Spatial and spectral features of the luminescence of liquid nitrogen stimulated by infrared lasers

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Abstract. Spectral features of cryogenic liquids, especially nitrogen, seem to be clearly investigated due to the wide application in science. On the other hand, material properties can really be different under intensive laser irradiation. During irradiation of liquid nitrogen with pulsed (pulse duration 20 ns) YaG: Nd 1064 nm laser with average power of 0.3 W we have found bright luminescence in the visible region with five narrow spectral lines. This phenomenon can be explained by the multiphoton excitation of nitrogen molecules and ions with infrared photons. Its spatial and spectral characteristics are attributed to Amplified Spontaneous Emission. The main features include super-linear dependence of the emission intensity on the intensity of the excitation radiation, limited amount of narrow spectral bands and conical geometry of the emission with the clear separation of the cones in correspondence with the spectral lines of the emission. This phenomenon manifests liquid nitrogen as the convenient substance of Kerr type for studies of various non-linear optical processes by means of nanosecond lasers instead of femtosecond lasers applied usually for these purposes.

1. Introduction
This paper is dedicated to one of the fields of light-matter interactions. R&D on the interactions of light and matter have the vast history starting from ancient centuries. At that time the great Greece scientist Aristotle became one of the first persons, who tried to apply transformations of light in practice. The legend tells that Aristotle destructed Persian ships attacking Greece with the beams of focused Sun light. During many hundreds of years which have passed from that moment the science and applications of the light matter interactions expanded fantastically and penetrated into all the fields of humanity activities [1-7]. Diagnostics of a wide variety of materials including inorganics, organics and bio-organics by means of combinations of optical microscopy and optical spectroscopy belong to the most popular branches of this work. Studies of photoelectrical and photochemical processes inducing transformations in electron and atomic-molecular systems in various materials form the next step. Development of lasers opened the new and highly productive branch of the light-matter interactions [8 – 12] including various kinds of laser technologies (cutting, drilling, welding, hardening, forming of nanoparticles by means of laser ablation and sublimation, etc.). Active interactions of laser beams propagating through various suspensions of nanoparticles in colloidal water solutions with these nanoparticles created wide sets of rather complicated nanostructures [9]. Irradiation of materials (solids, liquids, gasses) with femtosecond laser pulses opened a new branch of the light-matter interactions [13]. Several principally new phenomena have been discovered: filamentation of laser beams, conical...
emission of the luminescence light and ultrafast generation of the emission pulses with super-continuum optical spectrum. This our paper presents a set of new results concerning unusual features of the spatial and spectral distributions of the visible light emission of liquid nitrogen irradiated with nanosecond pulses of the YAG:Nd infrared laser with 1.064 µm wavelength. On the one hand the spatial distribution of this emission reminds the patterns observed in the cases of femtosecond irradiation. But on the other hand, the spectral features of these emissions demonstrate essential differences.

2. Experimental techniques

The infrared laser emitted 1.064 µm radiation by means of excitation of YAG:Nd crystal with the pulses of light. The mean optical power of the laser was about 0.3 W. Due to the optical amplifier the laser could be used in two kinds of the pulsed emission: millisecond and nanosecond (the duration of the pulses was about 20 nanoseconds). The laser beam had the transverse dimension about 5 mm. Several kinds of lenses were used for focusing of the laser beam (the focal lengths of the lenses were in the range 30 – 150 mm). Liquid nitrogen used in our experiments had the purity of the technical level and contained about 0.5 % inclusions of oxygen and argon. Three kinds of dewars for the laser irradiation of the liquid nitrogen were used in our experiments: the glass dewar with optically transparent walls, external diameter about 12 cm, the molten quartz dewar, external diameter about 4 cm and the metal dewar with two pairs of mutually perpendicular optical windows.

The observations of the propagation of the laser beam through the liquid nitrogen was made using the two schemes: the beam entered the glass or fused quartz dewar vertically top down. The propagation of the beam inside the nitrogen was observed in the horizontal direction via the transparent walls of the dewars. In the second scheme the beam entered the dewars horizontally via either through the transparent walls of the glass or silica dewars or through one of pairs of the windows of the metal dewar. The observations of the propagations of the beam were made in the horizontal direction perpendicular to the entering laser beam. Before the entering the dewars the beam could be focused with one of the lenses. In addition, the pattern of the radiation exiting the dewars was fixed and photographed at the screen with the plane perpendicular to the entering beam.

The spectra of the radiation emitted from the liquid nitrogen were registered by means of the spectrometer with the spectral resolution about 0.1 nm. The dynamics of the emission was registered by the photodiode and oscilloscope with the temporal resolution of about 1 ms. The dynamics of the patterns of the nitrogen emission was registered by the video camera with the temporal resolution of about 3 milliseconds.

3. Experimental results

During laser irradiation of liquid nitrogen in dewar with YAG:Nd pulsed laser (pulse duration 20 ns, average power 0.3 W) with the beam focused by the lenses in the both schemes of the irradiation we have revealed the bright emission of the liquid nitrogen in the visible spectral region. A bright white spot of the emission is seen clearly at the sub-surface region of the liquid. In the lower regions of the liquid the red color of the emission prevailed.

The spatial distributions of the emission were observed rather clearly when the laser beam entered the liquid nitrogen horizontally. The photos of these patterns are presented at Fig.1 and 3 (the beam propagates from the right side to the left).

In the situation presented at Fig.1 the laser beam was focused with the lens having the focal length of 7 cm. The focus point is placed at about 1/3 of the width of the picture from its right edge. Several features observed at this photo are as follows:

• Several small whitish spots are observed in the vicinity the focal point.
Figure 1. Luminescence of liquid nitrogen in glass dewar under horizontal irradiation of pulsed infrared laser. Laser beam goes from right to left.

Figure 2. The concentric series of the colored rings at the perpendicular projection of the emission exiting the dewar with liquid nitrogen.

• The reddish emission is seen clearly at the left side of the beam trajectory whereas the emission is not observed at the right side of the beam.
• The reddish emission at the left side has a form close to the narrow cone.

When we put a screen at the left side of the beam prolongation 5 cm apart from the exit of the beam from the dewar we observed that the cross-section of the visible radiation emitted from the liquid nitrogen looked like series of concentric circles corresponding to different wavelengths. Spectral analysis showed that in the center of this series the laser beam is situated with a wavelength of 1064 nm. Then the sequence of the rings from the center to the edge corresponds to the wavelengths of 852 nm, 711.7 nm, 610.9 nm, 610.3 nm and 534.7 nm respectively. The borders between these rings look like dark circles and can be seen clearly (Fig.2).

When we used the focusing lens with the focal length of 3.5 cm (instead of 7.0 cm in the
The study of the spectral composition of the radiation showed the presence of 5 narrow spectral lines with wavelengths at 852 nm, 711.7 nm, 610.9 nm, 610.3 nm, 534.7 nm, the accuracy of the measurements of the wavelengths is ±0.5 nm. Most notably, the half-width of these spectral lines is about 0.7 nm and the line broadening is quite small.

The measurements of the emission spectra of the bright flashes of the whitish spots appearing spontaneously in the trajectory of the laser beam showed that these spectra consist from several components: the broadened line of the emission of argon neutral atoms and of ionized argon atoms as well as the quasi-continuum plasma-like emission.

One more rather important experimental fact consists in the threshold-like and super-linear dependence of the light emission from liquid nitrogen on the intensity of the exciting laser irradiation. The nanosecond pulses do excite this emission whereas the millisecond pulses of the same wavelength and the same mean power do not. On the other hand, the dependence of the emission intensity on the excitation intensity is essentially super-linear and in the process of gradual decreasing of the excitation intensity the emission disappears abruptly below a certain
4. Discussion of the experimental results

The spatial and spectral distributions of the light emission from liquid nitrogen described above demonstrate several unusual features. First of all, the energies of the exciting photons (1.064 µm wavelength) are lower significantly than the energies of the emitted photons (say, for 534 nm emission line this deficiency is two times). At least two possible reasons of this deficiency are described in publications [14,15,16] – collapses of the bubbles of gaseous nitrogen produced by the intense laser irradiation and multiphoton excitation. The formation of the gaseous nitrogen bubbles during laser irradiation of liquid nitrogen manifests itself in the boiling-like behavior of the liquid nitrogen subjected to laser irradiation. Fig. 6 demonstrates the light scattering at the sphere from the gaseous nitrogen micro-bubbles in liquid nitrogen formed during its irradiation with the focused beam of continuous wave infrared CO$_2$ laser (the wavelength 10.6 µm, the optical power 70 W).

The bubbles formed in the liquid phase below its boiling temperature are non-equilibrium and should collapse. The difference of the internal energies between the gaseous and liquid phases is emitted partially via infrared or visible photons. When these non-equilibrium bubbles are formed by acoustical irradiation of liquids the light emission is called sono-luminescence [14]. In another case connected with the emission of photons during the fast structural transformation of materials from the phase with higher internal energy to the phase with lower energy is known as Perelman – Tatartchenko effect (PeTa-effect [15]). But, the spectral widths of the emission bands observed in the both of these cases are higher significantly than in our experiments. So, we assume that the excitation of the visible emission of liquid nitrogen excited by infrared lasers is produced by multi-photon mechanisms. Say, the emission lines presented at Figs. 4 and 5 can be excited by simultaneous absorption of two or three 1.064 µm photons [16]. The assumption about the multiphoton excitation explains the super-linear and threshold-like dependence of the liquid nitrogen emission. Moreover, it can be attributed to the explanation of the non-symmetrical distribution of the red emission along the laser beam (Figs.1 and 3). The red emission is observed at the left side from the focal point only. At the right side it is not observed, although the distributions of the exciting beam intensities before the focal region (the right side) and after it (the left side) should be symmetrical. The asymmetrical distribution of
Figure 6. Photograph of the formation of a structure of microbubbles in the form of a cloud at the site of incidence of the CW CO$_2$ 70W laser beam

the red emission manifests the necessity of achieving the threshold level of the exciting intensity for the start of the nitrogen emission. Naturally, this threshold level is achieved in the focal region first of all.

But the assumption about the multiphoton excitation is not sufficient for complete explanation of the spatial distribution of the emission concerning its narrow conical geometry and distinct separations of the cones corresponding to different emission lines (Fig.2). To resolve these problems, we attract the mechanisms of the Amplified Spontaneous Emission (ASE [17]) and of the filamentation of the intense laser beams propagating through optical refractive media [18]. ASE between two levels of any electron system appears when the density of excitations at the upper level becomes higher than the density at the lower level (the so called inverse distribution [17]). The filamentation occurs due to the positive feedback between the intensity of the light and non-homogeneity of the refraction index of the medium induced by this light. The phases of the electron excitations along this filament are determined by the propagating beam. If these excitations are transformed to the self-stimulated emission of the photons, the wave vectors of the emitted light waves should be in the spatial resonance with the double wave vector of the exciting photons. This means that due to the rule of conservation of the impulse the projections of the wave vectors of the emitted photons onto the axis of the exciting beam should be equal to the double wave vector of the exciting photons (for the two-photon excitation). So, the directions of the self-stimulated emissions of the separate spectral lines form discrete cone surface along the exciting beam. Due to the fact that the wave vectors of light waves are increasing with the decreasing of the wavelength the cones of the shorter lines are situated at bigger angles (Fig.2). This explanation of the conical emission observed in our experiments corresponds to the model of Cherenkov radiation excited in a certain substance by particles moving with the speeds higher than the speed of light in this substance [19].

The assumption of ASE explains the narrow spectral distributions of the emitted light and relatively small amount of the spectral lines observed in spite of the fact that the total amount of the emission lines of nitrogen molecules, atoms and ions is bigger significantly [20,21]. The self-stimulated emission (the so called super-luminescence) selects usually the most profitable ways of the radiative recombination.
Our preliminary studies of the spectral distributions of the white flashes emission show that these flashes are produced by the micro-inclusions of argon, which is present in ordinary air and in liquid nitrogen of the technical purity. In more detail the emission of impurities present in liquid nitrogen will be described later.

Conclusions

- We found the generation of the visible light emission in liquid nitrogen by nanosecond pulsed radiation of the infrared laser (the wavelength 1.064 \( \mu m \)). This generation is ascribed to the multiphoton excitation of nitrogen molecules and ions by the infrared radiation.

- This visible light emission of liquid nitrogen demonstrates several signs of the Amplified Spontaneous Emission: highly anisotropic spatial concentration of the emitted light flow around the direction of the exciting laser beam, the narrow widths of the spectral lines of the emission and severely limited amount of several spectral lines of the emission among rather a wide set of various possible channels of the radiative recombination of nitrogen, the super-linear dependence of the intensity of the emission on the intensity of the laser beam with the threshold intensity of the start of the emission.

- The visible light emission of liquid nitrogen is concentrated in the conical surfaces along the exciting beam having the general apex at the focal region of the laser beam. The cones corresponding to different wavelengths of the emitted light are separated clearly from each other following the rule of the phase synchronism: the projection of the wave vector of the emitted light onto the direction of the laser beam should be in resonance with the wave vector of the exciting radiation.

- The experimental results presented in this paper reveal liquid nitrogen as the flexible and convenient Kerr substance for generation of various non-linear optical phenomena by means of nanosecond lasers which usually are arranged only by means of femtosecond lasers.

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