

FEEDBACK DESIGN OF CONTROL ALGORITHMS FOR DISSOCIATION OF DIATOMIC MOLECULES

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Abstract

Two methods for dissociation of diatomic molecules based on nonperiodic excitation generated by feedback control mechanism are described and analyzed both analytically and by computer simulation. The first method of control design uses nonlinear resonance curve of the system to fulfill the resonance conditions at any time of excitation. The second method is based on the speed-gradient principle. Implementation of the proposed methods by pulse laser control is described. It is shown that both the resonant curve and the speed-gradient algorithms in ideal case (in the feedback loop) ensure dissociation with arbitrarily small intensity of the controlling field from almost all initial conditions. Efficiency of the proposed methods is demonstrated by simulation for example of hydrogen fluoride (HF) molecule dissociation. Simulations confirmed that new methods are more efficient than the existing algorithms based on harmonic (monochromatic) and linear chirping excitation both for the model case of single molecule and for an ensembles of molecules.

1 Introduction

Since the beginning of the 1990s a growing interest has been observed in the control problems for molecular systems in classical and quantum formulation [1, 2, 4, 3, 12]. One of the benchmark problems in the field is the dissociation problem for diatomic molecules [2, 5, 6, 7, 8]. In the paper [5] possibilities of dissociation a molecule by monochromatic (single frequency) laser field have been explored for the case of hydrogen fluoride (HF) molecule using Chirikov's resonance overlap criterion. In [6, 7] the case of two-frequency (two-laser) control field was investigated. It was shown that intensity of bichromatic field required for dissociation can be reduced compared to monochromatic case. In [8] the further reduction of the control field intensity has been demonstrated by means of chirping (frequency modulation) the laser frequency with constant chirping rate.

New possibilities for changing of physical and chemical properties are provided by using feedback for control design. In [2]

methods based on geometric control theory (inverse control) were proposed for control of molecular systems, including dissociation problems for diatomic and triatomic molecules. In a number of papers possibility of optimal control design is discussed. Two methods for dissociation of diatomic molecules design by feedback control based on resonance curve and speed-gradient principle were proposed in [9, 10].

In this paper new versions of the algorithms of [9, 10] are developed and analyzed. The first algorithm is based on the dependence of the natural frequency of the nonlinear molecule oscillations on its energy, further referred to as *energy resonance characteristics* or *energy resonance curve*. For control design the knowledge of the energy resonance curve is required. For the case of Morse potential this dependence is obtained in a simple analytical form. For other potentials, where the analytical solution is too complicated if not impossible, the energy resonance curve can be obtained numerically. Efficiency of the proposed algorithm for the case of HF molecule is illustrated by computer simulation. It is shown that the time of dissociation can be reduced significantly compared with such nonfeedback designs as harmonic excitation or linear chirping.

Second algorithm is based on the speed-gradient method [11]. Design of the algorithm does not rely on the shape of the potential energy of molecule and does not require precalculation of the energy resonance curve. In order to demonstrate applicability of the proposed methods to realistic experimental situations we compare one of the proposed design (speed-gradient algorithm) with the optimal linear chirping by simulating it for a molecular ensemble. The open-loop pulse control strategy is used that fits modern femtosecond laser pulse experimental technologies [12].

Note that the algorithms of [9, 10] are based on classical models of molecular dynamics. Classical models are often used instead of the quantum ones in dynamics calculations of molecular motion [13, 5, 6, 14, 15]. It was shown that classical and quantum dynamics give similar results for model systems with one or two degrees of freedom. Even when the expectation values of the quantum wave packet did not exactly correspond to the averages over classical trajectories, observables such as dissociation probabilities were shown to be quite similar for monochromatic [13, 5] and bichromatic [6] excitation. Recently the possibility of using classical models for feedback de-

sign was justified by comparison of the results obtained by simulation of classical and quantum-mechanical ensembles [16]. The problem statement and controlled system equations are given in Sec. II. In Sec. III the case of one molecule is studied. The known dissociation control algorithms (monochromatic excitation and linear chirping) and new control algorithms (resonance curve and speed-gradient methods) based on feedback design are considered. Efficiency of the feedback algorithms for the case of HF molecule is confirmed by computer simulation results. In Sec. IV the application of the feedback technique to the pulse control for a molecular ensembles is considered.

2 Model of the controlled system

Let us consider a diatomic molecular system under the action of the external laser field. Dynamics of such a system can be described by the following controlled Hamiltonian [2, 7]

$$H = \frac{p^2}{2m} + \Pi(r) - \mu(r) u(t), \quad (1)$$

where m is reduced mass, p is momentum, $\Pi(r)$ is potential of interatomic interaction, $\mu(r)$ is dipole moment of the molecule, $u(t)$ is intensity of external field. The value $u(t)$ serves as control variable. Transformation to Lagrangian form yields the following equation of molecular motion

$$m\ddot{r} = -\Pi'(r) + \mu'(r)u(t). \quad (2)$$

Let us use Morse form of the interatomic potential

$$\begin{aligned} \Pi(r) &= \\ &= D \left(e^{-2\alpha(r-r_e)} - 2e^{-\alpha(r-r_e)} \right), \end{aligned} \quad (3)$$

where D is the bond energy, r_e is the equilibrium interatomic distance. The corresponding force is

$$f(r) = -\Pi'(r) = 2\alpha D \left(e^{-2\alpha(r-r_e)} - e^{-\alpha(r-r_e)} \right). \quad (4)$$

For the dipole moment the linear approximation is used

$$\mu(r) = Ar, \quad \mu'(r) = A, \quad (5)$$

where A is constant. Thus the equation of motion (2) reads

$$\begin{aligned} m\ddot{r} &= 2\alpha D \left(e^{-2\alpha(r-r_e)} - e^{-\alpha(r-r_e)} \right) \\ &+ Au(t). \end{aligned} \quad (6)$$

In the vicinity of equilibrium $r \approx r_e$ equation (6) with harmonic excitation ($u(t) = E \cos(\omega t)$, where E and ω are strength and frequency of the external laser field) can be reduced to the equation of linear forced oscillations

$$m\ddot{r} = Cr + EA \cos(\omega t), \quad C \stackrel{\text{def}}{=} \Pi''(r_e) = 2\alpha^2 D, \quad (7)$$

where C is linear stiffness of the bond. The natural frequency of the linear system is

$$\Omega_0 \stackrel{\text{def}}{=} \sqrt{C/m} = \alpha \sqrt{2D/m}. \quad (8)$$

3 Dissociation control design

3.1 Nonfeedback control design

The simplest way to control molecular systems is monochromatic excitation with frequency of external laser field $\omega = k\Omega_0$, $k \leq 1$ (Ω_0 - natural frequency of the linearized system). This approach is well known and was investigated in a large number of publications. In this case equation of motion (6) takes the form

$$m\ddot{r} = -\Pi'(r) + AE \cos(\phi_0 + \omega t), \quad (9)$$

where ϕ_0 is the initial phase of control.

In a nonlinear system the resonance frequency is function of the amplitude of oscillations, or, in other words, it depends on the energy of the oscillator. Thus the faster dissociation can be achieved if the excitation frequency is changing (decreasing in our case) while the energy increases. The simplest control algorithm of this kind can be done by linear chirping:

$$\omega = \Omega_0 - \varepsilon t \quad (10)$$

where ε is a constant (chirping rate), which characterizes the speed of the frequency decrease. In this case equation of motion (6) takes the form

$$m\ddot{r} = -\Pi'(r) + AE \cos \varphi, \quad \dot{\varphi} = \omega(t) = \Omega_0 - \varepsilon t \quad (11)$$

or

$$m\ddot{r} = -\Pi'(r) + EA \cos\left(\phi_0 + \Omega_0 t - \frac{\varepsilon t^2}{2}\right), \quad (12)$$

where ϕ_0 is the initial phase of control.

Simulation results. We studied dissociation control algorithms by computer simulations for the case of hydrogen fluoride (HF) molecule that has become a benchmark problem for controlled dissociation. This study is useful for comparing the efficiency of existing and new methods. The parameters of the model (6), corresponding to HF molecule are as follows [2, 7]: $m = 1732$, $D = 0.2101$, $\alpha = 1.22$, $a = 1.75$, $A = 0.4541$. The intensity of external laser field was $E = 0.005$. All quantities are given in atomic units. The equation was integrated numerically by central differences method with time step $dt = T_0/200$ (integration with smaller time steps yields practically the same results). The initial molecule energy is $W_0 = -0.8689D = -0.1826a.u.$ (corresponds to 2nd energy state in quantum-mechanical model). The dissociation criterion for a molecule is exceeding of the molecule energy the value of dissociation energy $W_* = -0.1185D = -0.0249a.u.$ (corresponding to 15-th energy state in quantum-mechanical model). The initial conditions for excitation at the initial energy W_0 is molecule with the minimal interatomic distance, corresponding to this energy value (velocity is equal to 0), i.e. $r = r_{min}(\Pi(r_{min}) = W_0)$, $\dot{r} = 0$.

Note that efficiency of both methods depends on the parameters k_c (in case of monochromatic excitation) and k_l (in case of

linear chirping) and on the initial deviations between phases of control (i.e. ϕ_0 in both cases) and phases of molecular motion (for our initial conditions the initial phases of molecular motion are 0). This dependence corresponds to the following condition : for the fastest energy growth control function should be "in phase" with the molecular motion, or, in other words, signs of control and velocity should be the same during sufficiently long time. Simulation results show that the monochromatic excitation requires high intensity control, while the linear chirping method is not robust. More details can be found in [16].

3.2 Resonance curve control design

More efficient dissociation can be achieved by taking advantage of the feedback control. In this case the frequency of excitation is changing according to the oscillator energy so that at any amplitude of oscillations the excitation acts at the resonance frequency. Let $\Omega(W)$ be the natural frequency of the diatomic molecular oscillator at the specified energy W . We call the function $\Omega(W)$ *frequency-energy resonance function*. The graph of this function is called *resonance curve*. The key idea of our approach is that if the function $\Omega(W)$ is known and the energy $W = W(t)$ is observable. Corresponding control algorithm

$$u(t) = E \cos \varphi \quad \dot{\varphi} = \Omega(W) \quad \varphi(0) = \varphi_0 \quad (13)$$

gives following equation of motion

$$m\ddot{r} = -\Pi'(r) + EA \cos \varphi \quad \dot{\varphi} = \Omega(W) \quad \varphi(0) = \varphi_0. \quad (14)$$

Obviously, control algorithm (13) will give the desired excitation at the resonance frequency at any time instant.

The relation $\Omega(W)$ in principle can be calculated (analytically or numerically) for any known potential $\Pi(r)$ using the integral of energy.

Luckily, for Morse potential analytical calculations give the following simple relation between energy and natural frequency of Morse oscillator

$$-\frac{W}{D} = \left(\frac{T_0}{T}\right)^2 = \left(\frac{\Omega}{\Omega_0}\right)^2, \quad (15)$$

where Ω_0 is defined by (8), $T_0 = 2\pi/\Omega_0$, Ω and T are natural frequency and period of the diatomic molecular oscillator at the specified energy W . The control law (13) therefore takes the form

$$u(t) = E \cos \varphi \quad \dot{\varphi} = \Omega(W) = \Omega_0 \sqrt{-\frac{W(t)}{D}} \quad \varphi(0) = \varphi_0, \quad (16)$$

where $W(t)$ is the current value of the molecule energy.

Simulation results. Efficiency of the proposed control algorithm was confirmed by computer simulations for dissociation of the hydrogen fluoride (HF) molecule with the parameters and initial conditions as described above. Note that, like a previous case, efficiency of the method depends on the initial

deviation on a phase (i.e. deviation between initial phase of control and initial phase of molecular motion) and on the multiplier at the frequency. Experiments show that the best result takes place when multiplier is equal to 1 (it is natural because this method is based on the strict fulfillment of the resonance conditions). Besides, from Fig. 1.a we see the minimal dissociation time if the initial deviation on phase is approximately zero. Thus, we can see that if we have strict fulfillment of the resonance conditions and start to control "in phase" with the system, we obtain best results. Corresponding graph Fig. 1.b shows that the dissociation takes place at $t \approx 52T_0$. This result is better (≈ 1.2 times) than the best result, provided by the linear chirping method. Furthermore, from the Fig. 1.a we can see that the efficiency of the resonance control depends smoothly and monotonically on the initial phase deviation. Thus, the resonance control method can be made more robust than non-feedback control methods.

3.3 Speed-gradient control design

The underlying idea of the speed-gradient method (see [11]) is that moving along the negative gradient of the speed \dot{Q} of a given goal function $Q(x)$ provides decrease of \dot{Q} (x is the state vector of a controlled dynamical system). It may eventually lead to negativity of \dot{Q} which, in turn, yields decrease of Q and, eventually, achievement of the primary goal

$$Q(x(t)) \rightarrow 0 \text{ when } t \rightarrow \infty. \quad (17)$$

In the case of dissociation problem the natural goal of control can be expressed in terms of the molecule free energy. In order to control the system to the desired energy level W_* , the energy related goal function $Q = (W - W_*)^2$ can be chosen, where W is the energy of the considered molecule. Let us use the speed-gradient method in finite (relay) form. Performing calculations according to this method, we arrive at simple feedback laws:

$$u = -E(W - W_*) \dot{r}, \quad (18)$$

$$u = -E \text{sign}(W - W_*) \cdot \text{sign} \dot{r}, \quad (19)$$

where $E > 0$; $\text{sign}(W) = 1$ for $W > 0$, $\text{sign}(W) = -1$ for $W < 0$, and $\text{sign}(0) = 0$.

The control algorithm (19) can be further simplified if we eliminate energy (e.g., assuming that system energy do not exceed the dissociation threshold):

$$u = \gamma \text{sign} \dot{r}, \quad (20)$$

that looks like introducing negative Coulomb friction into the system.

Simulation results. Simulation was performed for the set of parameters and initial conditions corresponding to HF molecule as described above. Let us note, that control of that type is originally "in phase" with the system. In Fig. 2.a the results of the speed-gradient feedback control (20) are presented. Graph shows the energy as a function of time for the feedback

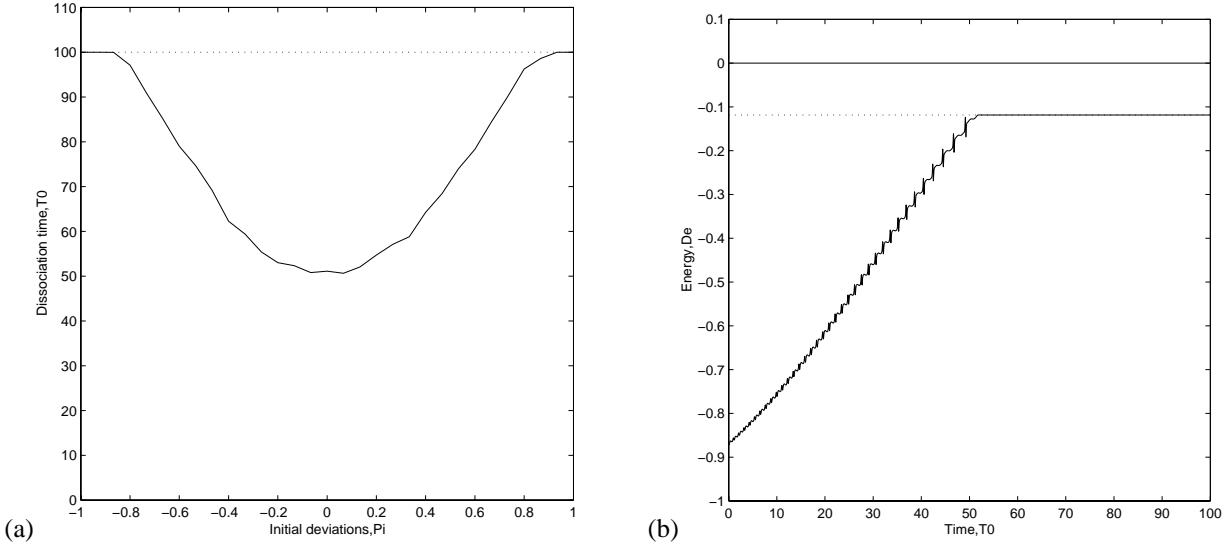


Figure 1: Excitation using resonance curve: (a) dependence of the dissociation time on the initial phase deviation, (b) excitation with zero initial deviation (“in phase”). Energy is measured in the units of the bond energy D , time is in the units of T_0 (natural period of linear oscillations), initial phase deviation - in π .

control (20). Obviously, this method provides the fastest dissociation at $t \approx 37T_0$. In Fig. 2.b we can see results of applying the speed-gradient type impulse with Gaussian envelope to the system. Such situation is more acceptable for real systems. Naturally, such adaptation gives a little worse results with dissociation at $t \approx 55T_0$. Graphs Fig. 3.a, Fig. 3.b show the corresponding control functions.

Thus the feedback control based on the speed-gradient method provides approximately 1.7 times faster dissociation than the best variant of the linear chirping. This method is also faster than the considered before energy-feedback method. However, since the direct implementation of the speed-gradient method is difficult, this method should be modified for experimental use. Such a modification is described below where simulation results for control of an ensemble of molecules are presented.

4 Properties of the controlled system

The following theorems show that both the resonant curve and the speed-gradient algorithms in ideal case (in the feedback loop) ensure dissociation with arbitrarily small intensity of the controlling field from almost all initial conditions.

Theorem 1. For the system (1), (16) with $(p_0, r_0) \neq (0, r_e)$ the control goal can be achieved for any sufficiently small value of E .

Theorem 2. For the system (1), (20) with $(p_0, r_0) \neq (0, r_e)$ the control goal can be achieved for any value of E .

The proofs are based on using $Q(x) = (H(x) - H_*)^2$ as a Lyapunov function. Note that achievement of the goal by the resonance curve algorithm is established under the “small control” restriction.

For practical applications the analytical results are not suffi-

cient. The evaluation of the algorithms in a more realistic situation is needed, when the feedback is applied only to precalculation of the controlling input. Such an analysis will be done in the next section.

5 Simulation of pulse control for molecular ensembles

In the real experiments obtaining the immediate feedback response is problematic. Therefore we precalculate the control function using the feedback technique for a selected representative molecule. Then this precalculated control function is used to control all the molecules in the ensemble (classical or quantum) in the open-loop mode during the specified time interval. The control method is used for shaping the laser pulses while between pulses the system remains uncontrolled. Such a control strategy corresponds to modern femtosecond laser pulse experimental technologies [12].

Let T_1 be pulse repeating time interval and the pause (time interval between pulses) be T_2 . Then the pulse duration will be $T_3 = T_1 - T_2$. We assume that the pause is long enough to allow the system to forget the influence of the previous pulse due to its ergodic properties. The following additional simplifying assumptions are used.

- Molecules do not interact with each other and with the boundary.
- The molecules are moving in one dimension along the force lines of external laser field, i.e. orientation and rotational effects are neglected.

Therefore the system is modeled as the system of N noninteracting Morse oscillators with parameters corresponding to HF molecule. The measure of efficiency is the fraction of the dis-

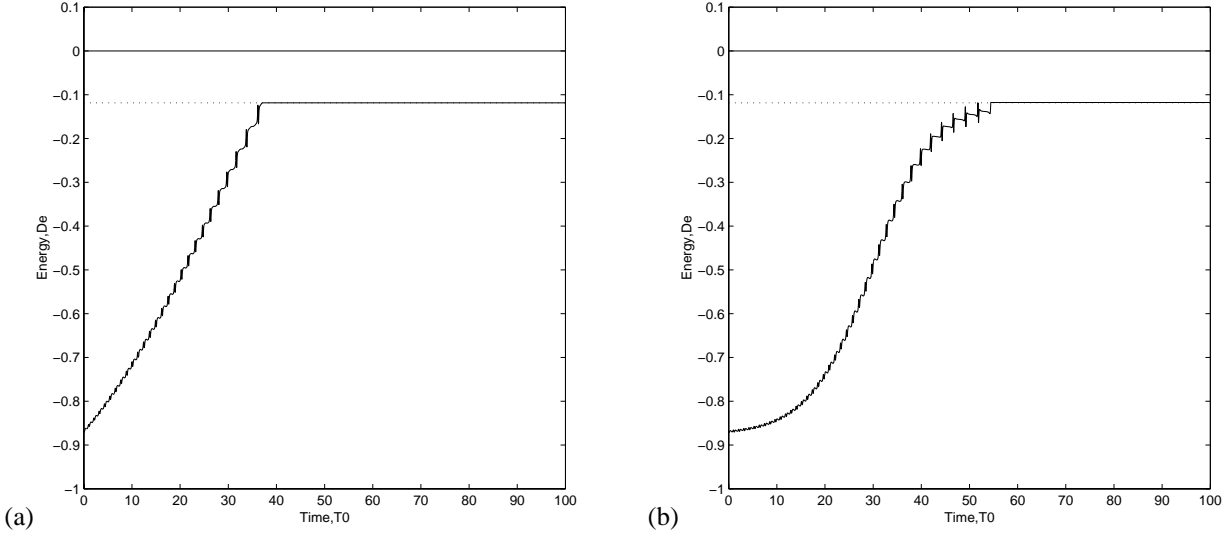


Figure 2: Excitation with speed-gradient feedback control: (a) using the speed-gradient method in form (20); (b) using speed-gradient type impulse with Gaussian envelope. Energy is measured in D , time is measured in T_0 .

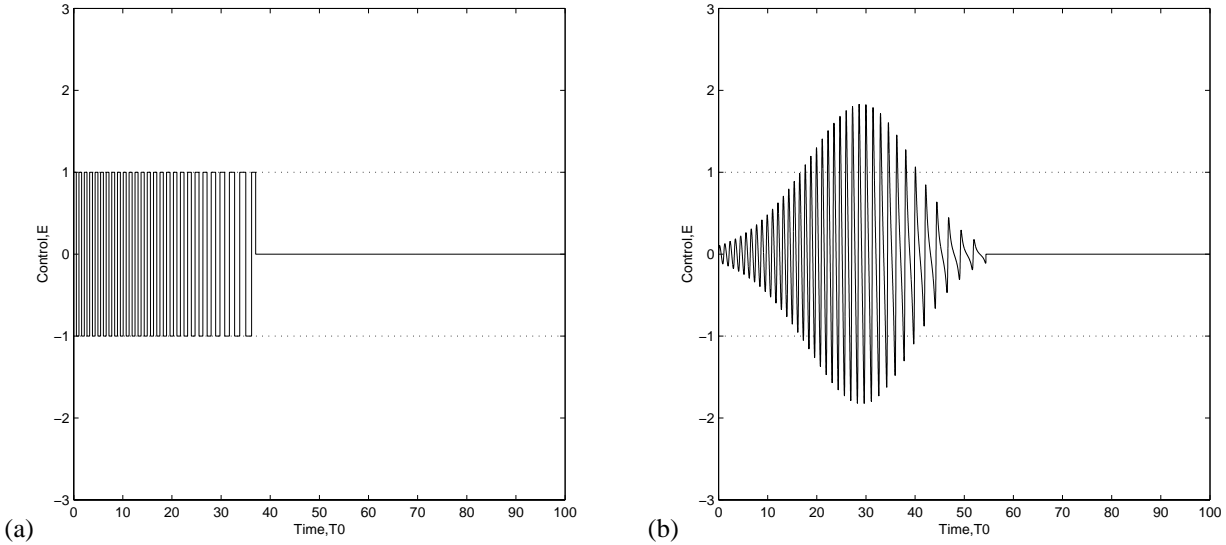


Figure 3: Speed-gradient feedback control functions: (a) speed-gradient method in form (20) ; (b) speed-gradient type impulse with Gaussian envelope. Control is normalized on E , time is measured in T_0 .

sociated molecules (percentage of the total number N). We establish the system parameters and initial conditions in accordance to the previous section (as much as possible). The dissociation criterion for a molecule is exceeding the energy value of $W_* = -0.1185D$. The low intensity control is applied: $E = 0.005$ a.u. The linear expression for the dipole moment $\mu(r) = Ar$ is used. To specify the initial conditions we assume that all the molecules have the same initial energy $W_0 = -0.8689D$ and their initial phases are chosen equidistantly in the interval $[0, T(-0.8689D)]$. Such a choice provides a good approximation for the uniform distribution of initial phases. In our experiments we took the following numerical data: $N = 1000$, $T_3 = 50T_0$, $T_2 = 150T_0$. Graph on Fig. 4.a shows the fraction of dissociated molecules for molecular ensemble under linear chirping pulse control with optimal chirping rate $\varepsilon = 0.01\varepsilon_0$ (this value of chirping rate, providing

the best result for control of this type, was obtained experimentally). Graph on Fig. 4.b shows the result of applying the speed-gradient pulse control to the ensemble (as representative molecule the one with median initial velocity was chosen).

It can be seen that the control using pulses designed by speed-gradient feedback method ensures significantly better efficiency compared with the linear chirping for the optimal value of the chirping rate ε .

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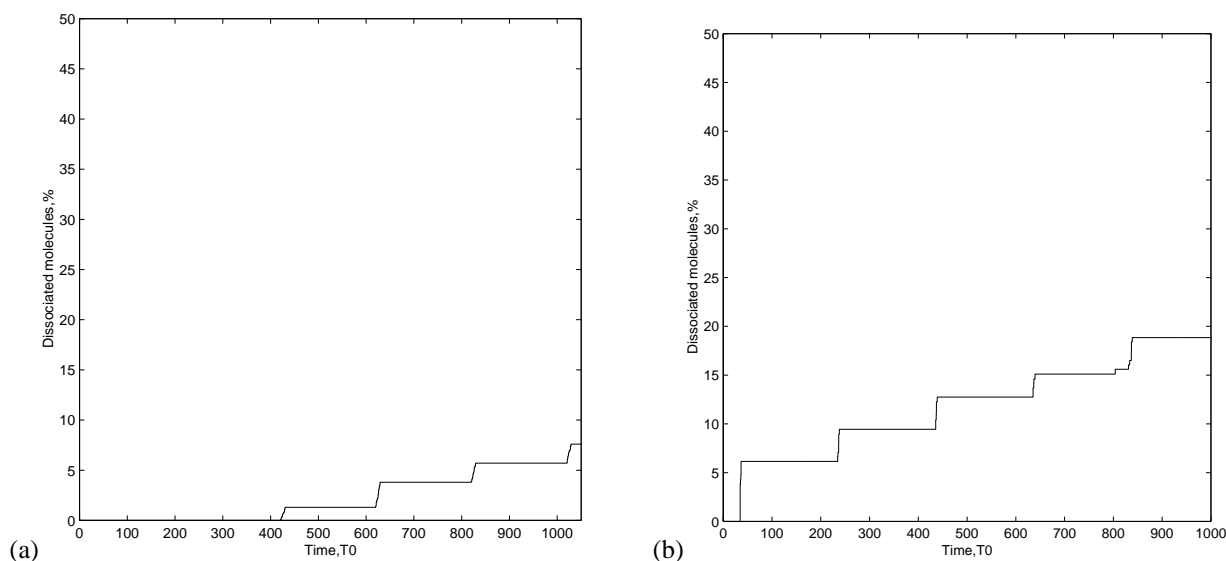


Figure 4: Excitation of the ensemble containing 1000 molecules at the excitation level of $E = 0.005$ a.u.: (a) pulse linear chirping with $\varepsilon = 0.01 \frac{\Omega_0}{T_0}$, (b) pulse speed-gradient control. Fraction of dissociated molecules - in %, time is measured in T_0 .

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