

Control of Chemical Reaction in High-intensity Laser Field^{*}

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Abstract: The prospects of control chemical reaction in high-intensity laser field are talked about here, and some experimental and theoretical designs are reviewed and discussed also.

Key words: High-intensity laser, ac-Stark effect, Control of chemical reaction

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1 Introduction

Significant advances have been made in recent years toward establishing the broad foundations and laboratory implementation of control over chemical reactions following the rapid development of ultrafast laser^[1]. There are two general reasons for considering control of quantum phenomena: first, to create a particular product that is unattainable by conventional chemical or photochemical means and second, to achieve a better fundamental understanding of atoms, molecules and their interactions. Since the closed-loop learning and feedback technique have been introduced into control of chemical reaction, the difference between the three theoretical control schemes: the coherent irradiative control scheme developed by Shapiro and Brumer (S-B scheme), the coherent laser pulse sequence control scheme initiated by Tannor and Rice (T-R Scheme) and the optimal laser pulse-shaping control scheme proposed by Shi and Rabitz (S-R scheme) becomes obscure in operation, even there is basic difference between the underlying theories of the three schemes^[2]. The closed-loop procedure has significant superiority: we need not to determine the de-

tails of laser control designs, especially for polyatomic molecule where we are unable to calculate accurately. Recently, experiments with closed-loop learning control have been successfully going in blind for manipulation of fluorescence signals, photodissociation products, and other applications^[3,4]. With the success of coherent control experiments emerging, it is time to consider whether some consistent rules for achieving control can be found. The rules no double comprise of some components coming from the historical three schemes demonstrated by several experiments, and will, we think, include some high-intensity laser field effects observed recently and others to be found in the future. The effects observed in high-intensity laser field lately out of question play an important role in control over chemical reaction with ultra-short laser pulses, which is first noticed in our laboratory by Lou enlightened by the results of Chen's experiment^[11]. Following we will state our points on chemical reaction control in high-intensity laser field by strong field effects, such as ac-Stark effect etc.

2 The concept of ac-Stark effect

Ac-Stark effect usually means the phenomena

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that the energy levels of atom or molecule are shifted in laser field in the papers of recent years, but not equal to the concept of dressed-state. The phenomena caused by ac-Stark effect fall into three categories: Autler-Townes splitting relative to two or several levels^[5], light induced potential such as the phenomena of bond-softening or -hardening^[6], and light shift or ac-Stark shift relative to molecular polarization^[7]. In papers the phenomena of energy level shifts falls under the first or third class are all named as ac-Stark shift, even there is some difference between the fundamentals of them. The control of chemical reaction in high-intensity laser field is usually realized by ac-Stark effect falling under later two categories till now. Usually the Rydberg states of the molecule exhibit obvious ac-Stark effect because the electrons of the Rydberg states are relatively far from the nucleus and are easy to be influenced by the external laser field, but the valence states not. Making good use of ac-Stark effects to steer population to target state will show intriguing and unexpected effectiveness.

3 The perspective into control of chemical reaction with ac-Stark effect

Even we could observe ac-Stark effect when molecules or atoms interact with any intensity laser field, certainly only sufficient intensity is capable of playing the role to steer population. Because ac-Stark effect is directly linked with the amplitude of laser field, we can expect some interesting experiment emerging with assurance along with the development of ultra-short laser. In fact, in 2000, Levis *et al.* reported that they had succeeded in selectively cleaving and rearranging bonds of some organic molecules with strong laser field up to 10^{13} W/cm² associated with the closed-loop technique^[8]. In their experiment, the high selectivity of control over the formation of CH₃CO from (CH₃)₂CO, CF₃ (or CH₃) from CF₃COCH₃ and C₆H₅CH₃ from C₆H₅COCH₃ demonstrated that strong laser field control has generic applicability for manipulating molecular reactivity because the tailored intense laser fields can dynamically shift many excited states into resonance which are not resonant with the frequency of laser field in the perturba-

tive regime. A strong-field laser with the magnitude about 10^{13} W/cm² is on the order of the valence electron's binding energy in the molecule, and this magnitude is a critical enabling feature for broad-scale application upon consideration of bandwidth required for the effective control of chemical reactions. The map of the theoretic exhibition for Levis *et al.*'s experiment is shown in Fig.1.

If we have known exactly the Hamiltonian of sample molecule and interaction between the high-intensity laser field and the molecule, we could steer the population to our target states by designing the optimal pulses that could not be attained with traditional photochemical method, even throwing away the closed-loop learning technique. Garraway *et al.* in 1998, with quantum wavepacket method, present a tempting model on Na₂ of Adiabatic Passage by Light-Induced Potential for transferring a WHOLE wave packet from one molecular potential of X¹Σ_g⁺ to the displaced ground vibrational state of 2¹Π_g^[9]. We all know that the Franck-Condon factor of ground vibrational states of X¹Σ_g⁺ and 2¹Π_g states is near zero and this population transferring cannot be attained with photon excitation in the perturbation regime. It is the strong ac-Stark effect in high-intensity laser field that brings forth this intriguing population transference. The authors are ingenious enough to make good use of the detuning, the counterintuitive sequence of the pulses and the ac-Stark effect, to realize the Adiabatic Passage of Light-Induced Potential along which the initial population moves as a ball ending up on the desired electronic state. The abridged general view is shown in Fig.2 and Fig.3.

The resonance in the multiphoton ionization result from ac-Stark shift has caused much interest since the short pulse laser appeared also^[7,10]. But all of these works are focusing on the essence of ac-Stark effect, or on measuring the magnitude of the energy shift in the process of ionization under certain intensity laser field^[7]. Nowadays the control of chemical reaction is one of hot topics in chemical physics subject, and we really can make the use of ac-Stark effect to select ionization path or to excite population to target state. To our knowledge, till now only Chen *et al.*

have reported on the control of the population excitation with Nitric Oxide molecule via ac-Stark effect in strong-field laser^[11]. In Chen's femtosecond laser experiment they fixed the central wavelength of the pump pulse at 380 nm and the probe at 260 nm to manipulate the population to transfer to one of the target states of NO : the third vibrational level of $A^2\Sigma^+$ or the ground vibrational level of $C^2\Pi$ by varying the magnitude of laser pulse. The states of $A^2\Sigma^+$ and $C^2\Pi$

are Rydberg states which exhibit the ac-Stark shift obviously are usually used to study the fundamental of ac-Stark effect. Because of the ambiguity about the short-lived photoelectron spectroscopy appeared in their experiment at current time, the paper is almost neglected in the related control theory forum. The maps about the experiment of Chen *et al.* are sketched in Fig.4.

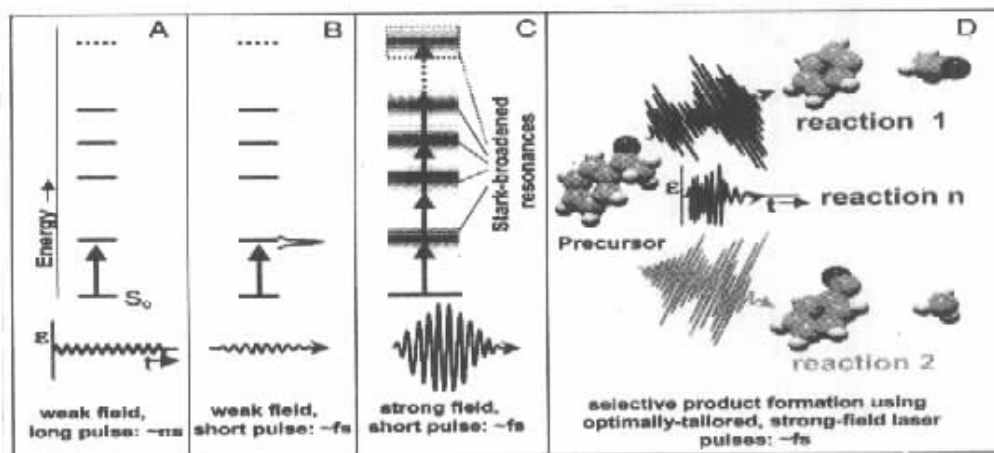


Fig. 1 Laser pulse schemes are shown for creating coherent molecular motion with sources of ever-increasing bandwidth and selectivity capabilities

The precursor molecule begins in the ground state and interacts with the electric field, $\epsilon(t)$.

- (A) In the weak field case, the molecule can only respond with the relevant molecular levels.
- (B) In this case, the shorter duration of the pulse helps to overcome resonance constrains.
- (C) The high-intensity, short-duration of the pulse creates sufficient dynamic power broadening of the molecular vibrational levels (denoted by light-gray bands) and multiphoton excitation to overcome any restrictions on resonant excitation.
- (D) This case indicates how optimal tailoring of the pulse in case C can be used to steer the molecular dynamics out one reaction channel versus another for high product selectivity. Controlled dynamics results from a combination of time-dependent ultrafast multiphoton excitation and Stark broadening of the molecular eigenstates^[8].

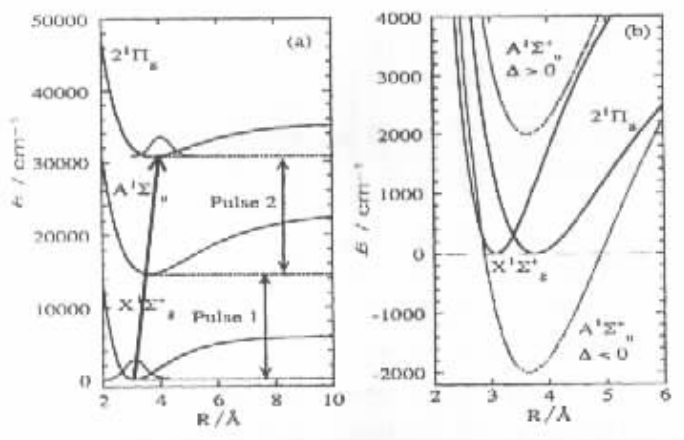


Fig. 2 (a) The three Na_2 potential energy surfaces used in our calculations : the $X^1\Sigma_g^+$ ground state, the $A^1\Sigma_u^+$ state as the first excited state, and the $2^1\Pi_u$ as the target state. The diagonal sloping arrow indicates the overall effect of the two laser pulses used and we could see clearly that the corresponding Franck-Condon factor is almost zero. (b) The dressed potentials. Here Δ indicates the detuning of the first pulse. We have set $\hbar\Delta = \pm 2000 \text{ cm}^{-1}$ and show the position of the intermediate $A^1\Sigma_u^+$ state (dotted line) with respect to the other two potentials (solid lines)^[9].

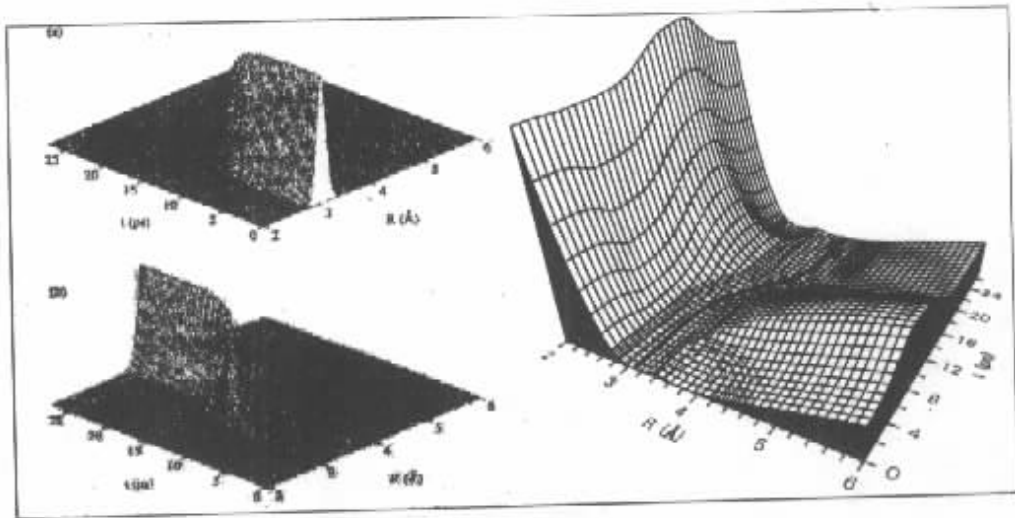


Fig.3 Left : The wave packet dynamics on (a) the $X \Sigma_g^+$ ground state and (b) the target state $2^1\Pi_g$. The wave packet motion has been determined from a fully quantum mechanical calculation. Note the steady displacement of the wave packet as it arrives adiabatically to the bottom of the lowest vibrational state of the $2^1\Pi_g$ state. Right : Space and time dependence of the light-induced potential responsible for the transportation of the wave packet (the direction of the dynamics is layout by bold solid line)⁹¹.

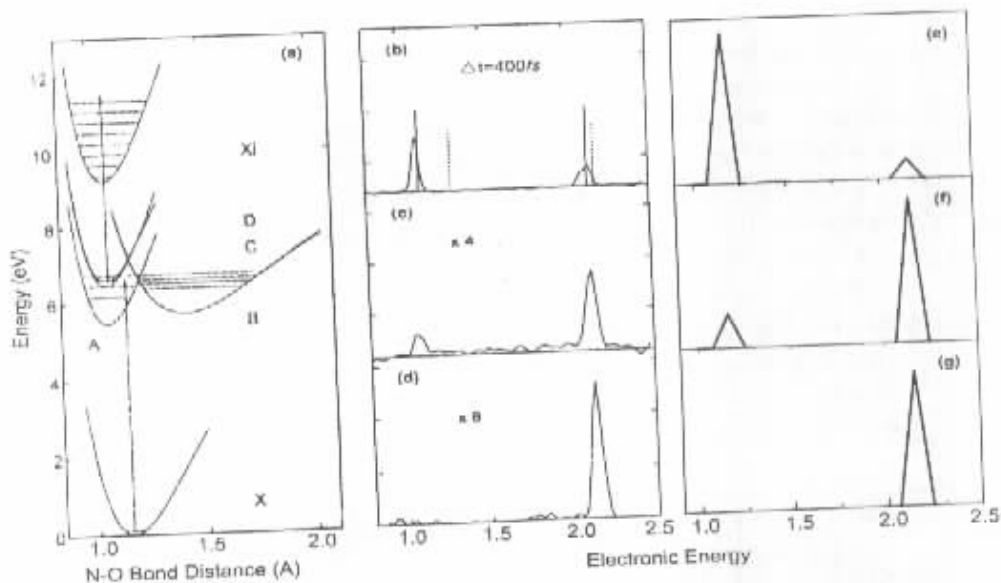


Fig.4 (a) NO potential energy curves. The plots at right are femtosecond time-resolved photoelectron spectra from 2 + 1 multiphoton ionization at fixed pump and probe wavelengths. The delay time between the central of the pump and probe pulses is $\Delta t = 400$ fs. Pump intensities are at 1.63×10^{13} W/cm² for (b) 3.0×10^{12} W/cm² for (c) and 8.0×10^{11} W/cm² for (d). The corresponding spectra calculated with wave packet model are sketched in right panel. The pump intensities and wavelengths are at 2.5×10^{13} W/cm² and 386 nm for (e), 4.0×10^{12} W/cm² and 386 nm for (f), and 8.0×10^{11} W/cm² and 386 nm for (g) in our calculation. We can see clearly that the population increases in $A \Sigma^+$ with enhancing intensity of the laser filed in these diagrams.

The experiment of Chen *et al.* verified the conjecture that it is possible to selectively excite a given energy level by varying the laser intensity. By one-dimensional quantum wave packet model, we have simulated the photoelectron spectroscopy of Chen's experiment, and the results are shown in Fig. 4. In Chen's experiment they varied the intensity of the pump pulse to change the energy shift and probed the population in the target state later, and they really realized the selectivity of population excitation. Enlightened by the experiment of Chen, apart from using strong-weak pulse pair we can employ three or more pulses, one of them with high-intensity, to tune given states into or out resonance at arbitrary time with fixed wavelength by varying the magnitude of the high-intensity pulse. The principle of Levis *et al.*'s closed-loop experiment that succeeded in cleaving and rearranging the bonds of some organic molecules with strong-field laser pulses is sufficiently explained by the phenomena in Chen's experiment. We are currently pursuing these possibilities of manipulating the population to a target state among several given states with strong-field laser pulses throw-

ing off the closed-loop technique.

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强激光场下化学反应的控制*

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摘要: 简要阐述了强激光场下的 ac-Stark 效应, 回顾、评论了近年来利用 ac-Stark 效应控制化学反应的几个典型实验和理论模型. 利用一维量子波包模型, 揭示了 NO 分子 Rydberg 态在不同光强下获得不同布居是由于强光场下产生的 ac-Stark 能移引起的. 并展望了利用 ac-Stark 效应进行激发态布居控制的可能性.

关键词: 强激光场; ac-Stark 效应; 化学反应控制

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