═══════════ **OPTICAL INSTRUMENTATION** ═══════════

Estimation of the Limiting Sensitivity of Laser Fragmentation/Laser-Induced Fluorescence Technique for Detection of Nitrocompound Vapors in Atmosphere

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Abstract—The limiting sensitivity of a technique for detecting vapors of nitrocompounds in the atmosphere based on laser fragmentation/laser-induced fluorescence is estimated in calculations with the developed kinetic model of the LF/LIF process. The calculations take into account the influence of atmospheric nitrogen dioxide as a limiting factor of the sensitivity of the technique in a real atmosphere. It is shown that if the concentration of nitrogen dioxide in the atmosphere does not exceed 10 ppb, the minimum detectable concentrations of nitrobenzene and *o*-nitrotoluene vapors are the ppb-level. It is also shown that the one-color excitation technique usually used for the detection of nitrocompounds does not allow attaining the maximal LF/LIF efficiency.
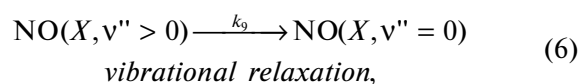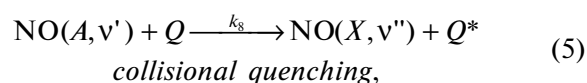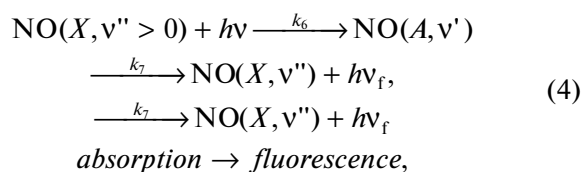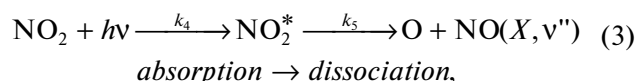
INTRODUCTION

The laser fragmentation/laser-induced fluorescence (LF/LIF) technique was first suggested in [1] for in situ detection of trace atmospheric gases. The technique is based on the effect of photodissociation of optically inactive molecules into fragments which are highly efficient in the LIF process. The technique is widely used for remote detection of various nitrocompounds [2−21].

Schematically, the LF/LIF process for an arbitrary nitrocompound (NC) can be represented as a sequence of photochemical reactions

$$NC + h\nu \xrightarrow{k_1} NC^* \xrightarrow{k_2} R + NO(X, \nu'') \quad (1)$$
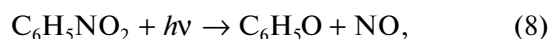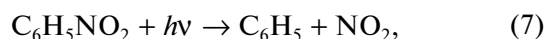*absorption → dissociation,*

$$\xrightarrow{k_3} R + NO_2 \; dissociation, \quad (2)$$

$$NO_2 + h\nu \xrightarrow{k_4} NO_2^* \xrightarrow{k_5} O + NO(X, \nu'') \quad (3)$$
absorption → dissociation,

$$NO(X, \nu'' > 0) + h\nu \xrightarrow{k_6} NO(A, \nu')$$
$$\xrightarrow{k_7} NO(X, \nu'') + h\nu_f,$$
$$\xrightarrow{k_7} NO(X, \nu'') + h\nu_f \quad (4)$$
absorption → fluorescence,

$$NO(A, \nu') + Q \xrightarrow{k_8} NO(X, \nu'') + Q^* \quad (5)$$
collisional quenching,

$$NO(X, \nu'' > 0) \xrightarrow{k_9} NO(X, \nu'' = 0) \quad (6)$$
vibrational relaxation,
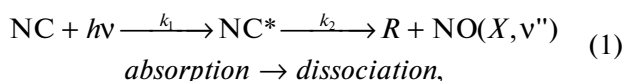
where k_i are the reaction rate constants; Q is the quencher molecule; X and A designate the ground and first electronically excited states, respectively; ν'' and ν' are the vibrational quantum numbers of the states X and A; h is the Planck's constant; and ν is the frequency.

Electronically excited NC* molecules produced in reaction (1) after absorption of a photon with the energy $h\nu$, which is significantly higher than the dissociation threshold, have sufficient or excess energy to dissociate into fragments. There are several ways (channels) of fragmentation of an excited polyatomic molecule. For example, in the case of photodissociation of nitrobenzene upon excitation in the wavelength range 220−280 nm [4], the most probable are channels of dissociation with the formation of NO_2, NO, and O:

$$C_6H_5NO_2 + h\nu \to C_6H_5 + NO_2, \quad (7)$$

$$C_6H_5NO_2 + h\nu \to C_6H_5O + NO, \quad (8)$$

$$C_6H_5NO_2 + h\nu \rightarrow C_5H_5 + CO + NO, \qquad (9)$$

$$C_6H_5NO_2 + h\nu \rightarrow C_6H_5NO + O. \qquad (10)$$

As is known the bonds between atoms in an excited nitrobenzene molecule are broken and redistributed, which lead to isomerization of the molecule and its transformation into phenylnitrite, followed by the breakage of the C−ONO, O−NO, and NO−O bonds and the formation of such fragments as NO_2, NO, and O, respectively [4, 6]. An alternative way of formation of NO_2, which competes with the nitro−nitrite rearrangement in a nitrobenzene molecule, is the radical abstraction of the NO_2 group by direct breakage of the C−N bond [22]. The nitro−nitrite rearrangement has a significantly lower activation enthalpy than the C−N bond breaking energy, which suggests that nitro−nitrite rearrangement can be one of the main channels for the decomposition of aromatic nitrocompounds.

Studies of the laser-stimulated fragmentation of nitrotoluene and dinitrotoluene (DNT) [23, 24] show that all isomers of these molecules have the same main fragmentation channels as nitrobenzene. However, in the case of *ortho*-isomers, an additional channel was observed with the formation of OH fragments [22, 24, 25]:

$$C_7H_7NO_2 + h\nu \rightarrow C_7H_6NO + OH. \qquad (11)$$

For DNT, the OH yield is maximal when both NO_2 groups are in the *ortho*-position relative to the methyl group (2,6-DNT). The appearance of a hydroxyl radical is explained by the intramolecular migration of a hydrogen atom from the methyl group to an oxygen atom of the nitro group, followed by breakage of the N−OH bond [22].

Reaction (3), in turn, describes the process of photodissociation of NO_2 fragments formed in reaction (2) and their dissociation into $NO(X^2\Pi)$ and $O(^3P)$ fragments. Dissociation of an NO_2 molecule becomes energetically possible at fragmenting radiation wavelengths <398 nm [26]. The absorption spectrum of the NO_2 molecule in the wavelength range <398 nm acquires a characteristic diffuseness, indicating the presence of predissociation.

The NO fragments produced in reactions (1) and (3) can obviously serve markers of nitrocompounds and form the basis of a technique for detecting molecules of nitrocompounds in the atmosphere. Several LF/LIF approaches to the detection of nitrocompounds are known, which differ in the ways of excitation of the fluorescence of NO fragments (4). However, since the process of molecular fragmentation is not selective, the same radiation source is often used for the fragmentation and for excitation of the fluorescence of NO fragments (one-color LF/LIF). The choice of a specific excitation scheme is mainly justi-

fied by the need for selective excitation of the fluorescence of precisely NO fragments, without involving atmospheric (background) nitric oxide. Otherwise, the sensitivity of the technique is significantly limited under real atmospheric conditions.

A variety of spectroscopic effects associated with violation of thermodynamic equilibrium during fragmentation and a significant redistribution of the populations of the vibrational−rotational states of NO fragments makes it possible to use several approaches to fluorescence excitation in them. The excess energy which appears after the R−NO bond of an excited molecule is broken is assumed to be partly spent on the excitation of the vibrational states of the NO fragments. According to [10], the ratio of populations of the vibrational levels $v'' = 0, 1, 2$, and 3 of the ground state of NO fragments, produced in the photolysis of nitrobenzene under the action of radiation at wavelengths of 226−259 nm, is $(v'' = 0) : (v'' = 1) : (v'' = 2) : (v'' = 3) \approx 1 : 0.3 : 0.1 : 0.02$. During the photolysis of *ortho*-nitrotoluene, dinitrobenzene (DNB), and DNT in the 220−250 nm range, $(v'' = 0) : (v'' = 1) : (v'' = 2) \approx 1 : 0.6 : 0.06$ [11, 13, 27].

Note that for background NO molecules in thermodynamic equilibrium, the population of vibrational levels obeys the Boltzmann distribution, and the ratio of the populations of the four lower levels at a temperature of 300 K is as follows: $(v'' = 0) : (v'' = 1) : (v'' = 2) : (v'' = 3) \approx 1 : 10^{-4} : 10^{-8} : 10^{-12}$. The distribution function of the population of NO fragments over the vibrational levels of the ground state significantly differs from the Boltzmann one, and this difference can be used for selective excitation of NO fragments. Excited vibrational states of NO fragments are manifested in their absorption spectra, where additional bands appear with the intensity several orders of magnitude higher than that for NO molecules in the equilibrium distribution. The atmospheric concentration of NO molecules can attain 100 ppb, and just it obviously determines the sensitivity limit of the LF/LIF technique when the fluorescence of NO fragments is excited from the zero vibrational level $X^2\Pi(v'' = 0)$. When fluorescence is excited from higher vibrational levels $X^2\Pi(v'' > 0)$, taking into account the ratio of the populations of the vibrational states of the background NO $(v'' = 0) : (v'' = 1) : (v'' = 2) : (v'' = 3) = 1 : 10^{-4} : 10^{-8} : 10^{-12}$, it becomes possible to significantly increase the sensitivity of the detection technique and ensure its noise immunity.

On the other hand, one should remember that, in addition to nitrogen monoxide, nitrogen dioxide is present in the real atmosphere in quite high concentrations (1−100 ppb). Being a source of noise which reduces the sensitivity of the LF/LIF technique, NO_2 molecules, like other nitrocompounds, supply NO fragments due to photofragmentation, which can participate in LIF (4):
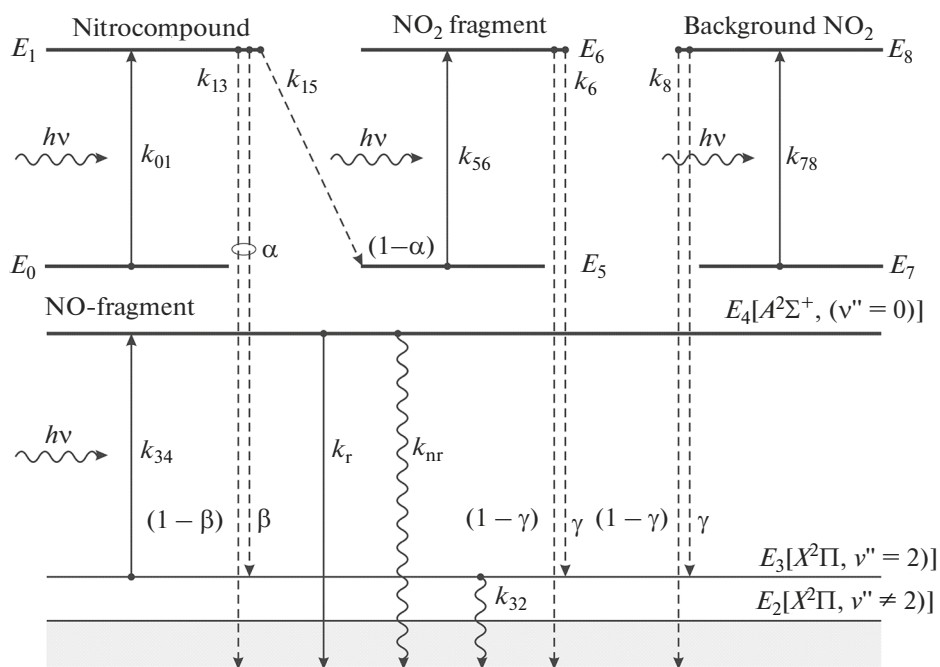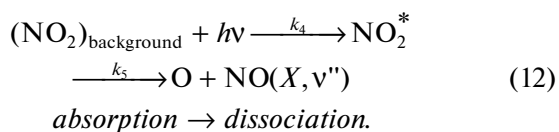
Fig. 1. Generalized diagram of the energy levels of molecules involved in the LF/LIF process.

$$(NO_2)_{background} + h\nu \xrightarrow{k_4} NO_2^*$$

$$\xrightarrow{k_5} O + NO(X,\nu'') \qquad (12)$$

$$absorption \rightarrow dissociation.$$

Results of studies of the photodissociation of the NO_2 molecule in the ultraviolet wavelength range are considered in [28, 29]. The distribution of NO fragments over vibrational states due to the fragmentation of an NO_2 molecule is shown to be inverse. In this case, the population of vibrational levels is significant up to the values $\nu'' = 8$. From the point of view of participation in LF/LIF, atmospheric nitrogen dioxide is a full-fledged nitrocompound that supplies NO fragments, which are indicators of the presence of nitrocompound vapors in the atmosphere in a LF/LIF detection technique. The concentration of atmospheric nitrogen dioxide largely determines the sensitivity threshold of the technique. That is why the assessment of this threshold and the search for ways to reduce it are key tasks in the development of the technique.
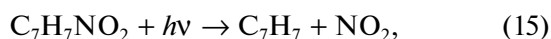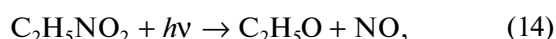
In order to determine the potential capabilities of the one-color LF/LIF technique for detecting nitrocompound vapors under real atmospheric conditions, the detection threshold of the technique is assessed taking into account atmospheric nitrogen dioxide fragmentation (12). Nitrobenzene and *ortho*-nitrotoluene are chosen for the study. These molecules are of interest as the simplest models of more complex nitrocompounds. The calculations were performed using a mathematical model of the one-color LF/LIF.
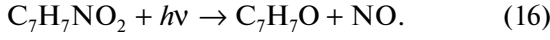
LF/LIF Model

The above features of the photodissociation of nitrobenzene and nitrotoluene have been taken into account when constructing the kinetic model of one-color LF/LIF. To visualize the process of laser fragmentation of nitrocompounds followed by the laser excitation of fluorescence of vibrationally excited $NO(X^2\Pi, \nu'' = 2)$ fragments, we show all possible processes as a sequence of transitions in the generalized diagram of the energy levels of a nitrocompound molecule, its main fragments NO and NO_2 molecules, and a background nitrogen dioxide NO_2 molecule (Fig. 1).

In the diagram, E_0, E_5, and E_7 denote the main states of the molecules, and E_1, E_6, and E_8 denote the dissociating states. The vibrational levels of a NO molecule are denoted as E_2 $(X^2\Pi(\nu'' \neq 2))$, E_3 $(X^2\Pi(\nu'' = 2))$, and E_4 $(A^2\Sigma^+(\nu' = 0))$. LF/LIF is presented as a sequence of inter- and intramolecular transitions with the corresponding rate constants k_{ij}, where i is the number of the initial state and j is the number of the final state.

Let us take into account that the main channels of dissociation of nitrobenzene and *ortho*-nitrotoluene under the action of radiation at a wavelength of 248 nm, according to [4, 22], are channels with the formation of NO_2 and NO fragments:

$$C_2H_5NO_2 + h\nu \rightarrow C_2H_5 + NO_2, \qquad (13)$$

$$C_2H_5NO_2 + h\nu \rightarrow C_2H_5O + NO, \qquad (14)$$

$$C_7H_7NO_2 + h\nu \rightarrow C_7H_7 + NO_2, \qquad (15)$$

$$C_7H_7NO_2 + h\nu \rightarrow C_7H_7O + NO. \qquad (16)$$

Part of NO fragments of nitrobenzene (14) and nitrotoluene (16) are formed at a rate of $\sim 10^7 \, s^{-1}$, while the rest is formed more slowly, at a rate of $\sim 10^4 \, s^{-1}$ [22]. According to estimates for both nitrocompounds, the approximate fraction of "fast" fragments of their total number (φ) is 0.7; and of "slow" fragments $(1 - \varphi)$, is 0.3.

The ratio of the numbers of "informative" NO and NO_2 fragments $[NO]/[NO_2] = 0.26 \pm 0.12$ for nitrobenzene and $[NO]/[NO_2] = 0.3 \pm 0.12$ for *ortho*-nitrotoluene [22]. Let us also take into account the participation in the LF/LIF process of atmospheric nitrogen dioxide molecules, which supply "false" NO fragments.

According to the diagram in Fig. 1, a nitrocompound molecule transits from the ground state E_0 into dissociating state E_1 during the radiation absorption and then dissociates into fragments NO and NO_2 (α is the fraction of NO fragments in the total number of fragments formed, $(1 - \alpha)$ is the fraction of NO_2 fragments). In turn, NO_2 fragments and background NO_2 molecules make transitions $E_5 \rightarrow E_6$ and $E_7 \rightarrow E_8$ during the radiation absorption and then dissociate into NO fragments. We set the quantum yield of NO_2 photodissociation equal to unity [26]. In this case, the population of the vibrational levels of the NO fragments is nonequilibrium. Let the constants β and γ denote the relative to level E_3 population of NO fragments formed during the fragmentation of nitrocompound and nitrogen dioxide molecules, respectively. Then, the relative populations with respect to other vibrational levels, conventionally combined into the level E_2, are $(1 - \beta)$ and $(1 - \gamma)$.

Depopulation of the level E_3 occurs due to both the collisional quenching of vibrational excitation by atmospheric components with the rate constant k_{32} ($E_3 \rightarrow E_2$ transition) and the transition of the NO molecule to the electronically excited state E_4 due to the radiation absorption. Relaxation of the E_4 level to the ground state is possible from both a radiative transition with the rate constant k_r and a nonradiative transition with the rate constant k_{nr}, which determines the fluorescence quenching factor.

In view of the foregoing, we write the system of kinetic equations which describe the LF/LIF in the considered nine-level model:

$$\frac{dN_0(t)}{dt} = -k_{01}N_0(t), \qquad (17)$$

$$\frac{dN_1(t)}{dt} = k_{01}N_0(t) \\ - \left(\varphi k_{13fast} + (1-\varphi)k_{13slow}\right)N_1(t) - k_{15}N_1(t), \qquad (18)$$

$$\frac{dN_2(t)}{dt} = \alpha(1-\beta) \\ \times \left(\varphi k_{13fast} + (1-\varphi)k_{13slow}\right)N_1(t) + k_{32}N_3(t) \\ + (k_r + k_{nr})N_4(t) + (1-\gamma)k_6N_6(t) \\ + (1-\gamma)k_8N_8(t), \qquad (19)$$

$$\frac{dN_3(t)}{dt} = \alpha\beta\left(\varphi k_{13fast} + (1-\varphi)k_{13slow}\right)N_1(t) \\ - (k_{32} + k_{34})N_3(t) + \gamma k_6N_6(t) + \gamma k_8N_8(t), \qquad (20)$$

$$\frac{dN_4(t)}{dt} = k_{34}N_3(t) - (k_r + k_{nr})N_4(t), \qquad (21)$$

$$\frac{dN_5(t)}{dt} = (1-\alpha)k_{15}N_1(t) - k_{56}N_5(t), \qquad (22)$$

$$\frac{dN_6(t)}{dt} = k_{56}N_5(t) - k_6N_6(t), \qquad (23)$$

$$\frac{dN_7(t)}{dt} = -k_{78}N_7(t), \qquad (24)$$

$$\frac{dN_8(t)}{dt} = k_{78}N_7(t) - k_8N_8(t). \qquad (25)$$

The values of the coefficients included in the system of equations are given in Table 1.

The system of kinetic equations was numerically solved using the MATLAB software package. The solutions found make it possible to trace the LF/LIF dynamics and estimate the efficiency of pulsed excitation.

Function $N_4(t)$ makes it possible to estimate the total number of photons spontaneously emitted by a unit volume of the model medium into a unit solid angle:

$$S = \int_0^{\tau_g} \frac{N_4(t)k_r}{4\pi} dt. \qquad (26)$$

Here, $\tau_g \geq \tau + 1/k_{nr}$ is the detection time and τ is the laser pulse duration.

RESULTS AND DISCUSSION

Fluorescence signals of informative NO fragments of nitrocompounds S_{NC} and of NO fragments of background nitrogen dioxide S_{NO_2} were calculated by Eq. (26). Figures 2 and 3 show families of lines corresponding to the ratio $S_{NC}/S_{NO_2} = 1$ and determining the nitrocompound vapor detection threshold $[NC]_{th}$ depending on the background nitrogen dioxide concentration at given values of the radiation energy density w. Calculations were performed at $\tau = 20$ ns.

The expression for estimating the detection threshold $[NC]_{th}$ at given concentrations $[NO_2]$ and w has the following form:

$$[NC]_{th} = [NO_2](A + B_1w + B_2w^2) + C, \qquad (27)$$

where $[NC]_{th}$ and $[NO_2]$ are in ppb; w is in mJ/cm^2; the values of parameters A, B_1, B_2, and C are given in Table 2.

Table 1. Input parameters of the kinetic model of the LF/LIF process of nitrocompounds (excitation wavelength 248 nm)

Parameter		Value	
		nitrobenzene	*ortho*-nitrotoluene
The absorption cross section of a nitrocompound molecule	σ_{abs}, 10^{-18} cm^2	18 [30]	14 [30]
The absorption cross section of the NO$_2$ molecule	σ_{NO_2}, 10^{-18} cm^2	0.009 [30]	0.009 [30]
The absorption cross section of the NO molecule	σ_{NO}, 10^{-18} cm^2	0.56	0.56
Weight coefficient	α	0.21 [22]	0.23 [22]
Weight coefficient	β	0.1 [10]	0.1
Weight coefficient	γ	0.1 [28]	0.1 [28]
Weight coefficient	φ	0.7**	0.7**
Absorption rate constant	k_{01}	$\sigma_{abs}F^*$	$\sigma_{abs}F^*$
Absorption rate constant	$k_{56} = k_{78}$	$\sigma_{NO_2}F^*$	$\sigma_{NO_2}F^*$
Absorption rate constant	k_{34}	$\sigma_{NO}F^*$	$\sigma_{NO}F^*$
Rate constant of dissociation NC$+ h\nu \rightarrow R + $NO:			
"fast" channel	k_{13fast}, s^{-1}	2.7×10^7 [22]	4.5×10^6 [22]
"slow" channel	k_{13slow}, s^{-1}	6.0×10^3 [22]	3.2×10^4 [22]
Rate constant of dissociation NC$+ h\nu \rightarrow R + NO_2$	K_{15}, s^{-1}	3.0×10^8 [22]	2.3×10^7 [22]
Rate constant of vibrational relaxation of NO($X^2\Pi(v' = 2)) \rightarrow$ NO($X^2\Pi(v'' = 0, 1)$)	k_{32}, s^{-1}	3.8×10^5 [31]	
Rate constant of dissociation NO$_2 + h\nu \rightarrow$ NO + O	$k_6 = k_8$, s^{-1}	2.5×10^{10} [32]	
Probability of radiative transition NO($A^2\Sigma^+) \rightarrow$ NO($X^2\Pi) + h\nu$	k_r, s^{-1}	4.9×10^6 [33]	
Probability of nonradiative transition NO($A^2\Sigma^+) \rightarrow$ NO($X^2\Pi$)	k_{nr}, s^{-1}	8.1×10^8 [34]	

 * $F = I/(h\nu)$ is the photon flux density; I is the intensity of laser radiation with a frequency ν.
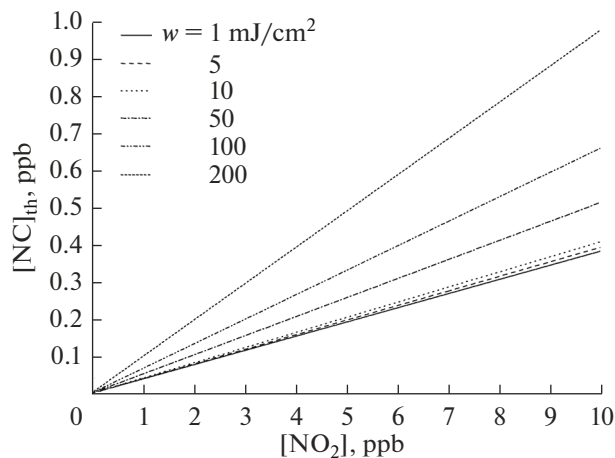** Determined from data [22].

Fig. 2. Detection threshold [NC]$_{th}$ for nitrobenzene vapors as a function of the atmospheric nitrogen dioxide concentration [NO$_2$] at given values of the radiation energy density.

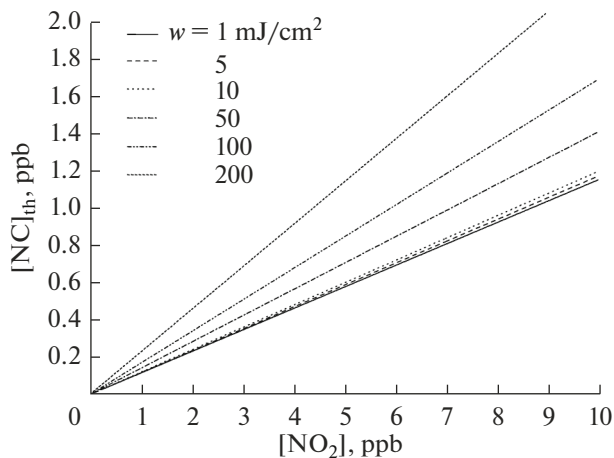**Fig. 3.** Detection threshold [NC]$_{th}$ for *ortho*-nitrotoluene vapors as a function of the atmospheric nitrogen dioxide concentration [NO$_2$] at given values of the radiation energy density.
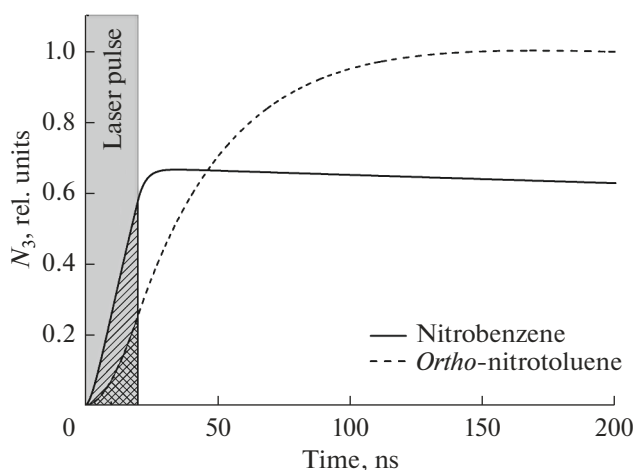
Fig. 4. Time dependence of the normalized population of NO fragments in the $X^2\Pi(\nu'' = 2)$ state, formed during fragmentation of nitrobenzene and *ortho*-nitrotoluene molecules by a rectangular laser pulse with a duration of 20 ns; $w = 10$ mJ/cm^2; $\lambda = 248$ nm.

As can be seen from Figs. 2 and 3, the detection threshold for nitrobenzene and *ortho*-nitrotoluene vapors [NC]$_{th}$ are at a level of 1 ppb for [NO$_2$] up to 10 ppb, and [NC]$_{th}$ for nitrotoluene is about three times higher than for nitrobenzene under the same conditions. The study of the photodissociation dynamics shows this difference to be due to the different rates of reaction (1) for these nitrocompounds. As a result, the total number of vibrationally excited NO($X^2\Pi$, $\nu'' = 2$) fragments $N_3(t)$ formed under the action of a laser pulse is also different (Fig. 4).

For the quantitative assessment, we use the ratio of the total number of NO fragments formed during the flash photolysis of nitrobenzene (NB) and nitrotoluene (NT) (see shaded areas in Fig. 4)

$$\eta = \frac{\int_0^\tau N_3^{\mathrm{NB}}(t)dt}{\int_0^\tau N_3^{\mathrm{NT}}(t)dt}, \qquad (28)$$

Table 2. The constants included in Eq. (27) for estimating the detection thresholds for nitrobenzene and *ortho*-nitrotoluene vapors

Constant	Value	
	nitrobenzene	*ortho*-nitrotoluene
A	0.03536	0.11274
B_1, cm^2/mJ	2.6×10^{-4}	5.2×10^{-4}
B_2, cm^4/mJ^2	1.9×10^{-7}	2.2×10^{-7}
C	0.001	0.001

which is equal to 2.96 at $\tau = 20$ ns and well agrees with the ratio [NB]$_{th}$/[NT]$_{th}$ = 3.09 (see Figs. 2 and 3) at $w = 10$ mJ/cm^2.

As can be seen from Fig. 4, during the flash photolysis of nitrocompound molecules, the formation of fragments continues even after optical excitation is ceased. In this case, the maximal concentration of NO fragments is attained in the time t_{max}, which is several times longer than the fragmenting pulse duration (20 ns). This is because polyatomic molecules do not usually directly dissociate upon light absorption in the region of spectral maxima. A large number of closely spaced electronic states and many vibrational modes lead to an increase in the probability of nonradiative transitions: internal and intercombination conversion. In this case, the time required for the energy concentration on a breaking bond (bonds) can be several orders of magnitude longer than, for example, a gap of 10^{-13} s required for dissociation of a di- or triatomic molecule [22, 32].

Thus, the one-color LF/LIF technique, where the fragmentation of nitrocompound molecules and the excitation of their NO fragments occurs for one laser pulse with the duration $\tau < t_{max}$, does not allow attaining the maximal efficiency of LF/LIF, although it is attractive due to the relative ease of implementation.

CONCLUSIONS

The results of this work show the background nitrogen dioxide to be a significant limiting factor of sensitivity of the LF/LIF technique when detecting nitrocompound vapors in the real atmosphere. For example, if the atmospheric concentration nitrogen dioxide does not exceed 10 ppb, then the detection thresholds for nitrobenzene and *ortho*-nitrotoluene vapors are of units of ppb.

As the calculations have shown, due to the inertia of dissociation of nitrocompound molecules into fragments, the formation of the latter continues under pulsed action even after the cease of optical excitation. The maximal concentration of NO fragments is attained in a time several times longer than a standard fragmenting pulse duration of 10–20 ns. Hence, we can conclude that the one-color LF/LIF technique does not provide for the maximal LF/LIF efficiency. It is likely that two-pulse excitation with a time lag between the action on nitrocompound molecules and their NO fragments is to increase the efficiency of the LF/LIF technique. We plan to experimentally verify this assumption in further research.

CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

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