

Statistical modeling of transspectral processes in laser sensing of the environment. 2. Laser-induced fluorescence

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A new form of the transfer equations (TE) is proposed based on theoretical studies, strictly speaking, a system of TE describing the process of wide-band radiation transfer in disperse media. Within the limits of the Monte Carlo method, an algorithm has been developed for numerically solving the above-mentioned TE system, which allows one to calculate the spatiotemporal and spectral characteristics of laser-induced fluorescence (LIF) under boundary conditions corresponding to real experiments. Numerical estimates obtained demonstrate the efficiency of the proposed method and confirm the necessity of taking into account the background due to multiple scattering in systems with wide field-of-view receiving optics. Further studies will deal with the account of the phenomena of resonance energy transfer at spontaneous fluorescence in multicomponent systems.

Introduction

At present, one of the methods providing the current information on ecosystem disturbances is remote laser sensing. Traditional technique of laser sensing is based on interpretation of range-resolved return signal due to the elastic scattering of radiation in a medium at one or more frequencies of the optical range.¹ During the past decade a natural tendency has evolved toward using a wide range of linear and nonlinear processes (transspectral processes) resulting in re-emission by the medium sounded at other frequencies.^{2,3}

Spontaneous Raman scattering⁴⁻⁶ and laser-induced fluorescence^{6,7} are the most significant phenomena among the linear processes.

Certain prospects are related with the use of the Mandelstam-Brillouin molecular scattering⁸ and hyperrayleigh scattering.⁹ The Ring effect¹⁰ and resonance Raman scattering⁶ should be taken into account in systems of passive optical sensing including the operating orbital systems ENVISAT and so on. It was shown in Ref. 11 that the Raman lidar allows obtaining regular information about spatial distribution of the majority of the main atmospheric parameters necessary for the analysis and forecast the state of air up to the heights of cirrus clouds.

In this paper, we shall analyze peculiarities of statistical modeling in the problem of wide-band radiation transfer in natural disperse media due to the spontaneous fluorescence, specifically, laser-induced fluorescence (LIF).

1. Overview

The problem considered has recently taken on special significance because LIF, as an optical

phenomenon, makes a good basis for the development of means to remotely detect a wide range of molecular compounds in the environment, including hazardous ones.¹²

It should be noted that *in situ* methods of fluorescence spectroscopy have been successfully used in analytical photochemistry and photobiology for a long time. A detailed list of such studies (more than 500 papers) can be found in the review given in Ref. 13. The methods of fluorescence laser diagnostics have gained a wide range of applications in medical and biological studies.^{14,15} The first successful experiments on remote lidar sensing using wide-band LIF have been carried out in studies of chlorophyll and phytoplankton in the near-surface ocean layer.¹⁶⁻¹⁸

First attempts of using fluorescence techniques in diagnostics of biogenic aerosols in the troposphere failed.¹⁹ For this reason, the author of the known monography⁶ arrived at a conclusion about unpromising use of the fluorescent lidar for remote sensing of small aerosol and gas impurities in the atmosphere as a complex multicomponent medium in view of high fluorescence quenching rate and relatively small sections of absorption.

The quenching processes are insignificant in the mesosphere and the methods of resonance fluorescence appeared efficient in application to monitoring concentration of OH radicals and metal vapor (K, Na, Mg, Fe).²⁰⁻²² However, use of new femtosecond laser sources^{22,23} in remote sensing and a new LIF stimulation procedure^{24,25} opened new opportunities for fluorescence lidars in optical investigations of the atmosphere.²⁶ The most fruitful field for application of the fluorescence lidars (FLIDAR in English transcription) is the monitoring of vegetation of the planet, which contains a broad

complex of active fluorophors responding to the metabolism processes.^{27,28}

Realization of effective remote methods for detection and identification of biogenic aerosols dangerous for people (spores, bacteria, viruses, etc.) has become an extremely urgent problem in recent years. According to the *in situ* laboratory measurements,^{29,30} LIF provides the highest sensitivity as compared to other methods. The lidar measurements under real atmospheric conditions are restricted yet by extremely short paths.^{31,32} These restrictions are connected not only with low spectral LIF intensity, but also with difficulties in correct interpretation of the obtained LIF spectra. The matter is that LIF spectra of proteins and even of living microorganisms often have a similar nature. Spectra in dense ground atmosphere are very broad and have no specific features. Moreover, at extended atmospheric paths, for instance, in helicopter sensing system,³³ LIF spectra have a tendency toward distortion and smoothing due to the interference and multiple scattering in the ambient natural aerosol. Technically, one can overcome these difficulties using the «pump-and-probe»-method,^{24,25} multispectral fluorescence,³⁴ multiphoton LIF,³⁵ fluorescence saturation effect,³⁶ and the high-frequency amplitude modulation of LIF.³⁷

Methodically, good prospects are connected with application of artificial neural network algorithms.^{38,39} However, the accuracy of classification and the desired pattern recognition (fluorophors)³⁸ appreciably depends on the errors in the information processed. The noise level of input data (LIF spectra) with a 3%-noise essentially worsens the result, and at 10%-error the results lose their uniqueness. For this reason, an attempt was made to estimate quantitatively the limits of possible standard spectra transformation of wide-band LIF under conditions of real atmospheric sensing paths. The estimation has been carried out on the basis of unsteady transfer equation by the Monte Carlo method.

2. Radiative transfer equation in the case of a wide-band radiation

In publications, there is no systematic description of the wide-band radiation transfer through the atmosphere formed by inelastic processes such as Raman scattering and fluorescence. Therefore, below we should briefly state the physical grounds of our approach and carry out a certain modification of the initial transfer equations for the short-wave radiation. As earlier,¹¹ we shall follow the phenomenological approach,^{6,40} whose fundamentals are in assumption that luminous energy is absorbed or elastically scattered in a dispersion medium. The absorbed fraction of luminous energy proportional to a certain absorption coefficient α , is converted into heat energy, the rest fraction is elastically scattered without energy loss. When there are fluorophors in the medium, a fraction of the absorbed energy is

reemitted as fluorescence for the second time. The fluorescence intensity depends on the intensity I_λ of incident radiation and many other parameters, including optical properties of the medium for a broad set of λ . The radiation transfer theory in a broad energy spectrum has been successfully developed in the neutronics.^{42,43,55}

The one-dimensional scalar transfer equation for solar radiation including the processes of *inelastic scattering* was stated for the first time in studies in Refs. 52 and 53. Note that in the above-mentioned studies, spontaneous fluorescence is treated as a process of inelastic scattering. In modern representations,^{47,54} the fluorescence is considered as a two-stage process: first a photon with wavelength λ is absorbed and then secondary emission at $\lambda' > \lambda$ takes place.

According to Ref. 47, let us write the stationary transfer equation in a scalar form including the basic transspectral processes:

$$\begin{aligned} & [\cos \vartheta \frac{d}{dz} + \sigma(\lambda)] I(\lambda, z, \mathbf{\Omega}) = \\ & = \frac{1}{4\pi} \int_{\mathbf{\Omega}'} G_M(\lambda, \mathbf{\Omega}', \mathbf{\Omega}) I(\lambda, z, \mathbf{\Omega}') d\mathbf{\Omega}' + \\ & + \frac{1}{4\pi} \sum_{i=R,F} \int_{\lambda' < \lambda} \int_{\mathbf{\Omega}'} G_i(\lambda', \mathbf{\Omega}', \mathbf{\Omega}) I(\lambda', z, \mathbf{\Omega}') d\mathbf{\Omega}' d\lambda', \quad (1) \end{aligned}$$

where $I(\lambda, z, \mathbf{\Omega})$ is the radiation intensity at wavelength λ at the point $\mathbf{r}(0, 0, z)$ for $\mathbf{\Omega}$; $G_M(\lambda, \mathbf{\Omega}', \mathbf{\Omega})$ is the volume coefficient of directed elastic light scattering, basically, the Mie-scattering;

$$G_i = G_R(\lambda', \mathbf{\Omega}', \mathbf{\Omega}) + G_F(\lambda', \mathbf{\Omega}', \mathbf{\Omega});$$

$G_R(\lambda', \mathbf{\Omega}', \mathbf{\Omega})$ is the volume coefficient of directed Raman scattering at λ' ; $G_F(\lambda', \mathbf{\Omega}', \mathbf{\Omega})$ is the coefficient of directed spontaneous fluorescence emission, $\sigma(\lambda)$ is the total extinction coefficient at λ , i.e.,

$$\sigma(\lambda) = \alpha(\lambda) + \sigma_S(\lambda). \quad (2)$$

Here $\alpha(\lambda) = \alpha_M(\lambda) + \alpha_F(\lambda)$, α_M is the absorption coefficient of the medium particles due to the heat dissipation, $\alpha_F(\lambda)$ is the absorption by the fluorophors, $\sigma_S(\lambda) = \sigma_M(\lambda) + \sigma_R(\lambda)$, $\sigma_M(\lambda)$ and $\sigma_R(\lambda)$ are the coefficients of elastic and inelastic (Raman) scattering. Usually (in a scalar case), G_M and G_R depend only on the scattering angle ϑ between the vectors $\mathbf{\Omega}'$ and $\mathbf{\Omega}$, i.e., on $\cos \vartheta = (\mathbf{\Omega}' \cdot \mathbf{\Omega})$.

In representing the total intensity as a sum of contributions due to elastic E and inelastic R and F scattering

$$I(\lambda, z, \mathbf{\Omega}) = I^E(\lambda, z, \mathbf{\Omega}) + \sum_{i=R,F} I^i(\lambda, z, \mathbf{\Omega}) \quad (3)$$

and introducing the operator

$$\hat{L}_\phi = \left[\cos\theta \frac{d}{dz} + \sigma - \frac{\sigma_S}{4\pi} \int G_M(\lambda, \mathbf{\Omega}', \mathbf{\Omega}) d\mathbf{\Omega}' \right] \phi, \quad (4)$$

the authors of Ref. 47 divide the transfer equation (1) into the system of equations for I^E and I^i :

$$\hat{L}I^E(\lambda, z, \mathbf{\Omega}) = 0, \quad (5)$$

$$\hat{L}I^i(\lambda, z, \mathbf{\Omega}) = \frac{1}{4\pi} \int_{\lambda' < \lambda} G_i(\lambda', \mathbf{\Omega}', \mathbf{\Omega}) I^i(\lambda', z, \mathbf{\Omega}') d\mathbf{\Omega}' d\lambda'. \quad (6)$$

Then Eqs. (5) and (6) are solved independently in the approximation of the so-called *transfer phase function*.⁵⁵ The obtained analytical estimations are of a special interest in the problems of spectral radiation balance in a turbid medium under conditions of natural illumination (sun, daylight sky background). However, Eqs. (1) and (6) are not informative in laser sensing of the environment using the LIF phenomenon, since they take into account the contribution of transspectral processes only in the short-wave spectral region $\lambda' < \lambda$, where λ is the wavelength, for which the solution of Eq. (1) is sought. In the case of a medium illumination by laser radiation, the secondary spontaneous fluorescence emission is found in the alternative region $\lambda' > \lambda$, since all the spontaneous processes are connected with photon energy dissipation. Figure 1 presents the spectra of absorption and fluorescence for a typical secondary plant metabolite.⁶²

Obviously, the spectral region of fluorescence is appreciably shifted to the long-wave spectral region and its contribution to the integrated expression (6) will be practically equal to zero

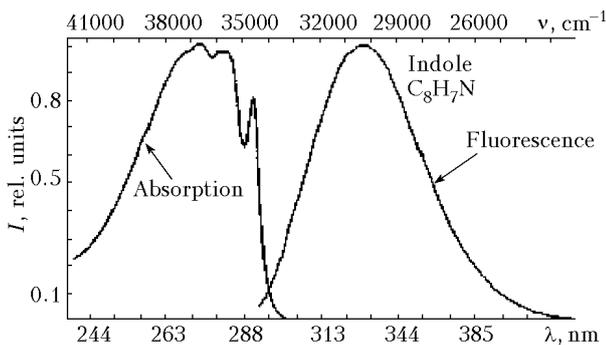


Fig. 1. Absorption and fluorescence spectra of indole excited at $\lambda = 266$ nm (Ref. 2).

Recent study⁵⁴ has demonstrated the potentialities of using a wide-band LIF of the organic matter dissolved in seawater in the spectral region $\Lambda = 355\text{--}600$ nm in the scheme of airborne lidar sensing of the near-surface ocean layer. The technique proposed assumes the approximate solution of two systems of equations (6) for $\lambda^{12} \in \Lambda$. Equation (5) for $\lambda = 355$ nm remains unused. Such an approach

needs for a more detailed mathematical substantiation, since solution of the transfer equation just for the elastic scattering describes the time-space distribution of fluorescence centers, probability and the level of their intensity. The concept of formal division of the wide-band radiation transfer into parts proposed in Ref. 47 is fruitful.

The Monte Carlo method,^{11,15,41–44,48} allows stating the problem more strictly excluding a series of simplified propositions.^{47,52–54} First, propagation of a short lidar signal at wavelengths of LIF excitation will be described by *unsteady* transfer equation in a 3D space:

$$c^{-1} \frac{\partial I(\mathbf{r}, \mathbf{\Omega}, t)}{\partial t} + \mathbf{\Omega} \nabla I(\mathbf{r}, \mathbf{\Omega}, t) = -\sigma(\mathbf{r}, \lambda) I(\mathbf{r}, \mathbf{\Omega}, t) + \frac{1}{4\pi} \int_{4\pi} G_M(\mathbf{r}, \mathbf{\Omega}', \mathbf{\Omega}) I(\mathbf{r}, \mathbf{\Omega}', t) d\mathbf{\Omega}' + \Phi_0(\mathbf{r}, t), \quad (7)$$

where $\Phi_0(\mathbf{r}, t)$ is the external source function.

Spectral intensity I_F of the subsequent fluorescence at $\lambda' \in \Lambda$ (Λ is the emission spectrum region) will satisfy the equation

$$c^{-1} \frac{\partial I_F(\mathbf{r}, \mathbf{\Omega}, \tau, \lambda')}{\partial \tau} + \mathbf{\Omega} \nabla I_F(\mathbf{r}, \mathbf{\Omega}, \tau, \lambda') = -[\sigma_M(\mathbf{r}, \lambda') + \alpha(\mathbf{r}, \lambda')] I(\mathbf{r}, \mathbf{\Omega}, t) + \frac{1}{4\pi} \int_{4\pi} G_M(\mathbf{r}, \mathbf{\Omega}', \mathbf{\Omega}) I(\mathbf{r}, \mathbf{\Omega}', t) d\mathbf{\Omega}' + \Phi_{L_0}(\mathbf{r}, \tau, \lambda, \lambda'), \quad (8)$$

where

$$\Phi_{L_0}(\mathbf{r}, \tau, \lambda, \lambda') = \frac{1}{4\pi} \phi(\lambda') \alpha_F(\lambda) q(\tau) \int_{4\pi} I(\mathbf{r}, \mathbf{\Omega}, \tau, \lambda) d\mathbf{\Omega}$$

is the function of external LIF sources distributed over the medium volume. According to Refs. 57 and 60, it will depend on the exciting radiation intensity, absorption cross section, quantum efficiency (quantum yield) of the fluorescence $\phi(\lambda')$, and quenching factor $q(\tau)$.

The system of Eqs. (7) and (8) is solved further by the Monte Carlo method. Photons from the external source (laser) go into the disperse medium according to the initial density $\Phi_0(\mathbf{r}, t)$.

3. Specific features of statistical modeling

The first phase of statistical modeling is in realization of the Markovian chain of random events adjusted by the kernel (7) in the generalized integral form (see below). In every next random interaction of the photon with a discrete medium center (molecule, particle) its energy can be scattered or absorbed. The following probability chain is possible:

a) scattering probability:

$$P_s(\lambda) = [\sigma_M(\mathbf{r}, \lambda) + \sigma_R(\mathbf{r}, \lambda)]/\sigma(\mathbf{r}, \lambda), \quad (9)$$

b) absorption probability:

$$P_a(\lambda) = [\alpha_M(\mathbf{r}, \lambda) + \alpha_F(\mathbf{r}, \lambda)]/\sigma(\mathbf{r}, \lambda), \quad (10)$$

c) probability of absorption by a fluorophor:

$$P_{cf}(\lambda) = \alpha_F(\mathbf{r}, \lambda)/\sigma(\mathbf{r}, \lambda), \quad (11)$$

d) reemission probability:

$$P_r = \phi(\lambda, \lambda')\alpha_F(\mathbf{r}, \lambda)/\sigma(\mathbf{r}, \lambda). \quad (12)$$

As soon as the “d” event occurs, the wandering process with elastic scattering at λ ceases.

The primary photon is absorbed, and in a certain time interval τ_p the secondary photon is emitted, as a rule, with lower energy at $\lambda' > \lambda$. Its subsequent interaction with medium will take place according to Eq. (8). A new wavelength is chosen on the basis of fluorescence spectrum, which represents the distribution function over frequencies $Y(v, v')$. It obviously should satisfy the normalization condition

$$\int_0^\infty Y(v, v') dv' = 1. \quad (13)$$

For the resonance fluorescence, the shape of the function $Y(v, v')$ has been studied in detail in Refs. 56 and 58 and is described, as a rule, by simple analytical expressions. The most common are the Doppler, Lorenz, and Voigt contours. The first spectral flux estimations for the Doppler profile have been by the Monte Carlo method in Refs. 58 and 59. In our paper,⁵⁹ the Doppler spectrum was used in the generalized form, which allows one to take into account the dependence on scattering angle in each interaction:

$$W(x_1, x_2, \mu) = \frac{C}{\sqrt{1-\mu^2}} \exp\left[-\frac{x_1^2 + x_2^2 - 2x_1x_2\mu}{1-\mu^2}\right], \quad (14)$$

where

$$x_1 = (v_0 - v_1)/\Delta v_d, \quad x_2 = (v_0 - v_2)/\Delta v_d;$$

v_1 and v_2 are the frequencies of incident and re-emitted photons, v_0 is the frequency of the exciting laser radiation; Δv_d is the Doppler spectrum half-width, μ is the cosine of the scattering angle, C is the normalization constant.

The spectrum of spontaneous LIF can have a rather complicated shape. There were attempts for the Raman spectra representation as a superposition of Gaussian distributions^{46,60}:

$$Y(v, v') = \frac{1}{\sqrt{2\pi} \sum_{i=1}^4 \alpha_i \delta_i} \sum_{i=1}^4 \alpha_i \exp\left[-\frac{(v' - v - \Delta v_i)^2}{2\delta_i^2}\right], \quad (15)$$

where α_i , δ_i , and Δv_i are the fitting factors.

In practice, the procedure (15) is rather cumbersome and ineffective in simulating the complicated LIF spectra. The function $q(\tau)$, entering into the transfer equation for LIF (8), specifies the time of fluorescence quenching. The best-known model of dipole resonance energy transfer was developed by Forster⁶¹ in 1948. It is based on assumption that medium contains arbitrarily distributed molecules of two types: donors and acceptors, each molecule has its own kinetics of fluorescence damping.

Analytically, it leads to the so-called law of the “extended” exponential curve⁴⁹:

$$q(\tau) = \frac{1}{\tau_d} \exp\left(-\frac{\tau_p}{\tau_d}\right) + \frac{1}{\tau_d} \exp\left[\xi \left(\frac{\tau_p}{\tau_d}\right)^{1/2}\right], \quad (16)$$

where τ_d is the mean lifetime of the donor's excited state; $\xi(N_a)$ is the parameter connected with concentration of acceptor molecules N_a , diffusion motion characteristics, and with other system and physical properties of the medium. The first term in Eq. (16) characterizes spontaneous emission of donors, the second one of acceptors. If the mean distance between the fluorophor molecules is larger than the so-called Forster radius,⁶¹ one can neglect the effect of fluorescence energy transfer. In particular, this condition is always satisfied in atmospheric problems and relation (16) is used in the abridged form without the second term.

By the wide-band radiation, we understand the secondary emission of metabolites caused by the effects of inelastic photon interaction with material medium, and not the laser radiation spectrum.

A set of transfer equations (7) and (8) is written in scalar approximation, i.e., ignoring the polarization effects. Nevertheless, its strict analytical solution has not been obtained yet. The Monte Carlo method⁴¹ is the most rational among the numerical methods. Although, the given method does not require the strictly written transfer equation,⁴² formation of the effective weighting algorithms of the method⁴³ is based on transformations of the integral transfer equation adequate to the initial problem. The transfer equation containing the spectral dependence of the estimated functionals is rearranged into the integral form,⁴³ where it conserves its canonical form of the Fredholm equation of the second kind:

$$f(x) = \int_X k(x', x) f(x') dx' + \psi(x), \quad (17)$$

where

$$X = \{(\mathbf{r}, \boldsymbol{\Omega}, t, \lambda) : \mathbf{r} \in Q \subset R^3; \\ \boldsymbol{\Omega} \in W = \{(a, b, c) \in R^3 : a^2 + b^2 + c^2 = 1\}, t \in T, \lambda \in \Lambda\},$$

or $X = Q \times W \times T \times \Lambda$ is the eight dimensional phase space, or

$$f = Kf + \psi, \quad (18)$$

$$f(x) = \sigma(x)I(x) \quad (19)$$

denotes the photon collision density. Further, in Eq. (17)

$$k(x', x) = \frac{w(\mathbf{r}', \lambda)g(\mu, \mathbf{r}', \lambda)\exp[-\tau(\mathbf{r}', \mathbf{r}, \lambda)]}{2\pi|\mathbf{r} - \mathbf{r}'|} \times \\ \times \delta(\Omega - \frac{\mathbf{r} - \mathbf{r}'}{|\mathbf{r} - \mathbf{r}'|}) \delta\left[t' - (t + \frac{|\mathbf{r}' - \mathbf{r}|}{c})\right], \quad (20)$$

where

$$w(\mathbf{r}', \lambda) = [\sigma_S(\mathbf{r}', \lambda) + \sigma_R(\mathbf{r}', \lambda \rightarrow \lambda')] / \sigma(\mathbf{r}', \lambda)$$

is the probability of a quantum survival, and

$$g(\mu, \mathbf{r}', \lambda) = \frac{\sigma_S(\mathbf{r}', \lambda)g_M(\mu, \mathbf{r}', \lambda) + \sigma_R(\mathbf{r}', \lambda)g_R(\mu, \mathbf{r}', \lambda)}{\sigma(\mathbf{r}', \lambda)}$$

is the weighted mean scattering phase function, $\mu = \cos(\theta)$, g_M and g_R are the scattering phase functions of the elastic and inelastic scattering normalized to unity

$$\tau(\mathbf{r}', \mathbf{r}; \lambda) = \int_0^l \sigma(\lambda, \mathbf{r}, l') dl'$$

is the optical length of the segment $l = |\mathbf{r}' - \mathbf{r}|$; c is the speed of light,

$$\psi(x) = p(\mathbf{r}_0)p(\Omega_0)p(t_0)p(\lambda_0)$$

is the multiplicative density of the external sources, $p(m_0)$ are the partial densities of the corresponding initial coordinates m_0 , it is natural that

$$\int_R p(m_0) dm = 1.$$

The Monte Carlo method rationality is in that it enables one to obtain estimations of both radiation fluxes and the linear functionals

$$I_\lambda = (f, \varphi) = \int_{D \subset X} f(x)\varphi(x) dx \quad (21)$$

over a preset region of phase space $D \subset X$ ($\varphi(x)$ is the characteristic function). Integration by the parts in Eq. (21) is realized in the course of simulation that essentially optimizes the computation process. The index subscript λ in Eq. (21) shows that spectral behavior of the backward scattering signal in the region of the hypothetical detector is of a special interest in the given problem. It is impossible to track insignificant variations of δI_λ over the range of narrow Raman scattering spectrum,¹¹ in the analog simulation scheme. In this case, one of the weighting methods connected with correlated sampling (method of depended testing) appears effective.²² The

secondary spectrum of spontaneous fluorescence is broad enough, and the correlated sample procedure becomes irrational. Henceforth, for simulation of the redistribution function entering into Eq. (13) in frequencies $Y(v, v')$, the canonical method of inverse functions⁴² is used in the tabular form.⁴⁷

One of the weighting methods, for instance, "analytical averaging",⁴² is used for realization of the discrete probability chain (9)–(12). It is assumed that in the process of random migration, the photon of the fundamental excitation wave at λ is always scattered on a particle or a molecule, and its statistical weight $\omega_n(\lambda)$ is reduced by $w(\lambda)$ in n th collision, i.e.,

$$\omega_n(\lambda) = \omega_{n-1}(\lambda)w(\lambda), \quad \omega_0 = 1. \quad (22)$$

The fraction $[1 - w(\lambda)]\omega_{n-1}(\lambda)$ of this weight remains in the medium as absorbed energy. According to Eq. (12), a photon absorbed by a molecule has the re-emission probability at the fluorescence wavelength λ' in the range of $Y(\lambda, \lambda')$. This probability is determined by the quantum yield $\phi(\lambda, \lambda')$. Correspondingly, the weight of fluorescence photon is

$$\omega_n(\lambda') = \omega_{n-1}(\lambda)[1 - w(\lambda)]\phi(\lambda, \lambda'). \quad (23)$$

With no available data on the spectral dependence $\phi(\lambda, \lambda')$ for the fluorophors selected in estimate calculations, but taking into account that this dependence is insignificant,⁵⁷ it is assumed that for the case of secondary metabolites $\phi(\lambda, \lambda') = \phi = \text{const} \approx 0.01 - 0.05$.

Generally speaking angular scattering of the fluorescence photons is anisotropic, especially, when the fluorophor molecules are inclusions into the material of aerosol particles.⁵⁰ However, since this anisotropy is weak in the approximation of scalar transfer equation, one can neglect it at the first stage of calculations. The secondary excitation of fluorescence does not take place at λ' . The following random migration of the photon occurs only due to elastic collisions. When the photon escapes the scattering medium, we return to the branching point and the process is recycled. The trajectory is broken when the photon at the excitation wavelength λ escapes the medium.

According to Ref. 57, spontaneous LIF is characterized by the finite decay time that leads to the increase of the photon free path l_n at each collision accompanied by the fluorescence in the scheme of statistical modeling. Ignoring the Forster effect,⁶¹ the formula (16) assumes direct conversion

$$l_n = c\tau \ln(1 - \alpha_n), \quad n = 1, 2, \dots, \quad (24)$$

where $\alpha_n \in [0, 1]$ is homogeneous.

Also, small phase volume of the detection region D of LIF and elastic scattering signals requires the use of the method of flux local estimation, whose

efficiency has been demonstrated many times, see, e.g., Refs. 11, 41, and 45.

The intensity of the fluorescence lidar return at the detector D is estimated using the statistical modeling as follows

$$I_{i,k}(\lambda) = 1/c\Delta t_k \int_{\Delta r^*} \int_{\Delta \Omega_i^*} \int_{\Delta t_k} I(\mathbf{r}, \boldsymbol{\Omega}, t, \lambda) d\mathbf{r} d\boldsymbol{\Omega} dt. \quad (25)$$

The detector is set by the set of field-of-view angles $\Delta \Omega_i^* = \sin \vartheta_i^i d\vartheta d\varphi$, space volume $\Delta r^* = \pi R_d^2$, and the time resolution grid $\Delta t_k = \Delta t_k c$.

4. Results of model estimates

The results of model estimates and their physical analysis will be presented completely in subsequent papers as well as the problems on identification of LIF spectra under conditions of active atmospheric disturbances based on the method of artificial neuron networks (ANN).

In order to illustrate the functionality of the Monte Carlo method algorithm proposed, let us give a calculation example connected with estimation of possible distortions of the fluorescence spectrum in one of the most significant secondary metabolites, 1H-Indole (indole).⁵¹ The indole is manifested in deciduous and herbaceous plants getting into the stressed state under the external action of a series of the chemically aggressive substances. Besides, the indole effectively fluoresces at excitation by the fourth harmonic of a Nd:YAG laser radiation at $\lambda_i = 266$ nm.

The detector parameters and other boundary conditions determining the region of required functionals (25) correspond to the real fluorescence lidar that is being operated at the Laboratory of lidar methods (IAO SB RAS) except for the estimations supplemented with results for the wide-angle

reception typical for the fluorescence lidar with a spectral device in the optical receiver. Traditional optical characteristics of the atmosphere, i.e., the coefficients of optical interaction effects in the medium and scattering phase matrices are preset on the basis of known optical models.⁴⁶

Figure 2 presents the spatially resolved LIF spectra calculated for the haze model $\sigma = 0.005 \text{ m}^{-1}$ containing the isotropically distributed fluorescence centers.

The spectral transformation (see Fig. 2) reflects the relative growth of the intensity in the short-wave part of the fluorescence spectrum ("the spectrum shift to the blue"). Transformation is the consequence of elastic multiple scattering of fluorescence radiation with increasing field-of-view angle of the detector: $\varphi_d = 0.001, 0.01745, \text{ and } 0.087$ rad. The depth from which the signal comes is specified by the curve numbers (1–6), being correspondingly 50, 100, 150, 200, 250, and 300 m. It should be noted that the curve maximum appeared in the short-wave part of the spectrum in Fig. 2c is completely caused by the multiple scattering signal and bears no useful information about the LIF spectrum. It makes considering the prospects of wide-angle systems of optical detection in lidar systems with caution.

Having in mind the use of ANN mathematical apparatus, in further studies we have reduced all the spectral curves in Fig. 2 to the probability density form, i.e., numerically normalized to unity. It also allows estimating visually the qualitative spectral transformation irrespective of the penetration depth of the lidar beam.

Acknowledgements

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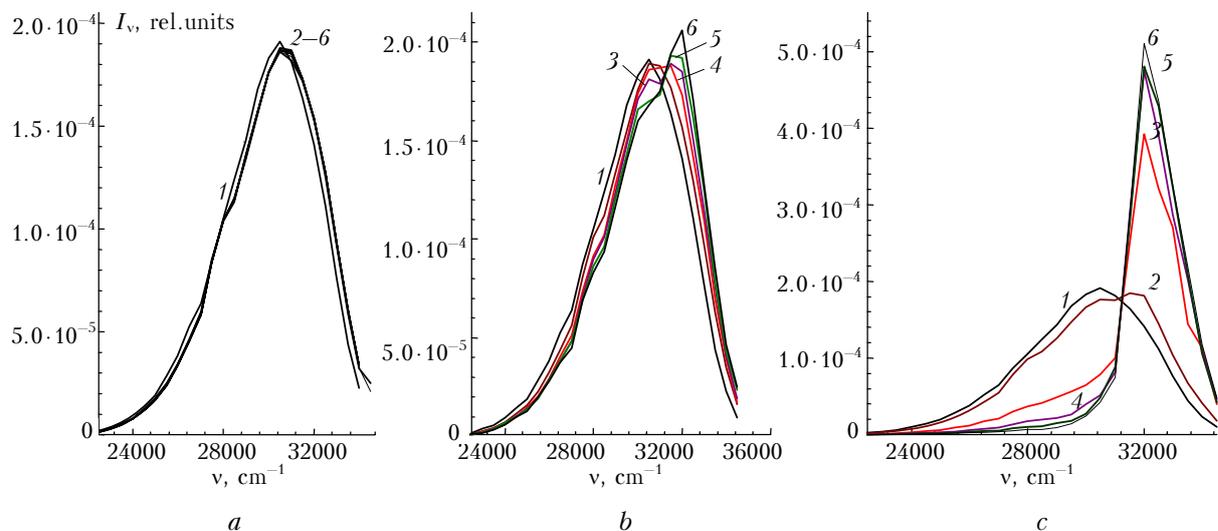


Fig. 2. Spatially resolved LIF spectra of indole: $\varphi_d = 0.001$ (a), 0.01745 (b), 0.087 rad (c).

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