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Generalized kinetics of laser-induced fluorescence versus standard approach

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ABSTRACT: We suggest generalized kinetics for the description of fluorescence induced by ultrashort laser pulses. This model is based on the expression for excitation probability at a given time obtained earlier in our papers. Proposed method is compared with standard approach which presumes that excitation probability is proportional to squared electric field strength in the laser pulse. Verification of generalized kinetics is made through the comparison with the exact solution of Bloch equations. It is shown that in the framework of the applicability of perturbation theory the results of generalized kinetics are in excellent correspondence with exact solutions while the standard approach gives much worse match.

PROBABILITY OF PHOTOEXCITATION AT A GIVEN TIME

Generalized kinetics

Let us consider the excitation of a quantum system (target) under the action of an electromagnetic pulse (EMP) in the framework of the applicability of perturbation theory and the dipole approximation. Using standard formulas [1], one can obtain the following expression for the probability of excitation of the target at a given time [2]

$$W(t,\tau)=\frac{c}{4\pi^2}\int_0^\infty d\omega\,\frac{\sigma(\omega)}{\hbar\omega}D(t,\tau,\omega), \tag{1}$$

$$D(t,\tau,\omega)=\left|\int_{-\infty}^{t}dt'\exp(i\omega t')\,E(t',\tau)\right|^2 \tag{2}$$

here $\sigma(\omega)$ is photoexcitation cross section of the target, *c* is light velocity, $E(t)$ is the electric field strength of EMP, t is pulse duration.

In the case of resonant excitation it is convenient to rewrite formulas (1)-(2) in the following form

$$W(t,\tau)=\omega_0\,\Omega_0^2\int_0^\infty G(\omega)\frac{\tilde{D}(t,\tau,\omega)}{\omega}d\omega, \tag{3}$$

$$\tilde{D}(t,\tau,\omega)=\left|\int_{-\infty}^{t}dt'\exp(i\omega t')\,\tilde{E}(t',\tau)\right|^2 \tag{4}$$

here $\Omega_0 = d_0 E_0/\hbar$ is Rabi frequency, d_0 and ω_0 are dipole operator matrix element and eigenfrequency of excited transition, E_0 and $\widetilde{E}(t) = E(t)/E_0$ are amplitude and dimensionless electric field strength of the pulse, $G(\omega)$ is spectral profile of the cross section.

Formulas (3)-(4) we use further for the description of generalized kinetics of photoprocesses in the field of ultrashort EMPs.

In what follows we assume Lorentzian spectral profile of excitation cross section

$$G(\omega) = \frac{1}{\pi T_2} \frac{1}{(\omega - \omega_0)^2 + T_2^{-2}}. \tag{5}$$

Here T_2 is phase relaxation time which determines the spectral width of homogeneously broadened transition $\Delta\omega_h = 1/T_2$.

Standard approach

Standard approach is based on the assumption that instantaneous probability per unit time of the photoprocess is proportional to the squared electric field strength at the given time moment, namely:

$$w_{st}(t) = \sigma(\omega_c) j_{phot}(t) = \sigma(\omega_c) \frac{c E^2(t,\tau)}{4\pi\hbar\omega_c} = \pi G(\omega_c) \Omega_0^2 \widetilde{E}^2(t,\tau), \tag{6}$$

here ω_c is carrier frequency of the pulse.

Then dimensionless probability is equal to

$$W_{st}(t,\tau) = \int_{-\infty}^{t} w_{st}(t')dt' = \pi G(\omega_c)\Omega_0^2 \int_{-\infty}^{t} \widetilde{E}^2(t',\tau)dt' \tag{7}$$

instead of the formulas (3)-(4) for generalized kinetics.

Note that in the monochromatic case one has

$$w_{mon} = \sigma(\omega) j_{phot}(\omega) = \sigma(\omega) \frac{c E_0^2}{8\pi\hbar\omega} = \frac{\pi}{2} G(\omega) \Omega_0^2 . \tag{6a}$$

This relation follows from (6) after averaging over oscillation period ($T = 2\pi/\omega$) of electromagnetic field in monochromatic radiation.

KINETIC EQUATION FOR THE POPULATIONS OF A TWO-LEVEL SYSTEM

Kinetic equation for the population inversion of a two-level system (TLS) can be written in the form [see e.g. 3]

$$\dot{N} + \frac{N - N_e}{T_1} = -2 w(t) N \tag{8}$$

here $N = N_2 - N_1$ is the population inversion at a given time, $N_{1,2}$ are populations of ground and excited states of TLS, N_e is equilibrium value of population inversion (without resonant radiation), T_1 is the population relaxation time, $w(t)$ is probability per unit time of the photo-induced process which is equal to

$$w(t)=\frac{d}{dt}W(t). \tag{9}$$

In the approximation of TLS, the normalization condition is

$$N_2+N_1=1. \tag{10}$$

The kinetic equation for the population of the upper level of the TLS under the assumption that $N_2^e=0$, taking into account equality (10), can be written as follows

$$\frac{dN_2}{dt}+\frac{N_2}{T_1}=w_i\left[1-2N_2\right]. \tag{11}$$

The solution of equation (11) is equal to

$$N_2(t,\tau)=\frac{1}{2}\left\{1-\frac{1}{T_1}\exp\left[-\frac{t}{T_1}-2W(t,\tau)\right]\int_{-\infty}^{t}\exp\left[\frac{t'}{T_1}+2W(t',\tau)\right]dt'\right\}. \tag{12}$$

here $W(t,\tau)$ is the excitation probability by EMP with duration t at the time moment *t* which is given by formulas (3)-(4) in the case of generalized kinetics or formula (7) in the framework of standard approach.

Neglecting the relaxation of the upper energy level of TLS ($T_1\to\infty$) formula (12) is simplified to

$$N_2(t,\tau,T_1\to\infty)=\frac{1}{2}\left\{1-\exp\left[-2W(t,\tau)\right]\right\}. \tag{13}$$

Note that in the limit of perturbation theory ($W(t,\tau)<<1$) it follows from (13) that $N_2(t,\tau)\cong W(t,\tau)$.

VERIFICATION OF GENERALIZED KINETICS MODEL

We verify our model using the comparison with the exact solution of Bloch equations which particularly determine the population of TLS upper level.

Calculations are made with the use of above formulas for the sodium atom excitation at the transition 3s-3p by exponential laser pulse:

$$E_{EP}(t,\tau)=\theta(t)E_0\exp(-t/\tau)\cos(\omega_c t) \tag{14}$$

here $\theta(t)$ is Heaviside step-function. This EMP provides the possibility to use relatively simple analytical expression for calculation. E.g. expression for D-functions (2) is the following

$$D_{EP}(t,\tau,\omega)\cong\frac{1}{4}\theta(t)E_0^2\tau^2\frac{1+\exp(-2t/\tau)-2\exp(-t/\tau)\cos\left[(\omega-\omega_c)t\right]}{1+\tau^2(\omega-\omega_c)^2}. \tag{15}$$

Note that (15) is derived in the rotating wave approximation which is valid if $\omega_c\tau>>1$.

Time dependences of upper level population calculated in the framework of different approaches are shown in Fig. 1-2 for different values of carrier frequency.

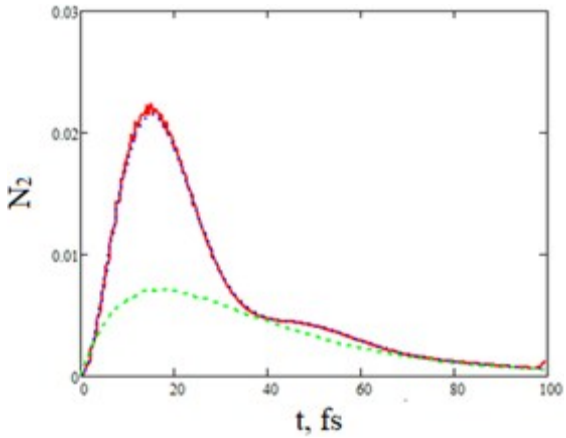

Fig.1.Time dependence of 3p level population of sodium atom calculated with the use of different approaches (off-resonance case): solid line – exact solution of Bloch equations, dotted line – generalized kinetics model, dashed line – standard approach; τ=24 fs, ω_c=1.904eV, Ω_0=0.0272eV

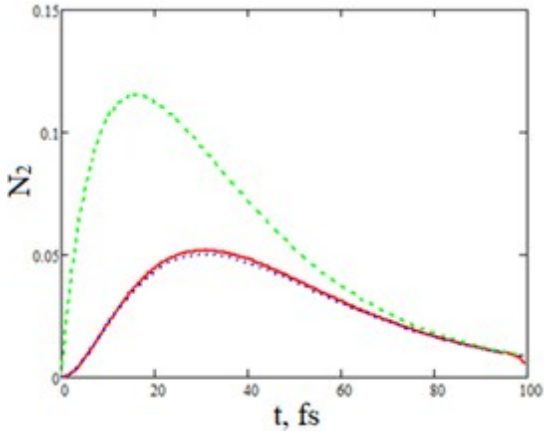

Fig.2. Time dependence of 3p level population of sodium atom calculated with the use of different approaches: solid line – exact solution of Bloch equations, dotted line – generalized kinetics model, dashed line – standard approach; τ=24 fs, $\omega_c=\omega_0$=2.013 eV, Ω_0=0.0272 eV

First of all one can see from these figures the excellent correspondence between results of exact Bloch solution and generalized kinetics model. At the same time standard approach gives much worse match. Note that in off-resonance case (Fig.1) there is shoulder in time dependence of upper level population while for near-resonance carrier frequency (Fig. 2) only one maximum appears.

It is noteworthy that in both cases, presented in Figs. 1-2, at large times ($t > \tau$) the population dependences on time $N_2(t)$ calculated by different methods are close to each other in magnitude.

It should be mentioned that generalized kinetics model is reasonable only in the framework of validity of perturbation theory when the following inequality for excitation probability holds

$$W(t,\tau) < 1. \tag{16}$$

Condition of applicability of this model (16) can be formulated in terms of pulse duration and Rabi frequency

$$\Omega_0 \tau < 1. \tag{17}$$

This relation should be valid at resonance carrier frequency. In off-resonance case the inequality (17) may be slightly weaker.

LASER-INDUCED FLUORESCENCE

We consider here the fluorescence of atomic sodium vapor at pressure $P=10^6$ Pa and temperature T=2000 K

induced by femtosecond laser pulse excitation on the 3s-3p electronic transition in Na atom. Under such conditions one can neglect the fine-splitting of 3p level and take into account only collisional broadening of the 3p-3s spectral line which is described by Lorentzian profile (5). Estimation shows that in this case the phase relaxation time is equal to $T_2 = 1067$ at. u. (25.6 fs). In what following we assume that $T_1 = T_2$.

The fluorescence volumetric power density is given by the relation

$$I_f(t,\tau) = \hbar\omega_0 \, An \, N_2(t,\tau) \tag{18}$$

here *A* is Einstein coefficient for spontaneous radiation at 3p-3s transition, *n* is concentration of sodium atoms. One can see from formula (18) that the time dependence of fluorescence signal is determined by the population of upper energy level 3p.

It is also of interest the fluorescence integral signal which is determined by the expression

$$S_f(t,\tau) = \int_{-\infty}^{t} I_f(t',\tau)\,dt' . \tag{19}$$

This quantity is usually used for the interpretation of experimental data.

The results of calculations of fluorescence integral signal as function of laser pulse duration are presented in Fig.3-4 in relative units for two values of carrier frequency (off-resonance and resonance) and large observation time (t > τ).

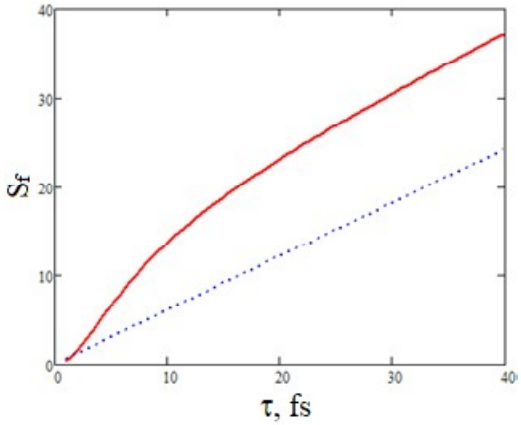

Fig.3.Integral fluorescence signal in sodium vapor as function of pulse duration calculated with the use of different approaches (off-resonance case): solid line – generalized kinetics model, dotted line – standard approach; τ=240 fs, ω_c=1.904 eV, Ω_0=0.0272eV

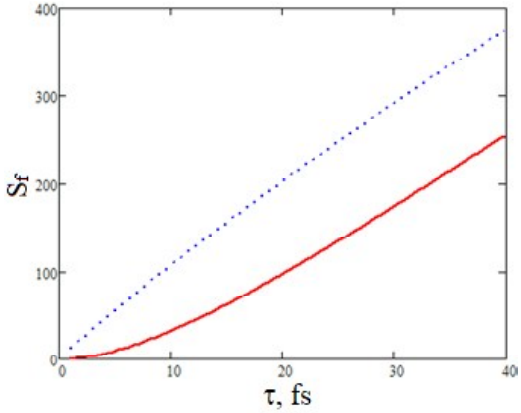

Fig.4. Integral fluorescence signal in sodium vapor as function of pulse duration calculated with the use of different approaches (resonance case): solid line – generalized kinetics model, dotted line – standard approach; t=240 fs, ω_c=ω_0=2.013 eV, Ω_0=0.0272eV

One can see from these figures that integral fluorescence signal calculated in the framework of standard approach is linear function of pulse duration both in off-resonance and resonance cases for large observation time ($t>\tau$). The same quantity calculated with the use of generalized kinetics model is nonlinear function of pulse duration especially for sufficiently short pulses ($t<15$-20 fs in considered case). This function is convex for off-resonance frequency (Fig.3) and concave for resonance one (Fig.4).

In particular, obtained dependences can serve as theoretical basis for experimental revealing a characteristic feature of fluorescence induced by ultrashort laser pulses, which is not described within the framework of the standard approach.

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References

[1] Landau L.D., Lifshitz E.M. Quantum Mechanics, Pergamon, 1974.

[2] V.A. Astapenko, Attosecond dynamics of photoexcitation of the Hydrogen atom by ultrashort laser pulses.// JETP 130 56-61 (2020).

[3] V.A. Astapenko Interaction of radiation with atoms and nanoparticles, Intellekt, 2010 (in Russian).