

Mathematical model of a two-stage process of laser fragmentation of nitrocompound molecules and subsequent laser-induced fluorescence of characteristic fragments

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ABSTRACT

The paper presents a mathematical model describing the kinetics of the two-stage process of laser fragmentation of vapors of nitrocompounds and subsequent nitric oxide (NO-fragments) laser-induced fluorescence. The use of the developed model in the lidar equation for the case of fluorescent objects allows to calculate the expected value of the lidar signal for a particular nitrocompound on the basis of spectroscopic information about the object of detection, parameters of the radiation propagation medium, and transceiver equipment parameters.

Keywords: nitrocompounds, laser fragmentation, laser-induced fluorescence.

The method of laser fragmentation/laser-induced fluorescence (LF / LIF) has a long history [1], but today it does not lose its attraction for the detection of very low concentrations of substances in the atmosphere, for example, the vapors of nitrocompounds (NC) [2-5].

The method of laser-induced fluorescence (LIF) is known for its high sensitivity, which makes it possible to detect the trace amounts of substances, and even the individual molecules. However, this method is not applicable for the detection of complex polyatomic molecules due to the high probability of non-radiative relaxation, characteristic of systems with many degrees of freedom. Application of the laser fragmentation together with LIF method can solve this problem and reduce the problem of detection of complex molecular compounds to the problem of finding the more simple molecules, whose spectroscopic properties are well studied and that have well pronounced resonances. The essence of the LF / LIF method is to dissociation the complex molecules into fragments by quanta of laser radiation with following resonant excitation of the laser-induced fluorescence of characteristic fragments.

To provide high noise stability of the method for detecting vapors of nitrocompounds in the real atmosphere, a method was proposed for the excitation of LIF of characteristic NO-fragments from the second vibrational level of the ground electronic state [1].

This approach is considered in this paper in description of the mathematical model of a two-stage process of LF/LIF.

The mechanism of laser fragmentation of NC-vapors followed by the excitation of the laser-induced fluorescence of NO-fragments can be conventionally represented as a series of transitions in the simplified diagram of energy levels of the NC-molecule and its main fragments - molecules of NO and NO₂ (Fig. 1).

The NC and NO₂ molecules are considered as simple two-level systems, where the lower level is a ground state (the E_0 and E_5 levels), the top level is the dissociative state (the E_1 and E_6 levels). The energy gap between the levels is conventionally taken to be equal to the quantum energy of the laser radiation with a wavelength of 247.87 nm.

The proposed model takes into account that the sensitivity of this detection method is limited by the atmospheric (background) nitrogen dioxide NO₂ that becomes a source of "false» NO-fragments in the process of laser fragmentation. In the diagram, the molecule of a background NO₂ is also presented in the form of a two-level system.

The structure of energy levels of an NO-fragment is represented as three vibrational levels ($v'' = 0, 1, \text{ and } 2$) of the ground state ($X^2\Pi$) and a vibrational level ($v' = 0$) of the first electron excited state ($A^2\Sigma^+$). The designations of the corresponding levels are given in the diagram.

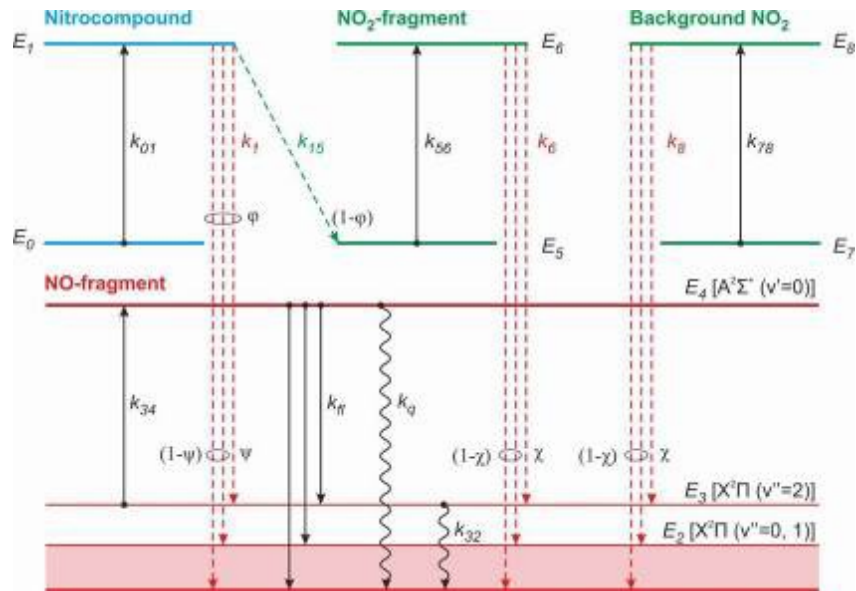


Fig. 1. Diagram of transitions in a two-stage process of LF / LIF

Absorbing a photon, an NC molecule transits from the ground state to the dissociative state E_1 with the absorption rate constant

$$k_{01} = \sigma_{fr} F. \tag{1}$$

Here σ_{fr} is the cross-section of absorption (fragmentation) of the NC molecule and F is the photon flux density in a laser pulse.

From the excited state E_1 , the NC-molecule is dissociated into fragments NO and NO_2 with the rate constants k_1 and k_{15} , respectively. We denote the fraction of NO-fragments in the total number of fragments with the constant φ . Then, the fraction of NO_2 -fragments is equal to $(1 - \varphi)$.

As a result of absorption of the laser radiation quantum, NO_2 -fragments transit from the ground state E_5 to an excited state E_6 with the absorption rate constant

$$k_{56} = \sigma_{NO_2} F, \tag{2}$$

where σ_{NO_2} is the absorption cross section of the NO_2 molecule at the wavelength of the laser radiation.

The photon energy of the laser radiation is much greater than the energy of the NO-O bond breaking. Therefore, if NO_2 -fragments transit into an excited state, they dissociate with the formation of NO-fragments. The quantum yield of the photodissociation is taken to be one. The dissociation rate constant of NO_2 -fragments is designated as k_6 .

The third channel for the formation of NO-fragments, along with the considered ones, is the photodissociation of the background nitrogen dioxide as a result of absorption of laser radiation (the transition $E_7 - E_8$). The rate constants of the absorption and photodissociation are marked as k_{78} and k_8 , respectively.

Populations of vibrational levels of NO-fragments formed as a result of dissociation differ from the equilibrium value. We designate the relative population of the second vibrational level (the E_3 level) of NO-fragments resulting from the dissociation of the molecules of nitrocompounds and NO_2 as the constants ψ and χ , respectively. The population of the lower vibrational levels, relatively united in the one level E_2 , we denote as $(1 - \psi)$ and $(1 - \chi)$, respectively.

In the course of time, the number of NO-fragments located on the vibrational level E_3 decreases as a result of quenching of the vibrational excitation by atmospheric components. In the diagram, this fact is illustrated by the transition $E_3 - E_2$ with the rate constant k_{32} .

Absorbing a photon of laser radiation, NO-fragments on the E_3 level transit in an electron-excited state E_4 with the absorption rate constant of

$$k_{34} = \sigma_{NO} F. \quad (3)$$

Here σ_{NO} is the absorption cross-section of NO-fragments located on the vibrational level E_3 at the wavelength of the laser radiation.

From the excited state E_4 , the molecule can transit to the ground state with a constant of the fluorescence rate k_{fl} , or it can make a nonradiative transition with the rate constant k_q due to the collisional quenching of fluorescence by atmospheric components.

We denote the time dependence of the population of E_i levels by $N_i(t)$, where $i = 0, 1, \dots, 8$. Given the equality of corresponding rate constants of absorption and fragmentation for NO_2 -fragments and background NO_2 molecules ($k_6 = k_8 = k_{fr}^{NO_2}$ and $k_{78} = k_{56} = k_{abs}^{NO_2}$), the kinetics of the considered process can be described by a system of linear inhomogeneous differential equations of the first order, and we have

$$\left\{ \begin{array}{l} \frac{dN_0(t)}{dt} = -k_{01} N_0(t); \\ \frac{dN_1(t)}{dt} = k_{01} N_0(t) - k_1 N_1(t); \\ \frac{dN_2(t)}{dt} = \varphi(1 - \psi) k_1 N_1(t) + k_{32} N_3(t) + N_4(t)(k_{fl} + k_q) + (1 - \chi) k_{fr}^{NO_2} N_6(t) + (1 - \chi) k_{fr}^{NO_2} N_8(t); \\ \frac{dN_3(t)}{dt} = \varphi \psi k_1 N_1(t) - N_3(t)(k_{32} + k_{34}) + \chi k_{fr}^{NO_2} N_6(t) + \chi k_{fr}^{NO_2} N_8(t); \\ \frac{dN_4(t)}{dt} = k_{34} N_3(t) - N_4(t)(k_{fl} + k_q); \\ \frac{dN_5(t)}{dt} = (1 - \varphi) k_{15} N_1(t) - k_{abs}^{NO_2} N_5(t); \\ \frac{dN_6(t)}{dt} = k_{abs}^{NO_2} N_5(t) - k_{fr}^{NO_2} N_6(t); \\ \frac{dN_7(t)}{dt} = -k_{abs}^{NO_2} N_7(t); \\ \frac{dN_8(t)}{dt} = k_{abs}^{NO_2} N_7(t) - k_{fr}^{NO_2} N_8(t). \end{array} \right. \quad (4)$$

We define the initial conditions. Suppose that at a time $t = 0$, when the leading edge of the laser pulse reaches the object medium, the population of the E_0 level is determined by the initial concentration of the NC vapors

$$N_0(t = 0) = N_0. \quad (5)$$

The population of the E_7 level at $t = 0$ is determined by the background concentration of NO_2 in the atmosphere

$$N_7(0) = N_{\text{NO}_2}. \quad (6)$$

Obviously, the populations of other levels are zero at $t = 0$.

$$N_1(0) = 0, N_2(0) = 0, N_3(0) = 0, N_4(0) = 0, N_5(0) = 0, N_6(0) = 0, N_8(0) = 0. \quad (7)$$

The time dependence of the population of each of the levels $N_i(t)$ can be found from the joint solutions of differential equations (4) with the initial conditions (5), (6), and (7).

Of practical interest is the time dependence $N_4(t)$ of the population of the E_4 level, i.e., the concentration of NO-fragments excited by laser radiation.

The use of the dependence $N_4(t)$ in the lidar equation for the case of fluorescent objects [6] allows to estimate the expected lidar signal for a particular nitrocompound on the basis of spectroscopic information about the object of detection, parameters of the radiation propagation medium, and parameters of the transceiver equipment.

Also, the model allows to estimate the contribution from the background NO_2 to the limitation of sensitivity of the detection method. This limitation is fundamentally irremovable when working in the real atmosphere.

The work was supported by the grant of the President of the Russian Federation for the state support of young Russian scientists (Contract No. 14.Y30.15.6286-MK).

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