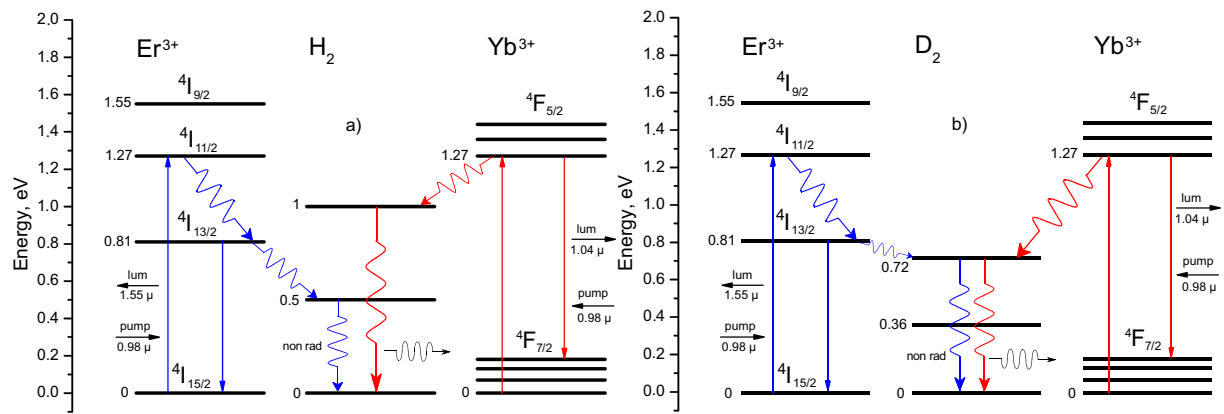


Fig. 10. Energy diagrams for Er<sup>3+</sup> and Yb<sup>3+</sup> f-electron terms in silica with imposed vibration levels of molecular hydrogen (a) and deuterium (b).

can cover in the course of random walk during the ion excitation lifetime.

Note that, caused by the Brownian motion, the non-exponential character of the luminescence decay curves arises at temperatures greater than 80–120 K, that is, when thermal motion starts to excite the rotational degrees of freedom of H<sub>2</sub> and D<sub>2</sub> molecules. Such a coincidence means that molecules with excited rotational degrees of freedom most likely accept energy upon coming into contact with the excited donor. This process is simply explained by the rotational component of molecular motion inside an interstitial void near an active ion. This rotational component determines the collision frequency and hence the probability of transferring energy from the excited electrons to molecular vibrations. This feature distinguishes the quenching mechanism under consideration from that associated with OH-groups bounded to the glass network, the latter being governed by electron-phonon coupling within the silica network.

## 5. Conclusion

Silica optical fiber with an activated core is a convenient object to study collisional luminescence quenching of active centers in silica via Brownian motion of H<sub>2</sub> and D<sub>2</sub> molecules dissolved in glass. The presence of Brownian motion in the glass was found to considerably affect the luminescence decay and cause the relaxation process to become non-single-exponential in nature, obeying the stretched exponential (Kohlrausch) law.

The phenomenon revealed may be explained by the appearance of an additional nonradiative relaxation channel for the excited rare earth ions incorporated in the glass network. The channel consists of the excitation of vibrational degrees of freedom of the diatomic molecules, followed by the subsequent transfer of the excitation to oscillations of the glass network. The effectiveness of the quenching depends on how similar the energies of electron excitations of the active centers are to the gap between vibration energy levels of the interstitial diatomic molecules.

The rate of quenching was found to depend on temperature and becomes nonzero at temperatures greater than ~100 K, which corresponds to the thermal excitation of the rotational degrees of freedom of H<sub>2</sub> and D<sub>2</sub> molecules. A rather small activation energy (considerably smaller compared to the interstitial molecules diffusion) highlights the fact that participating in the process are those dimers that at a given moment occupy interstitials in the glass network in proximity to the active centers.

The phenomenon described above would negatively affect the amplification characteristics of an active fiber. However, if the fiber operates in an ionizing radiation environment, hydrogen loading

significantly decreases the radiation-induced loss. The latter effect completely compensates the effect of luminescence quenching.

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