

Extinction of radiation by aerosol formations from laser luminophors

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The contribution of luminescent aerosol from laser luminophors to the total extinction of sounding laser fluxes was investigated, and some practical applications of such aerosol formations are considered.

Radiation propagation in the atmospheric surface layer is accompanied by the radiation extinction due to absorption, reflection, and scattering by gases and aerosol particles. The contribution of the gas medium to radiation extinction can be taken into account using data on atmospheric transmission windows.^{1,2} The presence of aerosol formations (AF) in the surface atmosphere requires various data (aerosol particle size, number density, chemical composition, etc.) to be known to consider the contribution of such a medium to extinction of a radiation flux at its long-range transportation.

This paper considers the effect of luminescent conversion on the extinction of radiation transported through aerosol formations, whose particles are laser luminophors (LL) having metastable energy levels. The data concerning some features of the technologies for creation of artificial AF and LL as well as their effect on signal extinction are presented. A technique is proposed for determining the concentration and size spectrum of particles from the recorded intensities of luminescence from aerosols after their exposure to radiation from an external source. The possibility of creating standard LL samples (SS) with a preset concentration and size spectrum is discussed along with possible practical applications.

Transformation of radiation characteristics (intensity, spectrum, etc.) is determined by the properties of a medium, it propagates through, and attenuation of the radiation intensity is characterized by the Bouguer law.^{3,6} Scattering of radiation with the wavelength λ by aerosols with the particle radius R is characterized by the real part of the medium refractive index n . Thus, at $R \ll \lambda$ (Rayleigh approximation) light scattering by particles is low, while at $R \sim \lambda$ the scattering efficiency coefficient Q_{scat} , according to the Mie theory,⁵ does not exceed two. If $R \sim 1 \mu\text{m}$, $Q_{\text{scat}} \sim 2$ and $N \sim 10^3 \text{ cm}^{-3}$, then the extinction due to scattering along the path $Z \sim 1 \text{ km}$ is

$$X_{\text{scat}} \sim Q_{\text{scat}} \cdot 2\pi R^2 N \sim 10^{-5} \text{ cm}^{-1},$$

which corresponds to the extinction of $\exp(-6.3)$.

At $R \gg \lambda$, optical characteristics of aerosol particles and their number density should be taken into account, according to Ref. 3, by the equation

$$Q_{\text{ext}} = 2[1 - 2/q \sin q + 2/q^2 (1 - \cos q)],$$

and the extinction $X_{\text{ext}} \sim \pi R^2 / 4 Q_{\text{ext}} N$. Here $q = 2\Delta n \rho = 2|n_1 - n_2| \pi R / \lambda$, n_1 and n_2 are the refractive index of the aerosol and air; λ is the radiation wavelength; N is the number density of aerosol particles with the radius R .

Extinction of radiation due to scattering is proportional to the particle cross section. If the particulate matter is LL, then the interaction of radiation flux with AF is accompanied not only by scattering, but also by absorption and appearance of luminescence spectral conversion by the 3- or 4-level energy scheme (through metastable levels) with the Stokes shift to the longwave region. In this case, every aerosol particle luminesces emitting the radiation within the full 4π solid angle and it can be considered as a point source. The process of absorption of radiation by LL aerosol particle is accompanied by conversion of a part of radiation energy into heat (radiationless slow conversion channel) and spectral conversion (re-emission – fast conversion channel) leading to extinction of the incident flux along the direction of propagation. Figure 1 explains, schematically, the radiation extinction by a particle and shows the main mechanisms of light interaction with AF from LL.

The excited state of optically transparent aerosols (and LL aerosols as well) usually involves a large number of electronic, vibrational, and rotational energy states. Therefore, the spectrum of luminescence of liquid and solid particles is observed in a wide wavelength range: tens and even hundreds of nanometers.

Radiation extinction in LL AF due to luminescent conversion is characterized by the ratio of the radiation pulse duration t to the lifetime of the excited state of active centers τ . This process is more efficient at $T = t/\tau \leq 1$ (Refs. 3–7), when the radiation energy absorbed by the aerosol medium has enough time to convert into the luminescent radiation emitted by particles to full solid angle. It

is just this property that characterizes the efficiency of radiation extinction in LL AF along a preset propagation direction.

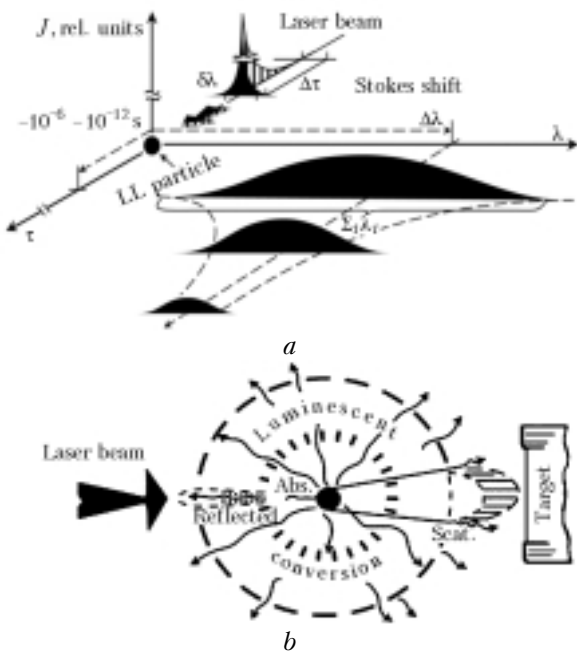


Fig. 1. Extinction of a laser signal by LL aerosol particle due to the luminescence spectral conversion in the full solid angle with Stokes shift to the longwave region (a); total extinction of sounding radiation by a target due to reflection, absorption, scattering, and luminescence conversion (b).

An experiment has been conducted to estimate the contribution of the luminescence conversion mechanism to total extinction of laser radiation at interaction with artificial LL AF (Fig. 2). A material for aerosols was a LiF alkali halide crystal (AHC) with and without color centers (CC). The lines of the laser emission used for remote sensing of the atmosphere are within their absorption bands.

A LiF crystal $\sim 2 \text{ cm}^3$ in volume was ground to powder. The fine fraction was separated with a mesh and the particle size ($R < 600 \mu\text{m}$) was determined with a microscope. A half of the powder was exposed to radiation from a gamma-ray source (dose of $10^5\text{--}10^7 \text{ rad}$) for production of various CC in aerosol particles.

Ruby ($\lambda \sim 0.69 \mu\text{m}$) and neodymium ($\lambda \sim 1.06 \mu\text{m}$) lasers operating in the free-running and repetitively pulsed modes were used in the experiment. To obtain the latter mode, LiF:F_2^{+-} modulators were placed in a laser cavity. This allowed us to obtain a series (from 40 to 10) of short (50–150 ns) pulses with a gap of 10–100 μs . In the experiments, we compared the amplitudes of the laser signal (normalized to the intensity of a reference signal) propagated through an aerosol cloud (2 cm long, 2 cm wide) consisting of unirradiated or γ -irradiated (having the corresponding CC) LiF particles. The experimental records depicted in Fig. 2b are indicative of the effect of LL AF on the total extinction of radiation due to luminescence conversion.

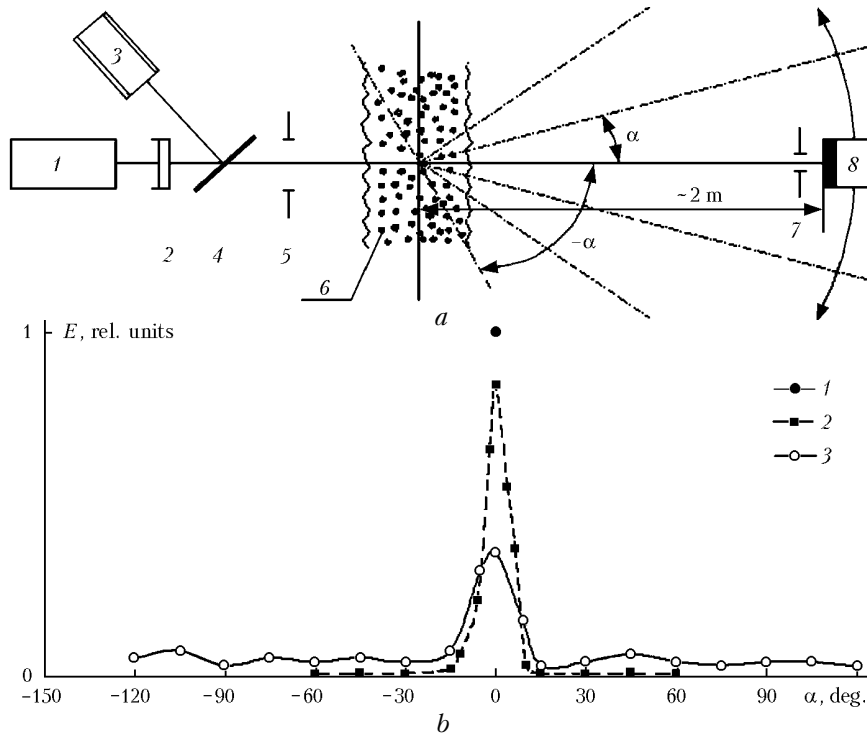


Fig. 2. Schematic of the experiment on studying the extinction of a laser signals by an ensemble of aerosol particles: laser 1, attenuator 2, reference receiver 3, beam splitter 4, diaphragms 5 and 7, aerosol formation 6, and a photodetector with a filter 8 (a); intensity of a laser signal and luminescence in dihedral angle (from 0 to 120°): no aerosol (1); unirradiated LiF particles (2); γ -irradiated LiF particles (3) (b).

Aerosols with LL properties can have natural origin being the result of interaction of seawater particles, industrial emissions, volcanic dust, and radioactive aerosols with electromagnetic and corpuscular fluxes of cosmic origin. Organic particles (for example, microorganisms) also can have the capability of fluorescing in the field of a light wave. Linear dimensions of aerosol formations can be large enough; therefore, even at low density of luminescent LL particles it is necessary to take into account their contribution to extinction of a laser signal.

Preparation of artificial LL AF and their practical applications

Media used as active media in liquid and solid-state tunable lasers fall in the class of LL with wide luminescence bands (tens to hundreds of nanometers). In the former case, organic dyes are dissolved in liquids with the given molar concentration. These solutions absorb UV and visible radiation and luminesce in the visible and near-IR regions. Organic dyes are readily assimilated by polymer solid-state matrices, which extend the feasibilities of creating multifunctional AFs. Another group of laser luminophors includes AHC with CC, metal ion doped oxide and fluoride crystals, as well as semiconductor compounds.

An LL aerosol particle with known physical, chemical, and optical characteristics after irradiation by an external source emits the radiation due to luminescence with the amplitude⁷:

$$J_1 = kN_1\tau h\nu\Omega \cdot 3/4 \pi R^3 \text{ [W]}$$

or

$$R = \sqrt[3]{V} = \sqrt[3]{J_1 \cdot 4 / 3\pi k N_1 \tau h\nu \Omega} \text{ [}\sqrt[3]{\text{W/cm}^3 \cdot \text{s}^{-1} \cdot \text{J} \cdot \text{s}^{-1}}\text{]},$$

where k is the LL quantum efficiency factor; N_1 is the number of active particles (ions, molecules, color centers, etc.) in the volume occupied by the aerosol particles $V = CA$ (C is the molar concentration; A is the Avogadro number); h is the Planck constant, τ is the lifetime of the LL excited state; R is the aerosol particle size; ν is the frequency of radiation within the luminescence spectrum; Ω is the solid angle of propagation of the luminescence.

An artificial LL AF can be prepared in the following way. A dosed amount ($C \sim 10^{-5}$ – 10^{-1} mole/l) of an organic dye, e.g., R6G, OX-17 is added to polyvinyl alcohol and a solution with the preset molar concentration of LL is prepared. A part of the solution is used to determine the optical and chemical characteristics: C , ν_λ , ν_1 , etc. The known (or recorded with a spectrophotometer) absorption spectrum ν_λ allows one to select a source for irradiation of the prepared medium in the peak of the absorption band and then to determine experimentally the luminescence spectrum using reference samples.

After determination of C , ν_λ , ν_1 and other characteristics, an aerosol formation is prepared. For this, a colloid solution colored with a dye is pulverized with an airstream atomizer and the aerosol particles produced are accumulated in a large-volume (tens of liters) sealed chamber. To accelerate the process of polymerization of polyvinyl alcohol, the pulverization zone is blown by warm air and irradiated by UV radiation of a mercury lamp. Liquid, atomized aerosol particles have near-spherical shape (due to the surface tension force), and, falling in the zone of UV irradiation, they quickly polymerize (depending on the particle diameter).

It was found experimentally that the time of polymerization (solidification) of the surface layer of particles with $R \leq 50 \mu\text{m}$ does not exceed 12–15 s. After preparation of an ensemble of aerosol particles, the calibration dependence of the luminescence signal amplitude on the particle size is determined. For this purpose, particles of different size are placed on the microscope slide and their mean diameters are determined. Then, particles are irradiated by an external source (e.g., $\lambda \sim 532 \text{ nm}$) with the controlled radiation intensity, the amplitude of the luminescence signals (within a fixed solid angle) is recorded with a PMT as a function of particle diameter, and the calibration curve is drawn (Fig. 3). It is linear and the tangent of its inclination angle depends on the molar concentration (concentration of active centers) of LL in the particle or the type of the dye used (the quantum efficiency k).

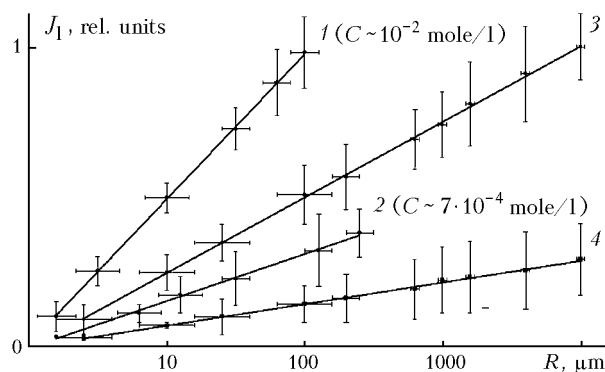


Fig. 3. Relative variation of the luminescence from laser luminophor aerosol particles as a function of particle size and LL molar concentration: OX-17 dye (1 and 2), for LiF:F_2^+ (3), for LiF:F_2^+ (the same particles after exposure UV radiation and hot air – the concentration of stable F_2^+ dye centers in LiF decreases due to radiative and thermal destruction) (4).

Similar AF can also be prepared from other classes of LL (e.g., AHC with CC), whose physical, chemical, and optical characteristics are well-known.⁸ For a more detail on handling the LL powders see Refs. 11, 12, and 14. It is possible to use LL with long lifetime of the excited state – the class of metal ion doped oxide or fluoride crystals,^{9,10} as well as semiconductor materials. It is a specific feature of solid-state LL matrices doped with metal ions that

their physical, chemical, and optical properties are constant, and this allows one to prepare artificial AF with stable characteristics from these materials.

In aerosol physics, a large number of problems involve determination of the concentration and size spectrum of particles. For obtaining reliable information on aerosol characteristics using some instrumental facilities, they should be properly tested and calibrated. This task is achieved by using standard samples (SS) made of monodisperse latexes $d \sim 1\text{--}10 \mu\text{m}$ on specialized aerosol generators (e.g., AG-1 [Ref. 13]). These latexes are small, and AF are prepared using the technique of atomization of a water suspension (water and latexes) in a gas flow through an atomizer, while calibration and testing are performed with the working standard of the particle number density¹³ in the range of $10^5\text{--}5 \cdot 10^8 \text{ m}^{-3}$. Instrumental facilities are tested only for the aerosol particles number density, while the size spectrum (dynamic range of a device) is determined numerically.

Consider the possibility of obtaining standard samples with the fixed values of concentration and particle size spectrum through the use of luminescent aerosol ensembles of LL. A technique and a laboratory setup for production of artificial aerosol ensembles of LL and recording of their calibration characteristics were proposed in Refs. 11 and 12. Using such a characteristic (see Fig. 3), one can pre-calibrate the channels of an amplitude analyzer (for example, AI-256) for any artificial LL AF. The signals recorded are normalized to the highest amplitude value, that is, to a particle of maximum size. Aerosol standard samples are certified using a system, resembling a sandglass in its shape and consisting of two spherical chambers (each up to several liters in volume) connected by a thin capillary channel (diameter $\sim 1 \text{ mm}$ and length up to 20 cm). This system is installed vertically, and the aerosol particles prepared are placed in the upper chamber. The particles move through the capillary from the upper chamber into the lower one under the effect of gravity in a slight airflow. The particles collected in the lower part of the capillary channel ($l \sim 1 \text{ mm}$) are irradiated. Luminescence from a particle is collected by a specialized optical system within a preset solid angle Ω and, after passage through an interference filter (polychromator), it is recorded with a photodetector. The signals are processed with an amplitude analyzer, each channel of which fixes the intensity of the luminescence signal (determined by the calibration curve), whose value is proportional to the size of the particle irradiated. The number of pulses counted in each analyzer's channel characterizes the size spectrum, while the total number of the amplitudes corresponds to the integral number density of particles in the prepared AF. Multiple repetition of this operation (alternation of the mutual position of the chambers to the opposite one) decreases the random errors and improves the reliability of certification of standard samples.

Another version of the SS preparation is the use of two-phase solutions, for example, solution of alcohol with the fine fraction of LiF:F₂ powder. The solution with suspended luminescent LiF:F₂ particles ($N \sim 10^1\text{--}10^4 \text{ cm}^{-3}$ and $d \leq 100 \mu\text{m}$) is pumped through a capillary (1–2 mm) and exposed to radiation of Ar⁺(488 nm) or Cu⁺(520 nm) lasers. Traversing the irradiation zone, LiF:F₂ particles absorb the pumping radiation and luminesce in the red spectral region. The amplitude of this reemitted radiation can be measured with a PMT after a polychromator. The intensity of luminescence proportional to the volume occupied by the particle is measured with an amplitude analyzer. With a cell consisting of two sealed chambers connected by a capillary and installed vertically or horizontally (in the latter case the liquid is pumped from one chamber to another by a pump), the particle size and the size spectrum can be determined as described above. By increasing the volume of solution (adding alcohol to the solution), one can obtain a two-phase solution, in which the specific number density of particles can vary within several orders of magnitude. This two-chamber cell containing a two-phase LL solution allows one to calibrate and test instruments, determine the efficiency of filters, etc.

The technique, whose basic principles are considered in Refs. 11 and 12 allows one to determine the total number of particles, their size, and the particle size distribution for any artificial LL AF, which can be stored in a sealed chamber and used in various applied problems, for example, as a standard sample for instrumentation calibration and testing, when checking the efficiency of fine filters, when studying turbulence in gases and liquids, etc. The practical usage of LL AF as elements of laser instrumentation has been already demonstrated^{14–17}: they were used as active media, passive modulators, soft apodizing diaphragms and luminescence transformers of radiation for matching the absorption spectra of active media and lamp sources of pump.

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