

Enhancement of the Raman lidar sensitivity using overtones of vibrational-rotational Raman bands of oxygen or nitrogen as the reference signals

S. M. Bobrovnikov^{a,b}, E. V. Gorlov^{a,b}, V. I. Zharkov^{*a}.

^a V.E. Zuev Institute of Atmospheric Optics SB RAS, Tomsk, Russia;

^b National Research Tomsk State University, Tomsk, Russia.

ABSTRACT

Influence of the vibrational-rotational Raman bands of molecules of the main components of the atmosphere (oxygen and nitrogen) on the sensitivity of Raman lidar is considered. A method is proposed of using the first overtones of the vibrational-rotational Raman bands of oxygen and nitrogen molecules as the reference signals for the measurement of low concentrations of chemicals in the atmosphere by the Raman method.

Keywords: Lidar, Raman scattering, gas analysis, atmosphere.

1. INTRODUCTION

The use of the matrix photodetector in the receiving opto-electronic system of the Raman lidar is justified due to the possibility of the simultaneous recording the spontaneous Raman spectra over the entire range of the Raman shifts¹. However, in the detection of ultra-weak Raman signals of small gas components, the elements of the photodetector matrix can be exposed to high-power optical Raman signals of molecules of main gas components of the atmosphere (oxygen and nitrogen), the intensity of which is 3-6 orders of magnitude higher.

Exceeding the permissible dynamic range of the signal variation can lead to a nonlinear operation mode of the photodetector, to the charge spreading over the adjacent matrix elements, and thus, to a distortion of the measurement results.

2. SUPPRESSION OF BACKSCATTERING RADIATION OF INTENSE COMPONENTS OF THE RAMAN SPECTRUM

On the other hand, the effect of backscattering radiation of intense components of the Raman spectrum on the grating and other optical elements of the polychromator will create additional noise in the recorded spectrum and limit the sensitivity of the lidar system². Therefore, for the correct measurement of low concentrations of pollutants and the implementation of the maximum level of the detection sensitivity of the Raman lidar, optical signals of intense Raman bands of the nitrogen and oxygen molecules should be blocked at the entrance of the spectrograph. For this purpose, it is sufficient to establish an additional interference filter between the telescope and spectrograph that suppresses the Raman bands of the nitrogen and oxygen molecules and transmits the working part of the spectrum (Figure 1). Spectral positions of the centers of the impact of Q -branches of the oxygen and nitrogen bands are 1556 cm^{-1} and 2331 cm^{-1} , respectively,

* zharkov@iao.ru

at the width of the impact zone of about 300 cm^{-1} (curve 1 in Figure 1). It is obvious that an additional filter should provide a high level of suppression of radiation in the range of Raman shifts from 1400 to 1700 cm^{-1} and from 2180 to 2480 cm^{-1} and have a high transmittance in the rest of the range of Raman shifts (curve 2 in Figure 1).

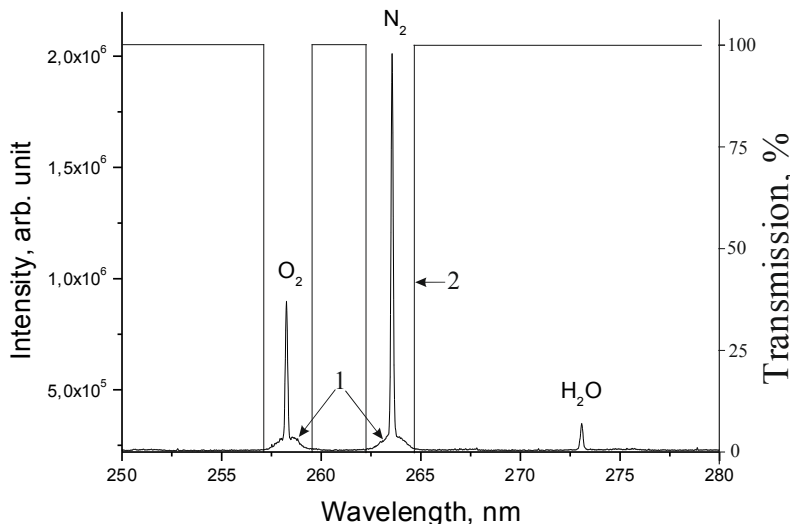


Figure 1. Raman spectrum of molecules of atmospheric air (curve 1) and the spectral characteristics of an additional spectral filter (curve 2).

3. THE SELECTION OF THE REFERENCE SIGNAL FOR MEASURING LOW CONCENTRATIONS OF CHEMICALS IN THE ATMOSPHERE BY THE RAMAN METHOD

As a rule, the lidar method for the determining the concentration of pollutants in the atmosphere with the help of Raman effect is based on the principle of measuring the ratio of the intensity of signal of Raman scattering by the molecules of a j -component of pollutants to the intensity of the reference signal - the signal of the Q -branch of the vibrational-rotational Raman bands of the nitrogen (or oxygen) molecules. In case of the suppression of intense responses of vibrational-rotational Raman bands of nitrogen and oxygen molecules, a question arises, how to select the reference signal. Obviously, the idea of using the Raman signals of water vapors or carbon dioxide is not very suitable, since the concentrations of the water vapor and carbon dioxide molecules in the atmosphere is not constant. Monatomic gases have no Raman responses. Concentrations of the other constant gas components of the atmosphere have lower values, than the threshold sensitivity of the Raman method (Table 1).

Table 1. Composition of dry air at the sea level³.

Gas	The volume content, %
Nitrogen	78.084
Oxygen	20.946
Argon	0.932
Water	0.5-4
Carbon dioxide	0.038-0.043
Neon	$1.82 \cdot 10^{-3}$
Helium	$4.6 \cdot 10^{-4}$
Methane	$1.7 \cdot 10^{-4}$
Krypton	$1.14 \cdot 10^{-4}$
Hydrogen	$5 \cdot 10^{-5}$
Nitrous oxide	$5 \cdot 10^{-5}$
Xenon	$8.7 \cdot 10^{-6}$

At the same time, in addition to the fundamental vibrational-rotational bands, the Raman spectra of the nitrogen and oxygen molecules also contain weaker bands associated with their overtones (Figure 2). For example, at the excitation at a wavelength of 488 nm, the ratios of the Raman cross-sections of *Q*-branches of the first overtone and the fundamental tone are 1×10^{-3} and 3.4×10^{-4} for nitrogen and oxygen, respectively⁴. It can be shown that the signal intensities of the first overtones of nitrogen or oxygen are comparable to the intensities of Raman signals of pollutants at their concentrations of the order of hundreds of ppm, which, obviously, will allow to carry out the relative measurements of intensities in the same scale.

That is why it was proposed to use the first overtones of the vibrational-rotational Raman bands of the oxygen or nitrogen molecules, as reference signals for measuring low concentrations of chemicals in the atmosphere by the Raman method. Then, the concentration of the pollutant in the atmosphere can be found from the expression:

$$C_x = \frac{I_x \cdot \sigma^o \cdot T^o(r) \cdot \eta^o \cdot K^o}{I^o \cdot \sigma_x T_x(r) \cdot \eta_x \cdot K_x} \cdot C^o, \quad (1)$$

where *I* are the intensities of the Raman responses, σ are the Raman cross sections, *C* is the concentration of molecules in the atmosphere, *T*(*r*) is the spectral transmission of the atmosphere, *r* is the distance from the lidar to the pollutant, η is the quantum efficiency of the photodetector, *K* is the transmittance coefficient of the receiving optical system of the lidar. The coefficients in equation (1) with the subscript *x* relate to the pollutant, and those with the superscript ^o relate to the first overtone of oxygen (nitrogen).

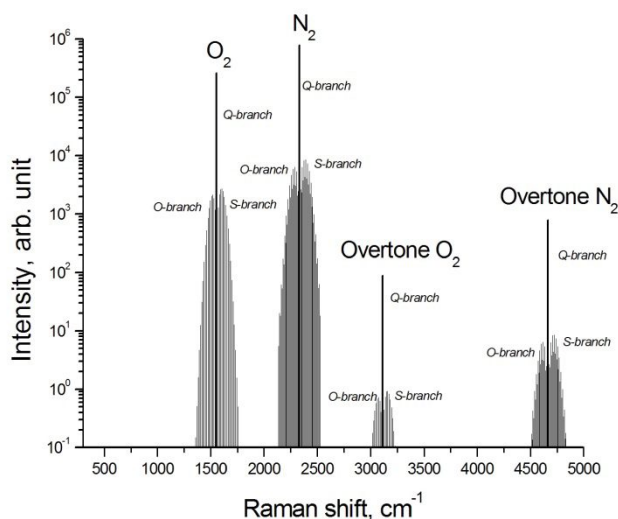


Figure 2. Vibrational-rotational Raman bands of oxygen and nitrogen molecules in the air and their first overtones.

4. CONCLUSIONS

The proposed method for reducing the dynamic range of the signal variation in the working spectral-analytical field of the matrix photodetector allows to ensure an optimum mode of photo detection and to achieve the maximum values of the Raman lidar sensitivity. Obviously, the Raman-lidar response of the first overtone of oxygen (see Fig. 2) will limit the lidar sensitivity in the range of Raman shifts of 3089 cm^{-1} . Thus, for example, with equal Raman cross-sections of molecules of the examined substance and nitrogen, the lidar sensitivity at the excitation at 488 nm can't be higher, than 100 ppm . Fortunately, the overtone of nitrogen lies outside the range of the possible Raman shifts and cannot affect the performance of Raman lidar.

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