Light-Induced Ultrafast Molecular Dynamics: From Photochemistry to Optochemistry

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ABSTRACT: By precisely controlling the waveform of ultrashort laser fields, electronic and nuclear motions in molecules can be steered on extremely short time scales, even in the attosecond regime. This new research field, termed “optochemistry”, presents the light field in the time-frequency domain and opens new avenues for tailoring molecular reactions beyond photochemistry. This Perspective summarizes the ultrafast laser techniques employed in recent years for manipulating the molecular reactions based on waveform control of intense ultrashort laser pulses, where the chemical reactions can take place in isolated molecules, clusters, and various nanosystems. The underlying mechanisms for the coherent control of molecular dynamics are explicitly explored. Challenges and opportunities coexist in the field of optochemistry. Advanced technologies and theoretical modeling are still being pursued, with great prospects for controlling chemical reactions with unprecedented spatiotemporal precision.

Even though photochemistry and optochemistry are both research areas dealing with the interactions of light and matter, the specific mechanisms of these interactions and the resulting chemical transformations are distinct.1−5 Light is considered as energy quanta, or photons, in photochemistry. First, lying at the foundation of photochemistry are two physical laws, i.e., (1) the Grotthuss−Draper law stating that the light must be absorbed by the molecule before a photochemical reaction can occur and (2) the Stark−Einstein law indicating that for every photon that is absorbed, only one molecule undergoes the subsequent photochemical processes. Second, in terms of light−matter interaction, upon absorption of a photon by a molecule, an electron of an occupied molecular orbital is promoted to a higher-energy molecular orbital to afford an excited state. Depending on its multiplicity, the energy deposited in the excited states of molecules can be dissipated either through photophysical processes, e.g., internal conversion, intersystem crossing, energy transfer, fluorescence, phosphorescence, or via photochemical pathways, such as homolysis, cycloaddition, isomerization, π−π stacking, and redox. Third, light sources driving photochemistry cover a diverse variety from sun light, incandescent bulbs, light-emitting diodes, arc lamps, CW lasers, to pulsed lasers with nanosecond to femtosecond pulse durations.6 Moreover, by modulating the wavelength of the irradiation sources, different chemical bonds can be selectively activated leading to the reaction specificity. Photochemistry is ubiquitous. Microscopically, photochemistry is at the core of ultrafast nonadiabatic molecular dynamics. For example, conical intersections, or degenerated electronic states of molecules, play an important role in the photostability of polyatomic molecular systems and provide pathways for ultrafast interstate crossing, typically on the femosecond time scale.7−12 Pump−probe spectroscopy is utilized in the areas of photochemistry for studying ultrafast dynamics near conical intersections.13−20 Another related new field of research concerns light-induced nonadiabatic processes, where several theoretical methods as well as experimental setups have been developed.21−24 On the macroscopic level, photosynthesis and vision involve elegant photochemistry from natural evolution. Complex photochemical processes are ongoing in the atmosphere and contribute to the formation of smog.25 Photochemistry has also been harnessed in organic synthesis of pharmaceutics,26−27 functional molecules, or polymers.28 Reversible photo-switchable molecules can be used as information storage materials.29 Photochemistry is at the core of various solar cells and photocatalysis.30−33 The light energy can also be used for disease treatment in photodynamic therapy.34−36

With the birth of ultrafast laser technology, advances in scientific instruments have opened up unexplored areas of research and applications.36 The electric force acting on electrons at the peak of an applied laser pulse is comparable to the internal Coulomb force acting on the bound electrons in molecular systems. Such laser fields can also provide a pulse.
duration down to the femtosecond or even attosecond level, thus enabling a visualization and manipulation of electron and nuclear dynamics under unprecedented temporal resolution. Although the chemical reaction generally occurs in the femtosecond scales, which corresponds to the inherent time scale of nuclear motion, it is the electron motion within the chemical bond that triggers and further determines the pathway and the outcome of a chemical reaction. Therefore, it is of crucial importance to understand the even faster electron dynamics—typically on the attosecond time scale—to observe, trace, steer, and control the chemical reaction in the microscopic manner. These could be realized based on precision manipulation of the waveform of ultrashort laser fields. The emerging field based on strong-field-driven molecular reactions, noted as optochemistry, depend heavily on the development of ultrafast lasing techniques and can uncover regions outside the realm of photochemistry.

In this Perspective, we introduce a series of work on the investigation of ultrafast molecular dynamics based on optical field manipulation. The target systems include, e.g., isolated molecules, clusters involving pure molecular species and with cooling mediums, as well as molecules in nanosystems. Related techniques and effects will be briefly introduced, and the future research directions will be previewed.

Waveform Control of Femtosecond Laser Fields. The electronic and nuclear dynamics taking place in the attosecond to femtosecond regime play crucial roles in optochemistry. Oscillation of the electric field of ultrashort laser pulses take place on the same time scales compared to the intrinsic time of electronic and nuclear dynamics within molecules. Given the transient intense field strength which is comparable to the intramolecular Coulomb field and the ultrashort temporal duration, coherent control of various chemical processes can be realized based on femtosecond laser fields. A waveform-controlled laser field could be constructed by coherent superposition of multiple frequency components or manipulation of specific light field parameters. In this section, a number of spatiotemporally tailored femtosecond laser fields will be presented.

**Few-Cycle Laser Fields.** A few-cycle laser pulse provides a key knob of control over the electron dynamics, known as the carrier-envelope phase (CEP). As shown in Figure 1a, the carrier wave (the oscillating field indicated by the red solid curves) determines the characteristic frequency of the laser pulse, and the ultrashort nature of the pulse introduces an additional envelope (indicated by the blue dotted curves) on top of the carrier that covers only a few optical cycles. The maximum of the envelope may or may not coincide with the peak of the carrier cycle, leading to a symmetric or asymmetric optical field of the ultrashort laser pulse. The optical response of electrons under few-cycle laser pulses with various CEPs would be different. The electron could then be driven while the molecule experiences dissociation, and in the end, the electron would localize at different atomic sites depending on the CEP.

Compression of the pulse duration has been realized by a couple of methods that can generate few-cycle femtosecond laser pulses. The most commonly used technique is based on spectral broadening in a hollow core fiber or filamentation and succeeding compression using state-of-the-art chirped mirrors. High-energy few-cycle pulses can be produced using this method and have been used widely in manipulating the subcycle electronic wave packet in molecular and solid systems. Optical parametric chirped pulse amplification was utilized to generate few-cycle pulses in the mid-infrared regime, where the tunneling process can be well-addressed. Recently, few-cycle pulses in the visible regime have been successfully achieved based on spectral broadening in thin silica plates.

**Two-Color Femtosecond Laser Fields.** Steering of the ultrafast molecular dynamics can be also accomplished by optical fields composed of a couple of phase-controlled frequency components. The specific waveform of the superimposed laser field can be tailored by tuning one or more of

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Figure 1. Waveform for few-cycle femtosecond pulses with (a) CEP = 0 and (b) CEP = π/2, linearly polarized two-color femtosecond laser fields with phase shifts at (c) ϕ = 0 and (d) ϕ = π/2, respectively.
One simple example is the superimposed two-color (TC) femtosecond laser field by combining the linearly polarized fundamental and the second harmonic (SH) frequency components, as shown in Figure 1c,d. Such a TC field can be sensitively reshaped and can be used to control various molecular dissociation processes. By simply turning the polarization directions of the two frequency components to an orthogonal geometry (as shown in Figure 2c), the electron excited by one color could be streaked by the action of the other color inserted in the perpendicular direction, therefore providing an extra degree of freedom for the directional control. Electron localization in the most fundamental hydrogen molecule was steered in two dimensions with attosecond precision using such laser pulses. TC field polarized in orthogonal directions could access photoelectron molecular dichroism and realize subcycle control of the chirality. Recently, bicircular TC laser fields were used for manipulating electron recollisions in strong laser fields. Such laser fields are obtained by coherently combining circularly polarized fundamental and SH frequencies. For instance, superposition of two counter rotating femtosecond pulses results in a clover waveform (Figure 2a). The underlying molecular dynamics driven by such laser fields is sensitive to the helicity and intensity ratio of the two colors.

**Polarization-Skewed Femtosecond Laser Fields.** Recently, a new kind of tailored laser field named polarization-skewed (PS) laser pulse has emerged. It proves to be very useful in resolving the ultrafast electron–nuclear dynamics during a molecular breakup. The PS field is composed of two time-delayed but partially overlapping orthogonally polarized laser pulses. As shown in Figure 2d, the polarization direction of the PS field gradually changes from the initial direction to its perpendicular direction as time evolves, thus providing the handles for the subcycle resolution and manipulation. On the other hand, coherent population transfer among various quantum levels of molecules can be effectively tailored by using the PS laser field, showing significant importance in the manipulation of molecular reactions where both parallel and perpendicular transitions are involved. One example is the excitation and ionization of the N2 molecule, where the ionization of N2 and subsequent population redistribution via photon-coupled perpendicular transitions from the ground state (X2πg) to the excited states (A2πu and B2Σu+) of N2+ take place. Several vibrational and electronic transitions between the Σ and Π states exhibit intrinsic orientation-dependent features which can be tailored in a unique way using the PS laser field.

**Ultrafast Dynamics in Isolated Molecules.** Interaction of light and isolated molecules is the basis for understanding the light-induced chemical reactions. An isolated molecule is a self-contained system with negligible coupling to external

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**Figure 2.** 3D Waveform for various tailored femtosecond laser fields: (a) counter-rotating two-color laser field, (b) corotating two-color laser field, (c) orthogonal two-color laser field, and (d) polarization-skewed laser field.
degrees of freedom, making its ultrafast dynamics relatively simple, trackable, and controllable. To explore the light-field-induced manipulation of molecular reactions, one would employ an ultrashort laser pulse, which has a broad spectrum covering many optical frequencies. For a molecule that has many electronic and ro-vibrational energy levels, this means a coherent population of multiple states. As long as the coherence persists through the chemical reaction, the coherent population of selected excited states via tailored laser pulses provides an important prospect for steering the bond breakage and formation during a chemical reaction.

Coherent Control of Chemical Bond Breakage and Formation. The central issue in chemical reactions is the bond breaking and formation, which originates from the electron dynamics across the molecule. On the one hand, instantaneous removal of electrons from a molecule would alter the potential between the nuclei and initiates the nuclear motion, resulting in fast variation of the molecular structure. On the other hand, the nuclear motion rearranges the remaining electrons and hence modulates their responses to the light. Within a polyatomic molecule, more than one bond is present. In this case, one can use a tailored laser pulse to selectively break a particular chemical bond, thus leading to designated chemical products. An example is the control of the breakup of the C$_2$H$_4$ molecules as intuitively shown in Figure 3,\textsuperscript{57–58} where removal of the HOMO and HOMO–2 electrons leads to a decomposition into two CH$_2^+$ ions while a removal of the HOMO and HOMO–1 electrons results in an H$^+$ ion and a C$_2$H$_3^+$ ion. The excitation probability to a certain excited state and the outcome of the reaction pathway could be well controlled by finely tuning the parameter of the applied laser pulses. Overall, the ultrashort laser pulses with duration of a few femtoseconds could initiate the reaction in the molecular system. The subsequent alteration to the structural and functional properties taking place on a longer time scale can then be well-controlled by a succeeding laser pulse with a controlled waveform and delay.

In addition to controlled breakup of chemical bonds, an ultrashort tailored laser pulse can also be exploited to facilitate controlled formation of chemical bonds within a molecule. It has been experimentally demonstrated that a few-cycle laser pulse can be employed to steer a preferred trend of proton migration in small hydrocarbon molecules such as acetylene, where a to and fro isomerization process between acetylene and vinylidene is accessible\textsuperscript{59,60} (see Figure 4). Furthermore, a direct formation of O$_2$ from CO$_2$ has been observed...
originating from the bending motion of the CO$_2$ molecule, which enables the formation of an O=O bond.\textsuperscript{61} The control of breakup and formation of chemical bonds is also possible even in a van der Waals complex, where an exotic ion-transfer channel (N$_2$Ar)$^+$→N$^+$/NAr$^+$ has been observed.\textsuperscript{62}

To realize a coherent probing and controlling of the stereo dynamics in chemical reactions, it has been shown that a laser-induced torque could align/orient and even rotate the molecules unidirectionally in space by triggering a coherent motion of the nuclear wave packet on the femtosecond or picosecond time scale.\textsuperscript{63−67} Recently, it was reported that the waveform-controlled two-color field could fix the molecular orientation of asymmetric-top molecules in three-dimensional space.\textsuperscript{68} As shown in Figure 5, the ionic momentum distributions of S$^+$ and O$^+$ generated via a Coulomb explosion imaging approach directly present the orientation of the SO$_2$ molecule in the laboratory frame. This approach is based on the nonlinear optical mixing process caused by the off-diagonal elements of the molecular hyperpolarizability tensor, and it is applicable to a variety of complex molecules, such as the chiral targets. It provides a new tool for the manipulation of light-induced molecular chemical reactions.

\textit{Attosecond Electron Dynamics in Molecules}. The coherent nuclei motion as well as the bond breaking and formation in strong laser fields are triggered by the extremely fast electron dynamics. Electrons exhibit intrinsic time scales much faster than the nuclear motion, into the attosecond domain. As shown in Figure 6, the charge redistribution inside the atoms or molecules can be directly visualized via attosecond metrology based on the attosecond light.\textsuperscript{69} After the removal of an electron, the remaining electrons, or charged holes, would undergo ultrafast rearrangement.\textsuperscript{70} The intramolecular charge migration could drive the electron cloud from one end of the molecule to the other end. It has been demonstrated to be visible through manipulating the CEP of the ultrashort laser pulse.\textsuperscript{39} Later, it was found that electron localization is possible even in a symmetric molecule within an optically symmetric laser pulse.\textsuperscript{71} Intuitively, it could be understood as being due to the laser-driven motion of the remaining bound electrons. In particular, as the molecule dissociates with the bond length increasing, the energy gap between its electronic states varies, leading to resonant absorption of photons at different internuclear distances. This results in coherent superposition of states with different inversion symmetry through the laser pulse, which in turn causes electron localization.

Tracking transient charge localization upon electron removal is however a difficult task because it involves a mixture of many one-hole configurations.\textsuperscript{72,73} The observation of ultrafast charge migration has been realized in, for example, phenylalanine and C$_2$H$_2$I molecules\textsuperscript{74,75} (see Figure 7) as a result of the development of attosecond technology. The unprecedented time resolution provided by attosecond pulses enables the measurement of the electron motion and its degree of coherence in molecular systems, offering powerful tools to detect and control the chemical reactions from the most fundamental perspective.

\textit{Photon Energy Deposition within the Electronic and Nuclear Degrees of Freedom}. Deposition of the photon energy to atoms and molecules is the primary step of the
interactions of radiation with matter. The details of the energy deposition process, in particular how the energy is distributed among the subsystems and various internal degrees of freedom, determine the subsequent ultrafast dynamics. Differing from the atom, the photon energy absorbed by a molecule, as shown in Figure 8, is shared by the electron and nuclei in a correlated fashion, resulting in multiple diagonal lines in their joint energy spectrum governed by the energy conservation.\(^\text{76} - \text{78}\) It clearly indicates that the molecule absorbs the photon energy as a whole, where more energy goes to the nuclei if the electrons take less. The participation of the multiple orbitals and the coupling of various electronic states alter the photon energy deposition dynamics, and the population of numerous vibrational states as the energy reservoir plays an important role in the photon energy absorption and deposition in a molecule. We note that both proper theoretical description and experimental investigation of this problem are very challenging especially in the case of medium-sized molecules, where the electron and nuclear dynamics should be treated on the same footing, while their respective dynamics takes place on different time scales.\(^\text{79} - \text{82}\)

**Ultrafast Dynamics in Clusters.** Atomic and molecular clusters show fascinating collective phenomena that bridge the gap of knowledge between isolated molecules and condensed-phase materials. Experimentally, clusters can be efficiently generated in a supersonic expansion through a cryogenically cooled nozzle. For instance, helium dimer (\(\text{He}_2\)), the most loosely bound ground-state molecule in the universe, has been studied as an intriguing quantum halo state system with a huge internuclear distance and minuscule binding energy.\(^\text{83}\) Large clusters with more than thousands of \(^{4}\text{He}\) atoms, termed helium nanodroplets, are considered to be an ideal quantum solvent for their unique properties of low temperature (~0.37 K) and negligible viscosity.\(^\text{84}\) Helium nanodroplets can be produced by expanding high-purity \(^{4}\text{He}\) gas through a small cryogenic nozzle into vacuum. The average sizes of droplets can be controlled by adjusting stagnation pressure, cold head temperature, and nozzle diameter. The helium nanodroplets provide a cold, weakly perturbing, and transparent environment for embedded molecules. Upon interaction with light, molecules, clusters, or complexes in helium droplets may first undergo excitation/ionization and then bond breakage or formation, leading to chemical activity. The technique of isolating molecules in superfluid \(^{4}\text{He}\) nanodroplets has been implemented in high-resolution spectroscopy in the past decades, in particular, for studying reactions at sub-Kelvin temperature. Complementary to the frequency-resolved spectroscopy, femtosecond pump–probe techniques have been used to explore the real-time ultrafast molecular dynamics inside helium nanodroplets. A coherent rotational or vibrational wave packet of molecules excited by femtosecond laser pulses was observed in helium nanodroplets, e.g., nonadiabatic molecular alignment\(^\text{85,125}\) and long-lived coherent vibration.\(^\text{86}\)

To date, a variety of frequency- and time-domain methods have been used to investigate the photo- or opto-chemical processes of molecules in helium nanodroplets. One key issue is to unambiguously identify the right events of various channels of the in-droplet molecules from the background molecules. It can be achieved by combining the in-droplet molecular beam generation system with the advanced reaction microscope of COLTRIMS,\(^\text{87}\) as shown in Figure 9. By measuring the ejected electrons and nuclear fragments in
coincidence, detailed insights of the ultrafast molecular dynamics in helium nanodroplets can be resolved into different channels. We recently used it to visualize in real time the light-induced molecular reactions in the droplets and to reveal their interactions with the surrounding helium liquid.

Ultrafast Molecular Dynamics in Nanosystems. The development of diverse functional nanostructures has brought tremendous opportunities for the manipulation of light and matter interactions. Thanks to the exciting progress in both ultrafast optics and nanophotonics, the emergence of ultrashort laser pulses with nanostructure provides an unprecedented interaction environment for molecules where considerable spatial gradient of the light field can be realized; therefore, novel dynamics can be initiated.\(^8\) It differs from the above-mentioned dynamics of isolated molecules or clusters. In the latter scenarios, the electromagnetic field a molecule can feel is spatially uniform, based on the fact that the size of molecule under consideration is much smaller than the focusing point of a laser beam. Situations can be completely different when the light–matter interaction takes place with the participation of nanostructures. For instance, when a dielectric nanoparticle interacts with femtosecond laser fields, the near-field enhancement can be induced around the nanostructure that changes dramatically on a femtosecond time scale. Local field distributions can be significantly tailored, and amplification by orders of magnitude could be realized. The molecular dynamics initiated by the induced near-field undergoes processes which have never been realized with conventional optical elements.

On the other hand, metallic plasmonic nanocavities exhibiting the ability to confine electromagnetic fields in volumes of subwavelength scales have promoted applications in single-molecule spectroscopy\(^9\) and nanofocusing.\(^10\) High sensitivity can be achieved because of the local field...
The surface of the nanostructure take the collected in coincidence. This opens a new avenue for the development in which data for electrons and ions are been obtained.100 It is crucial to explore the underlying dynamics on the beginning and to exert tremendous influence on the succeeding reaction of the whole nanosystem. Based on the interaction between the local field and materials. Utilizing state-of-the-art techniques to create small nanocavities and precisely oriented molecules in them, strong coupling between the light and molecule resulting in the formation of light-and-matter hybrid is demonstrated.93–95 These pioneering works shed light on manipulating molecular reactions in the strong-coupling regime within a photon prison.

In the following, we will introduce a few examples of exploring molecular dynamics in nanosystems, with the molecules either attaching to the surface of nanostructures or residing within the nanosystems. People have implemented the nanoparticle sources with a high vacuum velocity map imaging spectrometer to realize single-shot imaging of the momentum distributions of the resulting electrons or ions after the light and nanoparticle interactions.96–99 A reaction nanoscopy has been developed in which data for electrons and ions are collected in coincidence.100 This opens a new avenue for the investigation of femtosecond laser-induced chemical reactions on surfaces of aerosolized nanostructures.

Exposed to the strong laser fields, the molecules adhered to the surface of the nanostructure take the first step to response rather than the nanostructure itself. The surface molecules can interact with the most intense part of the enhanced near field, therefore having great probability to be excited at the very beginning and to exert tremendous influence on the succeeding reaction of the whole nanosystem. Based on these, it is crucial to explore the underlying dynamics on the “surface” molecules. Considering the initial charge distribution around the nanostructure and subsequent dynamics in the modified near field, the momentum distribution of protons from the dissociation of the molecules adhered on nanosphere surfaces can be utilized for the reconstruction of the nanoscale reaction yield landscape.99–101 The breakage of a hydrogen bond is one of the prototype chemical reactions in molecular systems. As shown in Figure 10, distinct momentum distributions with a feature of forward focusing can be obtained for the H⁺ ions generated from large isolated nanoparticles (with a diameter of about 300 nm) and from nanoparticle dimers composed with a pair of nanospheres. However, the laser intensity required to induce comparable ion yields in the above two cases can differ to a large extent. Because of the greater enhancement factor that a dimer system can reach, the corresponding laser intensity to initiate considerable ionization can be much lower. This indicates that by tuning the nanoscale landscape, the involved molecular reactions can be precisely tuned with high resolution.

Apart from the deprotonation process induced in nano-systems, detection of H⁺ ions forming in the strong field interaction of nanospheres via reaction involving two water molecules attached to the nanosurface has been reported (shown in Figure 11).102 In this study, nanoparticles provide a unique environment including nanoscale near-field enhancement, electron trapping, local charge interactions, etc. Complex molecular reactions via four different pathways were expected for the formation of trihydrogen cations, where hydrogen migration is necessary. It stands for the basic chemical process, i.e. hydrogen migration, induced in aerosolized nanoparticle systems in intense femtosecond laser fields. The trihydrogen cation is a highly important ion in aerosols and in space. Accessing the mechanism of H₃⁺ (D₃⁺) formation from water in nanosystems has profound implications for inorganic synthesis.

Beyond the prototype system of isolated nanospheres, plasmonic nanocavities composed of pairs of nanostructures have been developed to provide extreme confinement of light field within small volumes. For instance, two nanospheres approaching each other with a spacing of a few nanometers or below 1 nm can form nano/pico-cavities.103 Such a cavity can be also achieved by placing a nanoparticle above a metallic layer and separating the two by a thin dielectric spacer. The interaction between the nanoparticle and its induced image forms a nanoparticle-on-mirror cavity.104,105 Different shapes of nanostructures can be fabricated, such as bow-tie, rectangular, or spheres.106 In these cavities, extreme control of the light coupling with a single molecule can be reached with high precision. In a recent work, femtosecond laser-induced resonant tunneling through quantized energy levels in an individual quantum dot attached to a metal nanotip has been observed.107 (Figure 12a). Moreover, chiral light–matter interactions have been manipulated in 2D transition metal dichalcogenides in a single plasmonic nanocavity.108 (Figure 12b). The interaction between the optical field and low-dimensional materials can be dramatically enhanced because of the confinement which opens an avenue for single-molecule chemistry under ambient conditions.

A complete modeling of the strong-field response of nanosystems is still challenging because of the complex shape and presence of surrounding materials. A promising alternative is to investigate isolated nanoparticles in the gas phase, where the influence from the environment can be safely.
neglected. In principle, the related evolution can be described by the TDSE. However, full numerical solutions of TDSE for nanosystems is not feasible to date. One reason is the insufficiency of computation ability. Another reason is the lack of knowledge of the underlying physics. A theoretical description of the ultrafast electronic dynamics called the semiclassical Mie Mean-field Monte Carlo (M‡C) model has been developed,\textsuperscript{109,110} the details of which will not be included in this Perspective. In brief, the oscillating near field induced by the interaction between nanostructure and femtosecond laser field is obtained via the Mie theory, where the Coulomb interactions between free charges are described by the mean field. The near-field driven ionization probability is then determined from Ammosov–Delone–Krainov tunneling ionization rates. Electron trajectories are launched at the classical tunneling exit and integrated classically in the local fields. This theoretical model has been applied to describing the strong-field ionization from nanospheres\textsuperscript{111} and metal nanotips.\textsuperscript{112}

In closing, we mention another group of work involving ultrafast dynamics in large molecular systems in the nanometer regime. Interactions of large molecules with ultrashort laser pulses have been of fundamental importance to understand the properties of coherent control.\textsuperscript{113} Other than responding to the photon energy addressed by a weak optical field, a strong laser field can provide actions comparable to the Coulomb field that a valence electron can experience, therefore offering unprecedented opportunity to tailor the molecular dynamics at will. In general, after absorbing the photon energy from the external optical fields, the electron and nucleus in molecular systems undergo complex dynamics. Both the interactions among multiple charges and the coupling between the electronic and nuclear degrees of freedom make the physical picture more complicated compared to the cases for small molecules. Formal techniques based on molecular fragmentation cannot address the exact electronic dynamics anymore. However, upon measuring the angular-resolved photoelectron distributions it is possible to probe the electronic dynamics before the onset of significant nuclear motion.\textsuperscript{114}

Herein, we take C\textsubscript{60} fullerene as a candidate because of its distinct physical properties. C\textsubscript{60} can serve as a unique prototype with nanometer dimension and high degree of symmetry. The semiclassical and quantum dynamical calculation methods developed for atomic and molecular systems can be used to study the behavior of C\textsubscript{60} to a certain extent.\textsuperscript{115} Because of the large amount of electronic states existing in fullerene, techniques such as time-dependent density functional theory need to be implemented to obtain the electronic structure.\textsuperscript{116} Many interesting properties have been discussed for C\textsubscript{60} such as high polarizability,\textsuperscript{117} macroatom behavior,\textsuperscript{118} etc. Recently, super atomic molecular orbitals have been detected in the solid state and even in isolated gas-phase C\textsubscript{60} molecules when interacting with intense femtosecond laser pulses.\textsuperscript{119–121} With the advanced laser-induced electron diffraction\textsuperscript{122} technique, ultrafast molecular deformation in C\textsubscript{60} has been observed in femtosecond time scales, which paves the way toward recording macromolecular structures and dynamics with atomic spatiotemporal resolutions.\textsuperscript{123} Some mature techniques which were demonstrated in the dynamical control of simple molecules can be applied to complex molecular systems, where novel effects might be raised. For instance, by using the CEP-controlled intense few cycle laser pulses, the collective electron motion in C\textsubscript{60} can be tailored with attosecond resolution where characteristic electronic scattering processes were revealed.\textsuperscript{124} With the advent of various techniques on waveform control of ultrashort laser pulses, unlimited possibilities could be expected in complex molecular systems.

In conclusion, photochemistry is an extremely important branch of chemistry associated with chemical processes initiated by absorption of light. However, the precise control of photochemical reactions is inherently difficult owing to the fact that photochemistry starts with the treatment of light in the frequency domain, thereby producing an excited-state species. Compared with photochemistry, optochemistry has the advantages of manipulating the electronic and nuclear dynamics in the time domain down to the femtosecond (or even attosecond) time scale, therefore could manipulate chemical reactions in a fundamental way with an unprecedented temporal resolution.

With the flourishing of ultrafast laser techniques, strong-field manipulation of molecular dynamics has entered a new era. Steering of chemical reactions has been implemented through laser field manipulation of electronic and nuclear degrees of freedom. By employing state-of-the-art detection techniques, correlated electron–nuclear motion can be revealed which composes the most fundamental part of light–matter interactions. Even rich dynamical processes which are not easy to achieve in common cases can be revealed in complex systems. Particularly, extreme control of the light and matter coupling can be realized by careful design of the nanostructure and the waveform of the light field. This could offer unprecedented opportunities, e.g., single-molecule chemistry under ambient conditions. We have strong confidence that the related fields of research and applications are facing a prosperous future.

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