Laser sensing of HF molecules in the atmosphere: problems of numerical modeling

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The logarithm of Raman backscattering power as a function of sensing distance is numerically calculated for HF molecule with concentrations of 10^{16} and 10^{19} cm^{-3} at chosen wavelengths of YAG:Nd laser and the distance range 1–1000 m. The numerical solution of the lidar equation for DAS is obtained. Ranges of HF molecule concentration, sensing distances, and optimal conditions are determined.

Wide application of Raman scattering (RS), as well as differential absorption and scattering (DAS) lidars to IR sensing of trace gas molecules[1–7] suggests that such lidars might be used in the remote sensing of HF molecules in the atmosphere. In this work, the capabilities of such lidars in sensing HF molecules are estimated for different experimental conditions.

RS sensing of HF molecules

To choose an optimal Raman lidar system for measuring the atmospheric concentrations of HF molecules under different sensing conditions and to obtaine maximum RS power at the lidar photoreceiver, it is necessary to solve the RS lidar equation in the form[1]

$$P(\lambda,R) = P_{\mathrm{L}} K_1 \Delta R A_0 \times$$
$$\times T(\lambda_{\mathrm{L}},R) T(\lambda,R) \left[\frac{\mathrm{d}\sigma(\lambda_L)}{\mathrm{d}\Omega}\right] N_a / R^2, \qquad (1)$$

where P_{L} is the laser power; λ_{L} is the wavelength; K_1 is the lidar constant; $\Delta R = (c\tau_i)/2$ is the distance step; c is the wind speed; τ_i is the time of one measurement (its minimum is determined by the laser pulse length); A_0 is the area of the receiving telescope; $T(\lambda_{\mathrm{L}}, R)$ and $T(\lambda, R)$ are the atmospheric transmissions at the wavelengths of laser radiation and RS signal, respectively; $\mathrm{d}\sigma(\lambda_{\mathrm{L}})/\mathrm{d}\Omega$ is the differential cross section of RS for the studied molecule at the laser wavelength; N_a is the molecule concentration.

To calculate the power of Raman backscattering radiation by HF molecules, the fourth, third, second, and first harmonics of YAG:Nd laser at λ = 266, 355, 532, and 1064 nm were chosen. The wave number of RS band of HF molecule valence vibration is 3959 cm^{-1}. The values of atmospheric transmission at the laser and RS wavelengths were calculated by equations from Ref. 1.

The values of laser wavelengths, RS bands for these wavelengths, coefficients of atmospheric attenuation and photomultiplier's relative spectral sensitivity, calculated for the same laser wavelengths and RS bands of the studied molecule, are given in Table 1. Since experimental data on differential cross section of RS of HF molecules are lacking, these values have been assessed by the values of RS intensities of HF molecules[8] and are given in the last column of Table 1 with accounting for the $1/\lambda^4$-dependence.

Table 1. The values of laser radiation wavelengths, RS bands, coefficients of atmospheric attenuation, photomultiplier's relative sensivity, and differential cross sections of RS for laser wavelengths and RS-light by HF molecules

Radiator	λ, nm	$k(\lambda, R)$, km^{-1}	$\xi_p(\lambda)$	$S_b(\lambda)$, $\frac{\mathrm{Wt}}{\mathrm{m}^2 \cdot \mathrm{sr} \cdot \mathrm{nm}}$	$\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega} \cdot 10^{30}$, cm^2/s
Laser	266	0.785	–	–	2.576
	355	0.310	–	–	0.812
	532	0.160	–	–	0.161
	1064	0.118	–	–	0.010
HF	297	0.480	0.290	$6 \cdot 10^{-6}$	–
	413	0.220	0.945	0.000114	–
	674	0.145	0.270	0.009	–
	1838	0.095	0.540	0.0007	–

Other parameters were the following: the peak power of laser radiation $P_{\mathrm{L}} = 100$ kW; the distance step ΔR = 7.5 m for the measurement time 50 ns; the lidar constant K_2 = 0.495 at a wavelength of 532 nm [Ref. 1]; the area of the receiving telescope A_0 = 0.008 m^2.

Using these parameters in the lidar equation for RS,[1] numerical calculations were carried out for the HF molecule with concentrations of 10^{16} and 10^{19} cm^{-3} for the chosen wavelengths of the YAG:Nd laser and the distance range 1–1000 m. The calculation results are presented in the form of logarithmic curve of the Raman backscattering power against the sensing distance.

To calculate the solar background power by the equation from Ref. 9, the $S_b(\lambda)$ values for the chosen wavelengths were taken from Ref. 2 and are cited in the next to the last column of Table 1; the calculated background powers are shown in Fig. 1 by the straight lines parallel to the abscissa.

According to the calculations, the performance of RS lidars in the single-sensing of HF molecules with a concentration of about 10^{19} cm^{-3} in daytime are limited to the distances of 8, 10, 190, and 850 m at 1064, 532, 355, and 266 nm, respectively. Minimal concentrations of HF molecules, recorded in daytime, are about 10^{13} cm^{-3} at a distance of 1 m from the radiator, 10^{15} cm^{-3} – at a distance of 10 m, and 10^{17} cm^{-3} – at a distance of about 100 m.

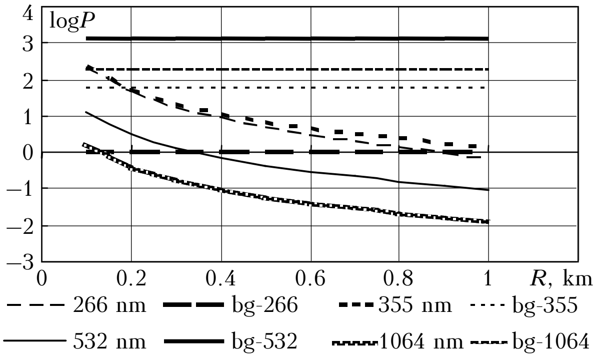

Fig. 1. The logarithm of the Raman backscattering power as a function of sounding distance from the range 0.1–1.0 km of HF molecules at the concentration $N_a = 10^{19}$ cm^{-3} for the chosen laser wavelengths. The background (bg) power level at the Raman lidar's photoreceiver is shown for the comparison.

Small values of differential cross sections of RS vibrational lines of gas molecules require rather large molecule concentrations to obtain a sufficient signal-to-noise ratio. Resonance absorption in the visible and IR spectral ranges has the largest interaction cross section[2] among all known spectroscopic effects.

This determines the capability of remote measurements of trace gases at large distances.

DAS sensing of HF molecules

In contrast to RS lidars, DAS lidars use two laser beams with different wavelengths, one of which falls into the maximum of molecule absorption band and another is beyond this band; the attenuation of the beams is determined by the elastic backscattering signals. The distribution of studied molecule concentrations in the atmosphere is calculated by the ratio of recorded DAS-lidar signals at these two wavelengths within quite narrow spectral range.[3,4]

To estimate capabilities of the method for sensing HF molecules, the lidar equation for DAS was numerically calculated[3] and ranges of molecule concentrations and sensing distances were determined.

Write the equation for the most general DAS case on the assumption that all the wavelength depended multipliers differ in the form[3]:

$$\int_0^R N_a(R)\,\mathrm{d}R = \frac{1}{2\sigma_0}\ln\left[\frac{P(\lambda_{\mathrm{L1}},R)P_{\mathrm{L0}}K_{10}\rho_0}{P(\lambda_{\mathrm{L0}},R)P_{\mathrm{L1}}K_{11}\rho_1}\right] - \frac{1}{\sigma_0}\int_0^R \left[k_{\mathrm{A}}(\lambda_{\mathrm{L0}},R) - k_{\mathrm{A}}(\lambda_{\mathrm{L1}},R)\right]\mathrm{d}R, \qquad (2)$$

where λ_{L0} and λ_{L1} are the excitation wavelengths, the former falls into the absorption band of HF molecule and the latter is beyond this band; $P(\lambda, R)$ is the power of the photodetected elastic backscattering signal at the wavelength λ_{L}, arriving from the distance R; ρ is the topographic target reflectivity, or the summary coefficient of elastic Mie scattering and Rayleigh molecular scattering; $k(\lambda_{\mathrm{L}}, R)$ are the atmospheric attenuation coefficients of laser radiation, defined by the equation[2]:

$$k(\lambda_{\mathrm{L}}, R) = k_{\mathrm{A}}(\lambda_{\mathrm{L}}, R) + N_a(R)\sigma_0(\lambda_{\mathrm{L}}). \qquad (3)$$

The first item here is the atmospheric attenuation coefficient at the laser radiation wavelength except for HF molecules and the second one is the product of HF molecule concentration and resonance absorption cross section of the molecule.

Determine the values of variables in Eq. (2) for our case.

The following wavelengths were chosen for DAS sensing of HF molecules: maximum of IR absorption band of the studied HF molecules of 2.3958 μm and the wavelength of rotational transition in the molecule $R(26)$ of 10.4578 μm [Ref. 10]. Calculations were carried out successively for pairs 2.4, 2.1 and 10.6, 2.1 μm.

To realize such lidar experimentally, pulsed YAG:Cr:Er, YAG:Cr:Ho, and CO_2 lasers can be used,[11,12] as well as the parametric $LiNbO_3$ oscillator with the second harmonic YAG:Nd laser pumping.[10]

Parameters in Eq. (2) have the following values:

– lidar constant $K_2 = 0.4$ at a wavelength of 1064 nm [Ref. 3];

– peak laser pulse power $P_{\mathrm{L}} = 10$ kW;

– sensing distances ranges R: 1 ... 5, 1 ... 100, and 100 ... 1000 m;

– molecular concentrations: 10^5 ... 10^{14} cm^{-3};

– attenuation coefficient $k_{\mathrm{A}}(\lambda_{\mathrm{L}}, R)$ is 0.09 km^{-1} at $\lambda = 2.1$ μm; 0.08 km^{-1} at $\lambda = 2.4$ μm; and 0.045 km^{-1} at $\lambda = 10.6$ μm;[2]

– resonance absorption cross section of HF molecules σ_0, assessed by the data from Ref. 2, is $1.923\cdot10^{-18}$ cm^2 at an excitation wavelength of 2.4 μm and 10^{-18} cm^2 at $\lambda = 10.6$ μm;

– reflectivity of topographic targets for mat surface, assessed by the data from Ref. 14, is 0.15, the summary atmospheric scattering coefficient is 10^{-7} [Ref. 4].

Spectral sensitivities of avalanche photodiode LFD-2 at the chosen wavelengths were taken from Ref. 13.

Using the above data, the ratio of DAS signal powers was numerically calculated by Eq. (2) depending on HF molecule concentrations in the range 10^5 ... 10^{14} cm^{-3} and sensing distances from 1 to 1000 m. The calculation results are given in Table 2.

According to Table 2, HF molecules with concentrations from the range 10^5 ... 10^{13} cm^{-3} can be sounded throughout the distance range and those with a concentration of 10^{14} cm^{-3} – at distances up to 100 m.

Table 2. The ratio of DAS signal powers when sensing HF molecules at $N_a = 10^5 \ldots 10^{14}$ cm^{-3} at distances of 1 ... 1000 m

N_a, cm^{-3}	R, m						
	1	5	10	50	100	500	1000
	$P(\lambda_{2.3958} R)/P(\lambda_{2.1}, R)$						
10^5	1.00002	1.00008	1.00016	1.0008003	1.001601	1.008032	1.016129
10^6	1.00002	1.00008	1.00016	1.0008003	1.001601	1.008032	1.016128
10^7	1.00002	1.00008	1.00016	1.0008001	1.001601	1.00803	1.016125
10^8	1.00002	1.00008	1.000122	1.0006079	1.001216	1.006096	1.012228
10^9	1.00002	1.000078	1.000156	1.0007811	1.001563	1.007838	1.015738
10^{10}	1.000016	1.000061	1.000122	1.0006079	1.001216	1.006096	1.012228
10^{11}	0.999982	0.999888	0.999775	0.9988776	0.997757	0.988833	0.97779
10^{12}	0.999635	0.998159	0.996321	0.9817388	0.963811	0.831686	0.691702
10^{13}	0.996181	0.981032	0.962424	0.8257196	0.681813	0.147342	0.02171
10^{14}	0.962289	0.825125	0.680832	0.1462848	0.021399		
	$P(\lambda_{10.6} R)/P(\lambda_{2.1}, R)$						
10^5	1.00009	1.00043	1.00086	1.004309	1.008637	1.043938	1.089806
10^6	1.00009	1.00043	1.00086	1.004309	1.008637	1.043938	1.089806
10^7	1.00009	1.00043	1.00086	1.004309	1.008637	1.043937	1.089804
10^8	1.00009	1.00043	1.00086	1.004308	1.008635	1.043927	1.089785
10^9	1.00009	1.000429	1.000858	1.004299	1.008617	1.043834	1.089588
10^{10}	1.000088	1.00042	1.00084	1.004209	1.008435	1.042894	1.087629
10^{11}	1.00007	1.00033	1.00066	1.003305	1.006622	1.033551	1.068227
10^{12}	0.99989	0.99943	0.998861	0.994316	0.988665	0.944594	0.892258
10^{13}	0.998092	0.990476	0.981042	0.908737	0.825802	0.384043	0.147489
10^{14}	0.980287	0.905227	0.819435	0.369465	0.136504		

To assess the solar background power at the lidar photoreceiver, the following $S_b(\lambda)$ values were chosen from Ref. 2: 0.00003 W/(m^2·sr·nm) for $\lambda = 2.1$ μm, $5 \cdot 10^{-6}$ W/(m^2·sr·nm) for $\lambda = 2.4$ μm, and 0.00002 W/(m^2·sr·nm) for $\lambda = 10.6$ μm.

Based on the comparison of the background power and laser radiation power with accounting for the attenuation of the signal, passing through the measurement volume, the following conclusion can be drawn. The background power does not overlap the photorecorded signal in all ranges of sensing distances and molecular concentrations when using a topographic target with a coefficient of 0.15, except for $N_a = 10^{14}$ cm^{-3}.

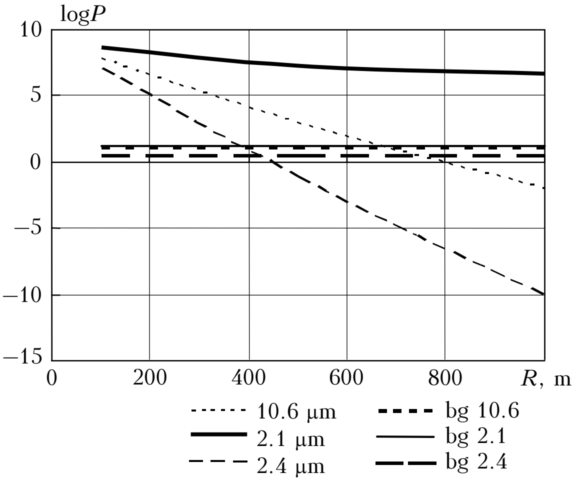

Fig. 2. Recorded signal of the scattered laser radiation passing through the measurement volume with the HF molecule concentration $N_a = 10^{14}$ cm^{-3}, at a topographic target with a coefficient of 0.15 as a function of sensing distance R. The horizontal lines correspond to the background power level at the lidar photoreceiver.

As is evident from Fig. 2, the detection of HF molecules with $N_a = 10^{14}$ cm^{-3} at $\lambda = 2.1$ and 2.4 μm is possible only at distances up to 420 m, at $\lambda = 2.1$ and 10.6 μm – up to 700 m.

The comparison of data from Table 2 and Fig. 2 shows that the background power does not virtually limit the capabilities of DAS lidars, therefore, the detection of HF molecules with $N_a = 10^{14}$ cm^{-3} is possible only at distances up to 100 m.

The situation differs in case of calculations at a summary elastic scattering coefficient of 10^{-7}. In this case, the background does not influence the sensing of HF molecules with concentrations of $10^5 \ldots 10^{14}$ cm^{-3} in the range 1 ... 100 m. For distances from 100 to 1000 m and HF molecule concentration from 10^5 to 10^{13} cm^{-3}, the useful signal exceeds the background one at distances up to 450 m, except for wavelengths of 10.6 and 2.1 μm, where HF molecules with concentration of 10^{13} cm^{-3} can be detected only at distances up to 400 m. When $N_a = 10^{14}$ cm^{-3}, possible sensing distances for HF molecules at $\lambda = 10.6$ and 2.1 μm are limited to 150 m and at $\lambda = 2.4$ and 2.1 μm – to 110 m (see Figs. 3 and 4).

A comparison of the calculation results and data from Table 2 allows the conclusion that in case of summary atmospheric scattering coefficient of 10^{-7}, HF molecules with $N_a = 10^5 \ldots 10^{13}$ cm^{-3} can be detected at the chosen wavelengths only at distances up to 450 m, with $N_a = 10^{13}$ см$^{-3}$ at $\lambda = 10.6$ and 2.1 μm – up to 400 m, and with $N_a = 10^{14}$ cm^{-3} – up to 100 m.

All calculations have been carried out for laser radiation power of 10 kW. An increase of the power will enhance the sensing efficiency proportionally to the order of increase. The use of a He–Ne laser with $\lambda = 2.3958$ μm and a power of 1 mW allows

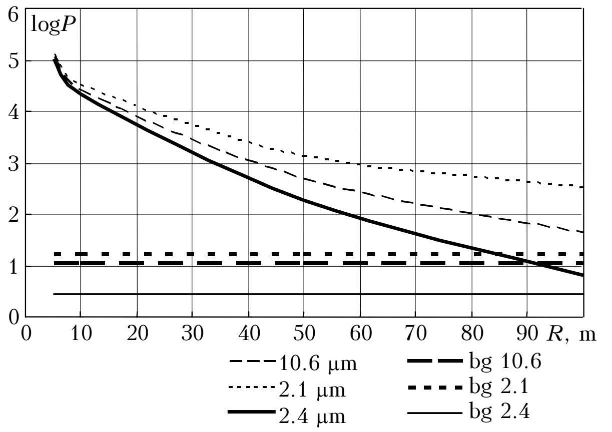

Fig. 3. Recorded signal of the scattered laser radiation passing through the measurement volume with the HF molecule concentration $N_a = 10^{14}$ cm^{-3}, at a topographic target with a coefficient of 10^{-7} as a function of sensing distance R (the range 1 ... 100 m). The horizontal lines correspond to the background power level at the lidar photoreceiver.

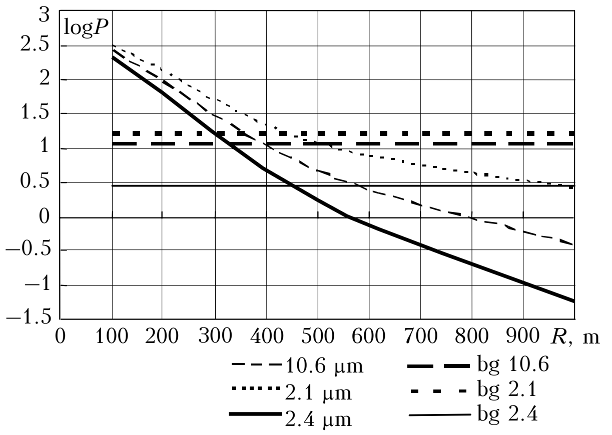

Fig. 4. Recorded signal of the scattered laser radiation passing through the measurement volume with the HF molecule concentration $N_a = 10^{13}$ cm^{-3}, at a topographic target with a coefficient of 10^{-7} as a function of sensing distance R (the range 100 ... 1000 m). The horizontal lines correspond to the background power level at the lidar photoreceiver.

sensing of HF molecules with $N_a = 10^5 \ldots 10^{14}$ cm^{-3} in the free atmosphere at a distance up to 0.3 m from the radiator. The background power exceeds the useful signal in case that the sensing distance increases.

Thus, the obtained results show the efficiency of HF molecules sensing with RS and DAS lidars. HF molecules with $N_a = 10^{13}$ cm^{-3} are detectable at distances up to 450 m.

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