Controlling Chemical Reactions with Laser Pulses
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ABSTRACT: One of the holy grails of contemporary science is to understand and manipulate chemical reactions to obtain desired products preferentially. To achieve this goal, chemists traditionally choose the correct starting materials and reaction conditions, but it often lacks selectivity and efficiency. A promising alternative is to design laser control schemes and apply them to guide and control chemical reactions. This mini-review attempts to provide theoretical insight into the laser-induced control of chemical reactions by highlighting some recent achievements, discussing the present challenges, and shedding some light on future prospects.

INTRODUCTION
Chemical reactions, the transformation of matter from reactants to products, is at the heart of chemistry. They usually consist of a sequence of elementary processes which ultimately result in the breaking and making of chemical bonds. Reactivity, the essence of chemistry, is a dynamic process resulting from the movement of electron(s) and nuclei under the influence of a force or potential. Molecular reaction dynamics is capable of providing deeper fundamental insight into a chemical process at a microscopic molecular level.1 With direct insight into the detailed evolution of a chemical process, along with the quest for advanced understanding, a chemists’ dream is to predict the behavior and control the outcome of the chemical reaction to enhance the yield of the desired product selectively. Although traditional thermodynamic techniques (e.g., variations in pressure and temperature) can assist and guide the reactants into particular product channels, they lack selectivity. With the possibility of generating electromagnetic laser pulses with a high level of control over their pulse characteristics, it has become possible to probe and steer the chemical reactivity due to their selectivity and high precision. They can guide a chemical reaction by delivering their energy to the reacting species at just the right moment to enhance or inhibit the reactivity. This is because the typical time scales of nuclear and electronic motions are on the order of femtoseconds (1 fs = 10−15 s) and attoseconds (1 as = 10−18 s), respectively, which exactly matches the pulse durations of modern laser pulses. In other words, chemical transformations can be fundamentally understood as femtochemistry if nuclear motion is involved or attochemistry if electronic motion is involved. Meanwhile, with the remarkable and decisive progress in femtosecond and attosecond laser technology, the investigation of ultrafast processes has received a major stimulus and the real-time observation of the transformation of matter at the atomic level has now become feasible.2

For unimolecular reactions, laser control can be achieved in three widely used ways. First, by optimal control theory3 (OCT), where a target operator is first constructed to calculate an optimal (shaped) laser field. This optimal field when applied to the system will result in a desired final state. OCT (pulse-shaping) leads to nontrivial, complex pulse shapes that are not accessible by conventional photochemical means. Experimentally, optimally tailored laser pulses are created via feedback from an experimental signal.4 Second, coherent phase control5 has been proven to be an experimentally easier alternative and enables a large range of yield control. It utilizes the phase coherence properties of a laser pulse (as opposed to traditional light sources) to alter the character of the prepared state, and thus the reaction outcome could be influenced. Moreover, coherent control provides deeper insight into the essential features of molecular reaction dynamics and quantum mechanical interference, which are necessary to achieve control in any elementary chemical process. Third, by exploiting the notion of mode-selective chemistry6 which relies upon the idea of utilizing laser light to induce selective excitation in specific bonds or modes of the reactant molecule that are closely coupled with (and communicate their energy to) the reaction coordinate to ultimately drive the outcome of the reaction in a desired direction. However, the implementation of this idea is impossible without having a sophisticated understanding of a...
fundamental and formidable phenomenon—intramolecular vibrational-energy redistribution (IVR) which dictates the pathways, rates, and properties of the energy distribution to different modes of the molecule and into the reaction coordinate, followed by the selective vibrational excitation of a particular mode or bond. Therefore, understanding and simulating vibrational energy flow on a molecular level with essential knowledge of the intramolecular couplings between different modes is of utmost importance and is a prerequisite to achieving the desired chemical transformation via mode-selective vibrational excitation. In special cases, when the molecular vibrations are largely independent, an easier way to promote the reaction to a particular product channel is by supplying energy to specific degrees of freedom of the reactant molecule (e.g., in the form of vibrational pre-excitation using laser light)

The recent availability of ultrashort, intense laser pulses comprising a few wave cycles has introduced a new parameter of importance—the carrier envelope phase (CEP) defined as the temporal offset between the maxima of the pulse envelope and the optical cycle. This is because the subsequent ultrafast dynamics is governed by the instantaneous magnitude of the laser field experienced by the irradiated system and not by the peak intensity corresponding to the pulse envelope, which remains unaltered. Experimentally, CEP is found to significantly affect many processes, including the ionization of atoms and molecules. Thus, for few-cycle pulses, CEP control plays a crucial role in influencing the reaction outcome and offers a new prospect in strong-field laser science.

This mini-review is organized as follows. Basic theoretical and computational details are briefly elaborated in Section 2. Some practical applications of laser control strategies are presented and discussed in Section 3. Section 4 concludes with a future outlook.

THEORETICAL AND COMPUTATIONAL DETAILS

The dynamics of a laser-induced chemical process can be theoretically studied either quasi-classically or quantum mechanically. Quasi-classical approaches involve solving the classical equations of motion in some form (Newton’s or Hamilton’s), where the prefix “quasi” indicates that the initial conditions are chosen in such a way that the energy in various degrees of freedom corresponds to the quantum mechanical energy. These methods are computationally cheaper, they can reproduce experimental results, in particular, for quantities which are averaged over thermal initial conditions, and often some unnoted processes are revealed by critically analyzing the individual trajectories which lead to valuable insights. Still, they have some shortcomings; they cannot reproduce the features arising from tunneling, resonances, and interference which are quantum mechanical in nature.

Recent developments in field chemistry and the birth of attochemistry have spurred enormous interest in solving the time-dependent Schrödinger equation, following quantum wave packet dynamics. It is analogous to the former description in the sense that an initial wave packet has to be prepared for a specified set of initial conditions, time evolve it, and extract the reaction attributes in the regions of interest. Moreover, a clear physical picture of the underlying microscopic dynamics (as snapshots) can be obtained by plotting the probability densities of the wave packet at various stages of time evolution.

While solving the time-dependent Schrödinger equation, it is always advantageous to separate the faster electronic motion from the slower nuclear motion, based on the Born–Oppenheimer approximation. This so-called adiabatic separation enables us to visualize a molecule as a set of nuclei moving on the instantaneous eigenstate, namely, the potential energy surface provided by the electrons. The gradients occurring on the potential energy surface quantify the forces acting on the atoms and molecules during a chemical transformation. Although many chemical reactions show adiabatic behavior (i.e., their dynamics are restricted on a single potential energy surface), under certain circumstances the Born–Oppenheimer approximation fails, resulting in the coupling between electronic and nuclear motion.

The various numerical/computational aspects related to dynamical methodologies are well documented in the literature (ref 13 and references therein); therefore, only a brief outline of the essential features is discussed below.

Time-Dependent Wave Packet Approach. The time-dependent wave packet approach involves numerically solving the time-dependent Schrödinger equation

$$i\hbar \frac{\partial}{\partial t} \Psi(R, t) = \hat{H} \Psi(R, t)$$

where $\hat{H}$ is the Hamiltonian operator of the system expressed as a sum of kinetic energy ($\hat{T}$) and potential energy ($\hat{V}$) operators, with the later being the potential energy surface within the Born–Oppenheimer approximation. For an explicitly time-independent Hamiltonian, the formal solution of eq 1 is given by

$$\Psi(R, t) = \exp(-i\hat{H}/\hbar)\Psi(R, t = 0)$$

For example, in the presence of an applied laser field $\vec{E}(t)$ the Hamiltonian (within the electric dipole approximation) is $\hat{H} = \hat{T} + \hat{V} - \vec{\mu}(R) \cdot \vec{E}(t)$ for static electric dipole $\vec{\mu}(R)$ and eq 3 becomes

$$\Psi(R, t) = \exp\left(-\frac{i}{\hbar}(\hat{T} + \hat{V})t - \int_0^t \vec{\mu}(R) \cdot \vec{E}(t') \, dt'\right) \Psi(R, t = 0)$$

The initial wave function, commonly chosen as a Gaussian function, represented as a coherent superposition of one or several eigenstates, is called a wave packet. The specific form of the initial wave packet is chosen on the basis of the initial conditions to be simulated. For example, in the case of unimolecular reactions it should describe the field-free initial states of the reactant molecule.

Quasi-Classical Trajectory Approach. A quasi-classical simulation consists of the following steps: (i) sampling of the initial conditions, (ii) numerical integration of the particle trajectories, and (iii) identification of the final state. To proceed with the sampling of initial values, first the quasi-
classical ground-state configuration is required, which can be obtained by a proper minimization of the system Hamiltonian using numerical techniques such as the downhill simplex method. Attainment of the global energy minimum can be confirmed by performing trials several times with various initial guesses of the particle configuration. With the ground-state configuration, an ensemble of random initial conditions are sampled (e.g., by applying random rotational matrices) in such a way that each set of positions and momenta shares the same total energy. Temporal evolution of the particle trajectories with different initial conditions (positions and momenta) is then followed by numerically solving the classical Hamilton’s equations of motion with the system Hamiltonian \( H \) as

\[
\frac{dr}{dt} = \frac{\partial H}{\partial p}, \quad \frac{dp}{dt} = -\frac{\partial H}{\partial r},
\]

\[
\frac{dR}{dt} = \frac{\partial H}{\partial P}, \quad \frac{dP}{dt} = -\frac{\partial H}{\partial R}
\]

(5)

where \( r \) and \( p \) and \( R \) and \( P \) are the positions and momenta of the electrons and nuclei, respectively. The final state analysis is relatively straightforward, and physical processes such as ionization and dissociation can be identified by simply calculating the probability of occurrence of that event.

### RESULTS AND DISCUSSION

Some simple applications of the laser control strategies are now discussed below, taking into account three different chemical processes.

**Photodissociation of HOD.** The photodissociation dynamics of HOD in the first absorption band is a well-studied reaction due to its unique characteristics. The dissociation occurs on a purely repulsive excited-state potential which is well separated from other electronic excited states, and the H–O–D bending mode is weakly coupled with the stretching modes (i.e., the dynamics can be simulated within a two degrees of freedom model). Moreover, it is the simplest example of a photoinduced reaction with chemically distinct products (\( D + OH \leftrightarrow HOD \rightarrow H + OD \)); therefore, this unimolecular reaction is considered to be a prototype for the chemically interesting scenario of bond-selective chemistry.

Starting with HOD in its vibrational ground state, breaking of the H–OD bond is always preferred over HO–D bond breaking. The mechanism behind this preferred O–H bond cleavage is mainly governed by the initial momentum distribution and is slightly affected by the smaller reduced mass associated with the O–H motion. In the weak-field (one-photon) limit, branching ratio \((H + OD)/(D + OH)\) strongly depends on the VUV excitation frequency, and it is always found to be \( \geq 2 \) over the entire range of the first absorption band. Thus, a key target of laser-controlled chemistry is to achieve a branching ratio of \( \leq 2 \) for this reaction.

HOD bond breaking can be selectively controlled by the following strategies: (i) A two-pulse control scheme, where an intense nonresonant infrared (IR) pulse first vibrationally excites the molecule and, at an optimal time delay, an ultrashort vacuum-ultraviolet (VUV) pulse transfers the molecule to the dissociative excited state. This approach is mainly based on the creation of nonstationary vibrational states in HOD by the nonresonant IR pulse. A further modification of this scheme by introducing chirped VUV pulses results in better yield control. (ii) A tailored intense VUV pulse directly transfers the molecule from its vibrational ground state to the excited state (as shown in Figure 1).

**Figure 1.** Ground and first excited state potential energy surfaces of water. The Franck–Condon wave packet is shown right after the instantaneous excitation. Reprinted with permission from ref 15. Copyright 2008 by the American Physical Society.

### Vibrational Excitation and (δ-Pulse) Photodissociation

Current laser technology can generate ultrashort (few-cycle) laser pulses with a temporal duration of a few femtoseconds (i.e., even shorter than any vibrational period in a molecule). Such ultrashort, intense laser pulses are an optimal tool for nonresonant vibrational excitation via the dynamic Stark effect, which is equivalent to impulsive stimulated Raman scattering. Thereby, first we consider the approach based on dynamic Stark control, where an ultrashort (3.5 fs) intense \((10^{14} \text{ W/cm}^2)\) nonresonant (800 nm) laser pulse induces the vibrational dynamics of HOD in the ground electronic state which, when followed by a properly timed ultrashort (δ-pulse) excitation, undergoes a Franck–Condon transition to the dissociative first electronically excited state. This will eventually help us to understand the extent of control that can be achieved with simple off-resonant vibrational pre-excitation. Moreover, the ease of realizing this two-pulse control scheme with any nonresonant laser pulse lends itself to convenient experimental implementation.

The photodissociation dynamics is theoretically studied by numerically solving the time-dependent Schrödinger equation (as discussed in Section 2.1) with the bond angle restricted to its equilibrium value. Under field-free conditions, we considered a randomly oriented molecule in space (e.g., corresponding to the rotational ground state). The initial nuclear wave packet in the electronic ground state is represented as a superposition of wave packets, each with different orientations in space. Since the electrons get significantly perturbed under intense nonresonant laser excitation, the first-order polarizability (field-induced dipole...
moment) components are taken into account in the interaction potential, along with the static electric dipole terms.

First, we investigate how the nonresonant laser excitation governs the vibrational dynamics of a randomly oriented HOD molecule. The expectation values of the OH and OD bond lengths as a function of time are plotted in Figure 2. The laser pulse is also plotted alongside (on an arbitrary scale) to visualize the onset of the vibrational dynamics. Clearly, the vibrational amplitudes are much smaller than expected with resonant laser excitation (i.e., when the laser center frequency is in resonance with a vibrational transition). This is because for resonant excitation the static dipole plays the main role, whereas for nonresonant excitation it is mainly via the induced dipole (polarizability) component of the interaction potential. This plot further indicates the characteristic vibrational time periods of 9.0 and 12.2 fs for the OH and OD bonds, respectively.

Since the vibrational amplitudes are smaller with nonresonant laser pulses, to further enhance the vibrational excitation, we applied the simple concept of laser pulse trains (i.e., a set of identical laser pulses, each of which is exactly the same as the single laser pulse previously used but with a proper time delay between each of them). We applied this idea, and at first we choose only two subpulses. The time delay between the subpulses is fixed at the respective time periods of OH (Figure 3(a)) and OD (Figure 3(b)) bond oscillations. Both subplots (a) and (b) indicate marked increases in the amplitude of the bond oscillations from the second pulse onward, where the increase in the OH bond oscillations shows up in subplot (a) and the increase in the OD bond oscillations shows up in subplot (b), since the time spacings are chosen accordingly. Moreover, subplot (b) further indicates a decrease in the OH bond oscillations due to improper time spacing.

With the vibrationally excited HOD molecule in the ground electronic state (Figures 2 and 3), we will now investigate the degree of selective bond breaking that can be achieved when a second laser pulse (δ pulse or VUV pulse) photodissociates it via the $\tilde{A}$ state. This is studied in a stepwise manner. First, we choose the single nonresonant vibrational excitation as reported in Figure 2 and shine a properly timed δ pulse. It is to be noted that a δ pulse is only used for convenience and any ultrashort pulse with a finite pulse duration of a few femtoseconds will give similar results. The dissociation dynamics is analyzed by measuring the outgoing flux along the two fragmentation channels, H + OD and D + OH, from which the branching ratio is calculated. A δ pulse timed at 24.8 fs (vertical dashed lines in Figure 2) following the nonresonant excitation gives 76.7% flux in the H + OD channel and 22.8% flux in the D + OH channel as revealed in Figure 4(a), which results in a branching ratio of 3.36, the upper limit that can be reached with a single nonresonant vibrational pre-excitation. However, if the δ pulse is timed at 19.7 fs (vertical dashed lines in Figure 2) following the nonresonant excitation, 72.1% flux in the H + OD channel and 27.5% flux in the D + OH channel are obtained as shown in Figure 4(b), with a branching ratio of 2.62 as the lower limit. To this end, we note that 19.7 fs (in Figure 2) corresponds to the time instant when the oscillating O−D bond is close to its equilibrium value, (i.e., the average

Figure 2. Expectation values of the O−H and O−D bond lengths as a function of time with single nonresonant pulse excitation. The laser pulse is also shown alongside (on an arbitrary scale). The vertical dashed lines are drawn at 19.7 and 24.8 fs. (See the discussion concerning photodissociation.) Reprinted from ref 16 with the permission of AIP Publishing.

Figure 3. The same as in Figure 2 except that now the laser pulse consists of two similar subpulses with pulse separations of (a) 9.0 and (b) 12.2 fs, respectively. The vertical dashed lines are related to the discussion concerning photodissociation. (See the text.) Reprinted from ref 16 with the permission of AIP Publishing.
as in Figure 3(a), and branching ratios of 3.58 and 2.47 are observed for Figure 3(b). Therefore, a more pronounced effect is noticed compared to the single pulse excitation at 80.6 fs with a pulse separation of 12.2 fs between each subpulse. The application of pulse trains with more than six subpulses will lead to even more controllability. Table 1 summarizes the lower limits of branching ratios obtained with nonresonant laser excitation followed by a δ pulse, along with the fluxes accumulated in the respective dissociation channels.

Vibrational Excitation and (VUV-Pulse) Photodissociation. Since nonstationary vibrational states are already created with nonresonant impulsive laser excitation, one way to improve the selectivity in controlling the branching ratio between the two fragmentation channels is to introduce a quadratic spectral chirp or, equivalently, a linear temporal chirp which corresponds to a time-dependent VUV excitation frequency.17

The time-dependent phase-coherent electric field $E(t)$ is given by

$$E(t) = E_0 \text{Re} \left[ \int_{-\infty}^{\infty} A(\omega) e^{i\phi(\omega)} e^{-i\omega t} d\omega \right]$$

(6)

where $A(\omega)$ is the real-valued distribution of frequencies and $\phi(\omega)$ is the real-valued frequency-dependent phase. The electric field in eq 6 corresponding to a Gaussian frequency distribution (centered at $\omega_0$) with a quadratic phase function takes the form

$$E(t) = E_0 \text{Re} \left[ \sqrt{\frac{\tau}{2\tau_0}} \exp \left( -\frac{t^2}{2\tau^2} - i\beta t^2/2 - i\omega_0 t \right) \right]$$

(7)

where $\tau$ is the pulse duration, $1/\tau_0$ is the frequency bandwidth, $\beta$ is the linear temporal chirp, and $\beta_0$ is the quadratic spectral chirp. Pulse shaping is employed by simple phase modulation of the frequency components of the excitation pulse without varying the frequency distribution. This is achieved by altering the spectral chirp $\beta_0$ of the VUV pulse which introduces a time-dependent frequency distribution of the field in eq 7. This in turn changes the magnitude of quantum mechanical interference terms in the interaction with matter and is the essence of coherent control.

With the laser pulse train containing six subpulses, a maximum vibrational excitation is noted. Therefore, now we try to find how a linear temporal chirp affects the branching ratio in the A state. Figure 5 shows the variation in the

![Figure 4](https://dx.doi.org/10.1021/acsomega.0c02098)  

**Figure 4.** Flux accumulated along the two dissociation channels as a function of time for δ-pulse excitations at (a) 24.8 and (b) 19.7 fs, respectively, with the vibrational excitation reported in Figure 2. The time axes indicate the time measured relative to the δ-pulse excitation. Reprinted from ref 16 with the permission of AIP Publishing.

Table 1. Lower Limits of the Branching Ratios Obtained from Nonresonant Vibrational Excitation Followed by a δ Pulse

| Pulse | H + OD | D + OH | (H + OD)/(D + OH) |
|-------|--------|--------|-------------------|
| 0 fs  | 0.745  | 0.251  | 2.97              |
| 1 pulse (19.7 fs) | 0.721  | 0.275  | 2.62              |
| 2 pulses (31.1 fs) | 0.708  | 0.286  | 2.47              |
| 6 pulses (80.6 fs) | 0.649  | 0.331  | 1.96              |

The time delay between the subpulses is 12.2 fs. Reprinted from ref 16 with the permission of AIP Publishing.
branching ratio as a function of quadratic spectral chirp $\beta_0$ and the full width at half-maximum (fwhm) of the unchirped VUV pulse ($\beta_0 = 0$). Here, the VUV pulse is centered at $t_c = 302.8$ fs with respect to the peak of the last (sixth) subpulse in the nonresonant laser pulse train. Clearly, a modulation of the branching ratio as a function of laser chirp is observed, and this modulation further depends on the bandwidth (fwhm) of the unchirped pulse. For fwhm = 5 fs, the branching ratio increases from 1.9 to 2.35 with the laser chirp. The effect becomes even larger as the pulse gets shorter, and the effect of chirping almost vanishes for pulse durations longer than 15 fs. When the time delay $t_c$ is replaced by $t_c + P_{OD}$, where $P_{OD}$ is the O–D vibrational period, essentially the same result is obtained as in Figure 5 due to the nearly stationary O–H oscillations.

Figure 6 shows the branching ratio with the VUV pulses now shifted by $t_c + (3/4)P_{OD}$. As a result, the relative phases in the initial vibrational superposition state differ from those in the earlier case. Thus, now the branching ratio is found to decrease from 3.4 to 2.33 as a function of the laser chirp (fwhm) of the unchirped pulse. For fwhm = 5 fs, the branching ratio increases from 1.9 to 2.35 with the laser chirp. The effect becomes even larger as the pulse gets shorter, and the effect of chirping almost vanishes for pulse durations longer than 15 fs. When the time delay $t_c$ is replaced by $t_c + P_{OD}$, where $P_{OD}$ is the O–D vibrational period, essentially the same result is obtained as in Figure 5 due to the nearly stationary O–H oscillations.

Figure 6. The same as in Figure 5, except now three-quarters of a vibrational O–D period has been added to time delay $t = t_c$ (details in the text). Reprinted from ref 17. Copyright 2019 with permission from Elsevier.

Table 2. Branching Ratios for Different Optimized Pulses

| $I$/(TW/cm$^2$) | (H + OD)/(D + OH) |
|----------------|------------------|
| 8              | 1.9              |
| 18             | 1.2              |
| 56             | 0.5              |

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as the lower limit. However, even smaller branching ratios can be obtained when the initial (nonstationary) vibrational state contains a larger excited-state population, for example, by adding more subpulses to the laser pulse train. This will allow for higher vibrational amplitudes/momenta in time-delay control or more comprehensive quantum interference control in chirped pulse excitation at a fixed time delay.

Direct Dissociation with Shaped Pulses. The photoinduced dynamics can also be controlled without considering any prior vibrational excitation of HOD. Utilizing the idea of optimized laser fields to guide and control reaction dynamics, preferential breaking of the O–D bond can be achieved with HOD initially in its vibrational ground state. The optimized laser pulse is calculated through a careful optimization of the time-frequency behavior via OCT with an objective of maximizing the D + OH channel population in the excited electronic state, under the constraint of constant field energy. It is based on an iterative procedure, and we choose a 5 fs Gaussian pulse with a center frequency of $\omega = 0.2738$ au ($\lambda = 166.5$ nm) as the initial pulse. The results were converged after 15 iterations. The branching ratios obtained at various (cycle-averaged peak) intensities are tabulated in Table 2.
To analyze the results corresponding to the branching ratio of 1.2, Figure 7 (upper panel) shows the optimized laser pulse whose cycle-averaged peak intensity is 18 TW/cm² at around 950 au and the Husimi transform (i.e., time−frequency behavior of the pulse, lower panel). The bandwidth essentially covers the entire first absorption band, and a positive chirp is noticed in the first part of the pulse. The ground- and excited-state populations as a function of time and the time-resolved branching ratio are plotted in the upper and lower panels of Figure 8. Roughly, more than 90% of the population is transferred to the excited state, where the first part of the pulse (up to 825 au) transfers about 50% of the population and the short pulse at around 950 au transfers the rest. The average branching ratio can be estimated to be \((1.83 + 0.75)/2 = 1.29\), in good agreement with the tabulated value. A closer look at the wave function in the electronic ground state indicates the creation of a nonstationary vibrational state with the momentum in the O−D stretch being transferred to the excited state. The mechanism involves a manipulation of the wave packet via a properly timed laser pump−dump−pump sequence between the ground and excited electronic states, with the excitation to the excited state taking place when the initial state is optimal with respect to position and/or momentum. Thus, preferential cleavage of the O−D bond can be achieved with optimally tailored intense UV pulses. The optimized laser pulse operates via a pump−dump−pump mechanism, where the bond-selective dumping to the electronic ground state creates nonstationary vibrational states in HOD.

**Photodissociation of IBr.** Now we consider the direct photofragmentation of IBr leading to atomic fragments in two different electronic states, specifically, nonadiabatic process I + excited-state potentials cross each other at an internuclear distance of about 6 au. Here we demonstrate the weak-field coherent control of the asymptotic states of dissociating IBr starting from the vibrational and electronic ground state.\(^\text{18}\) In the calculations, we start with a transform-limited pulse \((\beta_0 = \beta = 0)\) of duration 30 fs and then vary the linear spectral chirp \(\beta_0\) keeping the bandwidth fixed (similar to the coherent control approach for HOD). The laser-induced dynamics is calculated...
within first-order perturbation theory for the interaction with the field.

The total dissociation probability in the two channels (I + Br* and I + Br) and the relative yield of Br* (defined as Br*/(Br* + Br)) are plotted as a function of time in Figure 10 for different linear spectral chirps. The pulse envelope of the chirped pulses (in arbitrary units) is also shown alongside as a dashed curve. The relative yield is plotted after the decay of the pulse. Reprinted with permission from ref 18. Copyright 2014 by the American Physical Society.

![Figure 10](https://example.com/figure10.png)

**Figure 10.** Panel (a) shows the total dissociation probability, and panel (b) shows the relative yield of Br* as a function of time for different linear spectral chirps. The pulse envelope of the chirped pulses (in arbitrary units) is also shown alongside as a dashed curve. The relative yield is plotted after the decay of the pulse. Reprinted with permission from ref 18. Copyright 2014 by the American Physical Society.

To further explain the observations in Figure 10(b), the expectation values of interatomic distance $\langle x \rangle$ and the associated uncertainty $\Delta x$ are plotted as a function of time in Figure 11. Clearly, the chirp affects the wave packet spreading/focusing in a different way for the two electronic states, and remarkably, it also controls the average position of the wave packet. $^1$ For I + Br*, the positive chirp gives the smallest $\langle x \rangle$ and $\Delta x$ values, followed by the zero chirp and the negative chirp. Thus, the appearance of Br* at the “detector” will be delayed on going from negative to positive chirp as Figure 10(b) indicates.

![Figure 11](https://example.com/figure11.png)

**Figure 11.** Expectation values of the interatomic distances (panels (a) and (b)) and the associated spreadings (panels (c) and (d)) (in atomic units) as a function of time for different linear spectral chirps. Reprinted with permission from ref 18. Copyright 2014 by the American Physical Society.

The photofragmentation dynamics of IBr, in the weak-field limit, for a constant pulse energy can also be controlled by the time delay of a phase-locked two-pulse sequence and by a pure-phase modulation with a two-step excitation $X\rightarrow A\rightarrow B$ involving bound state A.$^2$ Furthermore, the origin of this CEP effect is analyzed, and mechanistic insights into the process are provided.

The carbon atom under study is irradiated with a three-cycle, 7.9 fs laser pulse of wavelength 800 nm, and a wide range of intensity values (10$^{14}$–10$^{17}$ W/cm$^2$) are considered. Since an exact solution of the time-dependent Schrödinger equation (taking into account both electronic and nuclear degrees of freedom) is limited to two-electron systems, alternative approaches are necessary to describe the laser-driven multi-electron dynamics. One easy alternative is to use quasi-classical models because they can explain the essential physics and have been found to be successful in interpreting many strong-field experiments. Thus, the laser-induced ionization dynamics is modeled within the quasi-classical Fermionic molecular dynamics approach, where the electrons are treated as classical.
point particles and two nonclassical momentum-dependent auxiliary repulsive potentials are introduced to take into account the classical phase-space constraints. These repulsive potentials prevent the electrons from visiting regions of classical phase space that are forbidden quantum mechanically. The laser-driven time evolution of the system is governed by the classical Hamilton’s equations of motion (as discussed in Section 2.2) using an adaptive fifth-order Runge–Kutta solver.

The final-state analysis is performed by computing the single electron energies. An electron is considered to be ionized if the single electron energy is positive over a sufficiently long time interval. Trajectories ($10^5$) were run at each laser peak intensity for different CEP values (0, 180, ±45, and ±90°), and the laser-induced ionization probabilities ($P_N$) are calculated.

Figure 12 shows the variation of ionization probabilities with the laser CEP at certain fixed laser intensities. Panels a and b, c and d, and e and f indicate single-, double-, and triple-ionizations, respectively. Statistical error bars are included to quantify the involvement of possible standard deviation errors (details in the text). Reprinted with permission from ref 22. Copyright 2019 by the American Chemical Society.

Figure 12. Variation of ionization probabilities with the CEP at certain fixed laser intensities. Panels a and b, c and d, and e and f indicate single-, double-, and triple-ionizations, respectively. Statistical error bars are included to quantify the involvement of possible standard deviation errors (details in the text). Reprinted with permission from ref 22. Copyright 2019 by the American Chemical Society.
double-ionization (NSDI) mechanism, where the first ejected electron recoils back to recollide with the parent atom and eject the second electron.\(^2\) With CEP = 45\(^\circ\), the attainment of the doubly ionized state is higher at early times, which indicates SDI to take place. On the other hand, a higher double-ionization probability at later times with CEP = 0\(^\circ\) indicates its preference toward NSDI. Overall, this gives a general overview of the vital role played by laser CEP in controlling the ionization dynamics, in particular, the SDI/NSDI ratio.

The above-mentioned mechanistic insight is further strengthened by Figure 14, where the electron–hole pair probability and the average angle of ejection between the two electrons are plotted as functions of laser CEP at the same intensity. This plot shows that these two properties are qualitatively anticorrelated. The higher average angle of ejection with CEP = 45\(^\circ\) ensures a lower chance for the electrons to recombine with the parent core; thereby, the final state primarily remains doubly ionized following a SDI event. However, for CEP = 0\(^\circ\), the average angle is the smallest. Therefore, there is a higher chance that at a later time the first ejected electron recoils back, collides with the parent atom, and recomines with it by electron–hole pairing to ultimately result in a single ionized product. To summarize, a simple variation in the CEP affects the angle of ejection of the electrons, and thereby it continues to offer new prospects in controlling electron dynamics on ultrafast time scales.

**CONCLUSIONS**

This mini-review provides theoretical insight into how laser light can be successfully applied to steer and control the course of chemical reactions. Some simple, practical applications of laser–matter interactions are discussed, which are vital and have a potentially huge impact in the field of chemistry. They offer a glimpse of the potential of these modern light sources in governing the fate of a chemical process.

In recent years, with the advent of ultrashort intense bursts of electromagnetic fields as a research tool, a formidable challenge is to theoretically describe the laser-induced complex correlation between the electronic and nuclear motions to understand the available strong-field experiments.\(^2\)\(^4\),\(^2\)\(^5\) A full quantum dynamical treatment of this correlated electron–nuclear motion involved in a chemical process is not a trivial task, and it becomes even more difficult as the complexity of the system increases. Currently, our investigations in this direction are in progress.\(^1\)\(^2\) This will eventually lead us to achieve the fundamental goal of controlling the reaction outcome with laser light and lay the foundation for the ultimate basis of using chemistry.

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**Notes**

The authors declare no competing financial interest.

**Biographies**

Diptesh Dey received his Ph.D. degree in 2017 from the Indian Institute of Science Education and Research Kolkata under the
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Ashwani K. Tiwari received his Ph.D. in 2007 from the Indian Institute of Technology Kanpur under the supervision of Prof. N. Sathyamurthy. During the period from May 2007 to April 2008, he was a postdoctoral researcher with Prof. Niels E. Henriksen at the Technical University of Denmark. From May 2008 to April 2010, he was a postdoctoral fellow with Prof. Bret Jackson at the University of Massachusetts, Amherst. He joined the Indian Institute of Science Education and Research Kolkata as an assistant professor in October 2010, and now he is a professor at the same institute. His research interests involve the dynamics of laser–molecule and molecule–metal surface interactions. Recently, he received the Chemical Research Society of India (CRSI) Bronze Medal for his creative work.

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