

Progress in sub-femtosecond control of electron localization in molecules

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Abstract. Recent advances in controlled generation of intense, ultrashort laser pulses in the femtosecond and attosecond time-scales have pushed new avenues of research in the coherent control of ultrafast electron dynamics in atoms and molecules. We present a topical review on the phenomenon of control of electron localization in small dissociating molecules. By creating and controlling coherent superposition of the symmetric and antisymmetric electronic states, it becomes possible to confine the evolving electron cloud onto a preferred nucleus, thereby steering the molecule towards a desired dissociation route. We discuss the origin of the idea and various mechanisms to achieve electron localization in small molecules. To highlight recent experimental progress, we explain how one can employ few-cycle IR pulses and different attosecond extreme ultraviolet (EUV) pulses in various ways to successfully demonstrate the control of electronic dynamics. Future research opportunities and challenges on this topic are envisioned.

Keywords. Attosecond physics; intense field; coherent control.

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1. Introduction

It has been a human curiosity to study and control fast moving objects compared to our natural biological time-scale of a few seconds. The ability to take snapshots of fast phenomenon not only provides deeper insight into its dynamics but also opens new opportunities to control them. In order to take snapshots of a fast process in time, one needs fast shutter that can generate flashes of light typically shorter than the relevant time-scale. The object appears quasistationary with such flashes thus minimizing blur in the image. On the other hand, due to the Heisenberg's uncertainty relation, the natural quantum dynamics becomes ultrafast with greater spatial confinement of the object. For example, the typical molecular rotational motion is in ps regime while its nuclear vibrational time-periods are in fs [1,2]. The electronic time-scale inside the molecule is much faster in the attosecond ($1 \text{ as} = 10^{-18} \text{ s}$) range. To give an example, the Bohr's revolution period for the hydrogen

atom is 24 as. Therefore, among various physical, chemical and biological processes, the electronic dynamics is the fastest. Its measurement and control are the key to understand many quantum phenomena [3,4].

Many recent technological innovations made it possible to generate ultrashort flashes of light reliably with a table-top system [5]. These pulses are typically many optical cycles long and can be made as short as a few fs. For example, the optical oscillation period of the electric field for near infrared (IR) wavelength at 800 nm is about 2.7 fs. In an ultrashort laser pulse with pulse width around 6 fs, there are hardly three oscillations. The smallest possible time resolution with such pulses is typically one optical cycle that has been termed as the femtosecond barrier [1]. Such few-cycle and many-cycle long fs pulses provided a great deal of information about the femtosecond-resolved molecular dynamics of chemical reactions. However, to directly measure and control electronic processes beyond the femtosecond barrier, one would require even shorter pulses of light. The femtosecond barrier was broken in the last decade by the new approaches that generated attosecond pulses in the EUV spectral range [1,2]. It became possible to generate attosecond pulses of light by exploiting extreme nonlinear interaction between intense IR pulses and atomic and bulk medium that produces very high-order harmonics of the fundamental IR pulse [1,2,6,7]. The high harmonic generation (HHG) generates a huge bandwidth in EUV and beyond in the form of highly energetic photons, the time-domain structure of which corresponds to the attosecond bursts of light. Depending on the magnitude and phases of the generated Fourier components, the synthesized waveform can be in different forms such as an isolated attosecond pulse or an attosecond pulse train [5]. Furthermore, since these pulses are intrinsically synchronized to the mother IR pulse, one gets a convenient reference to measure the attosecond time delay. These intense femtosecond pulses together with the attosecond pulses constitute key tools to capture and control electronic processes in atoms and molecules with unprecedented time resolution.

These femtosecond and attosecond laser-like pulses have provided fundamental new insight into quantum phenomenon on sub-fs times. For example, it has become possible to image molecular orbitals in N₂, O₂ [8], to measure tunnelling of electron in atoms [9,10], to measure attosecond electronic processes such as decay of molecular autoionization states [11,12], real-time observation of valence electron motion [13] etc. In addition to imaging the ultrafast electron dynamics, one can also control electronic processes on its natural time-scale. Many examples had been experimentally demonstrated [14–17]. Control of atomic photoionization due to the wavepacket interference using XUV and IR pulses [18,19] and demonstration of control of electron localization in small molecules [20–23], are just a few that can be mentioned. Clearly, with the advancement of attosecond science, novel insight is gained about quantum dynamics of the fundamental physical, chemical and biological processes.

In this topical review, we choose to summarize the recent progress in the phenomenon of control of electron localization in dissociating molecular ions. This contemporary research topic has attracted a great research interest in attoscience both theoretically and experimentally [24–32]. It demonstrates a new way of steering molecular dissociation into the desired channel by directly controlling the motion of electron cloud on its natural attosecond time-scale. After discussing the basics of the phenomenon of control of electron localization (EL), we shall focus on the three main experimental techniques that demonstrate the control of electronic dynamics in various small molecules.

2. Introduction to the phenomenon of control of electron localization in small molecules

To understand the basics of the phenomenon of electron localization in molecules, let us concentrate on the simplest diatomic molecule D_2^+ . It consists of two nuclei and a single delocalized electron that glues them together. The vibrational time-period of the molecule is several femtoseconds but the electronic time-scale is much faster in the sub-fs regime. The two most important electronic states in the molecule for us are the ground electronic state $1s\sigma_g$ and the first excited electronic state $2p\sigma_u$. The molecule remains stable when it is in the symmetric $1s\sigma_g$ electronic state but it dissociates into a neutral atom and a D^+ ion when excited to the antisymmetric $2p\sigma_u$ state. Two final dissociation channels are possible (figure 1). If the electron is localized onto, say, the left nucleus, the D^+ ion would be ejected in the right direction. Or else, if the electron is localized to the right nucleus, the D^+ ion would be ejected in the opposite direction. Therefore, by controlling the localization of the electron in a dissociating molecular ion, one can control the dissociation path and guide the molecule into a preferred final state.

A key requirement to control the electron localization (EL) is to create a coherent superposition of the two opposite symmetry electronic states, such as $1s\sigma_g$ and $2p\sigma_u$. When their linear superposition has a positive (negative) sign, the two wavefunctions cancel (add) on one of the nucleus thus localizing the electron onto the other nucleus. If, however, only one of the electronic state is excited this would lead to a delocalized electron with equal probability to be on both the nuclei. In other words, one can consider the localization control due to essentially an interference between two different quantum paths leading to the same final energy state during molecular dissociation. There are many

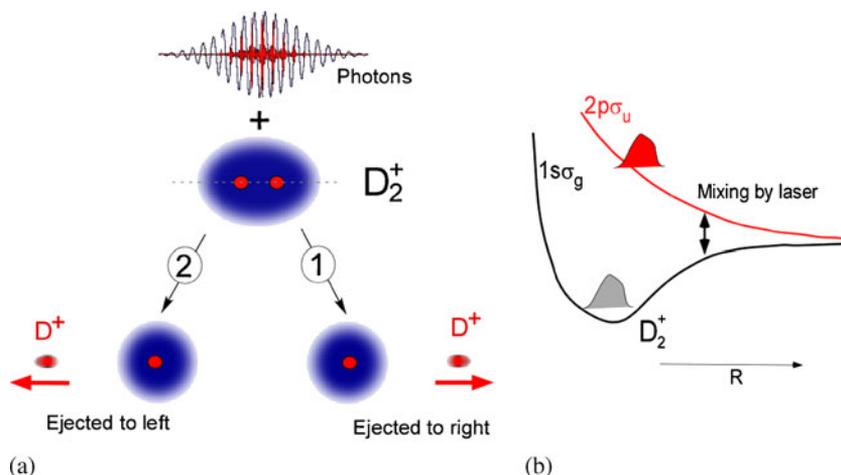


Figure 1. (a) The schematic description of electron localization in molecular fragmentation. A D_2^+ molecule subjected to EUV and IR pulses can fragment via two different channels. The localization of electron is the key to choose the desired pathway. (b) Schematic of the electronic energy level and laser-induced coherent mixing for the molecule.

different ways in which these interferences can possibly take place that give rise to various mechanisms of the EL as will be discussed later. The essential feature in all the mechanisms is to realize a coherent superposition of the symmetric and antisymmetric electronic states. It is equally important to vary the relative phase between them by means of a control parameter such as the time delay between IR and EUV pulses.

The degree of control of electron localization is quantified by defining an asymmetry parameter A [20, 22],

$$A(E, \tau) = \frac{[C_{\text{left}}(E, \tau) - C_{\text{right}}(E, \tau)]}{[C_{\text{left}}(E, \tau) + C_{\text{right}}(E, \tau)]}, \quad (1)$$

where $C_{\text{left}}(E, \tau)$ and $C_{\text{right}}(E, \tau)$ are the total D^+ counts ejected in the left and right directions, respectively. In an experiment these counts can be energy resolved as the control parameter is varied. The $C_{\text{left}}(E, \tau)$ and $C_{\text{right}}(E, \tau)$ can be theoretically computed from the probability to find the electron in the right and in the left nucleus [20, 25]. The asymmetry parameter lies between $-1 < A < 1$. Importantly, $A(E, \tau)$ depends on the control parameter τ and the energy of the ejected D^+ ion. Typically, the asymmetry is demonstrated to oscillate with the period of the optical cycle as the control parameter is varied. Furthermore, the oscillation contrast and phase, depends on the kinetic energy released of D^+ ions that bear the signature of the underlying mechanism. For all the mechanisms the universal signature of the control of EL in a molecule is the existence of oscillations with the period of the optical cycle (~ 2.7 fs). This has been demonstrated in many small molecules like H_2 , D_2 , and multielectron molecules like CO [21]. The phenomenon is now well established both theoretically and experimentally. In the following we shall review three main experimental techniques that have been used so far to achieve the control of EL successfully.

2.1 Control of electron localization using intense, phase-stabilized few-cycle pulses

The first pioneering experiment to demonstrate the phenomenon of control of EL on its natural time-scale was done by Kling *et al* [20]. The key tool used to control EL in dissociating D_2^+ molecule was the few-cycle (5 fs), linearly polarized intense IR pulse around 800 nm central wavelength. A dilute gas of D_2 molecules was exposed to the CE phase-stabilized laser pulses having intensity $I \simeq 10^{14}$ W/cm². The molecular ion D_2^+ was formed by removing an electron by means of various mechanisms. The D_2^+ was formed in the few-cycle IR pulse which controlled the electron localization when its CE phase was varied. Both the momentum of the ejected D^+ ions and their kinetic energy were measured that clearly identified the underlying mechanism of the electron localization.

A key signature of the electron localization was observed in the form of oscillations in the asymmetry parameter $A(E, \varphi)$ when the CE phase φ was varied. The dominant contribution to D^+ counts was found to be in 3–8 eV energy range that was attributed to the recollision excitation of the molecular ion. This means that the intense laser pulse first removed an electron from D_2 by tunnel ionization thus creating D_2^+ in its ground electronic state. The ionized electron returned to the D_2^+ ion due to the linearly polarized field. Its collision with the D_2^+ excited the molecule to $2p\sigma_u$ electronic state thus creating a coherent superposition of the ground and first excited electronic states. The recollision

mechanism was further confirmed experimentally by using circularly polarized IR pulse instead of the linear one. The observed oscillations in the asymmetry parameter vanished, thus confirming the central role of recollision in achieving the control of EL.

The CE phase-stabilized few-cycle 5 fs pulse is vital to achieve the control. It was observed that as the pulse duration increases from 5 fs to 8 fs, the degree of control was progressively lost because, in a few-cycle CE phase-stabilized pulse, the tunnel ionization of electron wavepacket takes place dominantly for a sub-optical cycle time interval near the peak of the electric field in full optical cycle. However, for a longer pulse many such electron wavepackets were launched for both half-cycles that cancelled the asymmetry. By varying CE phase one could precisely time the recollision wavepacket and hence vary the relative phase between $1s\sigma_g$ and $2p\sigma_u$ wavefunctions. While this technique is very efficient, it required controlled generation of few-cycle pulses with tunable CE phase. Using this technique the control of EL has been demonstrated in many molecules including the multielectron molecule like CO [33–36].

2.2 Exploiting a combination of isolated attosecond pulse and few-cycle IR pulse

An alternative promising experimental technique to achieve control of electron localization is the combined action of an isolated attosecond laser pulse and a few-cycle IR pulse in a molecular attosecond pump–probe experiment [22]. This technique requires generation of isolated attosecond pulse having 300–400 as duration with energy bandwidth spanning 20–40 eV. The isolated attosecond pulse was generated by intense few-cycle IR pulse. Due to the inherent synchronization between attosecond and IR pulses, no phase stabilization of the few-cycle pulse was required. Figure 2b shows the combined field of isolated attosecond pulse and IR pulse. The intensity of the IR pulse was weaker ($I \sim 10^{12}$ W/cm²) and its pulse duration was ~ 6 fs. The control parameter to achieve control of EL was the time delay between IR and EUV pulses. The signature of the electron localization was demonstrated in the form of oscillations in the asymmetry parameter $A(E, \tau)$ as the time delay between IR and EUV pulses were varied. The oscillations were observed over a large range of energy of ejected D⁺ ions. The experimental observations were well supported by the theoretical formalism described in [22].

The mechanisms of the electron localization were different from the previous case. Due to the large energy bandwidth of the EUV pulse (20–40 eV) and the simultaneous presence of the few-cycle pulse, two different mechanisms were identified. Mechanism I occurred when both the isolated attosecond pulse and IR pulse temporally overlap. However, mechanism II occurred when the IR pulse is much delayed compared to the EUV pulse. In mechanism I, the energetic EUV pulse excited two-electron autoionization states which decayed onto the ground electronic state $1s\sigma_g$. But the $2p\sigma_u$ state was populated by multiphoton EUV–IR excitation. These two states then mixed with each other and produced an asymmetry of electron localization as the time delay was varied. Mechanism II was slightly different. The EUV pulse first removed an electron from D₂ thus creating D₂⁺ molecule onto $2p\sigma_u$ state. The few-cycle IR pulse arrived several femtosecond later such that it could mix the $1s$ and $2p$ populations creating a linear superposition of these two states. Again, by changing the time delay between the IR and EUV pulses, one can vary relative phase between these two states thus controlling the electron localization. The

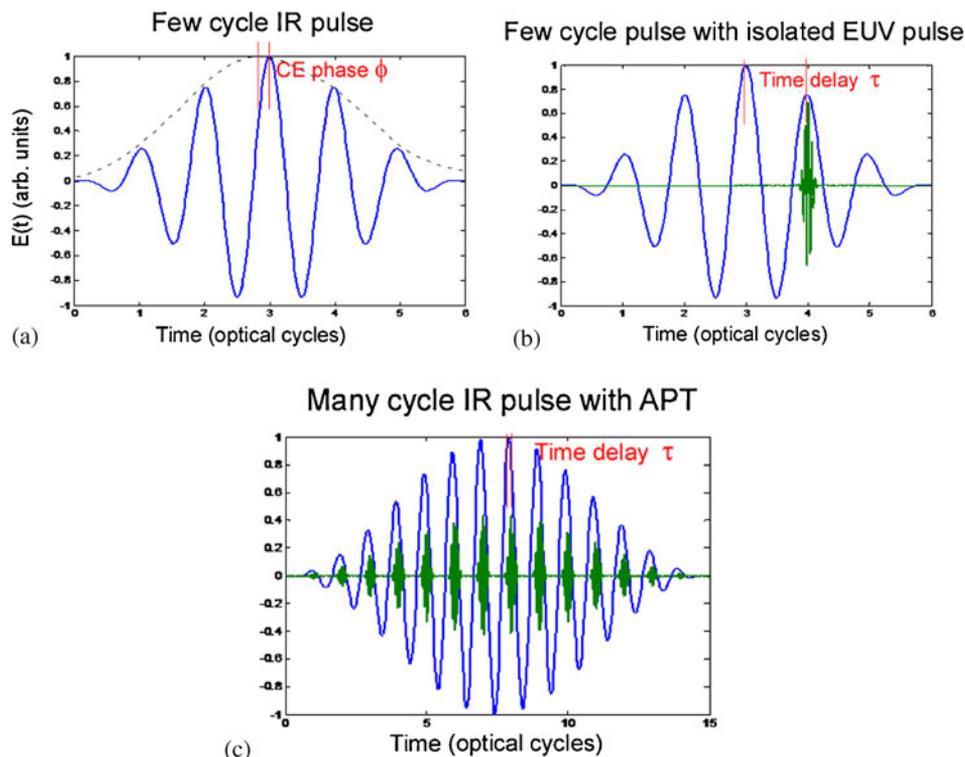


Figure 2. Three main tools used to demonstrate control of electron localization in a molecule. (a) A few-cycle IR pulse at around 800 nm central wavelength. Time is measured in units of optical cycle (1 oc = 2.7 fs). (b) A few-cycle IR pulse together with an isolated attosecond EUV pulse. (c) A many-cycle long IR pulse together with an attosecond pulse train. Note that the attosecond bursts happen once every optical cycle.

use of isolated attosecond pulse along with the IR pulse is a powerful technique that successfully exploits the latest sophisticated technological innovation in the ultrashort pulse generation.

2.3 Electron localization using a combination of many-cycle IR pulse and an attosecond pulse train

Unlike both the above techniques which required sophisticated few-cycle pulses, in this technique, a robust control was demonstrated using a combined action of a many-cycle (25–30 fs) long IR pulse with an attosecond pulse train (APT) [23]. Phase stabilization of the IR laser pulse was not required. Following the theoretical calculations by He *et al* [28], it was understood that to demonstrate the control of electron localization a special APT having one attosecond burst per optical cycle was required. The APT with one attosecond pulse per cycle would strobe the IR pulse for the same phase thus launching the electron wavepacket towards the same nuclei. This would lead to a greater probability

of electron localization compared to the case when two wavepackets are launched in the opposite directions. The control parameter in this experiment was the time delay between APT and IR pulses in a Mach–Zehnder-type interferometer set-up. In one of its arm the APT was synthesized by focussing 800 nm pulse with its second harmonic at blue using a BBO crystal [37–39]. This produced both even and odd harmonics thus creating an APT with one burst per IR cycle as shown in figure 2c. This APT was overlapped with a replica of the IR pulse and it was time delayed in fine steps of about 25 as. The produced ionic fragments (D^+) were collected and analysed using a reaction microscope [40,41].

First, the APT was characterized by recording the photoionization spectra of argon exposed to XUV pulses. That clearly demonstrated the existence of both the even and odd order 11th–17th harmonics. The individual bursts in the APT were about 300 as long and were separated by one optical cycle. Such an APT can strobe many-cycle IR pulse once per optical cycle at its fixed phase. This phase could be varied by tuning the time delay between IR and APT. The experimental signature of the asymmetry was again the oscillations in the asymmetry parameter with the period of one optical cycle versus the time delay between APT and IR pulses as in figure 3. The mechanism of the control was different from both the experiments discussed above. Due to the lower energy of APT harmonics, below $2p\sigma_u$ electronic state, the APT mostly produces D_2^+ ions in its ground electronic state. The IR pulse ($I \sim 10^{13}$ W/cm²) then mixed the $1s\sigma_g$ and $2p\sigma_u$ states thus creating a coherent linear superposition of these two states. Unlike

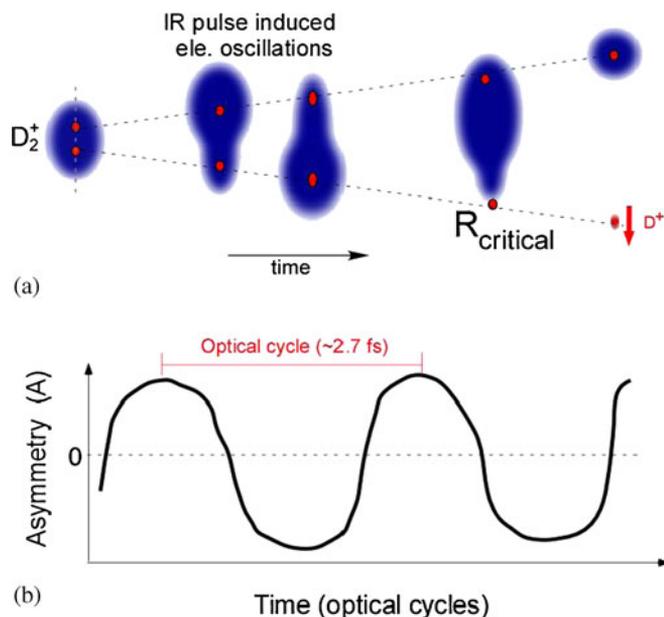


Figure 3. (a) Intuitive mechanism of electron localization in dissociating molecule. A D_2^+ molecule is subjected to EUV and IR pulses, can fragment via two different channels. The localization of electron is the key to choose the desired pathway. (b) Typical oscillations in the asymmetry parameter vs. a control parameter such as time delay.

other experiments, the produced coherent superposition was in the low energy channel for D^+ ions below 1 eV. By varying the time delay between APT and IR pulses, one could control the relative phase between coherent superposition states thus leading to the observed control of electron localization. The many-cycle IR pulse and APT offers a robust method for demonstrating the control of electron localization that can be potentially applied to other molecules due to the tunability of the APT [42,43].

3. Summary

In summary, with the advancement of ultrafast technology it has become possible to track and control electron dynamics on an attosecond time-scale. The control of electron localization in dissociating molecular ions exemplifies one of the many important demonstrations of the capability of the attoscience. The observed control was due to the creation of a coherent superposition of $1s\sigma_g$ and $2p\sigma_u$ states during dissociation of D_2^+ by various mechanisms. The use of few-cycle pulses, isolated attosecond pulses, and attosecond pulse train are the vital experimental tools to achieve the unprecedented time resolution. In future, it would be possible to demonstrate such control in many new, more complex molecular systems. As the complexity of molecules increases, we expect new techniques and mechanisms of control of electron dynamics. It would be challenging to see if such ideas can be realized in complex biomolecules that might find potential applications.

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