

# Amplification of the intensity of Raman scattering by ozone molecules during their photodissociation as a result of nonlinear two-photon absorption of XeCl laser radiation

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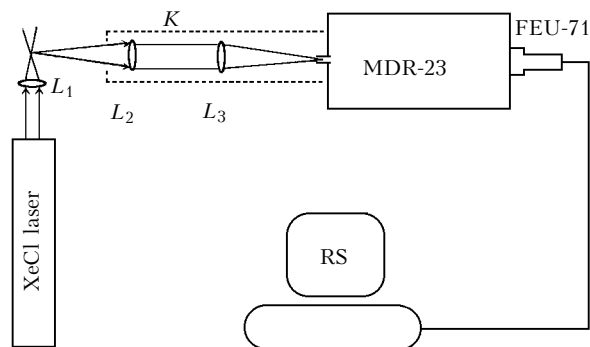
We present some results of laboratory studies on the amplification of Raman scattering by ozone molecules during their photodissociation due to nonlinear two-photon absorption of XeCl laser radiation at the wavelength of 308 nm at a lens focus. As laser radiation energy increases to 40 mJ and nearly breakdown conditions are achieved at the lens' focus, the experimentally observed amplification factor can reach five orders of magnitude.

As known, there exists resonance type of Raman scattering (RS) at excitation to the dissociation continuum.<sup>1</sup> In this case the instantaneous re-emission at the frequency shifts of the Raman scattering occurs before the molecular dissociates. In this case the cross section of RS can be increase by several orders of magnitude. This process has been experimentally observed for molecules of halogens ( $I_2$ ,  $Cl_2$ , etc.).<sup>2</sup> For the ozone molecule ( $O_3$ ) only theoretical estimates were made.<sup>3</sup> The estimates show that at  $O_3$  excitation higher than the dissociation threshold at the center of Hartley absorption band the resonantly amplified RS cross section of ozone molecule can reach the value of the order of  $10^{-24}$   $cm^2/sr$  that exceeds, approximately by five orders of magnitude, that of the RS cross section of nitrogen molecule. Although in the conventional mode the relationship between the ozone RS cross section and nitrogen RS cross section at one excitation wavelength is  $\sim 3.6$  (Ref. 1).

To experimentally check up theoretical calculations, we have investigated the amplification of the Raman scattering signal from ozone molecules at their photodissociation due to nonlinear two-photon absorption of XeCl laser radiation at the wavelength of 308 nm at a lens focus. The regime of two-photon absorption (about  $65000$   $cm^{-1}$ ) provides an unconditional excess of all the thresholds of photodissociation of ozone molecules at any energy state. The block-diagram of the experimental setup is shown in Fig. 1.

The XeCl laser radiation was focused using a lens  $L_1$  with the focal length of 85 mm. As laser radiation power exceeds 40 mJ, the spark breakdown occurred in the atmosphere at the lens' focus. The availability of a luminous spark provided a fine adjustment of the optical channel of RS signal recording just from this atmospheric volume. The spark image was constructed using two lenses,  $L_2$  and  $L_3$ , on the entrance slit of an MDR-23 monochromator. To remove possible lateral irradiation of the lens, the slit was shielded with a housing  $K$ . A photomultiplier tube (FEU-71) was set up at the exit slit. The photomultiplier (FEU-71) detected separate pulses of

photocurrent (photon counting mode). After optical adjustment the laser radiation power was gradually decreased until the spark disappeared in the focus.

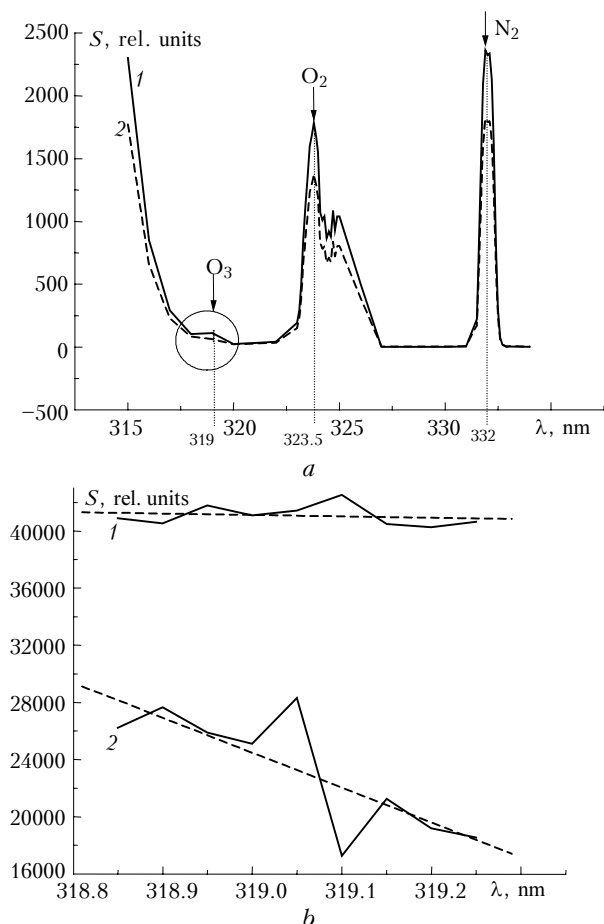


**Fig. 1.** Block-diagram of the experimental setup.  $L_1$ ,  $L_2$ ,  $L_3$  are the lenses;  $K$  is the protective housing.

Figure 2 shows the recorded spectra of RS signals at two energy levels of XeCl laser radiation. In the pre-breakdown regime at 40 mJ the RS signal from ozone in the range of 319 nm was precisely recorded, as denoted by a circle in Fig. 2a. However, this signal was not identified even at a 30% power decrease. This can be seen from the variation of the slope angles of the regression lines, shown in Fig. 2b, where signals are given in the area of RS ozone line recorded with the best spectral resolution and long duration of signal accumulation at each reading.

Figure 2a clearly shows the pedestal in the RS signals due to the wing of laser excitation line at 308 nm. On correcting these distortions, the ratio of the RS signals from ozone  $S(O_3)$  and nitrogen  $S(N_2)$  is  $S(O_3)/S(N_2) = 51/2301 \cong 0.022$ . In its turn,  $S(O_3)/S(N_2) = N(O_3)d\sigma'(O_3)/d\Omega/N(N_2)d\sigma(N_2)/d\Omega$ . Here  $N(O_3)$  and  $N(N_2)$  are the concentrations of the ozone and nitrogen molecules, and  $d\sigma'(O_3)/d\Omega$  and  $d\sigma(N_2)/d\Omega$  are the corresponding Raman cross sections. In this case the primed symbol for the ozone Raman cross section is

indicative of its resonant amplification before the photodissociation. Now we take the table values of the volume content of ozone and nitrogen in the surface atmosphere  $2 \cdot 10^{-6}$  and 78.09%, respectively.<sup>4</sup> Then the obtained ratio of cross sections  $d\sigma'(O_3)/d\Omega/d\sigma(N_2)/d\Omega$  at photodissociation of ozone molecules is  $0.7 \cdot 10^5$  that agrees well with the calculated estimates.<sup>3</sup>



**Fig. 2.** RS spectrum excited by the XeCl laser radiation at  $\lambda = 308$  nm at the lens'  $L_1$  focus. Pulse energy of 40 and 28 mJ (curves 1 and 2, respectively). Spectral distribution step  $\Delta\lambda = 0.1$  nm; the number of accumulated pulses  $n = 2000$  (a);  $\Delta\lambda = 0.05$  nm;  $n = 50000$  (b).

Such an amplification of the Raman signal from ozone molecules at their photodissociation supports the reliable detection of background concentrations of tropospheric ozone using lidars. It is clear that for practical realization of laser sounding of tropospheric ozone using Raman effect we need to consider more effective schemes of photodissociation of ozone molecules along the sounding path. For example, it can be expected that when using an excimer KrF laser and a high-pressure hydrogen ( $H_2$ ) cell, as a laser transmitter of a Raman lidar, emitting simultaneously along the sounding

path at the wavelengths of 248 nm (fundamental frequency), as well as at 277 nm and 313 nm (first and second Stokes lines of SRS in the  $H_2$  cell, respectively), laser photons at the fundamental frequency (248 nm) must provide for efficient photodissociation of the ozone molecules. It should be noted that for improving the efficiency of ozone photodissociation along the sounding path we can also use a supplementary  $CO_2$ -laser radiation at the wavelengths in the ozone absorption band at  $9.6 \mu m$  synchronously with the KrF laser radiation. Then radiation at the wavelength of 313 nm can be used as the test one for excitation of Raman signals from ozone and nitrogen at the wavelengths of 324 nm and 337 nm, respectively.

It should be noted that such a Raman lidar can provide more reliable data on the tropospheric ozone, at least in the atmospheric boundary layer, than the differential absorption lidar (DIAL) with the use of a KrF laser and a high-pressure hydrogen cell. The matter is that the laser sounding of tropospheric ozone by the differential absorption method using an on-line and off-line pair of wavelengths (for example, 248/277 or 277/313 nm) is very sensitive to spectral and, especially spatial inhomogeneities in the profile of aerosol scattering coefficients.<sup>5</sup> Under conditions of inhomogeneous aerosol atmosphere that is the most typical for the lower part of the atmospheric boundary layer, these vertical distributions are too complicated and strongly variable. Therefore, under such conditions the problem of correcting for aerosol the laser sounding data on tropospheric ozone obtained by the differential absorption method cannot be solved in full measure.<sup>6</sup>

Thus, the experimentally recorded amplification of the RS intensity by ozone molecules at their photodissociation by five orders of magnitude gives rise to real prospects for the development of a new method of RS laser sounding of tropospheric ozone, at least, in the lowest part of the atmospheric boundary layer as an alternative of UV lidar method of differential absorption.

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