

# Nonresonant interaction of molecules with femtosecond laser pulse

S.R. Uogintas

*Institute of Atmospheric Optics,  
Siberian Branch of the Russian Academy of Sciences, Tomsk*

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Nonresonant interaction of nonpolar molecules with femtosecond laser pulse is considered using the time-dependent perturbation theory. The solution for the density matrix is obtained in the fourth order of the perturbation; and a general expression for the field energy loss is found. The rigid rotor model is used to numerically calculate absorption by molecular nitrogen.

## Introduction

A nonresonant monochromatic field effectively does not cause any direct transitions in a quant system, because corresponding probabilities are rapidly oscillating time functions, and the energy conservation law in quantum mechanics results in vanishing of such probabilities at  $t \rightarrow \infty$ .

Nevertheless, the nonresonant field at a sufficient intensity is able to significantly affect atoms and molecules through exciting multi-quantum transitions occurring via intermediate virtual states. Multi-photon absorption, two-quantum processes of stimulated Raman scattering type, multi-photon ionization and dissociation can be considered as examples.

The nonresonant interaction with a laser pulse has its own features. While the carrier pulse frequency is far from atomic-frequency resonances, the amplitude spectral content can include frequencies, resonant to one or several of them, which can cause excitation of corresponding transitions.<sup>1</sup> A pulse spectrum is determined by its length, hence, the length is the key parameter, determining which transitions are most effectively excited in the interaction. Besides, different pulse length scales correspond to motion of different degrees of freedom of a quantum system with their specific character. This requires the use of different approximations and models to describe interactions versus pulse length.

In this work, we consider interactions between nonpolar molecules and pulses of length from hundreds to tens of femtoseconds. In this scale, characteristic electron travel times can be considered as rapid. This allows the approximation of slowly varying amplitude to be used and interaction with an electronic subsystem to be taken into account via its polarizability at the field carrier frequency. The consideration is limited to the fourth order of temporal perturbation theory, since the first nonvanishing correction to population levels of the electronic ground state appears in this order.

## 1. Molecules in a nonresonant field

Consider a molecule in the pulse field described by the electric field strength

$$\mathbf{E}(\mathbf{r}, t) = \frac{1}{2} E_0(\mathbf{r}, t) [\mathbf{e} \exp(i(\mathbf{kr} - \Omega t)) + \mathbf{e}^* \exp(-i(\mathbf{kr} - \Omega t))], \quad (1)$$

where the real amplitude  $E_0(\mathbf{r}, t)$  determines the time shape of the pulse and field strength distribution in a plane, normal to the propagation direction;  $\mathbf{e}$  is the complex polarization vector:

$$\mathbf{e}^* \cdot \mathbf{e} = 1. \quad (2)$$

In the long-wave approximation, the Hamiltonian of the molecule in the field has the known form

$$H = H_0 + V(t); \quad (3)$$

$$V(t) = -\mathbf{dE}, \quad (4)$$

where the dependence on  $\mathbf{kr}$  is to be omitted in Eq. (1) for the field  $\mathbf{E}$ . The carrier pulse frequency  $\Omega$  is nonresonant to the frequencies of inter-electronic transitions  $\omega_{m'}$  much larger than rovibrational ones. The field amplitude  $E_0(\mathbf{r}, t)$  is a slowly varying time function in the sense of fulfilling the condition

$$|\omega_{m'} \pm \Omega| \tau \gg 1, \quad (5)$$

where  $\tau$  is the characteristic pulse width. This condition allows expressing field interaction effects via dynamic polarizabilities of the ground electronic state at the carrier pulse frequency, as well as neglecting real processes of absorption to excited electronic states, which could occur in the presence in the spectrum of an envelope of frequencies, resonant to detuning from the electronic transition.

Consider an interaction with molecules having inversion centers, for which dipole transitions in the ground electronic state are forbidden by the selection rules:

$$\langle \mu | V | \mu' \rangle = 0. \quad (6)$$

The interaction with field is supposed to be quite weak; therefore, the consideration can be carried out within the perturbation theory, and ionization and dissociation processes can be neglected. Assume that the pulse length is much shorter than characteristic times of the molecular system relaxation. At the initial moment ( $t \rightarrow -\infty$ ), the molecule is at the thermodynamically equilibrium state, described by the density matrix

$$\rho^0 = \frac{1}{Z} \exp(-\beta H_0), \quad \beta = 1/k_B T. \quad (7)$$

In this case, temperatures are such that excited electronic states are efficiently unpopulated:

$$\beta E_e \gg 1. \quad (8)$$

Assume also that multi-photon resonances with electronic transitions do not occur in the considered orders of the perturbation theory.

Under the above assumptions, the processes of first order with respect to the field are absent in the ground state, and the main interaction mechanism will be processes of the type of the stimulated Raman scattering through virtual electronic states.

## 2. Motion equations

Write the motion equation for the molecule matrix density in interaction representation, neglecting all relaxation processes because of short pulse length:

$$i\hbar \dot{\tilde{\rho}}(t) = [\tilde{V}(t), \tilde{\rho}(t)]. \quad (9)$$

Isolate evolutions of ground and excited electronic states in Eq. (9). To do this, introduce projectors

$$P_g = \sum_{\mu} |\mu\rangle \langle \mu|, \quad P_e = \sum_n |n\rangle \langle n|, \quad P_g + P_e = 1. \quad (10)$$

Hereinafter, excited electronic states are enumerated with Latin letters and levels of ground state – with Greek ones. The identity

$$A = A_{gg} + A_{ge} + A_{eg} + A_{ee} \quad (11)$$

is correct for an arbitrary functional  $A$ . Here

$$A_{ij} = P_i A P_j, \quad i, j = e, g. \quad (12)$$

Substituting the density matrix in the form of Eq. (11), obtain the following set of equations:

$$i\hbar \dot{\tilde{\rho}}_{gg} = \tilde{V}_{ge} \tilde{\rho}_{eg} - \tilde{\rho}_{ge} \tilde{V}_{eg}, \quad (13a)$$

$$i\hbar \dot{\tilde{\rho}}_{ge} = \tilde{V}_{ge} \tilde{\rho}_{ee} - \tilde{\rho}_{ge} \tilde{V}_{ee} - \tilde{\rho}_{gg} \tilde{V}_{ge}, \quad (13b)$$

$$i\hbar \dot{\tilde{\rho}}_{ee} = \tilde{V}_{eg} \tilde{\rho}_{ge} - \tilde{\rho}_{eg} \tilde{V}_{ge} + \tilde{V}_{ee} \tilde{\rho}_{ee} - \tilde{\rho}_{ee} \tilde{V}_{ee}. \quad (13c)$$

It is evident from Eq. (13a) that evolution of the ground state is determined by the coherence created by the field between the ground and excited states. It follows from symmetry grounds that for systems with centers of inversion the series of perturbation theory for the density matrix of the ground state contain only even degrees of interaction operator, because matrix elements in Eq. (13a) are diagonal with respect to electronic state, and dipole transitions occur with the change of parity. The set of equations (13) can be simplified based on the following physical grounds. All molecules are in the electronic ground state at the considered temperatures, therefore, excited levels can be populated only due to transitions from the ground state; such processes are negligible in the absence of multi-photon resonances. Note that the first correction to the ground-state density matrix, caused by population of excited states (13c), appears only in the fourth order. Therefore, from set (13), assuming the absence of multi-photon resonances up to the fourth order, obtain a set of equations, describing evolution of the ground state  $\tilde{\rho}_{gg}$  and the coherence  $\tilde{\rho}_{ge}$ :

$$i\hbar \dot{\tilde{\rho}}_{gg} = \tilde{V}_{ge} \tilde{\rho}_{eg} - \tilde{\rho}_{ge} \tilde{V}_{eg}, \quad (14a)$$

$$i\hbar \dot{\tilde{\rho}}_{ge} = -\tilde{\rho}_{ge} \tilde{V}_{ee} - \tilde{\rho}_{gg} \tilde{V}_{ge}. \quad (14b)$$

Let us solve equations (14a) and (14b) by the iterative method. The initial population of excited electronic states can be neglected with a good accuracy, and the ground state density matrix  $\rho_{gg}^0$  can be taken as an initial condition. For definiteness, thermodynamic equilibrium position (7) was chosen as an initial condition. Nevertheless, the consideration is valid at any position, if excited levels are unpopulated and the initial coherence between the ground and excited states is absent.

## 3. Density matrix

In the first order of perturbation theory, the field interaction results in the coherence between the electronic ground and excited states:

$$\tilde{\rho}_{\mu n}^{(1)}(t) = \frac{i}{\hbar} \rho_{\mu \mu}^0 \int_{-\infty}^t dt' \tilde{V}_{\mu n}(t'). \quad (15)$$

Using the slowness condition (5), it is possible to take the field amplitude out of the integral in Eq. (15) and obtain the following equation:

$$\tilde{\rho}_{\mu n}^{(1)}(t) = -\frac{1}{2\hbar} \rho_{\mu \mu}^0 \mathbf{d}_{\mu n} E_0(\mathbf{r}, t) e^{i\omega_{\mu n} t} \left[ \frac{\mathbf{e} \mathbf{e}^{-i\Omega t}}{\omega_{\mu n} - \Omega} + \frac{\mathbf{e}^* \mathbf{e}^{i\Omega t}}{\omega_{\mu n} + \Omega} \right]. \quad (16)$$

The coherence (16) results in appearance of molecule average dipole moment, oscillating at the pulse carrier frequency<sup>2</sup>:

$$\begin{aligned} \langle d_i(t) \rangle &= \text{Sp} \rho^{(1)}(t) d_i = \\ &= \frac{1}{2} \sum_{ij} \rho_{ij}^0 E_0(\mathbf{r}, t) [(\alpha_{ij})_{ij} e_j e^{-i\Omega t} + (\alpha_{ij})_{ij}^* e_j^* e^{i\Omega t}], \end{aligned} \quad (17)$$

where

$$(\alpha_{ij})_{ij} = \frac{1}{\hbar} \sum_n \left[ \frac{(d_i)_{in} (d_j)_{ni}}{\omega_{n0} - \Omega} + \frac{(d_j)_{in} (d_i)_{ni}}{\omega_{n0} + \Omega} \right] \quad (18)$$

is the dynamic polarizability tensor of the electronic ground state.

We neglected the contribution of vibrational and rotational energies to the total energy, taking  $\hbar\omega_{ni}$  equal to the difference of electron energies:

$$\hbar\omega_{ni} \approx E_n - E_0. \quad (19)$$

The coherence (16) exists only for the time equal to pulse length and then is violated.

In the second order of perturbation theory, obtain

$$\tilde{\rho}_{ij}^{(2)}(t) = \left( -\frac{i}{\hbar} \right) \int_{-\infty}^t dt_1 [\delta \tilde{H}_{ij}(t_1) \rho_{ij}^0(t_1) - \rho_{ij}^0(t_1) \delta \tilde{H}_{ij}^*(t_1)] \quad (20)$$

for the ground state. The Schrödinger functional  $\delta H$  has the form

$$\begin{aligned} \delta H_{ij} = & -\frac{E_0^2(\mathbf{r}, t)}{4\hbar} \sum_n \left[ \frac{(\mathbf{d}_{in} \cdot \mathbf{e}^*)(\mathbf{d}_{ni} \cdot \mathbf{e})}{\omega_{ni} - \Omega} + \frac{(\mathbf{d}_{in} \cdot \mathbf{e})(\mathbf{d}_{ni} \cdot \mathbf{e}^*)}{\omega_{ni} + \Omega} \right. \\ & \left. + \frac{(\mathbf{d}_{in} \cdot \mathbf{e})(\mathbf{d}_{ni} \cdot \mathbf{e}) e^{-i2\Omega t}}{\omega_{ni} - \Omega} + \frac{(\mathbf{d}_{in} \cdot \mathbf{e}^*)(\mathbf{d}_{ni} \cdot \mathbf{e}^*) e^{i2\Omega t}}{\omega_{ni} + \Omega} \right]. \end{aligned} \quad (21)$$

Two first items in Eq. (21) describe processes of the type of the stimulated Raman scattering, while oscillating terms – two-photon absorption and emission.<sup>3</sup> Oscillated terms are usually neglected in the majority of optical problems using the rotary-wave approximation (secular approximation).<sup>4</sup> Note, that this approximation could be violated for very short pulses, which have frequencies resonant to  $|\omega_{ni} \pm 2\Omega|$  in the envelope spectrum. In this case, oscillations do not appear during interaction, and two last items have the same order that those describing the light scattering. In this work, we consider such processes, assuming  $|\omega_{ni} \pm 2\Omega| \tau \gg 1$ .

The functional  $\delta H$  is non-Hermitian because of its construction as a product of two interaction operators heterogeneous in time, which do not commute in general. Separating Hermitian and anti-Hermitian parts, the operator can be represented via the shift  $\delta E$  and the absorption  $\delta \Gamma$  operators<sup>4,5</sup>:

$$\delta H = \delta E - \frac{i\hbar}{2} \delta \Gamma, \quad (22)$$

where

$$\delta E = \frac{1}{2} (\delta H + \delta H^+); \quad \delta \Gamma = \frac{i}{\hbar} (\delta H - \delta H^+). \quad (23)$$

In this case, equation (14a) takes the form

$$i\hbar \dot{\rho}_{gg} = [\delta \tilde{E}, \rho_{gg}^0] - \frac{i\hbar}{2} \{ \delta \tilde{\Gamma}, \rho_{gg}^0 \}. \quad (24)$$

The first term in Eq. (24) describes unitary evolution of the density matrix, and the second one – departure from (arrival to) the ground state due to two-photon absorption (emission).

The  $\delta E$  operator becomes Hermitian and  $\delta \Gamma$  – zero in the approximation, at which field detuning from frequencies of electronic transitions is much greater than ranges of rovibrational structure:

$$|\omega_{ni} - \omega_{ni'}| \ll |\omega_{ni} \pm \Omega|, \quad (25)$$

The use of approximation (25) justifies reducing the set (13) to the simplified set (14). It follows from preservation of density matrix trace that an analogous component of arrival of the same order is to be omitted in Eq. (13c) for excited electronic states.

The  $\delta H$  operator in approximation (25) is reduced to the well-known equation for effective Hamiltonian, used in problems of optical pumping and molecule orientation<sup>1,4-6</sup>:

$$\delta H_{ij} = -\frac{E_0^2(\mathbf{r}, t)}{4} (\alpha_{ij})_{ij} e_i^* e_j. \quad (26)$$

For following calculations, it is convenient to represent this operator in the form reflecting its tensor structure with respect to the angular momentum operator:

$$\delta H_{ij} = -\frac{E_0^2(\mathbf{r}, t)}{4} T_{ij}. \quad (27)$$

Here the operator  $T$  is defined by the equation

$$T_{ij} = \sum_{\kappa=0}^2 (-1)^\kappa \left( \alpha_{ij}^\kappa \cdot \{ \mathbf{e}^* \otimes \mathbf{e} \}^\kappa \right), \quad (28)$$

where (... ..) means the scalar product of irreducible tensors and  $\{ \dots \}^\kappa$  – irreducible tensor product of  $\kappa$  order of two irreducible tensors.<sup>7</sup> An irreducible polarizability tensor has the form

$$\alpha_{ij}^\kappa = \frac{1}{\hbar} \sum_n \{ \mathbf{d}_{in} \otimes \mathbf{d}_{ni} \}^\kappa \left[ \frac{1}{\omega_{n0} - \Omega} + \frac{(-1)^\kappa}{\omega_{n0} + \Omega} \right]. \quad (29)$$

Effective Hamiltonian (27) describes transitions between different sublevels of the electronic ground state; transitions with change of vibrational state occur only when accounting for dependence of polarizability on vibrational coordinates. The scalar part ( $\kappa=0$ ) describes transitions with invariable rotational quantum numbers. The anti-symmetric part ( $\kappa=1$ ) is equal to zero for molecules with nondegenerate ground state<sup>2</sup> and in interaction with linear-polarized light. Rules of the rotational-number selection for the symmetric part ( $\kappa=2$ ) are the same as those for quadrupole transitions.

Finally, the following equation for the ground state density matrix in the second order is obtained:

$$\tilde{\rho}_{\mu\mu'}^{(2)}(t) = -\frac{i}{4\hbar} I_{\mu\mu'}(\mathbf{r}, t) \Delta\rho_{\mu\mu'}^0 T_{\mu\mu'}, \quad (30)$$

where  $\Delta\rho_{\mu\mu'}^0$  is the difference between equilibrium populations of the levels  $\mu'$  and  $\mu$ :

$$\Delta\rho_{\mu\mu'}^0 = \rho_{\mu\mu'}^0 - \rho_{\mu\mu}^0; \quad (31)$$

$$I_{\mu\mu'}(\mathbf{r}, t) = \int_{-\infty}^t dt_1 E_0^2(\mathbf{r}, t_1) e^{i\omega_{\mu\mu'} t_1}. \quad (32)$$

The density matrix  $\tilde{\rho}_{\mu\mu'}^{(2)}(t)$  describes coherence between sublevels of the ground state, which keeps after pulse propagation ( $t \rightarrow \infty$ ) and turns out to be proportional to the Fourier transform of the squared pulse amplitude  $E_0^{(2)}(\mathbf{r}, \omega_{\mu\mu'})$ :

$$\rho_{\mu\mu'}^{(2)}(\infty) = -\frac{i}{4\hbar} E_0^{(2)}(\mathbf{r}, \omega_{\mu\mu'}) e^{i\omega_{\mu\mu'} t} \Delta\rho_{\mu\mu'}^0 T_{\mu\mu'}. \quad (33)$$

Parameter  $E_0^{(2)}(\mathbf{r}, \omega_{\mu\mu'})$  plays the part of resonance factor – the field effectively excites transitions for which  $\omega_{\mu\mu'} \tau \leq 1$ .

The correction to the diagonal matrix elements is equal to zero in this approximation. To determine the correction, consider next orders of the perturbation theory.

Describe briefly the sense of the next corrections to  $\rho_{ge}$  without writing them explicitly. The second-order correction  $\rho_{ge}^{(2)}$  for centrally symmetrical media does not contribute to the dielectric susceptibility stipulated by the dipole current. It should be taken into account for finding the contribution of higher current multipoles, for which transitions between electron states occur without change of parity, e.g., the contribution of quadrupole moment. The third-order correction  $\rho_{ge}^{(3,1)}$ , resulting from the first term in Eq. (14b), determines cubic susceptibility and results in the third harmonic generation. Its contribution to the ground state reduces to a term proportional to the nonresonant second hyperpolarizability ( $\gamma$ ) of the

ground state. The correction  $\rho_{ge}^{(3,2)}$  from the second term in Eq. (14b) results in an addition to the cubic susceptibility, expressed via squared polarizability  $\alpha$ . All the above listed coherences are violated after the pulse has passed.

Neglecting the contribution concerned with the second hyper-polarizability, obtain the following equation in the fourth order for populations of the ground state:

$$\tilde{\rho}_{\mu\mu'}^{(4)}(t) = \frac{1}{16\hbar^2} \sum_{\mu''} (I_{\mu\mu''}(\mathbf{r}, t) + I_{\mu''\mu'}(\mathbf{r}, t)) \Delta\rho_{\mu''\mu}^0 T_{\mu\mu''} T_{\mu''\mu'}, \quad (34)$$

where

$$I_{\mu\mu'}(\mathbf{r}, t) = \int_{-\infty}^t dt_1 E_0^2(\mathbf{r}, t_1) e^{i\omega_{\mu\mu'} t_1} \int_{-\infty}^{t_1} dt_2 E_0^2(\mathbf{r}, t_2) e^{i\omega_{\mu\mu'} t_2}. \quad (35)$$

Decomposition of  $E_0^2(\mathbf{r}, t)$  in Eq. (35) into the Fourier integral, yields the equation for populations after pulse propagation:

$$\rho_{\mu\mu'}^{(4)}(\infty) = \frac{1}{16\hbar^2} \sum_{\mu''} |E_0^{(2)}(\mathbf{r}, \omega_{\mu\mu''}) T_{\mu\mu''}|^2 \Delta\rho_{\mu''\mu}^0. \quad (36)$$

## 4. Energy loss

Determine from Eq. (36) the field energy loss due to interaction with a molecule. The molecule-absorbed energy during the field interaction is defined as

$$\begin{aligned} \Delta Q(\mathbf{r}) &= \text{Sp} H_0 \rho^{(4)}(\infty) = \sum_{\mu} E_{\mu} \rho_{\mu\mu}^{(4)} = \\ &= \frac{1}{32\hbar} \sum_{\mu\mu'} \omega_{\mu\mu'} |E_0^{(2)}(\mathbf{r}, \omega_{\mu\mu'}) T_{\mu\mu'}|^2 \Delta\rho_{\mu\mu}^0. \end{aligned} \quad (37)$$

Assuming that the energy is independent of the projection of angular momentum  $m$  on the quantization axis, it is possible to sum over  $m$  implicitly in Eq. (37) and obtain the following equation:

$$\begin{aligned} \Delta Q(\mathbf{r}) &= \frac{1}{32\hbar} \sum_{v_1 v_2 j_1 j_2} \sum_{\kappa=0}^2 \frac{\langle v_1 j_1 | \alpha^{\kappa} | v_2 j_2 \rangle^2}{2\kappa+1} \times \\ &\times \left( \{ \mathbf{e}^* \otimes \mathbf{e} \}^{\kappa} \cdot \{ \mathbf{e}^* \otimes \mathbf{e} \}^{\kappa} \right)_{v_2 j_2 v_1 j_1} \left| E_0^{(2)}(\mathbf{r}, \omega_{v_2 j_2 v_1 j_1}) \right|^2 \Delta\rho_{v_2 j_2 v_1 j_1}^0, \end{aligned} \quad (38)$$

where subscripts  $v$  and  $j$  relate to vibrational and rotational states of the ground electron term, respectively; according to the Wigner–Eckart theorem, it is accepted that

$$\begin{aligned} \langle v_1 j_1 m_1 | \alpha_q^{\kappa} | v_2 j_2 m_2 \rangle &= \\ &= (-1)^{j_1 - m_1} \begin{pmatrix} j_1 & \kappa & j_2 \\ -m_1 & q & m_2 \end{pmatrix} \langle v_1 j_1 | \alpha^{\kappa} | v_2 j_2 \rangle. \end{aligned} \quad (39)$$

As an example, consider energy loss in interaction of a molecule of rigid rotor type with a linear-polarized pulse. Assuming nondegenerate ground state of the molecule and neglecting polarizability dependence on vibrational coordinates, obtain the contribution of only the second-rank tensor in Eq. (38):

$$\Delta Q(\mathbf{r}) = \frac{1}{240\hbar} \sum_{jj'} \left| \langle j \parallel \alpha^2 \parallel j' \rangle E_0^{(2)}(\mathbf{r}, \omega_{jj'}) \right|^2 \omega_{jj'} \Delta \rho_{jj}^0. \quad (40)$$

Calculating the reduced matrix element  $\langle j \parallel \alpha^2 \parallel j' \rangle$ , obtain

$$\langle j \parallel \alpha^2 \parallel j' \rangle = \sqrt{\frac{2}{3}} \Delta \bar{\alpha} \sqrt{(2j'+1)} C_{000}^{j'2j}, \quad (41)$$

where  $\Delta \bar{\alpha} = \bar{\alpha}_{zz} - \bar{\alpha}_{xx}$  is the polarizability of anisotropy in the molecular coordinates.

Summation in Eq. (40) is carried out over rotational states with  $j' = j \pm 2$  owing to selection rules for the Wigner coefficients  $C_{000}^{j'2j}$  [Ref. 8] and the population difference  $\Delta \rho_{jj}^0$ .

Summing over  $j'$ , obtain

$$\Delta Q(\mathbf{r}) = \frac{(\Delta \bar{\alpha})^2 B_e}{60\hbar} \sum_{j=0}^{\infty} (j+1)(j+2) \left| E_0^{(2)}(\mathbf{r}, \omega_{j+2,j}) \right|^2 \Delta \rho_{j+2,j}^0, \quad (42)$$

where  $B_e$  is the rotational constant of the molecule.

$$E_0(\mathbf{r}, t) = E_0 \mathbf{e} e^{-(t/\tau)^2} e^{-(r_{\perp}/r_0)^2} \quad (43)$$

for a linear-polarized Gaussian pulse. Integrating over the beam cross-section, obtain the ratio of energy, absorbed by the medium during interaction, to the unit length:

$$\frac{\Delta Q}{\Delta x} = \frac{(\pi \Delta \bar{\alpha} r_0 \tau)^2 n B_e S E_0^4}{480\hbar}, \quad (44)$$

where  $S$  is defined as

$$S = \frac{1}{Z} \sum_{j=0}^{\infty} (j+1)(j+2) \exp\{-[B_e(2j+3)\tau]^2\} \times \{\exp[-\beta \hbar B_e j(j+1)] - \exp[-\beta \hbar B_e (j+2)(j+3)]\}. \quad (45)$$

Generally speaking, it is necessary to take into account a degeneracy order of rotational levels, connected with nuclear spins,<sup>9</sup> in the statistical sum  $Z$  and in summation over  $j$  in Eq. (45) when considering molecules with the same nuclei. Thus, e.g., summation in Eq. (45) for the O<sub>2</sub> molecule is to carry out over only odd  $j$ . For the below-considered nitrogen molecule N<sub>2</sub> within high temperatures

( $\hbar B_e/kT \ll 1$ ), formula (45) can be used without change.

Expressing the pulse amplitude in terms of total field energy<sup>10</sup>:

$$E_f = \frac{c}{4\pi} \int_{-\infty}^{\infty} \int_S E^2(\mathbf{r}_{\perp}, t) dt dS = \frac{\sqrt{2\pi}}{32} c \tau r_0^2 E_0^2,$$

obtain the equation for energy loss:

$$\frac{\Delta Q}{\Delta x} = \frac{16\pi}{15\hbar} \left( \frac{\Delta \bar{\alpha}}{c r_0} \right)^2 n B_e S E_f^2.$$

Absorption of femtosecond pulse by atmospheric gases was studied in Ref. 11 with a PA technique. Using the experimental data<sup>11</sup>:  $\tau = 1.14 \cdot 10^{-13}$  s,  $r_0 = 2.5 \cdot 10^{-1}$  cm,  $T = 298$  K,  $n = 2.4 \cdot 10^{19}$  cm<sup>-3</sup>, and  $E_f = 10^4$  erg along with  $\Delta \bar{\alpha} = 0.71 \cdot 10^{-24}$  cm<sup>3</sup> [Ref. 12] and  $B_e = 3.8 \cdot 10^{11}$  Hz, we obtain the effective absorption coefficient for molecular nitrogen:

$$k = \frac{16\pi}{15\hbar} \left( \frac{\Delta \bar{\alpha}}{c r_0} \right)^2 n B_e S E_f = 1.65 \cdot 10^{-6} \text{ cm}^{-1},$$

which coincides with the experimentally measured one in the order of magnitude.

## Conclusion

Nonresonant interaction of nonpolar molecules with a femtosecond laser pulse, much shorter than characteristic electron travel times, has been considered in this work. Neglecting multi-photon absorption, the molecule density matrix has been obtained in the fourth order of the perturbation and the general expression for the field energy loss has been found.

As is known, the density matrix best describes the state of the quantum system; hence, the obtained equations can be used as input data for solution of many problems, concerned with the interaction of considered type, such as problems of pulse propagation in a medium, relaxation of molecular system after pulse propagation, determination of nonlinear susceptibility of a medium, orientation and alignment of molecules in a field, etc.

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