Lidar measurements of hydrogen fluoride concentration in atmospheric boundary layer

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Abstract. The possibility of measuring the concentration of hydrogen fluoride molecules in the range from $10^{14}$ to $10^{16}$ cm$^{-3}$ in the atmospheric boundary layer at probing distances up to 1.5 km is estimated, taking into account the spectral width of the instrumental function of the Raman scattering lidar. Computer simulation of the lidar equation for our experiment and the measurement time $t_d=100$ s made it possible to obtain computational solution of this equation for three values of the laser radiation wavelength, i.e. 405, 532, and 650 nm. It was concluded that the minimum concentration of hydrogen fluoride molecules $1.88 \times 10^{13}$ cm$^{-3}$ can be recorded at a wavelength of 405 nm and a distance of up to 100 m at a laser pulse repetition rate of 1 MHz and at a distance of up to 1500 m - $7.64 \times 10^{15}$ cm$^{-3}$. The concentration level of HF molecules equal to $1.5 \times 10^{14}$ cm$^{-3}$ at a laser radiation wavelength of 405 nm can be measured at a distance of up to 650 m, at a wavelength of 532 nm - up to 350 m and 650 nm - only up to 200 m during measurement time of 100 s.

1. Introduction

Exhaust gas emissions from ship power plants lead to pollution of the atmospheric boundary layer over the sea area. The use of lidar technologies [1] makes it possible to monitor this pollution and control the operation of both ship power plants and the port’s coastal infrastructure. Let us evaluate the possibilities of lidar systems for solving such problem using the example of hydrogen fluoride molecules, which have high toxicity and a low level of maximum allowable concentration (MAC) of the order of 0.02 mg/m$^3$ or about $1.5 \times 10^{14}$ cm$^{-3}$. The development of new remote sensing methods for measuring the HF molecule concentration in the atmospheric boundary layer at probing distances of up to 1.5 km requires the potential capabilities assessment of Raman scattering lidar for solving this problem.

A theoretical analysis of the methods of laser remote sensing of hydrogen fluoride molecules in the atmosphere was carried out in [2-4] and it was found that such lidar can be used for remote measurement of molecule concentration at a level from $10^{14}$ to $10^{16}$ cm$^{-3}$. A lidar equation for Raman scattering by gaseous molecules in the atmosphere with the allowance for the finite linewidth of the
laser was proposed in [4]. These studies showed that taking into account the finite linewidth of a real laser, the half-width of the Raman scattering band, and the instrumental function of the lidar makes it possible to obtain a solution of the lidar equation [4] for the case of a low concentration of the molecules under study.

Therefore, the purpose of this work is to estimate the concentrations of hydrogen fluoride molecules measured by such a lidar in the atmospheric boundary layer in the altitude range up to 1.5 km in the mode of synchronous photon counting and to select the optimal parameters of the lidar.

2. Raman scattering lidar

The optical diagram of a lidar similar to one presented in [3, 4] is shown in Fig. 1.

![Optical diagram of the Raman scattering lidar](image)

The second harmonic of the radiation of a YAG: Nd laser at a wavelength of 532 nm pumped by a semiconductor laser and diode lasers at the wavelengths of 405 and 650 nm with a laser pulse duration of 10 ns and a pulse energy of up to 10 μJ with a laser pulse repetition frequency f up to 1 MHz is used as a probe laser radiation [5]. Laser radiation 7 was directed along the axis of the receiving telescope, as in [4], and the Raman scattering by hydrogen fluoride molecules in the atmospheric boundary layer in the backward direction was collected by a Newton-type receiving telescope with a spherical mirror 1 with a diameter of 400 mm and focused by lens 9 onto the input 2 of the fiber input micro spectrometer 8 type FSD-8 operating under PC control. Part of the laser radiation was directed by a glass plate 4 through an interference light filter 5 to an optical receiver 6 the pulse U₀ of which was recorded by a data acquisition module on the PC to control the laser pulse energy and set the beginning of time measurement.

3. Lidar Equation for Raman Scattering

There will be described the lidar laser by the number of photons n₀ in a laser pulse sent into the atmosphere of duration t₀ and the laser generation line as a Gaussian function with a maximum at the frequency ν₀ and the line half-width Γ₀. Then the number of photons n(ν, z) of Raman scattering by the investigated hydrogen fluoride molecules with the concentration N(z) on the photodetector of the lidar can be calculated using the lidar equation for Raman scattering in the backward direction in the photon counting mode as in [3, 4] in the form of an integral in the range from (ν₀ - Γ₀) to (ν_R - Γ_R) [5]:

\[
n(ν, z) = n₀ \cdot c \cdot τ_0 \cdot G(z) \cdot ft₀ \cdot S₀ \cdot N(z) \cdot (dσ/dΩ) \int_{ν₀-Γ₀}^{ν_R+Γ_R} T₀(ν₀, z) \cdot T(ν_R, z) \cdot Φ(ν)A(ν)dv / 2z^2
\]

(1)
where \( n(v,z) \) is the number of photons recorded by the lidar photodetector at the Raman scattering frequency \( v_R \) from the probing distance \( z \); \( n_o \) is the number of photons at the laser radiation frequency \( v_0 \) determined by the expression: \( n_o = E_0 / h v_0 \), where \( E_0 \) is the energy of a laser pulse with the duration \( t_o \) different from \( t_i \), i.e. the duration of one measurement or the sync pulse duration and \( h \), i.e. the Planck’s constant. In addition, \( S_0 \) is denoted by the aperture of the cross section of the receiving telescope, and \( G(z) \) is the geometric function of the lidar [4, 5]. This function is completely determined by the parameters of the lidar optical system and quantitatively characterizes the degree of vignetting of the scattered radiation flux in the backward direction entering the optical receiver from the measuring volume of the atmosphere from a distance \( z \) [5] and is in the range of \( 0 < G(z) < 1 \). \( N(z) \) is the concentration of the studied molecules; \( t_i \) is the time of measurement or accumulation of signal and \( (d\sigma/d\Omega) \) is the differential cross section of the Raman scattering of the molecules under study: two factors, i.e. the transmission of the atmosphere - are equal, respectively [6, 7]:

\[
T_0(v_0, z) = \exp[-\int_0^z \alpha(v_0, r) dr] \quad \text{and} \quad T(v_R, z) = \exp[-\int_0^z \alpha(v_R, r) dr],
\]

where \( \alpha(v_0, r) \) and \( \alpha(v_R, r) \) are the attenuation ratio at the frequencies of laser radiation and Raman scattering by hydrogen fluoride molecules. Substituting these expressions the equation (1) can be presented in the following form:

\[
n(v, z) = \frac{c \tau_0}{2z^2} n_o S_0 G(z) N(z) f r \left( \frac{d\sigma}{d\Omega} \right) v_{Rs} \int_{v_0 - \Gamma_v}^{v_0 + \Gamma_v} \Phi(v') \exp\left[ -\int_0^z \left( \alpha(v_0, r) + \alpha(v_R, r) \right) dr \right] A(v') dv',
\]

where \( \Phi(v) \) is the distribution function of laser radiation photons in the lasing line [4] and can be represented by the Gaussian function

\[
\Phi(v) = \frac{1}{\sqrt{2\pi \Gamma_0}} \exp\left\{ -(v - v_0)^2 / (2 \Gamma_0^2) \right\}
\]

(3)

In addition, there will be considered the case when the instrumental function of the lidar or the spectral transmittance of the lidar receiving system \( A(v) \) [4, 5] also has a Gaussian shape with a maximum at the frequency \( v_R \) of the Raman scattering band of hydrogen fluoride molecules with a half-width \( \Gamma_\alpha \), which is greater than \( \Gamma_R \) and \( \Gamma_0 \):

\[
A(v) = \frac{K_t \xi(v)}{\sqrt{2\pi \Gamma_0}} \exp\left\{ -(v - v_R)^2 / (2 \Gamma_\alpha^2) \right\}
\]

(4)

where \( K_t \) is the lidar constant at the frequency \( v_0 \) of laser radiation, measured experimentally in [4] and \( \xi(v_R) \) is the relative spectral sensitivity of the optical receiver at the frequency \( v_R \) corresponding to the band of Raman scattering of light by hydrogen fluoride molecules. Then the equation (2) could be presented in the following form:

\[
n(v, z) = \frac{C}{z^2} N(z) \mu_d I(v, z)
\]

(5)

In expression (5), the constant \( C \) is defined as:

\[
C = \frac{c \tau_0}{2} S_0 f
\]

(6)

and some function \( I(v, z) \) has the form:
\[ I(v, z) = G(z)n_0 \int_{v_0 - \Gamma}^{v_F \Gamma} \left( \frac{d\sigma}{d\Omega} \right) \exp \left[ - \int_0^z \left( \alpha(v_0, r) + \alpha(v_F, r) \right) dr \right] A(v') \, dv' \]  

(7)

It is assumed that \( \Phi(v) = 1 \) when the half-width of the lasing line is much less than the half-width of the instrumental lidar function. This approximation is quite valid for industrial lasers and spectrometers [4, 6]. Let us make some transformations, assuming that the differential cross section for Raman scattering and the attenuation ratio of laser radiation in the atmosphere are molecular constants, the first exponent insignificantly depends on frequency and can be removed from the integral, and the remaining integral in expression (7) can be transformed into integral of errors [4], then the expression (7) could be presented in the following form:

\[ I(v, z) = G(z)n_0 \left( \frac{d\sigma}{d\Omega} \right) \cdot 0.34K_4 \xi(v) \exp \left[ - \int_0^z \left( \alpha(v_0, r) + \alpha(v_F, r) \right) dr \right] \]

(8)

Now let us express the value of the concentration of molecules \( N(z) \) from equation (5) taking into account (6) and (8) as

\[ N(z) = \frac{n(v, z)z^2}{Ct_I I(v, z)} \]

(9)

Let us consider a homogeneous atmosphere and single scattering [4-6]. The value of the maximum of the stretching vibration band of the HF molecule was taken from [4, 8] and is equal to 3959 cm\(^{-1}\). The value of the differential cross-section for the Raman scattering of the hydrogen fluoride molecule \( \frac{d\sigma}{d\Omega} \) for the selected wavelengths of laser radiation 405, 532, and 650 nm were estimated from the data [4] and the value \( 2.98 \times 10^{-30} \) cm\(^2\) for a wavelength of 435.8 nm and calculated taking into account the dependence \( \frac{1}{\lambda^2} \) [4], and for the wavelengths of interest to us are given in Table 1.

**Table 1.** Wavelength and frequency values of laser radiation and Raman scattering of hydrogen fluoride molecule, the differential cross section of Raman scattering, the attenuation ratio for these wavelengths in the atmosphere, and relative spectral sensitivity values of the optical receiver.

| Wavelength (\( \lambda \), nm) | Differential cross section \( \frac{d\sigma}{d\Omega} \) \( 10^{30} \) cm\(^2\) | Attenuation ratio \( \alpha(v_0, z) \), km\(^{-1}\) | Attenuation ratio \( \alpha(v_F, z) \), km\(^{-1}\) | Relative photo receiver spectral sensitivity \( \xi(v) \) |
|-------------------------------|-------------------------------------------------|---------------------------------|---------------------------------|---------------------------------|
| 650                           | 461.54                                          | 0.60                            | -                               | -                               |
| 875.2                         | 342.78                                          | -                               | -                               | -                               |
| 532                           | 563.91                                          | 1.34                            | 0.16                            | -                               |
| 673.9                         | 445.17                                          | -                               | 0.14                            | 0.2                             |
| 405                           | 740.74                                          | 4.01                            | 0.24                            | -                               |
| 482.3                         | 622.02                                          | -                               | 0.18                            | 0.8                             |

Table 1 also presents the attenuation ratio values for these frequencies \( \alpha(v_0, z) \) and \( \alpha(v, z) \) from [4, 6, 7, 9]. The cross section of the mirror of the receiving telescope was 0.126 m\(^2\), and the distance step was 7.5 m for a time of one measurement of 50 ns during which 200 photons can be recorded.

**4. Computer Simulation Results and Discussions**

To begin with, let us perform a computer simulation of equation (9), assuming that in our case \( G(z) \) is equal to 1 and the measurement time for our experimental situation is \( t = 100 \) s. Let us find a numerical
solution to the equation (9) for three values of the laser wavelength 405, 532 and 650 nm and the sensing distance from 100 m to 1500 m. The results of the equation solution (9) for this case are shown in Figure 2.

Figure 2. Diagrams of the dependence of concentration of hydrogen fluoride molecules in the atmosphere calculated according to equation (9), (on a logarithmic scale, in cm$^{-3}$) on the probing distance $z$(in m) for laser wavelengths 405 (3, 5), 532 (2) and 655 (1) nm and measurement times of 100 s (1, 2, 3) and 103 s (5) for the selected option of the Raman lidar. The MAC level is a straight line (4).

It can be seen from the diagram in Figure 2 that an increase in the concentration of the studied molecules is observed in the range of wavelengths as 405-532-650 nm due to the strong spectral dependence of the values of parameters included in equation (9). In this case, this concentration value sharply increases by about 1.5 orders of magnitude for the first 500 m. The minimum concentration of hydrogen fluoride molecules $1.88 \times 10^{13}$ cm$^{-3}$ can be obtained at a wavelength of 405 nm and a sensing distance of up to 100 m; for a distance of up to 500 m this value is $5.56 \times 10^{14}$ cm$^{-3}$; for 1000 m it is 2.74 1015 cm$^{-3}$, and for 1500 m the value is $7.64 \times 10^{15}$ cm$^{-3}$ at a laser pulse repetition rate of 1 MHz and a distance step $\Delta z=7.5$ m. In this case, the concentration level of $1.5 \times 10^{14}$ cm$^{-3}$ can be recorded as MAC at a laser radiation wavelength of 405 nm and a sensing distance of up to 650 m, at a wavelength of 532 nm - up to 350 m and 650 nm - only up to 200 m. It is obvious [4] that further decrease in the concentration of the studied molecules is possible due to an increase in the repetition frequency of laser pulses $f$ or an increase in their energy $E_0$. If the measurement time $t_d$ is 1000 s, then the level of $1.5 \times 10^{14}$ cm$^{-3}$ can be depicted at a distance of 1500 m as curve (5) in Figure 2.

5. Conclusion
Thus, hydrogen fluoride molecules in the atmospheric boundary layer can be detected by a Raman scattering lidar, and the laser radiation wavelength of 405 nm and the lidar parameters can be selected for remote measurement of the concentration of the studied molecules at a level of $10^{14}$ cm$^{-3}$ at a sensing distance of up to 500 m.

The minimum concentration of hydrogen fluoride molecules $1.88 \times 10^{13}$ cm$^{-3}$ can be recorded at a wavelength of 405 nm and a distance of up to 100 m at a laser pulse repetition rate of 1 MHz and a
measurement time for our experimental situation $t_d = 100$ s. At a distance of up to 1500 m in this experimental situation, it is only $7.64 \times 10^{15}$ cm$^{-3}$. The MAC concentration level equal to $1.5 \times 10^{14}$ cm$^{-3}$ at a wavelength of laser radiation of 405 nm can be measured at a distance of up to 650 m, at a wavelength of 532 nm - up to 350 m and 650 nm - only up to 200 m. And an increase in the measurement time up to 1000 s leads to an increase in the sensing distance up to 1500 m for this concentration level of the hydrogen fluoride molecule.

As a result of the work, it can be concluded that the concentration level of the studied molecules of $10^{14}$ cm$^{-3}$ will be recorded during the measurement 100 with this option of the Raman scattering lidar.

The use of lidar technologies, as well as the results obtained, make it possible to monitor pollution over the water area of seaports and control the operation of both ship power plants and the port’s coastal infrastructure [1, 10].

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