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Raman lidar system for the hydrogen molecules remote sensing in atmosphere

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Computer simulation of the Raman lidar equation for measurement of the hydrogen molecules at the concentration level of $10^{13}\,\text{cm}^{-3}$ and higher in atmosphere at the ranging distances up to 100 m in the synchronous photon counting mode and selection of such a lidar optimal parameters have been fulfilled. It is shown that for hydrogen molecules concentration of $N(z) = 10^{13}\,\text{cm}^{-3}$ measurement at the distances from 5 to 100 m the measurement time t is in the range from 3.83 s to 26.5 min, for measurement of concentration $N(z) = 10^{15}\,\text{cm}^{-3}$ — from 38 ms to 15.9 s and for the concentration measurement of $N(z) = 10^{17}\,\text{cm}^{-3}$ — already from 0.4 ms to 160 ms, respectively.

Keywords: Raman lidar, hydrogen molecule, concentration, ranging distance, laser radiation wavelength.

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Introduction

The great prospects of using hydrogen as a new type of clean fuel [1] require systems to control its leakage from cylinders and pipelines, especially at pumping points. In the real atmosphere, the mole fraction of H_2 molecules is $5 \cdot 10^{-7}$ [2] or about 0.5 ppm, corresponding to a countable concentration of $1.345 \cdot 10^{13}\,\text{cm}^{-3}$. However, remote monitoring and measurement of concentrations at such levels is a great challenge [3].

Design of new laser systems and methods for measuring hydrogen molecule concentrations at the level of concentrations at around $10^{13}\,\text{cm}^{-3}$ and higher in the atmosphere based on a Raman light scattering lidar requires selection of an optical circuit and optimal selection of parameters of individual elements of such a lidar. Earlier in paper [4], as a result of analysis of methods of laser sensing of hydrogen molecules in the atmosphere, it was found that a Raman light scattering lidar can be used for remote measurement of the concentration of molecules at such a level at distances up to hundreds of meters. The paper [5] proposed a lidar equation for Raman light scattering by gas molecules in the atmosphere, taking into account the finite width of the generation line. It turned out that taking into account the finite width of the generation line of a real laser, the ratio of the widths of the Raman light scattering bands and the lidar hardware function allow us to clarify the solution of such a lidar equation [5].

The objectives of this paper are to evaluate the possibility of measurements of hydrogen molecule concentrations by a Raman light scattering lidar at $10^{13}\,\text{cm}^{-3}$ and higher in the atmosphere at sensing distances up to 100 m in synchronous photon counting mode and the choice of optimal lidar parameters.

Raman light scattering lidar

Optical circuit of the proposed version of Raman light scattering lidar is biaxial, as in [2,3]; it is given in Fig. 1.

Sensing radiation is radiation of the third and second harmonics of YAG–Nd-laser (with pumping by semiconductor laser with wave lengths 355 and 532 nm) and semiconductor laser with wave length 405 nm, with pulse duration 10 ns and energy in the pulse up to 1 mJ at successive frequency of laser pulses f up to 100 kHz [2,3]. Laser radiation it1 was directed parallel to the axis of the receiving telescope at a distance of 150 mm, as in [2], and the radiation of Raman scattering by hydrogen molecules in the atmosphere in the backward direction was collected by a Newton type receiving telescope with a spherical mirror *9* of 200 mm diameter, and focused by a lens lens *8* into a fiber light guide *6* and directed through an interference light filter *7* to the photoelectric detector *8*. The output of the photoelectric detector is connected to the input of the synchronous detector, the signal U_1 from which is fed to the input of the analog-to-digital converter and then the microcontroller.

Part of the laser radiation was directed by a glass plate *5* and a totally reflecting mirror *4* through an interference light filter *3* to the photoelectric detector *2*, the voltage U_0 from which was recorded by the data acquisition board in the PC to control the laser pulse energy and form the beginning of measurement time counting.

Wave lengths and frequencies of laser radiation and bands of Raman light scattering by hydrogen molecules, differential cross section of vibrational Raman scattering (VRS) for such bands, coefficients of attenuation in the atmosphere at these wave lengths and relative spectral sensitivity of a photoelectric detector

Wave length, λ, nm	Frequency, ν, GHz	Differential cross section VRS $(d\sigma/d\Omega)$, 10^{30} cm^2	Coefficient of attenuation $\alpha(\nu_0, r)$, km^{-1}	Coefficient of attenuation $\alpha(\nu_R, r)$, km^{-1}	Relative spectral sensitivity of photoelectric detector $\xi(\nu)$
355	845.1	21.7	0.31		
389.3	809.5			0.28	0.52
532	563.9	4.3 ± 0.9 — 21%	0.17		
683.2	439.1			0.14	0.86.25 photomultiplier
405	740.7	12.8	0.24		
487.1	615.9			0.19	0.89

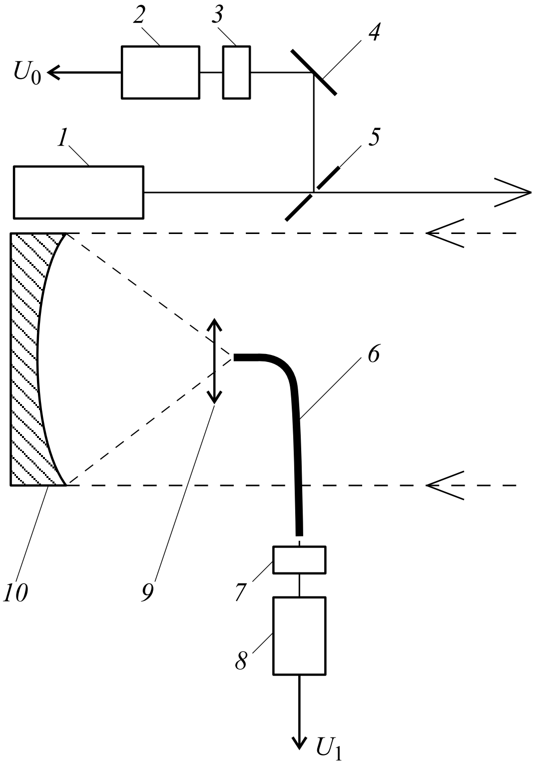

Figure 1. Optical circuit of Raman light scattering lidar: *1* — laser, *2, 8* — photoelectric detectors, *3, 7* — interference light filters, *4* — totally reflecting mirror, *5* — glass plate, *6* — fiber light guide, *9* — lens objective, *10* — spherical mirror of receiving telescope.

Lidar equation for Raman light scattering

We will characterize the lidar laser by number of photons n_0 in the pulse of laser radiation sent to atmosphere with duration of τ_0, and we will consider the laser generation line as Gaussian with maximum at frequency of ν_0 and half-width Γ_0. Then the number of photons $n(\nu, z)$ of Raman light scattering radiation by studied hydrogen molecules with concentration $N(z)$ on the lidar photoelectric detector may be produced from a lidar equation in the backward direction in photon counting mode in the form of an integral in the interval from $(\nu_0 - \Gamma_0)$ to $(\nu_R - \Gamma_R)$ [5]:

$$n(\nu, z) = n_0 c \tau_1 G(z) f t S_0 N(z) (d\sigma/d\Omega) \int\limits_{\nu_0-\Gamma_0}^{\nu_R+\Gamma_R} T_0(\nu_0, z)$$

$$\times T(\nu_R, z) \Phi(\nu) A(\nu) d\nu / 2z^2, \tag{1}$$

where $n(\nu, z)$ — number of photons recorded by a photoelectric detector of the lidar at frequency ν_R of Raman light scattering from sensing distance z, n_0 — number of photons at frequency ν_0 of laser radiation. Besides, S_0 — area of receiving aperture of the telescope, $G(z)$ — geometric factor of lidar [2,3]. This factor is determined by parameters of lidar?s optical circuit [2,3] and is within the limits of $0 < G(z) < 1$. Further, $N(z)$ — concentration of studied molecules, t — time of signal measurement or accumulation, $(d\sigma/d\Omega)$ — differential cross section of Raman light scattering by studied molecules. Two other multipliers — atmospheric transmission (as in [2,3]) — are accordingly equal to

$$T_0(\nu_0, z) = \exp\left[-\int\limits_0^z \alpha(\nu_0, r) dr\right],$$

$$T(\nu_R, z) = \exp\left[-\int\limits_0^z \alpha(\nu_R, r) dr\right],$$

where $\alpha(\nu_0, r)$ and $\alpha(\nu_R, r)$ — coefficients of attenuation at frequencies of laser radiation and Raman light scattering by hydrogen molecules

$$n(\nu, z) = n_0 \frac{c\tau_0}{2z^2} G(z) f t S_0 N(z) \frac{d\sigma}{d\Omega}$$
$$\times \int\limits_{\nu_0-\Gamma_0}^{\nu_R+\Gamma_R} \exp\left[-\int\limits_0^z \{\alpha(\nu_0, r) + \alpha(\nu_R, r)\}dr\right] \Phi(\nu')A(\nu')d\nu', \tag{2}$$

where $\Phi(\nu)$ — function of distribution of laser radiation photons in the generation line [6]; in our case it is Gaussian and may be recorded as

$$\Phi(\nu) = \frac{1}{\sqrt{2\pi}\Gamma_0} \exp\left[-\frac{(\nu - \nu_0)^2}{2\Gamma_0^2}\right]. \tag{3}$$

Besides, we will consider that hardware function (or spectral transmission ratio of lidar receiving system$A(\nu)$ [2,3,5]) has Lorentzian form and is tuned precisely for frequency ν_R of Raman light scattering band by hydrogen molecules with half-width Γ_a, which is more than Γ_R and Γ_0,

$$A(\nu) = \frac{K_1\xi(\nu_R)}{\pi} \frac{\Gamma_a}{(\nu - \nu_R)^2 + \Gamma_a^2}, \tag{4}$$

where K_1 — lidar constant on frequency ν_0 of laser radiation, measured experimentally in [3], and $\xi(\nu_R)$ — relative spectral sensitivity of the photoelectric detector at frequency ν_R of Raman light scattering radiation. Let us assume that $\Phi(\nu) = 1$, when generation line half-width is much lower than half-width of lidar hardware function [5]. Let us rewrite equation (2) in the form of

$$n(\nu, z) = \frac{B}{z^2} N(z) t I(\nu, z), \tag{5}$$

this formula includes constant B,

$$B = \frac{c\tau_1}{2} S_0 f, \tag{6}$$

and function $I(\nu, z)$,

$$I(\nu, z) = n_0 G(z) \frac{d\sigma}{d\Omega}$$
$$\times \int\limits_{\nu_0-\Gamma_0}^{\nu_R+\Gamma_R} \exp\left[-\int\limits_0^z \{\alpha(\nu_0, r) + \alpha(\nu_R, r)\}dr\right] A(\nu')d\nu'. \tag{7}$$

Further, assuming coefficients of attenuation on frequencies of laser radiation and Raman light scattering by hydrogen molecules $\alpha(\nu_0, r)$ and $\alpha(\nu_R, r)$ as hardly dependent on frequency, let us rewrite function (7) in the form of

$$I(\nu, z) = n_0 G(z) \frac{d\sigma}{d\Omega} \exp\left[-\int\limits_0^z \{\alpha(\nu_0, r) + \alpha(\nu_R, r)\}dr\right]$$
$$\times \int\limits_{\nu_0-\Gamma_0}^{\nu_R+\Gamma_R} A(\nu')d\nu', \tag{8}$$

where the last integral

$$\int\limits_{\nu_0-\Gamma_0}^{\nu_R+\Gamma_R} A(\nu')d\nu' = \frac{K_1\xi(\nu_R)\Gamma_a}{\pi} \int\limits_{\nu_0-\Gamma_0}^{\nu_R+\Gamma_R} \frac{d\nu'}{(\nu' - \nu_R)^2 + \Gamma_a^2}$$
$$= \frac{K_1\xi(\nu_R)\Gamma_a}{\pi} \frac{\pi}{2\Gamma_a} = \frac{K_1\xi(\nu_R)}{2}. \tag{9}$$

Then the formula (8) takes the form of

$$I(\nu, z) = n_0 G(z) \frac{d\sigma}{d\Omega} \frac{K_1\xi(\nu_R)}{2}$$
$$\times \exp\left[-\int\limits_0^z \{\alpha(\nu_0, r) + \alpha(\nu_R, r)\}dr\right]. \tag{10}$$

We also assume that the differential cross section of Raman light scattering can be assumed constant within the frequency integration interval, as are the attenuation coefficients at the frequencies of the laser and Raman light scattering by hydrogen molecules [7]. Let us express from equation (2) the measurement time t as a measure of the lidar system efficiency and consider the spectral and concentration dependencies of this equation solution:

$$t = \frac{n(\nu, z)z^2}{BI(\nu, z)N(z)}. \tag{11}$$

Next, we will consider single Raman light scattering and a homogeneous atmosphere [2,3,7]. The maximum values of the band of valent H−H-vibrations of hydrogen molecules are $4161\,\mathrm{cm}^{-1}$ according to [2–4,8], and the wavelengths of bands of vibrational Raman scattering by hydrogen molecules were calculated for all wavelengths of laser radiation; they are listed in the table.

Values of differential cross sections of Raman light scattering $(d\sigma/d\Omega)$ for all molecules and selected wavelengths of laser radiation (355, 532 and 405 nm) were determined according to data experimentally measured in [2,8] at room temperature and normal pressure at wave length of radiation 532 nm, $(d\sigma/d\Omega) = (4.3 \pm 0.9) \cdot 10^{-30}\,\mathrm{cm}^2/\mathrm{sr}$, and for the wave lengths of interest for us are calculated with account of dependence $1/\lambda^4$ [3]. All these values are given in the table. Values of attenuation coefficients for these frequencies $\alpha(\nu_0, z)$ and $\alpha(\nu, z)$ from [9] are also collected in the table. Cross section of lidar receiving telescope mirror was $0.031\,\mathrm{m}^2$, and pitch along distance — 7.5 m for the time of single measurement 50 ns.

Solution of lidar equation and discussion of results

Let us solve numerically equation (11), assuming that $G(z)$ in our case is equal to 1 and concentration of hydrogen molecules $N(z)$ is in the range of $10^{13}-10^{17}\,\mathrm{cm}^{-3}$. For our experimental situation for the time of measurement t, 200 photons [6] could be registered.

For this case let us solve equation (11) for three values of wave lengths of laser radiation (355, 532 and 650 nm) at successive frequency of laser pulses 100 kHz, energy in the pulse 1 mJ in the range of sensing distances from 5 to 100 m. Results of equation (11) solution for this case are presented in Fig. 2 in the form of dependence between measurement time t and sensing distance z.

Curves of Fig. 2 show increase of measurement time t in a row of wave lengths of laser radiation 405–532 — 355 nm at the account of spectral dependence of values in equation (11), at the same time the measurement time drastically increases for the first 20 m approximately by an order.

Let us consider numerical solution of equation (11) for the range of concentration of hydrogen molecules $N(z)$ from 10^{13} to $10^{17}\,\text{cm}^{-3}$. For this purpose let us solve equation (11) for wave length of laser radiation 405 nm as the best version according to data of Fig. 2. Results of equation (11) solution are presented in Fig. 3. Measurement time t for our experimental situation diminishes inversely to concentration of hydrogen molecules $N(z)$, as it follows from equation (11), and increases approximately by two orders with increased sensing distance z from 5 to 100 m.

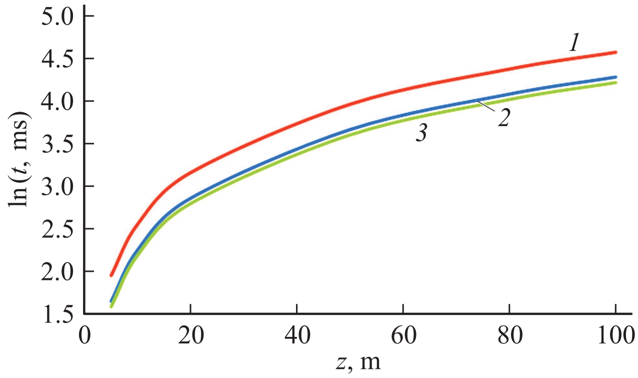

Figure 2. Curves of dependence calculated according to equation (11) between time of measurement t for hydrogen molecules with concentration $N(z) = 10^{15}\,\text{cm}^{-3}$ (in logarithmic scale, in ms) and distance of sensing z (in m) for wave lengths of laser radiation 355 (*1*), 532 (*2*) and 405 nm (*3*) when atmosphere is sensed by the Raman light scattering lidar.

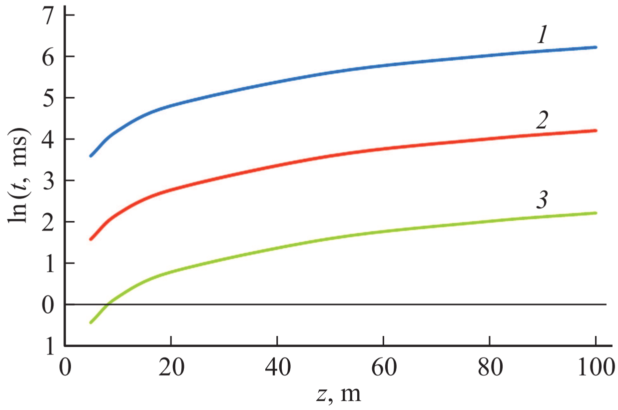

Figure 3. Curves of dependence calculated by equation (11) between measurement time t (in logarithmic scale, t in ms) for hydrogen molecules at their concentrations $N(z)$ 10^{13} (*1*), 10^{15} (*2*) and $10^{17}\,\text{cm}^{-3}$ (*3*) from sensing distance z (in m) for wave length of laser radiation 405 nm for the same experimental situation.

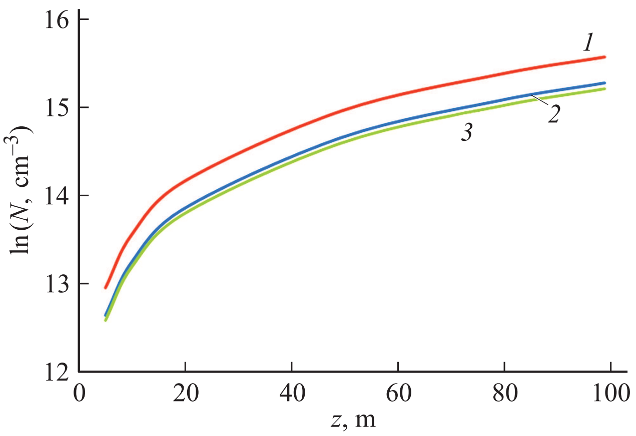

Figure 4. Curves of dependence calculated by equation (12) between hydrogen molecules concentration $N(z)$ (in logarithmic scale, in cm^{-3}) and sensing distance z (in m) for the same measurement time $t = 10$ s for wave lengths of laser radiation 355 (*1*), 532 (*2*) and 405 nm (*3*) for the same experimental situation.

The dependence of hydrogen molecule concentration $N(z)$ on the sensing distance z for the same measurement time $t = 10$ s for all wave lengths of laser radiation may be represented more visually by expressing value $N(z)$ from equation (11):

$$N(z) = \frac{n(\nu, z)z^2}{BI(\nu, z)t}. \tag{12}$$

Then let us perform numerical solving of equation (12) for hydrogen molecule concentrations $N(z)$ from 10^{13} to $10^{17}\,\text{cm}^{-3}$, measurement time 10 s and all wave lengths of laser radiation. Results of equation (12) solution are presented in Fig. 4.

Curves in Fig. 4 show that for sensing distances up to 100 m and measurement time 10 s the range of concentration variation makes around three orders from 10^{13} to $10^{17}\,\text{cm}^{-3}$ for the entire range of sensing distances z to 100 m.

As it follows from the produced results, for measurement of concentration of hydrogen molecules $N(z) = 10^{13}\,\text{cm}^{-3}$ in the sensing range from 5 to 100 m the measurement time t is in the range from 3.83 s to 26.5 min, for measurement of concentration $N(z) = 10^{15}\,\text{cm}^{-3}$ — from 38 ms to 15.9 s and for measurement of concentration $N(z) = 10^{17}\,\text{cm}^{-3}$ — from 0.4 μs to 160 μs.

This means that depending on the expected real concentration at a given probing distance, it will be possible to choose the parameters of the laser, telescope, and photoelectric detector by measurement time to create the required lidar system of Raman light scattering by hydrogen molecules. Such a choice is determined by the spectral dependence of the differential cross sections of the band of vibrational Raman scattering by hydrogen molecules, atmospheric attenuation coefficients at these wavelengths and the relative spectral sensitivity of the photoelectric detector.

Everywhere in the calculations, the laser pulse successive frequency was 100 kHz and the time per measurement was 50 ns or pitch by distance $\Delta z = 7.5$ m. It is obvious that a further decrease in the concentration of the molecules under study is possible by increasing the successive frequency of the laser pulses f or by increasing their energy E_0.

Conclusion

Thus, the results obtained allow us to choose the optimal parameters of the laser and Raman light scattering lidar for sensing of hydrogen molecules in the atmosphere at sensing distances up to 100 m. And they are in good agreement with the results of our previous papers [4]. To sense hydrogen molecules with concentrations $N(z)$ from 10^{13} to $10^{17}\,\mathrm{cm}^{-3}$ in the sensing range from 5 to 100 m, measurement time from 400 ns to 26.5 min is sufficient, which can be realized in one Raman light scattering lidar under specific experimental conditions [3,4]. Therefore, by selecting the measurement time at the expense of the parameters of the same lidar variant, it is possible to increase the sensing distance of the required concentrations of hydrogen molecules in the atmosphere.

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Conflict of interest

The authors declare that they have no conflict of interest.

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