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Laser Pulse Sequence Effects on Selective Ionization in Three-Level Systems Driven by Coherent Radiation Fields

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Abstract. Using the time-dependent Schrödinger equation we investigate the effect of different pulse sequences of two lasers on selective ionization in three-level systems driven by coherent radiation fields. It is assumed that inhomogeneous broadening as well as the radiative decay can be neglected during the laser pulses. We demonstrate to what an extent the selectivity given by the absorption or relaxation process can be increased by coherent interaction during the first step and different timing of the incoherent interaction during the second step of a two-step photoionization. A comparison is made with the rate-equation results. We could show that utilization of coherent excitation for high ionization selectivity is most efficient if the two laser pulses do not overlap.

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Two- and three-level systems play a fundamental role in our understanding of absorption of radiation. The typical scheme of a two-step photoionization process involves the transition from the ground electronic state to an intermediate excited state and the subsequent ionization of the excited atom/molecule by visible, UV or VUV laser radiation. Using two different lasers this can be accomplished without ionizing ground-state species.

The excitation scheme is shown in Fig. 1. Nonradiative transitions described by a relaxation constant γ compete with the ionization from the excited state described by k_1.

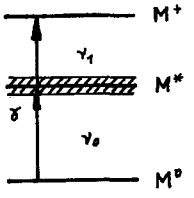

Fig. 1. Scheme of two-step photoionization

The selectivity of two-step photoionization through intermediate electronic states is governed by the electronic absorption spectra. A great improvement of selectivity is achieved by the use of supersonic cooled molecular beams.

The sequential excitation process can be varied by different pulse sequences. Such pulse sequences are an additional tool to increase the selectivity given by the absorption or relaxation process. The aim is a high selectivity at sufficient ionization efficiency [1–4]. In a former paper [2] using rate equations we investigated the effect of three different pulse sequences on selective ionization. Provided that the excitation process is incoherent we showed that there exists an optimum combination of pulse sequence, pulse duration and delay time for given conditions. Rate equations are adequate, when each subsequent step has a higher probability and there is no return from the ionized state. If one assumes a system coherently driven by the laser-field rate equations are insufficient and the Bloch equation formalism of the density matrix or the time-dependent Schrödinger equation should be applied. Then Rabi oscillations of the level populations can be achieved as a function of laser intensity, detuning and dephasing processes [4–14].

It is known that in a two-level system coherent interaction strongly increases the selectivity of the excitation process of two species compared with incoherent interaction [15].

We want to demonstrate to what an extent these coherent interaction properties are damped and the high selectivities are diminished if a third level is incoherently coupled by different timing. We investigate the special pulse sequences between exciting and ionizing lasers, as shown in Fig. 2. In pulse sequence A the lasers act simultaneously. In pulse sequence B the second laser is

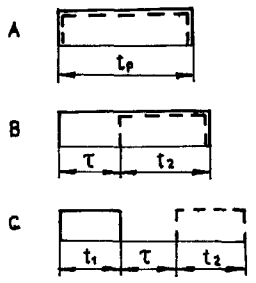

Fig. 2. Pulse sequences (—— first laser, ----- second laser)

switched on after a delay time τ additionally to the first one for a duration t_2. In pulse sequence C the second laser is switched on after a delay time τ with respect to the end of the first pulse. In this case the pulse durations of the first and second laser are denoted as t_1 and t_2, respectively.

Using time-dependent Schrödinger equation we investigate the effect of these pulse sequences on selective two-step photoionization and compare it with rate-equation results. To simplify this comparison we assume that inhomogeneous broadening as well as radiative decay processes can be neglected during the laser pulses and that the radiation fields are coherent: Erosion of coherence should only be caused by radiationless transitions and ionization.

The influence of fluctuations of the laser field and the effect of inhomogeneous broadening have been investigated in detail in [7, 15], respectively.

1. Time-Dependent Schrödinger Equation

In our two-step excitation process three levels are included. The third level (ionic state) participates in the dynamics of the two lower levels via a kinetic rate equation.

For a system which is coherently driven a wave function is adequate to describe its time evolution. The population-loss mechanism can be taken into account via complex energies of the states. When pure dephasing is significant during the excitation process, then density matrix description (Bloch equations) should be applied.

We restrict our discussion to a model system where line broadening is mainly caused by non-radiative processes described by the relaxation constant γ. A further broadening mechanism emerges, if a second, ionizing laser couples to the intermediate level with a rate constant k_1 which depends on the cross section of the intermediate to the ionic state and the laser intensity of the second laser.

We assume that the rotating-wave approximation can be applied, which is consistent with the assumption that each laser beam drives only its own transition [12, 16]. So the time evolution of the two lower levels can be described by the Hamiltonian

$$H=\begin{pmatrix} 0 & -\omega_R/2 \\ -\omega_R/2 & \Delta-i\gamma/2-ik_1/2 \end{pmatrix}. \tag{1}$$

$\omega_R=\mu E_0$ is the Rabi frequency which is proportional to the field strength E_0 and the transition-dipole moment μ ($\hbar=1$). Δ is the detuning between laser and transition frequency.

The wave function for this two-level system can be written as

$$|\psi(t)\rangle=c_0(t)|\varphi_0\rangle+c_1(t)|\varphi_1\rangle, \tag{2}$$

where $|\varphi_0\rangle$ and $|\varphi_1\rangle$ are the eigenfunctions of the ground and intermediate state, respectively. $|c_0(t)|^2$ and $|c_1(t)|^2$ are the corresponding occupation probabilities.

Without damping and in resonance, $|c_1(t)|^2$ oscillates with $\sin^2(\omega_R t/2)$ [17, 18].

In a general case we have

$$\begin{aligned}|c_1(t)|^2=P_1(t)&=|\langle\varphi_1|U(t,t_0)|\varphi_0\rangle|^2\\&=\left|\sum_j\langle\varphi_1|j\rangle\exp(-i\varepsilon_j(t-t_0))\langle\bar{j}|\varphi_0\rangle\right|^2\end{aligned} \tag{3}$$

and the ionization probability is evaluated by

$$P_i(t)=k_1\int_0^t|c_1(t')|^2dt' \tag{4}$$

if the two pulses coincide. $|j\rangle$ and ε_j are the eigenvectors and eigenvalues of H, respectively. They are complex, because H is non-Hermitian. $\{|j\rangle\}=D\{|\varphi\rangle\}$ and $\{|\bar{j}\rangle\}=(D^{-1})^+\{|\varphi\rangle\}$ is complementary to the basis $\{|j\rangle\}$ [17]. At time $t_0=0$ all species are assumed to be in the ground state.

2. Ionization Probabilities at Different Pulse Sequences

The expressions (3, 4) are valid for the pulse sequence A, and must be modified for the pulse sequences B and C. In pulse sequence B two different time evolution operators $U^{(1)}$ and $U^{(2)}$ must be applied characterized by $k_1=0$ and $k_1\neq0$, respectively. For the occupation probability of the intermediate state after the laser pulses, i.e. after the delay time τ and the time t_2, in which both lasers act, one obtains

$$\begin{aligned}|c_1(t_2,\tau)|^2&=|\langle\varphi_1|U^{(2)}(t_2,0)U^{(1)}(\tau,0)|\varphi_0\rangle|^2\\&=\Big|\sum_{j^{(1)}}\sum_{j^{(2)}}\langle\varphi_1|j^{(2)}\rangle\langle\bar{j}^{(2)}|j^{(1)}\rangle\langle\bar{j}^{(1)}|\varphi_0\rangle\\&\quad\times\exp(-i\varepsilon_j^{(1)}\tau)\exp(-i\varepsilon_j^{(2)}t_2)\Big|^2.\end{aligned} \tag{5}$$

The ionization probability is then

$$P_i(t_2,\tau)=k_1\int_0^{t_2}|c_1(t_2',\tau)|^2dt_2'. \tag{6}$$

In pulse sequence C the occupation probability (3) after the pulse duration t_1 relaxes (during delay time τ) to

$$|c_1(\tau,t_1)|^2=|c_1(t_1)|^2\exp(-\gamma\tau). \tag{7}$$

In this case the ionization probability can be evaluated analytically and reads after the end of the second pulse (duration t_2)

$$\begin{aligned}P_i(\tau,t_1,t_2)&=k_1|c_1(\tau,t_1)|^2\\&\quad\times\{1-\exp[-(\gamma+k_1)t_2]\}/(\gamma+k_1).\end{aligned} \tag{8}$$

3. Relations to Rate Equations

We compare our results with those obtained by using the rate equations [2]

$$dN_0/dt = -k_0(N_0 - N_1),$$
$$dN_1/dt = +k_0(N_0 - N_1) - \gamma N_1 - k_1 N_1, \quad (9)$$
$$dN_i/dt = +k_1 N.$$

The quantities $N(t)$ represent the time evolution of the populations of the corresponding states, the k's are transition rates given by $k = \sigma \times I$ with σ being the cross section [cm^2] and I the laser flux [photons/(cm^2 × s)].

In this case the occupation probability of the intermediate state and the ionization probability can be expressed by

$$P_1(t) = N_1(t)/N_0(0) \quad (10)$$

and

$$P_i(t) = N_i(t)/N_0(0). \quad (11)$$

$N_0(0)$ is the initial ground-state population and $N_1(0) = N_i(0) = 0$.

The selectivity of the excitation and ionization process of two species a and b can be written as

$$S_1(t) = P_1^a(t)/P_1^b(t) \quad (12)$$

and

$$S_i(t) = P_i^a(t)/P_i^b(t), \quad (13)$$

where the $P(t)$ have to be replaced by either probabilities resulting from the Schrödinger equation or from rate equations.

For equivalence between the parameters of the rate equations (k_0, k_1, γ) and Schrödinger equation $(\Delta, \omega_R, k_1, \gamma)$ the following relation can be derived using the Wilcox-Lamb method [6, 19]:

$$\omega_R^2 = 4k_0[(k_1+\gamma)^2/4 + \Delta^2]/(k_1+\gamma). \quad (14)$$

Figure 3 shows the differences between rate-equation and Schrödinger-equation results as to the occupation and ionization probabilities (3, 4) and (10, 11), which mainly influence the selectivity of the pulse sequences. It is also demonstrated that the ratio between k_1 and ω_R affects P_1 and P_i in a different way. For simplicity, we used $\gamma = 0$ and $\Delta = 0$. If $k_1 > \omega_R$ Rabi oscillations cannot be formed and rate-equation and Schrödinger-equation results are similar (a). If $\omega_R > k_1$ oscillations of P_1 arise and influence P_i (b). At very large $\omega_R \gg k_1$ strong Rabi oscillations of P_1 take place but P_i corresponds to the rate-equation result $P_i = 1 - \exp(-k_1 t/2)$ because of the decoupling of the two transitions (c). If $\gamma \neq 0$ and $\Delta \neq 0$ the oscillations of P_1 are additionally damped and changed in frequency [18]. Therefore, the conditions for P_1 as to oscillations become more complicated.

For the comparison of the pulse sequences we used a fixed parameter set k_0, k_1, and γ of the rate equations. Thus, according to (14), different possibilities to choose ω_R and Δ are given. Figure 4 demonstrates the influence of this parameter choice. It shows the rate-equation

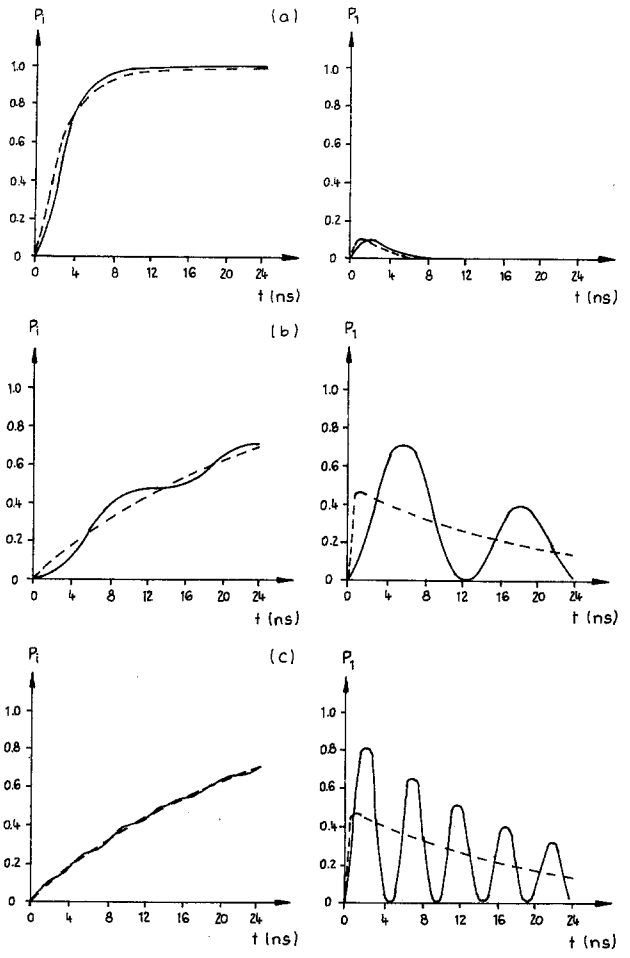

Fig. 3. Ionization and occupation probability (P_i and P_1) at (**a**) smaller, (**b**) larger, and (**c**) very large Rabi frequencies compared with ionization rate constant k_1 ($\gamma = 0$). (**a**) $\omega_R = 10^9\ s^{-1}$, $k_1 = 2.5 \times 10^9\ s^{-1}$; (**b**) $\omega_R = 5 \times 10^8\ s^{-1}$, $k_1 = 10^8\ s^{-1}$; (**c**) $\omega_R = 5 \times 10^9\ s^{-1}$, $k_1 = 10^8\ s^{-1}$ (——, Schrödinger equation; - - - - -, rate equations)

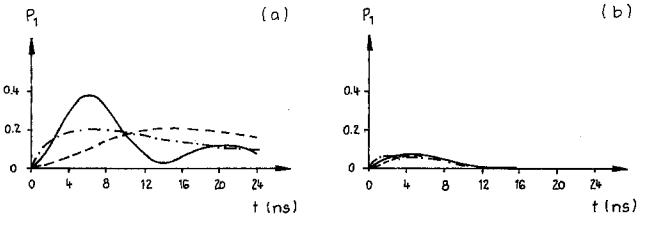

Fig. 4. Effect of detuning on occupation probability P_1 in Schrödinger-equation results at $k_0 = 10^8\ s^{-1}$ and $\gamma = 2 \times 10^8\ s^{-1}$. (**a**) $k_1 = 0$; (**b**) $k_1 \neq 0$ (——, $\Delta \neq 0, \omega_{R1}$; - - - - -, $\Delta = 0, \omega_{R2}$; · · · · · ·, rate-equation result)

results (10) and the corresponding Schrödinger-equation results (3) in dependence on Δ. First, we put $k_1 = 0$. At $\Delta \neq 0$ an oscillating occupation probability appears contrary to $\Delta = 0$ for the same k_0 and γ. Only if k_1 is large, strong relaxation equalizes the results.

Varying k_1 during the pulse sequences affects rate constant k_0 in (14) because ionization shortens the lifetime of the excited state and causes additional line broadening.

A fixed k_0 can be taken for all three pulse sequences if one sets

$$\Delta^2 = \gamma(k_1 + \gamma)/4 . \tag{15}$$

If the detuning strongly deviates from this value k_0 must be varied.

Differences in k_0 or γ of the two species a and b assumed in our rate-equation calculations as either $k_0^b = x k_0^a$ and $\gamma^b = \gamma^a$ or $\gamma^b = x\gamma^a$ and $k_0^b = k_0^a$ (with $x = 1.2$, 2 or 5, for example) now must be transformed into differences of the parameters used in the Schrödinger-equation approach by means of (14). Provided that the detunings expressed by (15) are nearly the same, different k_0, i.e. different absorption cross sections, result in different Rabi frequencies $\omega_R^b = \sqrt{x}\,\omega_R^a$ which correspond to different transition-dipole moments between the electronic states. If the absorption cross sections coincide but there are differences in the relaxation of the intermediate state relation (14) leads to Rabi frequencies and detunings (15) which depend on γ.

4. Results and Discussion

For the rate constants k_0, k_1, and γ we assumed in correspondence to our calculations in [2] the following values: $k_0 = 10^8\,\mathrm{s}^{-1}$, $k_1 = 10^9\,\mathrm{s}^{-1}$, and $\gamma = 2 \times 10^8\,\mathrm{s}^{-1}$.

Under the above-mentioned conditions the first transition can be driven coherently if relaxation acts ($\gamma \neq 0$) and ionization is absent ($k_1 = 0$). When the second laser is switched on, an incoherent interaction with the laser field takes place.

The pulse sequences are compared at the same laser intensities and on the basis of maximum selectivity at a given efficiency of ionization. For efficient ionization we set $t_2 = 15$ ns in the sequences B and C.

Figure 5 shows the ionization probabilities (4, 6, and 8) and the corresponding selectivities (13) due to different transition-dipole moments for the three pulse sequences A, B, and C. In sequence C we set $\tau = 0$ because it has no influence on the selectivity concerning transition-dipole moments and absorption cross sections of the exciting step, respectively. The values of the peak selectivities were taken from 0.1 ns time steps.

Figure 6 shows the ionization probabilities and selectivities at constant k_0 if there are additionally different relaxation rates of the excited state as described in part 3.

For pulse sequence A both lasers act simultaneously. Coherence effects during the first transition are destroyed by the relaxation γ and the ionization k_1. That is why no Rabi oscillations occur, and results of the rate equations [2] and Schrödinger's equation are similar.

For the pulse sequences B and C first only the exciting laser acts and the coherence destroying effect of k_1 is absent. For the same Rabi frequency as in sequence A now oscillations of the occupation probability P_1 take place until the second laser is switched on. Therefore, peaks in the selectivity of the occupation probability S_1 appear in contrast to rate-equation results. These peaks can be seen for different ω_R in Fig. 5 at the sequence C because we

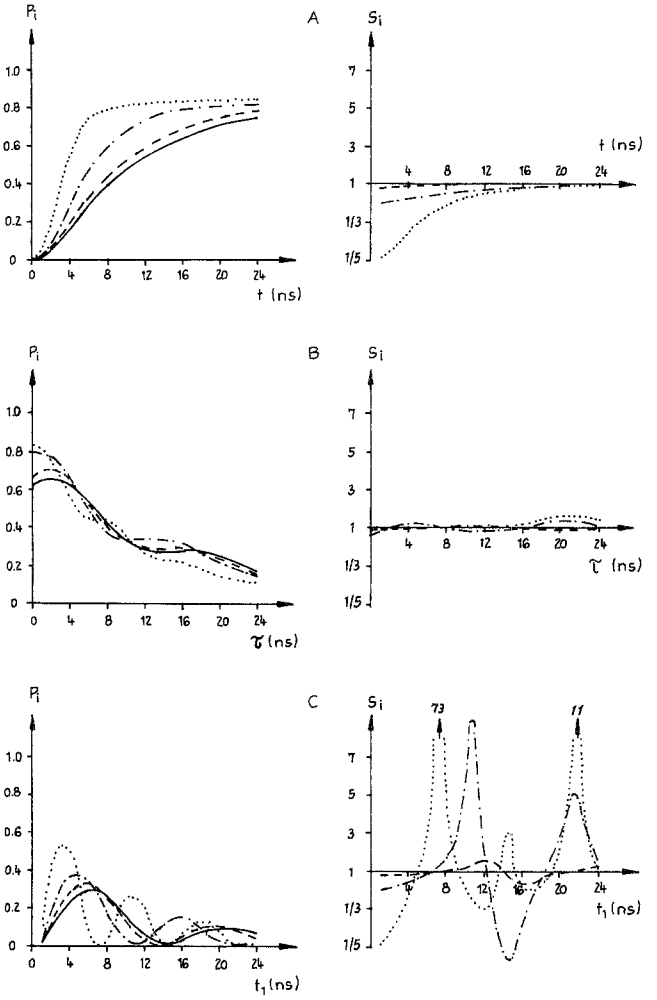

Fig. 5. Ionization probability P_i and selectivity S_i due to different transition-dipole moments ($\mu^b = \sqrt{x}\mu^a$) as a function of pulse sequence (**A, B, C**), pulse duration (t, t_1) and delay time (τ) (——, μ^a; - - - -, μ^b ($x = 1.2$); - · - · -, μ^b ($x = 2$); ····· μ^b ($x = 5$)

have here $S_1 = S_i$. They are demonstrated in Fig. 7 where additionally γ is different.

For the pulse sequence B these high selectivities cannot be transformed to high ionization selectivities. The overlap of the two laser pulses during t_2 is necessary for sufficient ionization, but smoothes the peaks of selectivity in dependence on t_2. This is also the case if the excitation during t_2 remains coherently because the occupation probability is much more oscillating than the ionization probability (Fig. 3b). Table 1 illustrates to what extent the high occupation selectivity is reduced by ionization if the two laser pulses overlap during t_2. Therefore utilization of coherent interaction properties for selective ionization is most efficient in sequence C, where ionization takes place without exciting ground-state species and therefore occupation instead of ionization probability is employed for high ionization selectivity. Moreover, sequence C has the advantage that a larger intensity of the first laser leads in a two-level system to more intensive Rabi oscillations and therefore to higher selectivities. In a three-level system stronger Rabi oscillations not always lead to more

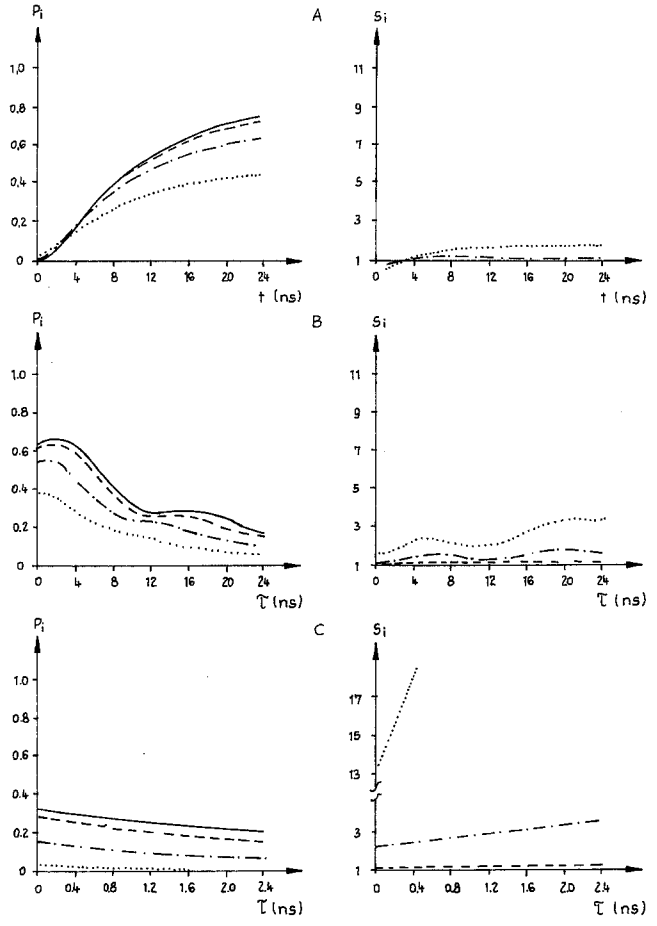

Fig. 6. Ionization probability P_i and selectivity S_i due to different relaxation rates ($\gamma^b = x\gamma^a$) as a function of pulse sequence (**A**, **B**, **C**), pulse duration (t), ($t_1 = 6$ ns) and delay time (τ) (—— γ^a; - - - - - γ^b ($x = 1.2$); - · - · - · γ^b ($x = 2$); · · · · · · · · γ^b ($x = 5$) (for additional differences in μ and Δ, see text)

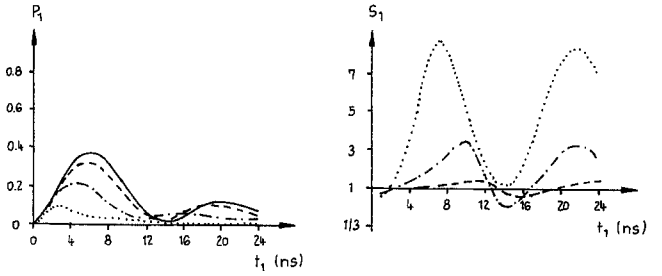

Fig. 7. Occupation probability P_1 and selectivity S_1 due to different relaxation rates as a function of t_1 (other parameters, see Fig. 6)

Table 1. Ionization selectivity of sequence B due to different transition dipole moments of two molecular species as a function of t_2 compared with the occupation selectivity at $\tau = 7$ ns and $t_2 = 0$

t_2 [ns]	P_i	S
0	–	36.7
1	0.21	15.3
2	0.28	3.6
3	0.31	1.8
4	0.33	1.2

oscillating ionization probabilities. Figure 3c shows that the effect of a high Rabi frequency consists in an approach to rate-equation results.

The preference of sequence C is in contrast to rate-equation results where also sequences A or B can give better selectivities [2]. That is why it is important whether the first transition is driven coherently or incoherently.

Because we only consider radiationless transitions and ionization as phase destroying processes the results of coherent and incoherent excitation can be compared in the same time scale, e.g., in the nanosecond range as applied in our calculations. This simplifies the comparison between Schrödinger- and rate-equation results, and makes it more transparent. For real physical situations, however, with significant additional homogeneous and inhomogeneous line broadenings coherence effects can be expected only on a much shorter time scale, i.e. at higher intensities and shorter pulse durations. In this case the obtained results have to be transferred to a time scale in which a coherent excitation of the first step can be achieved. The conclusions concerning optimum pulse sequences do not alter as long as a coherent excitation is possible. If inhomogeneous broadening is significant during coherent excitation it affects the size of the selectivity [15]. In those cases in which dephasing effects are so strong that coherent excitation cannot be achieved rate-equation results are adequate.

5. Summary

Using time-dependent Schrödinger equation we have shown to what extent coherent interaction properties of the first transition and different timing of the incoherent interaction of the second transition affect the selectivity in three-level systems with line broadening mainly caused by radiationless transitions and ionization, respectively. The equations have been solved in the rotating-wave approximation and compared with rate-equation results. The investigation of three different pulse sequences has been demonstrated that the coupling of a third level strongly reduces the achieved high selectivity in a coherently excited two-level system if the two pulses overlap. So pulse sequence C is always the most selective provided that the intensity of the first laser is high enough to induce Rabi oscillations and its pulse duration is properly chosen depending on the differences in detuning, transition dipole moments or relaxation rates.

In the rate-equation description Rabi oscillations do not appear and it is not obvious, which pulse sequence is the most selective one. Here a partial or complete overlap can be more selective as calculations showed. So the choice of a special pulse sequence to achieve high selectivity in two-step photoionization is strongly influenced by the type of the interaction during the first transition.

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