Dissociation of Diatomic Molecule by Energy-Feedback Control

Alexander Fradkov, Anton Krivtsov, Alexander Efimov

Institute for Problems of Mechanical Engineering,
Russian Academy of Sciences,
61 Bolshoy ave., V.O., St. Petersburg, 199178, Russia.
Fax: +7(812)321-4771, Tel: +7(812)321-4766,
E-mail: alf@ipme.ru

December 26, 2001

Abstract

New method for dissociation of diatomic molecule based on nonperiodic excitation generated by energy-feedback control mechanism is proposed. The energy-feedback control uses frequency-energy (FE) relation of the natural oscillations to fulfill the resonance conditions at any time of excitation. Efficiency of the proposed method is demonstrated by the problem of dissociation of hydrogen fluoride (HF) molecule. It is shown that new method is more efficient than methods based on constant frequency and linear chirping excitation.

Keywords: diatomic molecule, dissociation, control, feedback.

1 Introduction

During last decade a growing interest has been observed in the control problems for molecular systems in classical and quantum formulation [1, 2, 3]. One of the simplest problems of that type is dissociation problem for diatomic molecule [3, 4, 5, 6, 7, 8]. It often serves as a benchmark for comparison of classical and quantum calculations. In the paper [4] 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 [5, 6] the case of two-frequency (two-laser) control field was investigated. It was shown that intensity of two-frequency field required for dissociation can be reduced compared to one-frequency case. In [8] the further reduction of the control

*The authors acknowledge support of the Russian Foundation of Basic Research (grant RFBR 99-01-00672) and of the Program of basic research N 19 (project 1.4) of the Presidium of RAS.
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. In methods based on geometric control theory (inverse control) were proposed for molecular systems. In the papers a general method for investigation of physical systems by means of feedback controlling actions was proposed. It was shown in by example of the problem of escape from a potential well that feedback allows to reduce control intensity required for overcoming a potential barrier by several orders of magnitude. It appears that using speed-gradient method for design of feedback control action allows to achieve desired level of energy by excitation of intensity inversely proportional to the system dissipation degree. Particularly, for conservative systems it allows to reach any energy level by (ideally) arbitrarily small control action.

In this paper the algorithm of the feedback frequency chirping of the controlling field frequency is proposed based on dependence of the natural frequency of the nonlinear molecule oscillations on its energy, further referred to as frequency-energy characteristics or frequency-energy curve (FE-curve). On-line implementation of the algorithm requires measurement of molecule energy only. This can be easily generalized for an ensemble of molecules, replacing exact energy of the separate molecule in the control criterion by the average energy per single molecule. However, for control algorithm design the knowledge of the frequency-energy relation is required. In this paper a classical Morse potential is considered, which allows obtaining this relation in a simple analytical form. For other potentials, where the analytical solution is too complicated or impossible, the frequency-energy relation 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 when using proper feedback excitation.

2 Basic equations

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

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

(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. E.g. for monochromatic control field \(u(t) = E \cos(\omega t)\), where \(E\) and \(\omega\) are strength and frequency of the external laser field. Substitution of (1) into Hamilton equations

$$\frac{\partial r}{\partial t} = \frac{\partial H}{\partial p}, \quad \frac{\partial p}{\partial t} = -\frac{\partial H}{\partial r},$$

(2)
yields the following equation of molecular motion

\[ m\ddot{r} = -\Pi'(r) + \mu'(r)u(t). \] (3)

For the case of harmonic excitation equations of motion is as follows:

\[ m\ddot{r} = -\Pi'(r) + E\mu'(r)\cos(\omega t). \] (4)

Let us use Morse form of the interatomic potential

\[ \Pi(r) = D \left( 1 - e^{-\alpha(r-a)} \right)^2 - D \left( e^{-2\alpha(r-a)} - 2e^{-\alpha(r-a)} \right), \] (5)

where \( D \) is the bond energy, \( a \) is the equilibrium interatomic distance. The corresponding force is

\[ f(r) = -\Pi'(r) = 2\alpha D \left( e^{-2\alpha(r-a)} - e^{-\alpha(r-a)} \right). \] (6)

The dipole moment can be represented in the form \[6, 13\]

\[ \mu(r) = A r, \quad \mu'(r) = A, \] (7)

where \( A \) and \( \xi \) are the known constants. Thus the equation of motion \[4\] reads

\[ m\ddot{r} = 2\alpha D \left( e^{-2\alpha(r-a)} - e^{-\alpha(r-a)} \right) + EA \left( 1 - 4\xi r^4 \right) e^{-\xi r^4} u(t). \] (8)

For sufficiently small \( \xi \) the simplified expression for dipol potential can be used:

\[ \mu(r) = Ar, \quad \mu'(r) = A, \] (9)

In the vicinity of equilibrium \( r \approx a \) equation \[8\] with harmonic excitation can be reduced to the equation of linear forced oscillations

\[ m\ddot{r} = Cr + E\mu'(a)\cos(\omega t), \quad C \overset{\text{def}}{=} \Pi''(a) = 2\alpha^2 D, \] (10)

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

\[ \Omega_0 \overset{\text{def}}{=} \sqrt{C/m} = \alpha\sqrt{2D/m}. \] (11)

3 Control of the dissociation process

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:

\[ \omega = \Omega_0 - \varepsilon t \] (12)
where $\varepsilon$ is a constant (chirping rate), which characterizes the speed of the frequency
decrease. In this case equation of motion (11) takes the form

$$m\ddot{r} = -\Pi'(r) + E\mu'(r) \cos \varphi, \quad \dot{\varphi} = \omega(t) = \Omega_0 - \varepsilon t.$$  \hspace{1cm} (13)

(Note that in this case the representation $\varphi = \omega t$ is not valid since the frequency $\omega$ is not
constant.

More effective dissociation can be achieved by taking advantage of the feedback control.
In this case the frequency of excitation can be changed according to the oscillator energy
so that at any amplitude of oscillations the excitation will act 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 curve of FE-curve. It contains
important information about dynamics of the molecular motion. The key idea of our
approach is that if the curve $\Omega(W)$ is known and the energy $W = W(t)$ is observable then
control algorithm

$$m\ddot{r} = -\Pi'(r) + E\mu'(r) \cos \varphi, \quad \dot{\varphi} = \Omega(W)$$  \hspace{1cm} (14)

will give the desired excitation at the resonance frequency at any time instant.

The relation $\Omega(W)$ in principle can be calculated for any known potential $\Pi(r)$ using
the integral of energy, which is realized when the external force is absent

$$\frac{1}{2} m\dot{r}^2 + \Pi(r) = W \quad \Rightarrow \quad T = \sqrt{2m} \int_{r_1}^{r_2} \frac{dr}{\sqrt{W - \Pi(r)}},$$  \hspace{1cm} (15)

where $W$ is a constant value of energy, $T$ is period of the oscillations, $r_1$ and $r_2$ are the
minimum and the maximum possible values of radius $r$ for the specified potential energy
(the solutions of the equation $\Pi(r) = W$). If period $T$ is known then frequency can
be obtained as $\Omega = 2\pi/T$. Obviously integral (15) can not be calculated analytically
for arbitrary potential and the desired relation $\Omega(W)$ should be evaluated by numeric
integration.

Luckily for the Morse potential (5) the integral can be evaluated analytically in the
following way. Substitution $\zeta = \zeta(r) = e^{\alpha(r-a)}$ transforms the integral (15) in the case of
Morse potential to the simple form which can be easily integrated

$$T = \frac{1}{\alpha} \sqrt{\frac{2m}{D}} \int_{\zeta_1}^{\zeta_2} \frac{d\zeta}{\sqrt{\frac{W}{D} \zeta^2 + 2\zeta - 1}} = \frac{\pi}{\alpha} \sqrt{-\frac{2m}{W}}.$$  \hspace{1cm} (16)

The above formula is valid if $W < 0$. Otherwise, the motion of the system is not peri-
odic, since the molecule dissociates. Equation (16) provides the following simple relation
between energy and natural frequency of Morse oscillator

$$-\frac{W}{D} = \left( \frac{T_0}{T} \right)^2 = \left( \frac{\Omega}{\Omega_0} \right)^2,$$  \hspace{1cm} (17)
where $\Omega_0$ is defined by (11), $T_0 = 2\pi/\Omega_0$. The control law (14) therefore takes the form

$$\dot{\phi} = \Omega(W) = \Omega_0 \sqrt{\frac{W(t)}{D}}.$$  \hspace{1cm} (18)

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

4 Calculations

Efficiency of the proposed control algorithm was confirmed by computer simulations for dissociation of the hydrogen fluoride (HF) molecule that has become a benchmark problem for controlled dissociation [3, 6, 13]. The parameters of the model 8, corresponding to HF molecule [3, 6, 13] are as follows: $m = 1732$, $D = 0.2101$, $\alpha = 1.22$, $a = 1.75$, $A = 0.4541$, $\xi = 0.0064$, $E = 0.1$. All quantities are given in atomic units. The initial condition for excitation is molecule equilibrium at the bottom of the potential well: $r = a$, $\dot{r} = 0$. The equation was integrated numerically by central differences method with time step $dt = T_0/160$ (integration with smaller time steps yields practically the same results.

![Energy vs Time for resonance and optimal frequency](image)

Figure 1: Excitation at constant frequency: a) resonance frequency $\omega = \Omega_0$, b) optimal frequency $\omega = 0.841\Omega_0$. Energy is measured in the units of the bond energy $D$, time is in the units of $T_0$ (natural period of linear oscillations).

The result of excitation at the resonance frequency is shown in Fig.1a. The graph shows that the motion is quasiperiodic and maximum value of energy, which can be achieved by this method, is $-0.68D$. Since the natural frequency of the molecule is decreasing when the energy is growing, more efficient excitation can be achieved at lower frequencies. It is even possible to dissociate the molecule if the excitation frequency is close to $0.841\Omega_0$ — see Fig.2a. The figure shows that at $t \approx 13.5T_0$ the energy crosses the zero level, and at $t = 14.5T_0$ the energy becomes a positive constant. This practically means...
that the potential energy is negligible and atoms are moving in the opposite directions with constant velocities (total dissociation). However this result is not structurally stable: small variation in the excitation frequency can noticeably increase the dissociation time and even break the dissociation.

![Energy vs Time Graph](image1)

**Figure 2:** Excitation with linear frequency chirping: a) $\varepsilon = 0.0157 \frac{\omega_0}{T_0}$, b) $\varepsilon = 0.059 \frac{\omega_0}{T_0}$ (the chirping rate, which provides the fastest dissociation). Energy and time are measured in units of $D$ and $T_0$.

Fig. 2a,b correspond to linear frequency chirping (12) at two different chirping rates. The dissociation is also achieved, but it is slower than in the previous case and the results are very sensitive to the variations of $\varepsilon$. Additional flexibility to the chirping process can be added by using the relation $\omega = \omega_0 - \varepsilon t$, where $\omega_0$ is a constant less than $\Omega_0$. Optimal selection of both parameters is a pretty complicated task. In more detail this problem is investigated in [8].

In this paper we will concentrate on the feedback chirping, based on the frequency-energy curve (17). Fig. 3a shows the energy as a function of time for the feedback control (18). At the initial stage the energy is growing faster than in other cases, but after the level about $W = -0.5D$ is reached, the efficiency of the excitation decreases so that dissociation is not realized. Probably this phenomenon is caused by wrong phasing which prevents the molecule dissociation although the resonance condition is always fulfilled. Indeed, the sign of the multiplier $\mu'(r)$ in equation (4) due to formula (7) is changing for high energies, so that the excitation starts acting in the opposite phase. To overcome this difficulty the following algorithm can be used: when the energy of the molecule reaches some certain value $W^*$, then the sign of the excitation force is permanently changing to the opposite. The result of such an excitation is shown in Fig. 3b. The dissociation is achieved at $t = 10T_0$, which is faster than in all previous cases.
Thus for the selected level of control ($E = 0.1$ a.u.) the best result is obtained for feedback excitation. However excitation with shifted constant frequency gives the competitive result. The situation changes if we consider lower level of excitation. If this level is sufficiently small then excitation at any constant frequency can not provide the dissociation. On the contrary, excitation with changing frequency can in principle give dissociation for any arbitrarily small level of control. For illustration let us consider the 5 times smaller control then in previous calculations: $E = 0.02$ a.u. In this case dissociation at a constant frequency is not possible. Results of linear chirping and feedback control excitation are given in Fig. 4. For simplicity these calculations use approximation $\mu'(r) \approx \mu'(a)$. The plots show that both methods provide dissociation. However, linear chirping achieves dissociation at $t = 89T_0$, while energy-feedback control achieves it at $t = 34T_0$. Thus the feedback control provides more than two times faster dissociation then the best variant of the linear chirping.

Although the proposed algorithm requires measurement of molecule energy only, its on-line implementation requires changing controlling action at the time intervals less then $10^{-12}$ s. This can be achieved with modern ultrafast lasers. The approach can be easily generalized to control of an ensemble of molecules, replacing exact energy of the separate molecule in the control objective by the average energy per single molecule.

References

[1] Chemical Physics. v.267, 1-3, (2001). Special Issue: Laser Control of Quantum Dynamics.
Figure 4: Excitation with lower level of control ($E = 0.02$ a.u.) and constant value of dipole moment a) linear chirping with $\varepsilon = 0.0091 \frac{\omega_0}{T_0}$, b) feedback control (using frequency-energy relation). Energy and time are measured in $D$ and $T_0$.

[2] Rabitz, H., R. de Vivie-Riedle, M. Motzkus, and K.Kompa. Whither the Future of Controlling Quantum Phenomena? Science, 288, (2000), 824–828.

[3] Chen Yu, P.Gross, V.Ramakrishna, H.Rabitz, K.Mease and H.Singh Control of classical regime molecular objectives – applications of tracking and variations of the theme. Automatica 9, (1997), 1617–1633.

[4] Goggin M.E., Melloni P.W. Driven Morse oscillator: Classical chaos, quantum theory and photodissociation. Phys.Rev. A, V.37 (3), 1988, 796–808.

[5] Goggin M.E., Melloni P.W. Phys.Rev. A, V.37 (3), 1988, 796–808.

[6] Guldberg A., Billing G.D. Laser-induced dissociation of hydrogen fluoride. Chem.Phys.Lett., v.186 (2-3), 1991, 229–237.

[7] Krempl S., Eisenhammer T., Hubler A., Mayer-Kress G., Milloni P.W. Optimal stimulation of a conservative nonlinear oscillator: classical and quantum-mechanical calculations. Phys.Rev.Lett., v.69 (3), 1992, 430–433.

[8] Liu W.-K., Wu B., Yuan J.-M. Nonlinear dynamics of chirped pulse excitation and dissociation of diatomic molecules. Phys.Rev.Lett., v.75 (7), 1995, 1292–1295.

[9] Fradkov A.L. Exploring nonlinearity by feedback. Physica D. 1999, V.128, N 2–4. pp.159–168.

[10] Fradkov A.L. Feedback resonance in nonlinear oscillators. Proc. 5th Europ.Contr.Conf., Karlsruhe, 1999.
[11] Fradkov A.L., Pogromsky A.Yu. *Introduction to control of oscillations and chaos*. (World Scientific Pub. Co, Singapore, 1998).

[12] Fradkov A.l., Miroshnik I.V., Nikiforov V.O. (1999) *Nonlinear and adaptive control of complex systems*. Dordrecht: Kluwer Academic Publishers.

[13] Stine J.R., Noid D.W. *Opt. Commun.*, v.31, 1979, 161.