Topical Review

H₂: the benchmark molecule for ultrafast science and technologies

Heide Ibrahim^{1,4} , Catherine Lefebvre¹, André D Bandrauk²,
André Staudte³ and François Légaré^{1,4}

¹ Institut National de la Recherche Scientifique, Centre Énergie, Matériaux et Télécommunications, 1650 Boulevard Lionel-Boulet, Varennes, J3X 1S2, Canada

² Laboratoire de Chimie Théorique, Faculté des Sciences, 2500, Boul. de l'Université, Université de Sherbrooke, QC, J1K 2R1, Canada

³ Joint Laboratory for Attosecond Science of the National Research Council, University of Ottawa, 100 Sussex Drive, Ottawa, Ontario, K1A 0R6, Canada

E-mail: ibrahim@emt.inrs.ca and legare@emt.inrs.ca

Received 13 October 2017, revised 7 December 2017

Accepted for publication 13 December 2017

Published 26 January 2018

Abstract

This review article focuses on imaging and controlling ultrafast dynamics of the hydrogen molecule and its cation, initiated by ultrashort laser pulses. We discuss the mechanisms underlying these dynamics and theoretical methods to describe them. A broad variety of defining and influencing theoretical and experimental results is presented. We put special emphasis on the required experimental techniques, many of which have been developed in view of imaging the fastest of all nuclear dynamics.

Keywords: hydrogen molecule, ultrafast dynamics, femto chemistry, electron localization, control, ultrafast imaging, ionization

(Some figures may appear in colour only in the online journal)

1. Introduction—the tiny but powerful hydrogen molecule

One would imagine that after decades of research and more than 7000 publications mentioning the H₂ molecule or its cation H₂⁺ in their title since the 1970s, everything is known about this little molecule—but no, interest remains incessant since every new insight opens up new challenges and questions. The hydrogen molecule H₂ serves as a benchmark system because it is the only molecule that can be fully investigated in theory, and is at the same time accessible in experiment. Compared to other molecules its theoretical description is simple, allowing to quantum mechanically fully describe the correlated electrons and nuclei. Experimentally, on the other hand, it requires parameters that are very challenging due to the rather extreme photon energies and timescales involved. The hydrogen molecule shows the fastest

vibrational dynamics—and has therefore triggered the development of experimental techniques to probe them with sufficient temporal resolution. H₂ also serves as a benchmark system because it is the molecule showing the strongest isotope effect—no other molecule can almost double its mass by adding an additional neutron to its atoms. This molecule shows in the most elegant way how theory and experiment can benefit from each other and mutually trigger new techniques leading to continuous development on both sides.

This key model in molecular photonics exhibits complex dynamics due to its various degrees of freedom occurring on different natural timescales: (a) the rotational degree of freedom at picoseconds (1 ps = 10⁻¹² s), (b) the vibrational one at femtoseconds (1 fs = 10⁻¹⁵ s), and (c) the electronic one at attoseconds (1 as = 10⁻¹⁸ s). With the current laser technology, pulses of few femtoseconds and even attoseconds duration are now routinely available. It is thus possible to image and control in real time the coupled ultrafast electronic–nuclear (i.e.

⁴ Authors to whom any correspondence should be addressed.

vibronic) dynamics of the smallest and lightest of all molecules, H_2 .

For an overview on the general interaction mechanisms of hydrogen and other small molecules with strong laser fields, we refer to references [1–3], where the mechanisms and pictures discussed in the following (ionization, dissociation, adiabatic or non-adiabatic views, etc) are explained in great detail. Other reviews in the past have covered specific aspects of the dynamics of small molecules in laser fields from both, theoretical, and experimental perspectives: topics contained the dynamics of H_2^+ in intense laser fields [2, 4, 5], molecular imaging [6–8], theoretical methods for attosecond electron and nuclear dynamics [9], as well as dissociative ionization (DI) leading to coherent control [10]. In our review, we have tried not to focus on one particular facet of imaging or controlling the ultrafast dynamics of H_2 and H_2^+ , but to rather give a comprehensive overview on the history and the state of the art of this continuously developing field.

Without claiming to be exhaustive, we have selected a small fraction out of those thousands of publications mentioned, which provides—from our perspective—the deepest insight, especially into the ultrafast dynamics occurring in this very special molecule.

In the next section, we will discuss the different ionization and dissociation mechanisms occurring due to the interaction with strong ultrashort laser pulses, together with the main theoretical models that have been developed to describe those processes. In section 3, we will discuss experimental imaging techniques and results for vibrational and electronic wavepacket dynamics. And finally, in section 4, we will focus on the various means to control those dynamics of electrons and nuclei.

2. Theory of H_2 in intense laser fields

In this short background overview, we cover the basic mechanisms when the one-electron molecule H_2^+ , and the two-electron molecule H_2 are subjected to a strong laser field $\mathcal{E}(t) = \mathcal{E}_0 f(t) \cos(\omega t + \phi)$, with $\mathcal{E}_0$ being the maximum amplitude, $f(t)$ the envelope function, ω the carrier frequency, and ϕ the carrier-envelope phase (CEP). These mechanisms are essential to understand, image, and control the ultrafast time-dependent non-perturbative and nonlinear dynamics of molecules.

We note that the rotational motion of the diatomic linear molecules H_2/H_2^+ with respect to the polarization of the laser pulse is a process that is relatively slow compared to its other degrees of freedom. A full rotation of H_2 around the axis of a linearly polarized laser field takes 0.281 ps [11]. In this review, we concentrate on the complex and ultrafast coupled vibronic dynamics, which occurs on the significantly faster femtosecond timescale, and where the rotational degree of freedom can be assumed to be frozen. For an in-depth review of molecular rotational dynamics in strong laser fields we refer the reader to [12] and references therein.

Nevertheless it is important to stress that the ionization dynamics, i.e., the promotion of H_2 to H_2^+ or the subsequent ionization of the cation to the Coulombic state ($\text{H}^+ + \text{H}^+$), can

strongly depend on the alignment of the molecule with respect to the laser field. In both cases, the ionization is maximum for parallel alignment, involving σ_g symmetry-type molecular orbitals. To study the molecular alignment dependence of ionization dynamics one can either align the molecule actively into the laboratory frame, or choose a subset of specific molecular alignment, i.e. after a measurement was performed on an isotropic ensemble of molecules. Active alignment of H_2 has been achieved, e.g. through the kicked-rotor-approach [13]. Alternatively, a specific molecular alignment could be selected from the dissociation following ionization (e.g. [14, 15]), as we will discuss in the next section.

The ultrafast nuclear dynamics is defined by vibrational motion, where a diatomic molecule comprises only one vibrational mode. For H_2 , the period of the ground vibrational state is 8 fs, corresponding to 4401 cm^{-1} , for the heavier D_2 molecule this period is slowed down to 11 fs. The fastest vibration in the cation H_2^+ occurs at 14.5 fs (corresponding to a vibrational energy of 2321 cm^{-1}) [16]. As the molecule stretches to a longer internuclear distance R , it can reach a point where the nuclei are too far apart and the electron–proton Coulomb attraction becomes too weak for binding, resulting in molecular dissociation. While for small internuclear distances the electron is shared equally between both protons, at a certain stretching during the dissociation process it will localize on one of them. With an appropriately intense laser field, this dissociation process can be controlled through nonlinear molecule–radiation interaction, leading either to enhancement or suppression.

In the photoionization of H_2 , the timescale of the electron removal is of critical importance for the following dynamics in the molecular ion. In single photon ionization, the electron removal is assumed to be instantaneous and therefore the ground state vibrational wavefunction is vertically projected onto the manifold of electronic states in H_2^+ . Such an instantaneous ionization typically creates a vibrational wavepacket in each accessed electronic state of the molecular ion simultaneously [17].

In the multiphoton ionization of H_2 and in particular in the tunneling regime, where the strong field distorts the electronic potentials, a vibrational wavepacket is typically created only on the ground state of the molecular ion due to its energetically large separation from the excited states. Furthermore, the composition of the ionized vibrational wavepacket differs from the pure Franck–Condon distribution caused by single photon ionization [18]. The reason for this departure from the single photon picture has been attributed to the highly nonlinear dependence of the ionization step on the ionization potential [18–20]. However, for practical purposes a vertical ionization step is often assumed in modeling the initialization of the H_2^+ nuclear wavepacket [21, 22]. In this case, the ground state wavefunction of H_2 is projected onto the cation H_2^+ , resulting in a coherent superposition of vibrational states. However, advanced calculations allow now to fully describe the two relevant steps: (i) ionization and (ii) dissociation, taking the two electrons [23–29] and both nuclei into account, as described e.g. in [30–32].

The nonlinear, non-perturbative interaction of femtosecond laser pulses with H_2 leads to interesting coupled electronic:nuclear dynamics due to the special configuration of

the neutral and cation potential energy surface (PES). One illustration of the electronic–nuclear coupling is that the equilibrium internuclear distance of the cation is strongly shifted towards larger R due to a stronger Coulomb repulsion, as compared to the neutral. Because of this, the promoted wavefunction is initially positioned on the steep repulsive wall of the electronic ground state potential of the cation. This steep potential induces an acceleration of the resulting vibrational wavepacket towards larger R , and drives it towards the outer turning point where dissociation might occur in the presence of the laser field. As discussed in this review, this vibrational motion can be imaged and controlled with laser pulses.

Once ionized, there are various processes that occur in H_2^+ . Its ultrafast dynamics is described by the time-dependent Schrödinger equation:

$$H(\mathbf{r}, \mathbf{R}, t)\Psi(\mathbf{r}, \mathbf{R}, t) = i\hbar \frac{\partial}{\partial t}\Psi(\mathbf{r}, \mathbf{R}, t), \quad (1)$$

with the molecular Hamiltonian being:

$$H(\mathbf{r}, \mathbf{R}, t) = T_N + T_e + V_{\text{eN}} + V_{\text{int}}. \quad (2)$$

This is a multidimensional many body problem, where the Hamiltonian $H(\mathbf{r}, \mathbf{R}, t)$, and the molecular wavefunction $\Psi(\mathbf{r}, \mathbf{R}, t)$, depend on the coordinates $\mathbf{r} = \{x_1, y_1, z_1\}$ of the electron and on the nuclear coordinates $\mathbf{R} = \{X_1, X_2, Y_1, Y_2, Z_1, Z_2\}$ of the 2 protons.

T_N and T_e are the kinetic energy terms of the protons and electron, respectively. V_{eN} describes the electronic–nuclear Coulomb attraction and $V_{\text{int}} = \mathbf{r} \cdot \mathcal{E}(t)$, in length gauge, is the laser-molecule interaction potential that induces a time-dependent radiative coupling. This coupling is non-perturbative with the strong laser fields considered (field strength higher than $10^{12} \text{ W cm}^{-2}$). H_2^+ , as well as H_2 , have no permanent dipole moment. The only dipole that exists is the one induced by the coupling of the electronic states with the laser field. With this type of laser excitation considered, the dynamics can be reasonably described with only the ground and the first excited electronic state of the cation H_2^+ , because all the other states are energetically well separated. The ground state $1s\sigma_g$ or $1\sigma_g$ (depending on the notation), will be termed σ_g in the following; accordingly, we will refer to the first excited state $2p\sigma_u$ or $2\sigma_u$ as σ_u . The corresponding PES are ${}^2\Sigma_g^+$ for the σ_g state, and ${}^2\Sigma_u^+$ for the σ_u state. These σ_g and σ_u states are coupled through a transition dipole moment $\mu_{gu}(\mathbf{R}) = -e\langle u|\mathbf{r}|g\rangle = R/2$, with R being the internuclear molecular distance and $|g\rangle$ and $|u\rangle$ referring to two electronic states in bra-ket notation, respectively. This was predicted first by Mulliken in 1939 and referred to as a charge resonance transition [33]. It describes a parallel transition which is maximum when the molecular axis is parallel to the laser field.

In the situation of a slowly varying laser field (slow with respect to the vibrational period of the molecule, i.e. $\omega \ll \omega_{\text{vib}}$), the interaction with the laser pulse can be described with the adiabatic quasi-static picture, i.e., in the time representation. Considering cases where the laser oscillation frequency (ω) is smaller than the Bohr frequency (i.e. the energy difference between the σ_g and the σ_u states), the 2×2

matrix of the instantaneous electronic Hamiltonian can be diagonalized at each position in R . The effective force acting on the nuclear motion, at each time, can be evaluated. This results in a deformation of the PESs describing the first two electronic states of the molecule by the time- R -dependent coupling between the σ_g and σ_u states. This quasi-static picture is illustrated in figure 1 for different laser intensities.

These light induced potentials are following the laser field oscillations, such that within one optical period, the PESs encounter two extrema where they are either converged to zero ($\mu_{gu} = 0$) or far apart ($\mu_{gu} = \mathcal{E}_0$) at large R . As seen in figure 1, with increasing laser intensity, the coupling also increases, resulting in a stronger deformation of the instantaneous PESs. This deformation opens the barrier, and the wavepacket can escape, leading to light induced dissociation. This barrier to dissociation lowers with increasing laser intensity, and at the same time its position moves towards smaller R . To give an example, at $1 \times 10^{13} \text{ W cm}^{-2}$, $\mathcal{E}R$ equals 1.8 eV ($\sim 15\,000 \text{ cm}^{-1}$) at an R of 4.0 a.u. ($\sim 2.1 \text{ \AA}$). In comparison with the ground vibrational frequency of H_2^+ (2321 cm^{-1}), this emphasizes that the laser–molecule interaction is non-perturbative already at such a moderate intensity (moderate with respect to the intensity of $\sim 1 \times 10^{14} \text{ W cm}^{-2}$, required for the ionization from H_2 to H_2^+).

Since the wavepacket created by ionization of H_2 is formed due to a superposition of many populated vibrational states of the σ_g ground electronic state, components of the wavepacket that are slightly below the dissociation threshold might tunnel through the barrier. Since this motion of the PESs follows the periodic oscillation of the laser field, it is possible to synchronize it with the components of the wavepacket undergoing dissociation. In some situations, the wavepacket will reach the barrier at the time the electric field is maximal such that the barrier is widely open. The vibrational components in front of the barrier will easily escape the Coulomb attraction and drive the molecule to dissociation. In the quasi-static picture, this is referred to as barrier-lowering (BL) mechanism; experimentalist refer to this mechanism as Bond softening (BS), a term we will introduce soon. In the opposite case, the wavepacket can reach the dissociation barrier at a time when it is closed because the electric field is zero. This leads to a reflection of the wavepacket at the barrier, thus pushing it back towards smaller R . This mechanism is named dynamical dissociation quenching [34]. This oscillatory motion between the closed dissociation barrier and the steep branch of the PESs at small R can be well controlled by choosing the appropriate wavelength of the driving laser field [34], which was also experimentally verified [35]. Since the field oscillation changes with wavelength, the right choice enables the right timing between creation of the H_2^+ wavepacket and its arrival time at the outer turning point.

When the exciting laser wavelength gets shorter, the oscillation of the laser field becomes so fast that the vibrational wavepacket can no longer follow the time-dependent PESs such that the adiabatic picture does not hold anymore. The laser-molecule interaction in this regime is therefore better described in the reciprocal momentum representation,

Figure 1. Quasi-static picture: field free potential energy curves for the ground state σ_g and the first excited state σ_u of the cation H_2^+ (solid black line), as well as adiabatic curves modified by laser pulses of three different intensities: $10^{10} \text{ W cm}^{-2}$ (dashed blue), $10^{12} \text{ W cm}^{-2}$ (dashed purple), and $10^{13} \text{ W cm}^{-2}$ (dashed red). The stronger the laser intensity is, the stronger the deformation of the adiabatic potentials. The energy splitting at large internuclear distances R is defined by $\mathcal{E}R$, as depicted by the red arrow.

Figure 2. Potential energy curves of H_2^+ dressed by n photons (wavelength = 800 nm), reaching from $n = -\infty$ to $+\infty$. Shown are diabatic (diabaticity in R , black curves) and adiabatic dressed potentials (adiabatic in R , blue dashed curves). The first Floquet block describes two antagonistic dissociation mechanisms where population from vibrational states (sketched in black solid lines) escapes through the dissociation barrier of the lower adiabatic potential (bond softening (BS)) or is trapped in the potential well of the upper adiabatic one (vibrational trapping (VT)). At higher laser intensities, other dissociation channels open up due to the absorption of additional photons, involving further Floquet blocks, and leading to the mechanism of above-threshold-dissociation (ATD). On the right hand side, possible 1–3 photon pathways are indicated, as well as their relative kinetic energy release (KER) contributions.

instead of the time representation. We thus refer to the dressed-states molecule or the Floquet picture [36, 37].

In the Floquet theorem [38], the Hamiltonian has a temporal periodicity coming from the periodic oscillation of the laser field. The two first electronic PESs, corresponding to σ_g and σ_u , are described by states dressed by an integer number of photons n , with n varying from $-\infty$ to $+\infty$. Following the parity rule, the nuclear amplitude χ_n^g refers to vibrational levels of the electronic state σ_g dressed by n photons, and is coupled to χ_{n-1}^u of σ_u dressed by $n-1$ photons.

To describe these dressed states as products of electronic states and photon states, we will use the notation $|g\rangle|n\rangle$ and $|u\rangle|n-1\rangle$, respectively.

In one dimension, as illustrated in figure 2, this corresponds to a set of PE curves shifted by n photons, following their respective parity, i.e. $|g\rangle$ is shifted in energy by $n = 0, \pm 2, \pm 4, \dots$ photons of the laser frequency ω and $|u\rangle$ is shifted by $n = \pm 1, \pm 3, \pm 5, \dots$ photons. A negative number of photons corresponds to photon absorption, while a positive number corresponds to photon emission. The diabatic dressed PESs (solid black lines in figure 2) cross at the internuclear distance R_c with the energy separation between successive crossings being 2ω . When diagonalizing the coupled diabatic dressed PESs, one obtains adiabatic PESs (blue dashed lines). In this Floquet picture we refer to an adiabaticity in R , in contrast to the quasi-static picture, where the adiabaticity is in time. At first, let us consider only the first Floquet block of diabatic PES, i.e. the pair of the $|g\rangle|n\rangle$ potential curve coupled to the $|u\rangle|n-1\rangle$ one, whose energy splitting at very large internuclear distances corresponds to $\hbar\omega$. After diagonalization, two adiabatic dressed PESs are obtained with an avoided crossing at R_c . Now the lower adiabatic dressed potential encounters a barrier to dissociation. The stronger the coupling due to higher laser intensity, the lower this barrier becomes. The transition rate between the dressed PESs at R_c [39] can be obtained using the standard Landau-Zener equation [40, 41].

When the laser field is turned on, vibrational states of the initial wavepacket are projected onto field-induced resonances. These resonances are metastable states of the dressed potentials coupled to the continuum that have a finite lifetime. The dynamics of these resonances on the coupled dressed PESs is the key to understand the different mechanisms leading to molecular dissociation [42]. For instance, the resonances in front of the avoided crossing escape easily the Coulomb attraction and give rise to dissociation of the molecule. As this softens the molecular bond, this mechanism is referred to as bond softening (BS) [43]. BS is the term used in the Floquet representation and corresponds to the BL mechanism discussed previously in the quasi-static picture. For the remainder of this article we will utilize only the term BS. On the other hand, the upper adiabatic dressed potential shows a potential well, which can accommodate a bound state—or long-living resonances. The stronger the coupling is, the longer these resonances can be trapped in this adiabatic state. This is the vibrational trapping mechanism, also called bond-hardening [2, 44, 45].

In most cases where the dressed picture is appropriate to describe the laser-molecule interaction, very few Floquet blocks are sufficient to describe the underlying processes. We note that this representation is numerically most useful for nearly monochromatic laser fields at large ω [2]. But even for broadband laser pulses it still serves well as a picture, in explaining the peak broadening of dissociation channels observed when using ultrashort pulses, due to the large manifold of dressed states involved. Additional dissociation pathways are opened by absorption of more than one photon. Indeed, the dressed state $|g\rangle|n\rangle$ is also coupled to $|u\rangle|n-3\rangle$, while $|u\rangle|n-1\rangle$ becomes coupled to $|g\rangle|n-2\rangle$, and so on. For instance, the low energy resonances associated with low vibrational components of the initial wavepacket, that are trapped in the potential well of $|g\rangle|n\rangle$ can escape after the molecule absorbs 3 photons, giving rise to fragments with much higher kinetic energies. Similarly, these same resonances can absorb 3 photons and then reemit one photon, driving the molecule to dissociation with a net absorption of 2 photons. This also gives rise to specific kinetic energies of the fragments originating from the same initial low energy vibrational components, as indicated on the right hand side of figure 2. This nonlinear process is called the above-threshold-dissociation (ATD) [46, 47]. ATD corresponds to the vibrational analog of above-threshold ionization. In both processes, more photons are absorbed than required to initiate the respective process, dissociation or ionization. The dressed states of the Floquet picture have been experimentally explored by studying and controlling ATD by Wang, McKenna and co-workers [48–50]. In order to distinguish ATD from e.g. recollision induced contributions, they have separated the steps of ionization and dissociation by the use of an H_2^+ ion beam. Those papers show that, when varying pulse duration and intensity, one can study and control the occurrence and pathways of higher-order ATD. The shorter the pulse duration, down to few-cycle pulses, the stronger the higher-order ATD contribution gets. On the other hand, for longer pulses on the order of 100 fs, even at high intensity, the BS channel dominates. Apart from pulse duration, also bandwidth and chirp (i.e. different frequencies of an ultrashort laser pulse arriving at different times) play an important role in the observed kinetic energy release (KER) [51, 52].

In practice, theoretical models start from the H_2^+ molecule, and thereby separate tunnel ionization from vibronic dynamics. In contrast, apart from few cases where e.g. ion beams are used [48–50], experiments almost always require the ionization process from H_2 to the cation, such that the ionization and dissociation processes are intrinsically linked given standard pulse durations on the order of 30 fs and the H_2^+ vibrational period of 14.5 fs. Therefore, when discussing experimental data, all processes leading to dissociation are referred to as DI.

We have discussed the two main pictures to interpret laser-induced ultrafast vibrational dynamics and its control. The main parameters to control dissociation in both, the adiabatic and the Floquet picture, are wavelength, frequency and intensity of the driving laser field. With multi-cycle femtosecond pulses, the vibrational dynamics and the

Figure 3. Charge resonant enhanced ionization. (a)–(c) Lowest two dc-field-induced levels of H_2^+ , $1\sigma_+$ and $1\sigma_-$, in the effective potential $V_c(R) + \mathcal{E}R$ for the different internuclear distances indicated with red (6 a.u.), green (10 a.u.) and blue (14 a.u.) in the calculated ionization rate shown in (d). Figure adapted with permission from [54]. Copyrighted by the American Physical Society.

dissociation of H_2/H_2^+ have been studied widely in the 90s [1, 4]. Over the last decade, the increasing availability of intense few-cycle pulses at 800 nm, with CEP stabilization, and more recently at longer wavelength, have opened new frontiers for imaging and controlling the ultrafast vibrational dynamics of the smallest molecule on its natural timescale, as will be discussed in the following sections.

Next, we will introduce another important nonlinear effect, charge resonance enhanced ionization (CREI). H_2 and H_2^+ are two-center molecules, i.e., the molecular potential consists of two Coulomb potential wells. The molecular orbitals are described as a linear combination of atomic orbitals of the two protons. For strong field ionization, the two most important orbitals are the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). As H_2^+ dissociates in the strong laser field, the internuclear separation increases and the molecular orbitals are distorted. The molecular

Coulomb potential and the laser field form a barrier to further ionize H_2^+ . Examples of field-distorted potentials at different internuclear distances are depicted in figure 3 together with the levels of HOMO and LUMO in the localized basis ($\sigma_+ \propto \sigma_g + \sigma_u$; $\sigma_- \propto \sigma_g - \sigma_u$). We note that these σ_+ and σ_- dressed electronic states correspond to laser localization [53] of a delocalized electron in a molecular orbital, approximately equal to the atomic orbitals 1sa or 1sb localized on proton a or proton b. This leads to the potentials shown in figure 3.

In this figure, the state σ_- is the HOMO, down-shifted by $\mathcal{E}R/2$ (Stark effect), while σ_+ is the LUMO, up-shifted by the same amount. The energy separation between these light induced states is $\mathcal{E}R$ as depicted in figures 1 and 3. $\mathcal{E}R$ can be seen as the energy difference in classical PES for the electron being localized on the left or on the right hand side.

At short internuclear distance, the bound electron of H_2^+ follows the laser field adiabatically, tunneling between both

Figure 4. Experimental time of flight (TOF) spectra showing the effects of dissociative ionization: bond softening (BS), above-threshold dissociation (ATD) and charge resonance enhanced ionization (CREI) in the H^+ peak upon ionization with laser light, linearly polarized along the TOF axis. The ratio of these features varies with pulse intensities. Figure adapted with permission from [73]. Copyrighted by the American Physical Society.

sides of the molecule as the laser field oscillates. As the molecule vibrates towards larger R , the electron can no longer follow the laser field and gets trapped, ending its route in the upper potential well. This leads to electron localization and thus DI, but also acts as the trigger of enhanced ionization [55] or CREI [54, 56, 57], as it is called in reference to the charge resonance transitions first described by Mulliken [33]. A qualitative picture for an enhanced ionization mechanism of a molecule in a strong laser field was proposed by Codling *et al* in 1989 [58] to explain low energy fragments in the triple ionization of dissociating N_2 .

CREI explains the high ionization rate of H_2^+ from 6 to 10 a.u. of bond length (~ 3 to $5 \text{ \AA}$), which is about 3 to 5 times the ground state equilibrium distance. Within this range, the energy of the orbital is at or above the barrier, explaining the significant increase of ionization rate. In particular, around 6 a.u., the electron is ionized through above-barrier ionization,

which is a process that is strongly dependent on laser intensity [3, 59]. This ionization dynamics strongly depends on the alignment of the molecule with respect to the laser polarization since the σ_g and σ_u states are coupled through a parallel transition. Selecting molecules perpendicular to the laser field allows to suppress electron localization and CREI. For H_2 , CREI has been also numerically predicted by two-electron *ab initio* simulations in both, single and double ionization [24].

More recently, Takemoto and Becker studied the laser driven electron dynamics in H_2^+ with a solution of the time-dependent Schrödinger equation for fixed nuclei in one dimension [60] and two dimensions [61]. Both papers predicted multiple sub-cycle ionization bursts which are contrary to the previous understanding of CREI as an adiabatically driven two-level system. Using Bohmian trajectories, the same authors were able to show that these multiple attosecond

Figure 5. (a) Relevant potential energy curves for H₂ and its ions. Ionizing H₂ forms a dual wavepacket. One is a vibrational wavepacket on the ground state of H₂ (shown). The other is an electron wavepacket that moves in the laser field. The vibrational wavepacket evolves for Δt until H₂⁺ is excited by inelastic scattering caused by the returning electron wavepacket. (b) Observed (symbols) and calculated (solid line) kinetic energy spectrum for the energetic protons caused by inelastic scattering. The agreement confirms the time dependence of the recolliding electrons. The dashed lines show the contributions from the first (long dash, $\Delta t \sim 1.7$ fs) and third electron return (short dash, $\Delta t \sim 4.5$ fs). Reprinted with permission from [14].

ionization bursts are caused by a transient attosecond localization of the electron on either proton [62]. These ionization bursts were later confirmed experimentally in cold target recoil ion momentum spectroscopy (COLTRIMS) experiments on laser driven H₂⁺ from an ion source [63, 64] and H₂⁺ that was prepared from neutral H₂ in the same laser pulse [65]. These works initiated a number of subsequent studies [66–72].

As a summary of the effects discussed in this section, the experimental results from Alnaser *et al* in figure 4 show how those DI channels and CREI depend on laser intensity for pulses at 800 nm [73]. While for low intensity the BS channel dominates, with increasing intensity ATD takes over. For the highest intensity the CREI channel is the most dominant one. The relative ratio of those channels gives thus an estimate of the laser intensity on target in an experiment.

In addition to the bound electronic dynamics launched by the ionization of H₂ to H₂⁺, discussed above, there is an electron in the continuum that is subjected only to the laser field and does not feel the influence of the Coulomb potential anymore. This photoelectron follows the oscillation of the laser field $\mathcal{E}(t) = \mathcal{E}_0 f(t) \cos(\omega t + \phi)$. The more intense the field, the further this electron travels away from its parent ion. Its classical maximal displacement is defined by $\alpha = \mathcal{E}_0 / \omega^2$. As an example, at an intensity of 3.5×10^{14} W cm⁻² and a wavelength of 800 nm, the electron travels up to 1.6 nm away from the core.

Within one optical cycle, the laser field oscillates and $\mathcal{E}(t)$ changes its sign every half cycle. As a result, the electron trajectory changes direction and the electron returns to the parent ion. This process is called rescattering or recollision. The electron can recombine, scatter elastically or inelastically.

Elastic rescattering gives rise to laser-induced electron diffraction (LIED) [74, 75] and photoelectron holography [74, 76, 77]. Inelastic rescattering is responsible, for example, for non-sequential double ionization (NSDI) [78, 79]—one of the hallmark processes of attosecond science. NSDI is characterized by an enhancement of the double ionization rate (e.g. from H₂ to H₂²⁺) which cannot be explained by two

sequential ionization steps, both steps described in the single active electron approximation, where the two electrons are emitted one after another and independently of each other. It is thus rather the correlated action of both electrons that leads to this enhancement. At lower intensities the NSDI rate exceeds sequential ionization by many orders of magnitude [78]. However, NSDI will subside above a certain intensity and the double ionization can be described in an independent electron model (e.g. [80]). Experimentally, it was difficult to detect NSDI in the proton energy spectrum because of CREI, the extremely efficient and thus dominant sequential double ionization channel of H₂⁺, visible in figure 4. In 1999, Trump and co-workers identified a weak, high energy proton group in the time-of-flight spectrum as a potential candidate for NSDI [81]. Difficulties in modeling the combined electron–nuclear dynamics of the real H₂ molecule limited the comparability with experiment [28]. The next experimental indication for NSDI was the observation that the high energy protons were emitted isotropically with respect to the linearly polarized laser pulses [82]. Very soon thereafter, the ellipticity dependence of the ion yield confirmed NSDI as the mechanism responsible for the high energy protons [14, 83–86]. By selecting only those high energy protons, Alnaser *et al* were also able to reproduce the archetypical knee-structure in the double ion yield [85]. Modeling the combined electron–nuclear dynamics in H₂ with quantum [87–89] and classical models [90] allowed a detailed analysis of the NSDI mechanisms such as multiple recollisions, and recollision induced excitation. Furthermore, theory specifically addressed NSDI in few-cycle optical pulses [91, 92], the alignment dependence of NSDI [93–95] and its wavelength dependence [96].

Finally, upon recollision there is a probability that the electron recombines and emits photons of higher frequencies than the incident laser frequency. This process is the molecular high-order harmonic generation (HHG) [97]. The maximum energy of the returning electron is 3.17 Up (for electrons returning after 2/3 of an optical cycle), with $Up = \alpha^2 \omega^2 / 4$ being the ponderomotive energy [98], which defines the cut-off

of the HHG spectra. E.g., at $1 \times 10^{14} \text{ W cm}^{-2}$, and 800 nm, Up equals 6 eV. Molecular HHG differs from the atomic one in that the harmonic emission is influenced by the two-center structure of the electronic potential. HHG in H_2 is additionally influenced by the motion of the nuclei on the ground electronic state due to its fast nuclear dynamics. When selecting those harmonics close to 3.17 Up, which are generated near zero field, the returning electron sees an almost undistorted potential [30, 31, 99].

The processes described above will play an important role in the experiments discussed in the following sections. The choice of an appropriate laser field, especially the laser polarization, represents a knob to turn the coupling between σ_g and σ_u on or off. As an example discussed in the next section, in the ‘molecular clock’ experiments [14, 15], this coupling needs to be suppressed which is achieved by choosing a laser field perpendicularly polarized to the molecular axis. On the contrary, for controlling the electron localization, this coupling is essential, as we will see in section 4.

3. Imaging nuclear dynamics—techniques and results

When it comes to experimentally detecting molecular dynamics in real time, the primary condition to be fulfilled is that the critical timescale of the system cannot be faster than the temporal resolution of the excitation and the detection mechanism. Consequently, the first nuclear dynamics were studied in heavy molecules like NaI, due to their rather slow vibrational oscillation [100], matching the <100 fs pulse duration available at that time. The femtosecond pump–probe technique introduced in these experiments has become a standard for almost all time-resolved experiments. A first laser pulse (pump) triggers a dynamic event whose effect is being interrogated by a second laser pulse (probe). The purpose of the probe pulse is to project the instantaneous state of a dynamically evolving system onto observables that can be read out by the detection process, which is—in general—slower by several orders of magnitude than the dynamics of interest. The shorter the pump and probe pulses, the higher the temporal resolution. Depending on the chosen detection mechanism however, pulses too short might generate state assignment problems due to their broad energy bandwidth which is intrinsically linked to ultrashort pulses. Thus, the second challenge is to find the appropriate detection mechanism to trace dynamics and to even image them. While techniques like laser-induced fluorescence [101] represent a great tool to trigger and detect molecular systems with transitions in the UV to the near infrared (NIR) range, one would need a pump wavelength of $\sim 100 \text{ nm}$ [102] to reach the first excited state of the neutral H_2 molecule—a challenge even today as we will see later [103–106], but not accessible 20 years ago. The desire to resolve vibrational and electronic dynamics in H_2 has thus triggered two branches of development—shorter laser pulses, and advanced and creative imaging techniques, which will be introduced in the following.

Given the above discussed limitations of a conventional pump–probe approach with respect to H_2 and the

inaccessibility, until recently, to launch dynamics in the excited states of the neutral molecule, researchers have first studied dynamics on the ground state of the H_2 cation. Early approaches in investigating its ultrafast nuclear dynamics were making use of electrons recolliding with the parent ion upon exposure to an intense laser field [14, 15, 107]. As described at the end of section 2, upon tunnel ionization of an atom or molecule, under certain conditions the driving field will bring the freed electron back to its origin where it recombines with the parent ion under the emission of radiation—the atomic [98, 108] or molecular [97] HHG discussed previously. While the HHG process is being extensively studied to generate attosecond pulses and compact x-ray sources [109, 110], it also plays a major role for the development of ultrafast imaging approaches and the hydrogen molecule has served as a prototype for developing these techniques.

The recombining electron reveals detailed information about the nuclear dynamics of the molecule it was originating from, encoded in the molecular HHG signal. To extract this information, a complete pump–probe experiment is performed within a single optical cycle of the laser field. The tunnel ionization step acts as the pump and starts the ‘molecular clock’ in the form of a simultaneously launched vibrational wavepacket in the cation. The time at which the electron returns to the parent ion defines the probe step and stops the clock. Information on the nuclear dynamics can be read out in two ways:

1. The proton kinetic energy produced by inelastic scattering contains information about the internuclear distance at the probe delay; higher proton energy means a smaller internuclear distance.
2. The energy of the emitted harmonics corresponds to a certain pump–probe delay; the intensity of HHG is suppressed when the internuclear distance changes during the pump–probe delay.

This first principle was introduced in 2002 by Niikura *et al* using sub-laser-cycle electron bunches generated by 50 fs laser pulses [14]. When the electron returns to the parent ion (after about 2 fs for 800 nm light), it can inelastically scatter, producing excited states of H_2^+ , or further ionize the ion (dotted arrow in figure 5(a)). In [14] recollision induced mainly a population transfer to the σ_u state, resulting in the dissociation of the H_2^+ ion. Since the vibrational period of H_2^+ is 14.5 fs [16], the molecule stretches for the first 7 fs after ionization. This increase in internuclear separation is observed in a decrease of proton energy, and has been shown to resolve the temporal structure of the recollision wavepacket (see figure 5(b)). In order to precisely define the molecular clock, a nearly field free propagation of the vibrational wavepacket was obtained by turning off the coupling between the σ_g and σ_u states via a selection of only those molecules which are aligned perpendicular with respect to the laser field. At the same time, this decoupling suppresses the dominant CREI channel to uncover the sought-after weak recollision signal. This model of the molecular clock assumes that the initial vibrational wavepacket is projected promptly onto the

Figure 6. Pump–probe experiment within a sub-laser-cycle. (a) Ionization forms correlated electronic and vibrational wavepackets near each peak of the laser field. (b) The vibrational wavepacket moves on the $D_2^+(X^2\Sigma_g^+)$ surface while the laser field causes the electron wavepacket to recollide (represented by a thick arrow in (a) and (b)). Inelastic scattering during recollision probes the vibrational wavepacket’s position. Measured is the kinetic energy of the D^+ fragments. (c) Measured wavepacket position as a function of time. To associate the laser wavelength with the time of recollision, the mean time of recollision for the first electron micro-bunch at each laser wavelength is used. The solid line is the calculated nuclear position as a function of time for a wavepacket evolving as discussed in (b). Reprinted with permission from [15].

σ_g state of the H_2^+ because tunnel ionization is confined to the crest of the laser field, resulting in a temporal resolution on the order of few-hundred attoseconds [111]. On the contrary, in the other extreme regime of single-photon ionization with attosecond pulses, it was recently shown that the settling time of an H_2^+ vibrational wavepacket can be on the order of 1 fs through an XUV–pump XUV–probe experiment by Nabekawa and co-workers [112].

To read out the molecular clock with the highest precision, details on the ionization channels involved are important and have been investigated in [113], discussing the question of how to distinguish contributions from dissociation and Coulomb explosion, which might both lead to fragments with very similar kinetic energies.

Using the process of inelastic scattering it was further proposed to tune the wavelength of the driving laser field to vary the pump–probe delay. The delay changes linearly with the laser wavelength and the 3.17 Up electron returns at 2/3 of the optical cycle. Using this approach, ultrafast molecular imaging was demonstrated with a spatial resolution of 0.05 Å together with a temporal resolution of ~ 200 as, again using standard multi-cycle laser pulses [15]. Like for figure 5, this experiment took advantage of the correlation between the continuum electron and the nuclear wavepacket formed during the ionization process. By varying the laser wavelength from 800 to 1850 nm, different recollision times and thus different time delays were investigated and the corresponding internuclear distances between the two deuterium atoms in the cation were determined, as explained in figure 6. Figure 6(c) was obtained from the wavelength-dependent position of the KER maximum resulting from the first recollision

Figure 7. Encoding of nuclear dynamics within harmonic spectra. Upper panel: the trajectory of the ionized electron differs depending on the exact time of ionization. Three possible electron trajectories labeled 1–3 are shown, which recollide with the molecular ion after delays Δt_1 , Δt_2 , and Δt_3 , with increasing kinetic energy E_1 , E_2 , and E_3 , resulting in the emission of increasingly higher frequency photons after recombination (shown as the 17th, 25th, and 33rd harmonics for the purpose of this illustration). Figure from [107]. Reprinted with permission from AAAS.

Figure 8. Sketch of a position and time-sensitive detector for ion detection in coincidence, composed of a time-of-flight mass spectrometer, a 2D delay line detector, molecular gas jet and time delayed laser pulses.

(figure 6(b)), and compared with the field free motion of the nuclear wavepacket on the σ_g state.

A few years later, this concept had been extended to molecular HHG by Baker and co-workers, which represents the second approach to image vibrational dynamics [107]. In HHG, depending on the phase matching conditions, the short or the long trajectories can be optimized [114]. For both trajectories, there is direct mapping between time and HHG photon energies, with the time being the delay between tunnel ionization and recombination. The resulting photon energy from this recombination probes the internuclear distance at a given time delay. This means that within those spectra, a range of pump–probe delays can be probed simultaneously, thus encoding ultrafast nuclear dynamics as depicted in figure 7. Because of this mechanism, the nuclear dynamics information is encoded in the amplitude modulation of the spectra. The method with a temporal resolution of ~ 100 as was verified by exploiting the isotope effect on the different dynamics for H_2^+ and D_2^+ before applying it on bigger molecules [107].

Recently, another observable to extract nuclear dynamics and structural information of molecules with HHG was investigated. Originating from laser driven nuclear motion in isotopic molecules like H_2^+ and D_2^+ , the HHG signal experiences a frequency shift. As discussed previously, for HHG, nuclear motion during the ionization and recombination steps plays an important role. The recombining electrons can be affected by a change between the orbital they are originally ionized from and the orbital they are recombining with. Rather than in the amplitude modulation discussed before [107], the ongoing nuclear dynamics can also manifest itself as a frequency modulation [115]. Depending on the pulse intensity, different effects can lead to either a blue or a red shift of the emitted harmonics. This frequency shift can e.g. be influenced by the pulse envelope: the rising part might lead to a blue-shift, while the falling part can induce a red shift. Very recently, this effect has also been observed in experiments [116, 117].

Figure 9. (a) Potential energy surface of D_2^{n+} sketching the experimental concept. (b) D^+ kinetic energy (KE) spectra for a pump–probe delay of 0 fs (square) and 12 fs (triangle). The dotted curve is the expected kinetic energy spectrum for $\Delta t = 12$ fs. (c) Ratio of high KE, D^+ is the total number of D^+ counts having $\text{KE} > 7$ eV divided by total D^+ counts (square). Calculated time-dependent average internuclear distance ($\langle R \rangle$ in Å) as a function of time on $\text{D}_2^+ \text{X}^2\Sigma_g^+$ (solid line). $I_{\text{pump}} \sim 3 \times 10^{14} \text{ W cm}^{-2}$, $I_{\text{probe}} \sim 1 \times 10^{15} \text{ W cm}^{-2}$. Reprinted with permission from [120]. Copyright (2005) by the American Physical Society.

While exploiting the intrinsic temporal resolution linked to the recolliding electron provided a breakthrough in imaging of the nuclear motion, this task was further pushed by the use of advanced imaging detectors in combination with the availability of intense few-cycle laser pulses in the 1990s [118, 119].

Coulomb explosion imaging (CEI) was the first technique that succeeded in imaging ultrafast dynamics using a conventional pump–probe approach with sufficient temporal resolution [120]. Representative of all correlation techniques, we will discuss CEI in detail in the following, as the underlying principle is very similar to all of them. CEI is based on the idea that upon very fast removal of electrons the left behind molecular ions dissociate quickly due to Coulomb repulsion between the positively charged nuclei. Depending on the ionization mechanism used and the mass of the involved atoms, this technique can freeze the information on the position of the fragments at the moment of Coulomb explosion. To obtain the required fast ionization step, one initial approach was to pass strongly accelerated molecular ions through a thin foil to strip-off several electrons at once. Using this approach, the energy-angle distribution of protons of a breaking-up hydrogen molecule was obtained at the end of the 1970s [121]. While this technique provides excellent spatial resolution, it lacks the temporal aspect. On the contrary, the use of table-top ultrafast lasers allows for dynamic studies with high temporal resolution—the removal of electrons upon the strong field interaction with a few-cycle laser pulse [122]. For molecules composed of heavy fragments like I_2 [123], this technique allows for a very accurate reconstruction of the geometrical structure at the moment of interaction with the probe pulse. For lighter fragments, one can still deduce significant knowledge on their geometrical arrangement. We refrain from recapturing the existing

Figure 10. (a) Illustration of the Lochfrass mechanism, as well as the absolute phase imprinted of a ground state vibration wavepacket by R -selective depletion. (b) Ion yield for D_2^+ (upper curve) and $D^+ + D$ channels, respectively, as functions of the delay between two 7 fs pulses of $4 \times 10^{11} \text{ W cm}^{-2}$ intensity. Reprinted figure with permission from [20]. Copyright 2006 by the American Physical Society.

literature on CEI and refer to introductory review articles [124, 125]. Reference [124] instructs on the care one has to exercise when deducing information using fs laser pulses to ionize the molecule under investigation. Interesting aspects of the time-resolved CEI technique include the fact that no frequency analog, connected by a Fourier transformation, exists (like in conventional pump-probe spectroscopy) due to the strong field interaction involved in the ionization step. In comparison with other techniques to measure geometric structures like electron or x-ray diffraction, in CEI a similar spatial resolution of around $\sim 0.3 \text{ Å}$ can be obtained. Provided sufficient statistics due to repeatability, CEI provides the ability of routinely measuring the effects of a single molecule exploding during one laser shot, compared to the large amount of scattered data one needs to collect at once in diffraction experiments. At the same time, CEI is advantageous in terms of temporal resolution, since it benefits from routinely available few-fs NIR laser pulses. In electron diffraction experiments in general, either space charge [126] or jitter effects between the required electronic equipment and the laser limit the temporal resolution, even though the latter had been recently pushed to below 50 fs [127]. Conventional x-ray diffraction is restricted by much longer pulse durations available at synchrotrons or typical free electron lasers (FEL) [128]. However, with sufficiently bright attosecond pulses or new generation FELs, also this field will experience a strong boost [129].

As soon as more than one positively charged particle is involved, CEI opens up the door to correlate molecular fragments, such that one can deduce which fragments were originating from exactly the same molecule. An exemplary CEI chamber is depicted in figure 8. An electric field guides the ions from the interaction volume of the supersonic gas jet with the laser beam onto a position and time-sensitive detector. From the ion time of flight (TOF) measured in a mass spectrometer with a micro channel plate (MCP) stack, together with the two-dimensional position information obtained with a delay line detector, the starting momentum of fragments can be calculated. One can obtain the full 3D

information on momentum vectors and energies for routinely three or four [130], even up to five [131] fragments stemming from the same molecule.

While the CEI technique is restricted to the detection of positively charged nuclear fragments, when combining two time- and position-sensitive detectors in one spectrometer, complete measurements of the three-dimensional momentum vectors of electrons and ions become possible. This technique is known as COLTRIMS or as reaction microscopy [125, 132]. The same electric field which guides the positively charged ions to one direction, accelerates the electrons, whose velocities are reduced in a magnetic field, in the opposite one. The ability to obtain molecular frame photoelectron angular distributions (MFPADs) makes COLTRIMS a very powerful tool for studying electron dynamics. However, in contrast to CEI, the coincident measurement of electron and ion momenta in COLTRIMS typically restricts the accessible charge state to doubly ionized systems. In practice, in COLTRIMS, the energy dispersing spectrometer field is also considerably lower ($1\text{--}20 \text{ V cm}^{-1}$) than in a CEI ($>20 \text{ V cm}^{-1}$) in order to preserve momentum resolution in both electrons and ions. Although the CEI and COLTRIMS techniques are very powerful in reconstructing 3D momentum vectors of single particles, it comes at the price of reduced energy resolution (due to the anode wired grids) and very long acquisition times which also require excellent stability of the optical setup. Another technique to image charged particles is velocity map imaging (VMI), where, under certain symmetry conditions, the 3D momentum distribution of either electrons or ions can be reconstructed from a single 2D image for one selected fragment's mass (selected via a certain TOF window in the acquisition) [133–135]. High electrostatic fields and an electrostatic Einzel-lens guide the charged particles towards the detector. In VMI, the charged particle detection is typically accomplished with a combination of an MCP stack and a phosphor screen, which is imaged by a CCD camera. With this technique, a much higher data-throughput at higher energy resolution can be achieved than with a CEI or COLTRIMS system. However, this comes at the cost of

Figure 11. Image of the nuclear wavefunctions of H_2^+ . (a) Measured vibrational energy E_{vib} versus internuclear distance R calculated from the kinetic energy release of the dissociation as described below. The potential energy curve of H_2^+ (σ_g) is shown as the green line. (b) Theoretical spatial density of the nine lowest vibrational states numerically calculated using the Born–Oppenheimer approximation. Reprinted with permission from [147].

losing the information on correlations between particles. Some experiments discussed in the following [136] and in the control section of this article were performed using the VMI technique [137–141].

In 2005, the first molecular movie of a nuclear wavepacket oscillating on the ground state of D_2^+ with a period of 24 fs was captured using CEI [120]. Figure 9(a) depicts the principle of fragment ion energy distributions based on the projection of a wavepacket on one electronic state (e.g., in the cation) to another electronic state of a different charge species (e.g., the dication) leading to Coulomb explosion. Depending on the energy difference between the projected position of the wavepacket on the final state and the dissociation level, the kinetic energy released will be higher (in

Figure 12. Imaging of a vibrational wavepacket undergoing dissociative ionization. (a) Imaging of the instantaneous nuclear wavepacket with a single attosecond XUV-pump and a 7 fs NIR probe pulse through proton kinetic energy release, (b) same nuclear dynamics probed by a 35 fs NIR pulse. (c) and (d) show relevant vibrational levels (v^+) and released energies (E) in potential energy surfaces dressed by a long NIR pulse. Figure adapted with permission from [136]. Copyrighted by the American Physical Society.

general at shorter distances between fragments) or lower (larger distances). The key to perform these experiments was access to both, intense few-cycle laser pulses, and coincidence imaging. As discussed in the background section, selecting molecules perpendicular to the laser polarization allows suppressing the coupling between the σ_g and σ_u states, resulting in an almost field-free wavepacket motion on the σ_g state only. Later on, the collapse at 250 fs and the revival at 500 fs of the H_2^+ vibrational wavepacket have been observed [142–144].

Those experiments have well resolved the fastest dynamics accessible at those days, and still they were limited by the laser pulse duration. Even with few-cycle pulses, the observed dynamics is distorted due to ultrafast nuclear motion on the ground electronic state of D_2^+ . Using the concept of the molecular clock, it was shown that even when using sub-8 fs pulses, it takes 4 fs to explode the D_2 molecule [84, 145], which is already long enough to significantly stretch the bond length. Considering longer pulse durations, already at 30 fs (the typical pulse duration out of a titanium–sapphire amplifier), the molecule reaches the critical distance for CREI. In that case, the KER spectra become almost independent of the pulse duration. As discussed in the background section, the trigger for CREI is electron localization. Indeed, in a very recent publication by Xu *et al* it was experimentally

Figure 13. Observation of a double structure in CREI. The measured delay-dependent KER spectra when pump and probe polarization axes are parallel (a) and perpendicular (c) to each other. The probe intensity for perpendicular polarization is approximately five times higher than for parallel one, as less intense pulses produced no significant EI signal in the cross-polarized configuration. Energy-integrated delay-dependent ionization yields with parallel (b) and cross (d) polarized pump and probe. Note the double-peak structure for parallel polarization. Reprinted with permission from [150].

demonstrated that electron localization in H_2^+ is already completed within 15 fs after ionization of the neutral [146], which explains why CREI remains almost independent on the pulse length beyond a few 10s of fs.

In addition to the vibrational dynamics in D_2^+ , Ergler *et al* observed the nuclear dynamics in the ground state of the neutral D_2 molecule with a period of 11 fs [20], based on the Lochfrass mechanism [19], as shown in figure 10(a). Rather than creating a vibrational wavepacket in the neutral charge state by direct excitation (which was experimentally not achievable at that time), they have ionized the molecule. In the Lochfrass mechanism, the R -dependent ionization rate of D_2 leads to a reshaping of the initial neutral ground state wavefunction. This is intrinsically connected with populating higher lying vibrational states of the neutral which leads to a nuclear wavepacket that evolves in time. It is the dynamics of this D_2 wavepacket that was imaged via ionization to the cation when varying the pump–probe delay.

The CEI experiments discussed so far have succeeded in mapping a change in internuclear distance due to an evolving vibrational wavepacket created either in the cation or in the neutral of the D_2 molecule. Details on the populated vibrational states of such a wavepacket were unveiled by Schmidt and co-workers [147] exploiting the accuracy of the COLTRIMS technique. They have spatially imaged the nuclear wavefunction of several levels of vibrationally hot H_2^+ , as shown in figure 11. The experimentally obtained internuclear distance R is not directly accessible, but could be deduced from energy measurements with such high resolution that not only the final state, but also the initial vibrational state could be assigned (figure 11(a)). Reconstructing the spatial positions from the measured energies beautifully matches the theoretically calculated eigenstates (or vibrational wavefunctions) of an anharmonic oscillator (figure 11(b)).

The composition of such a vibrational wavepacket was analyzed in a combined experimental and theoretical approach by Kelkensberg and co-workers [136]. Based on the VMI technique, the time dependent DI of H_2 was imaged, as shown in figure 12. By Fourier transformation of the measured proton KER, the instantaneous components of the vibrational wavepacket created by an isolated asec pump pulse in the hydrogen cation could be retrieved, thanks to the use of a few-cycle NIR probe pulse (figure 12(a)). On the contrary, by using a longer probe pulse [26, 136], the interference structures required for the wavepacket snap-shot smear out due to the evolution of the nuclear wavepacket (figure 12(b)). The lowering of the dissociation barrier discussed in section 2 occurs here due to the rising amplitude of the long NIR laser pulse. This, and the influence on the vibrational levels contributing to the observed kinetic energy signal is visualized in the dressed potential energy curves for well separated (figure 12(c)) and overlapping pulses (figure 12(d)). In the case of (c) the wavepacket is about to experience all NIR pulse amplitudes during its evolution, including the strongest lowering of the dissociation barrier (dashed red curve), while in (d) the maximum of the NIR pulse envelope is long gone by the time the wavepacket reaches the—now higher—dissociation barrier (dotted red curve).

Another recent experiment on the time-resolved DI of H_2 focused on imaging the instantaneous molecular geometry, by measuring the photoelectron angular distribution [148]. The wavelength and intensity dependence of DI of H_2 in particular was investigated by Hu and co-workers [149]. They have e.g. studied how the kinetic energy released in the different channels of the fragmentation process (BS and ATD) is shifted towards smaller energies with increasing wavelength. They assigned the observed wavelength- and intensity-

Figure 14. Schematic view of sub-cycle electron wavepacket (EWP) interferences. When a molecule is exposed to a two-color laser field, shown as the magenta line, EWPs will be released around the field's peaks. In a unit cell of the pulse, the EWPs released during each half cycle (t_1 and t_2) will lead to the same final momentum p , which leads to interference fringes in the momentum space. Reprinted with permission from [158].

dependence of the proton spectra to a selective excitation of different vibrational levels of H_2^+ in intense laser fields.

Recently, the elusive double peak structure in the R -dependence of strong field CREI was observed in a few-cycle pump–probe experiment [150]. Those two maxima in the ionization rate had been predicted by the fixed-nuclei theoretical model [54] but its origin remained unclear. Because it could not be observed experimentally using 40 fs pulses [151], it was ascribed for a long time to be an artifact due to the fixed-nuclei approximation. Finally, this uncertainty could now be cleared up thanks to the use of few-cycle pulses; the experimental observation of an energetic splitting and thus of two corresponding internuclear separations of 3.4 and 6.3 Å at which the ionization probability for H_2^+ is maximized in the case of parallel polarization (figure 13) confirms the validity of the fixed-nuclei approximation in this context. Furthermore, the striking difference between parallel (a, b) and perpendicular (c, d) relative polarization for pump and probe pulses reconfirms the importance of the σ_g/σ_u coupling in understanding the DI dynamics, as discussed in the theory section. The resulting ionization rate dependence in (b) for parallel polarization closely follows the initial theoretical predictions discussed in section 2 (see figure 3(c)), [54]). Furthermore, the case of perpendicular polarization (figure 13(d)) matches with polarization dependent numerical simulations performed by the same group [56].

Another path to observe electronic and nuclear dynamics is to study photoelectron distributions. Any two-dimensional photoelectron image that is recorded, for example, with a VMI or COLTRIMS spectrometer, represents a combined energy and angle resolved spectrum. Different parts of such a spectrum provide different insights. Strong field photoelectron holography [65] is based on the interference of low energy, scattered and unscattered photoelectrons. Experimentally first implemented in 2010, it was expected to provide insight into sub-cycle ionization dynamics [152].

However, the holographic interferences in H_2 were only recently studied by experiment [77] and theory [72]. In the experimental investigation, Haertelt *et al* [77] created a differential hologram from holographic images of different alignments of H_2 . The alignment was deduced from the proton momentum, exploiting the axial-recoil approximation for the DI channel [153]. The DI channel preferentially selects those molecules from a randomly aligned ensemble that are aligned along the polarization. However, a sufficiently wide distribution of alignments can still enable the examination of angle dependent effects. The differential hologram allowed unraveling the weak interference between backscattered and forward scattered photoelectrons. This approach enabled the suppression of otherwise dominant forward scattering contributions. Hereby, electrons emitted from different quarter cycles of a laser field interfere with each other as signal and reference waves to unveil molecular dynamics. In such a differential backscattering hologram the authors not only observed the ultrafast nuclear motion of the stretching molecular ion after ionization, but also discovered that the backscattered trajectory is sensitive to the electronic character of the molecular ion, as they distinguish the different contributions of ATD and BS dissociation channels for the two isotopes.

The photoelectron angular distribution alone is already a powerful measure to study electron dynamics. To understand how tunnel-ionized photoelectrons are influenced by the doubly charged, two-center Coulomb potential, the asymptotic momentum distribution of these electrons is studied in strong field-MFPADs. To this end, Spanner *et al* [65] doubly ionized hydrogen molecules with 800 nm, circularly polarized laser pulses. In order to disentangle the contribution of each ionization step from the total MFPAD, the authors relied on the assumption that the photoelectron from the neutral molecule does not depend on the subsequent path of the molecular ion. By subtracting the MFPAD of singly ionized, dissociated molecules from doubly ionized molecules, the authors isolated the MFPAD of the second ionization step. This procedure revealed a previously unexpected light-induced sub-optical cycle electron dynamics. This experiment required the information of alignment of the molecules with respect to the laboratory frame. This can either be accomplished by aligning molecules in the laboratory frame using impulsive alignment with non-ionizing femtosecond laser pulses (e.g., [154]). However, due to the low polarizability of H_2 , the achievable degree of molecular alignment via rotational excitation with a femtosecond laser pulse is very weak [13]. Hence, for H_2 the molecular alignment in the laboratory frame has been deduced *a posteriori* from the proton momentum in the DI channel of H_2^+ [70, 77, 153, 155] and from the Coulomb explosion of H_2^+ [63–65, 156].

In a theoretical approach by Palacios and co-workers, a complete description of the coupled electron and nuclear dynamics in H_2 was extracted. This is based on wavepacket interference in the cation resulting from pump–probe type excitation with EUV laser pulses. The advantage of using such a high photon energy is that one can interrogate the system without potential energy distortions due to strong field effects from the laser pulses [157]. Recent laser technology

Figure 15. (a) 4.8 fs FWHM 800 nm laser pulse; (b) time-dependent potential energies V_1 and V_2 of the quasi-static states during molecular dissociation of D_2 in the presence of the laser field depicted in (a). The green curve shows the probability for a diabatic transition given by the Landau–Zener formula, and defines three regions where the dynamics is primarily adiabatic (light blue), primarily diabatic (light pink) or mixed (light green). (c)–(e) Population dynamics during dissociation shown for (c) the field-free nuclear wavefunctions $\Psi_g(R, t)$ (black) and $\Psi_u(R, t)$ (red), (d) the quasi-static wavefunctions $\Psi_1(R, t)$ (black) and $\Psi_2(R, t)$ (red) and (e) the localized wavefunctions $\Psi_{\text{left}}(R, t)$ (black) and $\Psi_{\text{right}}(R, t)$ (red). Reproduced from [165] with permission of the PCCP Owner Societies.

has opened up the door to realize such EUV laser pulses with sufficient energy and temporal resolution [109, 110], as will also be briefly discussed in the following section.

In order to studying electron dynamics with attosecond resolution, one does not always require EUV laser pulses. Also pulses being orders of magnitude longer than the dynamics of interest can be utilized, when taking advantage of phase differences induced, once those light pulses are combined—e.g. in a two-color laser field. Based on those interferences, Xie and co-workers have studied sub-cycle interferences of electron wavepackets, when ionizing H_2 with a two-color laser field composed of 800 (ω) and 400 nm (2ω) pulses [158], as depicted in figure 14.

When tuning the relative phase, such two-color fields cannot only be used for measuring molecular dynamics, but can also be employed, as will be discussed in the following section, for the control of electron localization and vibrational dynamics—the underlying mechanisms of previously discussed phenomena such as BS or CREI.

4. Controlling ultrafast dynamics

The steering of electronic and nuclear processes with light has been always one of the main goals in ultrafast science. In order to achieve control over either electronic or nuclear populations, a control over the waveform of the employed light is necessary. For nuclear wavepackets this can often be achieved in a two pulse experiment: through the delay between the envelope of femtosecond pulses, rotational (e.g., [13]) and vibrational [150, 159] populations are directed. Also three-pulse experiments to control the dissociation yield were implemented [142]. For very light molecules such as H_2^+ , the difference frequency between two overlapping laser pulses can control the nuclear wavepacket [35]. In every case, the manipulation of nuclear dynamics arises from the ability to coherently modify electronic states. To steer electronic populations on the other hand, one controls in general the electric field rather than the envelope of a light pulse. We will discuss the different means to realize such control fields in the following, as well as the current status of experiments that achieve active control over the dynamics of H_2^+ and its isotope D_2^+ .

In the molecular frame, every single molecule experiences electron localization upon excitation with an oscillating light field. In the laboratory frame however, the measured average electron distribution on either side will always be symmetric, if neither the exciting light field nor the detector are sensitive to directionality to break this symmetry. In general, it is thus not inherently predetermined whether it will be the left or the right atom of a two-atomic molecule that will lose its electron due to dissociation upon photoionization. By introducing an artificial asymmetry in the system, e.g. due to the excitation with a strong, asymmetric laser field, this intrinsic symmetry can be broken, and electrons can be preferentially localized in the laboratory frame on one side or the other. Alternatively, the asymmetry can also be introduced in the detection, as will be shown later. As discussed in the background section, the hydrogen cation can be treated as a two-level system consisting of the ground gerade σ_g and the first excited ungerade σ_u electronic states. Following radiative coupling of those two states, their coherent superposition can be generated, leading to the electron localization on either side of the molecule depending on the relative phase of the states. The resulting field-free electronic wavepacket of H_2^+ is defined by the phase relationship (φ) and the relative population (c_1 versus c_2) between both states:

$$|\Psi_{\text{tot}}\rangle = c_1|1s\sigma_g\rangle + e^{-i\varphi}c_2|2p\sigma_u\rangle. \quad (3)$$

Steering the coupled electron–nuclear motion in a dissociating H_2^+ molecule requires the phase of the exciting electric field to be stabilized on the sub-cycle level. In the following, we will discuss various experiments offering such a (sub)fs resolution; possibilities cover (i) the coherent superposition of two laser fields of different color with adjustable and locked relative phase, (ii) CEP locked few-cycle laser pulses, as well as (iii) the use of attosecond pulses in the presence of a moderately intense NIR fs pulse. For a

Figure 16. (a) Theory prediction by Charron *et al* [169]. Dissociation probabilities in the $\{H^+ + D(1 s)\}$ (solid line) and $\{H(1 s) + D^+\}$ (dashed line) channels in the forward (upper panel) and backward (lower panel) directions in the low frequency domain as a function of the phase ϕ between the fundamental radiation ($10.6 \mu\text{m}$) and the second harmonic ($5.3 \mu\text{m}$) of a CO_2 laser. The pulse width is 113 fs. For each chosen phase the forward and backward dissociation probabilities for a particular fragment are obtained by angular integration of the 3D angular distributions over $0^\circ \leq \theta \leq 90^\circ$ and $90^\circ \leq \theta \leq 180^\circ$, respectively, where θ denotes the angle between the dissociation and the polarization axis. (b) Experimental results showing TOF spectra expanded about the H^+ (solid line) and D^+ (dashed line) arrival peaks for $\phi = 0$ (upper panel), $\phi = 0.6\pi$ (central panel), and $\phi = \pi$ (lower panel). The optical electric field $[E_1 = E_2]$ is plotted over two optical cycles in the inset of each graph for the corresponding value of the two-color relative phase [171]. Figure (a) reprinted from [169], with the permission of AIP Publishing. Figure (b) reprinted with permission from [171]. Copyright (1995) by the American Physical Society.

very detailed and recent review on sub-fs directional control of chemical processes in molecules in general, we refer to the paper of Alnaser and Litvinyuk [160], and for the H_2 molecule in particular, the paper by Li *et al* [161] as part of this special issue.

To coherently control electron localization, two fundamental conditions have to be fulfilled: firstly, the *spatial overlap* between both nuclear wavepackets propagating along these two potential curves must be maintained. In the case of molecular hydrogen, this condition can be satisfied because the σ_g and σ_u states of the cation are nearly degenerate at large internuclear distances where dissociation occurs, such that the two wavepackets will spatially overlap there. Those wavepackets will however only interfere with each other, when they arrive at the same time in the dissociation region, thus secondly, *temporal overlap* is required. Such a spatio-temporal overlap of wavepackets stemming from electronic states of opposite parity is likely to occur when their kinetic energy distribution is similar. Theoretical efforts have demonstrated that such a kinetic energy overlap—leading to coherent control—can be achieved from the interference between dissociation pathways. Each pathway is populating electronic states of different parity via the concurrent net absorption of n and $n + 1$ photon(s) in the presence of a strong laser field [162], as was discussed in the context of the Floquet picture in section 2.

The interference of those two dissociative pathways which defines the electron localization has been directly observed by Staudte and co-workers, encoded in the

structured proton kinetic energy spectra associated with CREI [163, 164]. Kelkensberg and co-workers have modeled semi-classically the interaction between the molecular potential and the electric field of the laser pulse that lead to the electron localization during dissociation as shown in figure 15. The field depicted in (a) leads to time dependent potential energies of the two involved quasi-static states given in (b). The corresponding effects on populations of those states and on new, localized wavefunctions is shown in panels (c)–(e). The described electron localization originates from the behavior of the dissociating wavepacket at the laser-induced avoided-crossings that are well-described by the Landau–Zener formula as discussed in section 2.

As a measure for the strength of the induced asymmetry in electron localization one requires an asymmetry parameter A , very often in the normalized form, ranging from 0 (equal distribution) to ± 1 (complete localization on one side or the other):

$$A(\varphi, E) = \frac{N_{\text{left}}(\varphi, E) - N_{\text{right}}(\varphi, E)}{N_{\text{left}}(\varphi, E) + N_{\text{right}}(\varphi, E)}, \quad (4)$$

with N_{left} and N_{right} being the number of fragments emitted to the left and right in the laboratory frame, with a kinetic energy E and for a specific relative phase φ of the asymmetric exciting laser field, e.g. the CEP, or between the two-color components ω and 2ω forming such a field.

Almost 30 years ago, the first theoretical suggestion of an experiment to control a unimolecular reaction was proposed by Shapiro, Hepburn and Brumer [166]. The authors

Figure 17. Comparison of different electric fields with baseline indicating the zero field value. (a) Few-cycle pulse as used for CEP control experiments. (b) Long femtosecond pulse with vanishing difference between up and down components and unsuitable for a control experiment. (c) Two-color field with 30% SHG contribution and the same pulse duration as (b)—here, the up/down asymmetry is maintained throughout the complete pulse.

proposed to control the dissociation outcome of a model molecule with an asymmetric laser field formed by two frequencies, the fundamental and its third harmonic ($\omega + 3\omega$). Slightly modified to the combination of ω and 2ω , this mechanism was soon adapted to the cation of the hydrogen molecule in both, theory [167–170] and experiment [171], as shown for two prominent examples in figure 16.

Based on these theoretical predictions, the first experiment controlling the directionality of electron localization during dissociation was performed in 1995 using picosecond lasers and a two-color scheme [171]. The effect of electron steering appeared in the TOF measurements shown in figure 16(b) where the sub-peaks at shorter times correspond to protons (left peak ensemble, solid line) and deuterons (right, dashed line) flying towards the detector, while the sub-peaks at larger TOF correspond to fragments initially flying away from the detector. The electric field of the TOF spectrometer is guiding those fragments with a certain delay towards the detector, thus even this relatively simple experiment already beautifully demonstrates the effect of phase control on electron localization, leading to a control of proton emission in the laboratory frame. Soon after, this experiment was further extended to the femtosecond pulse regime by Thompson and co-workers, where they detected both, electron and ion energies showing their counter-oscillation [172]. The first 2D asymmetry map of KER versus phase for a two-color experiment was presented by Ray and co-workers [138], as will be shown later.

Figure 18. Principle of a dissociation control experiment. (a) Scheme of the reflection principle associated to the formation of D^+ ions from bond softening (red KE region), above-threshold dissociation (blue KE region), three-photon dissociation (green KE region), charge-resonance-enhanced ionization (orange KE region) and recollision-excitation (purple KE region). Capital letters correspond to different pathways and roman numerals indicate different control channels as discussed in the text. Blue arrows indicate absorption of 2ω photons, red arrows of ω photons (b) left panel: experimentally deduced asymmetries for the detected D^+ fragments at an intensity of $8.3 \times 10^{13} \text{ W cm}^{-2}$ and right panel: corresponding logarithmic energy distribution. (c) Averaged asymmetries for the specified KER cuts.

Figure 19. Selection of different dissociation channels showing up in different control experiments to observe the steering of proton emission in the D_2 cation. The ‘control-piano’ can be played differently, depending on the chosen laser pulse wavelength and shape of the electric field. The color scale indicates preferential left (up) and right (down) emission of the D^+ with blue and red, respectively. Green indicates no preference of emission direction. (a) 800 nm CEP controlled [137], (b) two-color laser field composed of 400 nm/800 nm pulses [138], (c) mid-IR two-color field with 900 nm/1800 nm [176], and (d) mid-IR CEP controlled laser field at 2100 nm [175]. Note that, apart from (d) they all follow the linear energy axis from 0 to 4 eV shown on the left. (d) Covers the same energy range but, as indicated on the right, on a logarithmic scale for low energies. (a) From [137]. Reprinted with permission from AAAS. (b) Figure adapted with permission from [138]. Copyrighted by the American Physical Society. (c) Reprinted with permission from [176] and (d) figure adapted with permission from [175]. Copyrighted by the American Physical Society.

Figure 20. Mechanisms that lead to asymmetry in EUV–infrared dissociative ionization. (a) Asymmetry caused by the interference of a wavepacket launched in the σ_u state by direct EUV ionization or rapid ionization of the Q_1 $^1\Sigma_u^+$ doubly-excited states by the NIR pulse and a wavepacket in the σ_g state resulting from autoionization of the Q_1 $^1\Sigma_u^+$ states. Blue arrows indicate the effect of the EUV pulse and red arrows that of the NIR pulse; purple lines and arrows signify dynamics that is intrinsic to the molecule. (b) Close-coupling calculations in which direct photoexcitation to the σ_g state has been excluded, supporting the notion that the Q_1 autoionizing states have an important role in the localization dynamics. (c) Asymmetry caused by the interference of a wavepacket that is launched in the σ_u state by direct EUV ionization and a wavepacket in the σ_g state that results from stimulated emission during the dissociation process. (d) Time-dependent asymmetry from a two-level calculation in which the wavefunction of the dissociating molecule is considered to be a coherent superposition of the σ_g and σ_u states. Reprinted by permission from Macmillan Publishers Ltd: nature [139], copyright (2010).

Figure 21. Interplay between dissociation and ionization of the hydrogen cation. (a) Time-dependent density of the nuclear wavepacket, displayed as a color map. The white and red lines represent the average internuclear distance and velocity, respectively. (b) Dependence of dissociation and ionization probabilities on the time delay. The wavelength, pulse duration, and peak intensity of the delayed probe laser are 1600 nm, 13.5 fs, and $1 \times 10^{14} \text{ W cm}^{-2}$, respectively. Taken with permission from [192].

Alternatively, also an interferometric one-color approach can lead to control of the fragmentation of H_2^+ due to different dissociation pathways (ω , 2ω) [159]. Two 795 nm pulses of 25 fs duration out of an interferometer were adjusted in time to lead either to constructive interference (relative time delay of 14.0 fs between the two pulses) or destructive interference (14.5 fs delay). At these time delays the pulses partially overlap, and depending on their delay, the electric field is tailored.

A very elegant way to control the dissociation outcome of DI of H_2 was demonstrated by Niikura and co-workers in 2003 [35]. There, the control was accomplished via the difference frequency between two NIR colors from an optical parametric amplifier. The difference frequency causes a variable modulation of the pulse envelope which can be adjusted to control the dissociation yield.

Experimentally, the two-color technique to shape an electric field is the easiest one to implement, since it comes with the smallest demands on pulse characteristics and stabilization compared to CEP controlled or attosecond pulses, as discussed in the following. The two-color approach also enables to tailor the electric field of a laser pulse on a much longer timescale. As visualized in figure 17, the differences of up and down components of the CEP-stabilized electric field shown in (a) vanish for a long pulse duration (b), while they are imprinted on every single cycle of a two-color field and remain present even for multi-cycle pulses (c).

Consequently, the first control experiments taking advantage of a few-cycle laser field succeeded about a decade later than the two-color experiments. An initial control experiment by Alnaser and co-workers used laser pulses of different duration (8–30 fs at 800 nm) and intensity [73]. By properly adjusting pulse duration and laser intensity, a single spectrum can show Coulomb explosion of H_2 proceeding

through three different processes: CREI, sequential ionization, and rescattering-induced double ionization. The first and ground breaking control experiment with a CEP stabilized few-cycle laser field was presented two years later by Kling and co-workers [137].

Building on those early approaches, there is still a continuous interest in this simple, yet beautiful type of control experiment, presently with the tendency of moving the excitation wavelengths towards the mid infrared spectral range. In this case, the duration of a single optical cycle (e.g. 7 fs at a wavelength of $2.1 \mu\text{m}$) closely matches the arrival time of the vibrational wavepacket at the outer turning point (~ 7 fs in the case of H_2^+), which leads to the highest degree of control of electron localization [173–176].

In addition to this temporal matching, new dissociation pathways open up because of the smaller photon energy related to a longer excitation wavelength. This is exemplarily illustrated in figure 18(a) for a two-color excitation of 900 nm in combination with 1800 nm [176]. The interference of different pathways with each other can be controlled by the asymmetric laser field. These pathways cover the previously discussed mechanisms of:

- BS (red KER region, pathways E and G, control channel I),
- ATD (blue KER region, e.g. combination of pathways C and F, control channel II),
- three-photon dissociation (green KER region, pathways B and C, control channel III),
- recollision-excitation (RCE, purple KER region, pathway A, control channel IV), where the ionized electron recollides with the molecular ion leading to the highest KER fragments that can be controlled.

The region of CREI (orange KER region, pathway H) shows up, as well. This channel cannot be controlled, since the final state of this process is the Coulomb state, thus both fragments carry the charge.

Out of the measured kinetic energy distribution of ionic fragments versus the relative phase of the two-color field an asymmetry map is reconstructed, as e.g. shown in figure 18(b) for the deuterium molecule. The discussed different control channels are separated by a π phase jump as pointed out in the KER integrated representation of figure 18(c).

An impressive variety of similar control experiments has been performed in the past ten years, investigating the influence of parameters like intensity, pulse duration, polarization direction and wavelength with either CEP control [137, 140, 177, 178], or two-color control combining $\omega + 2\omega$ fields [138, 176, 179, 180], or $\omega + 3\omega$ [181]. We also refer to the review article by Sansone *et al* on attosecond time-resolved electron dynamics in the hydrogen molecule [182]. Out of this collection, four exemplary studies are presented in the overview of figure 19, to highlight the diversity of DI channels one can control when playing on the piano of PES of the H_2 molecule.

Once it is possible to control electron localization, one can think of observing the very moment when it occurs. Very recently, Xu *et al* have imaged this electron localization in

real time by using a variable time delay between two 5 fs, CEP controlled laser pulses from a Mach–Zehnder-type interferometer. Varying the time delay between pump and probe pulses allowed the authors to prove that the electron localization in H_2^+ is terminated within 15 fs at an internuclear distance of about 4 Å [146].

An alternative possibility to induce a control of the electron localization takes again advantage of an asymmetry in the excitation process—but this time due to an extremely short—attosecond excitation in combination with a strong NIR laser pulse. The attosecond element can either be an attosecond pulse train (APT) [141, 183–187] or an isolated attosecond pulse [139]. Representatively for all of them, the latter is briefly discussed in the following: the initial photoionization to a variety of electronic states of the cation by an isolated attosecond pulse is controlled by a time-delayed few-cycle NIR pulse [139]. As depicted in figures 20(a) and (c), two different mechanisms can lead to charge localization, with the NIR pulse either influencing the photoionization (a) or dissociation (c) of the molecular ion. Fragments at high kinetic energy are only there in the presence of the EUV pulse and vary with changing time delay. The corresponding measured and calculated asymmetry in the deuteron KER is shown in plots (b) and (d), respectively.

Recently, this concept has been extended by Nabekawa *et al* to an XUV–pump–XUV–probe experiment, employing a rather intense APT of ~ 4 fs for both, ionization and dissociation [141]. In the experiment, the first APT launched the H_2^+ wavepacket on the σ_g ground state. The second APT then projected the population onto either the first or second excited dissociative state, i.e., the σ_u and $2p\pi_u$, respectively. The broad bandwidth of the APT causes an overlap of the KER spectra of both dissociation pathways. By varying the time delay between pump and probe APT the KER spectrum was modulated, i.e., certain spectral components of the dissociation pathways were suppressed and others enhanced.

Naturally, the energetic width of attosecond pulses is so large, that some of the harmonics might lead to background contributions. Therefore, future experiments require spectrally tailored attosecond pulses, which asks for the extension of femtosecond to attosecond pulse shaping.

While in general, people study the asymmetry of a dissociation process as a function of the phase in control experiments, it is also possible to study the overall dissociation yield as a function of relative CEP and kinetic energy released. A general theory of CEP effects was developed in [188] and reformulated in [162]. Based on these theoretical developments, Xu *et al* suggested an experimental approach to detect the protons emitted in both directions and thus to define the combined dissociation yield [178]. When controlling the asymmetry of a dissociation direction, paths of n photon absorption interfere with paths of $n + 1$ photons, which leads to a 2π periodicity. In contrast, the control over dissociation yields requires the interference of paths populated by n and by $n + 2$ photons, which results in a π periodicity with the phase.

All the previously discussed mechanisms follow the same principle to imprint a certain distortion onto a symmetric

molecular system via an asymmetric laser field. In this case, the detection integrates over the total outcome. However, a different route to asymmetry in the reaction products has been also taken over the last decade [17, 65, 77, 153, 156, 189, 190]: rather than asymmetric excitation combined with symmetric detection, a symmetric excitation together with an asymmetric detection mechanism becomes possible by taking advantage of the ultimate strengths of electron–ion coincidence techniques. When studying electrons and ions in coincidence, one can fix the direction of the departing electron with respect to the left behind hydrogen and proton and thus has access to the molecular frame and the ability to detect this naturally occurring asymmetry. In other words: while the conventional control experiments described up to now introduce an asymmetry in the laboratory frame with symmetric detection in the molecular frame, these experiments keep molecules in the laboratory frame symmetric, but take advantage of the asymmetry they can detect in the molecular frame.

Exploiting this ansatz, Lafosse and co-workers have observed an asymmetry in the photoelectron angular distribution due to autoionization of higher excited states of the hydrogen cation (Q_1 and Q_2) which leads to a superposition of gerade and ungerade electronic states at large internuclear distances [189]. While all the previously discussed control mechanisms rely on the presence of a laser field being well defined in time, it was shown by Martín *et al* [17] that based on this second control mechanism, even a single photon could induce a breaking of the symmetry. To observe this effect, electrons and ions need to be detected in coincidence. Under these conditions, it can be seen that the photoelectron is preferentially ejected in the same direction as the H^+ .

Hence, the reconstruction of the molecular frame from coincidence detection of the ionization fragments lends itself to photoionization with either synchrotron radiation [189], single photon excitation [17], symmetric, circularly polarized laser fields [65, 153, 156], symmetric, linearly polarized laser fields [77], or the retroaction of the transient field of the photoelectron by Waitz *et al* [190]. The latter work is based on the theory work by Serov *et al* [191] stating that the retroaction of a photoelectron might be capable of breaking the symmetry on which side of the remaining H_2^+ ion the bound electron localizes: this asymmetry is induced by the transient field of photoelectrons of very low energy. They are slow enough that the wing of their Coulomb potential can interact with the molecule at the moment of dissociation, inducing a transient polarization in the molecular ion. In this special case, the steps of ionization and dissociation can no longer be separated. Experimentally, it was observed that the remaining bound electron preferentially localizes on the site opposite to the ejected electron [190].

The mechanisms on the control of electrons discussed here are always inseparably linked to the motion of nuclei. This is also the case in the experiments of Ranitovich and co-workers, who have investigated the control possibilities of molecular ionization and dissociation via the interference of electronic wavepackets in both, ionic states and in the neutral, using pump light from a high harmonic source [103]. This represents a continuation of the experiments imaging DI of

the nuclear wavepacket, discussed in the previous section [136]. They could select the population of certain electronic states, which has led to a steering of nuclear wavepackets defining the outcome of dissociation or ionization processes.

This competitive behavior and nuclear dependence of dissociation and ionization of H_2^+ has also been studied theoretically by Jiang and co-workers [192]. By varying the time delay between two mid-IR laser pulses (2.4 and 1.6 μm), they have triggered nuclear dynamics of higher lying vibrational states of the σ_g cationic state. Those populations are further promoted by the probe pulse to either the σ_u state where dissociation occurs or to the dication via ionization. The resulting interplay of ionization and dissociation probabilities is shown in figure 21.

5. Perspective

This concludes our review on recent activities to image and control electronic and nuclear dynamics on this small molecule. Despite continuing efforts over the last three decades, the research into how the hydrogen molecule responds to intense optical fields is far from being completed. As laser technology and thereby waveform control improves, previously unresolved questions can be addressed.

Recently, the production of Rydberg states in the wake of an intense laser pulse has gained increasing attention. Highly excited states in neutral and ionized atoms or molecules were known to be produced by an intense laser pulse already in the early 1990s (e.g. [193, 194]). However, further experiments were hampered by the inherently difficult detection of the residual internal energy in strong laser fields. This difficulty arises in processes that are proceeding through absorption of many photons, where the total energy is not defined in contrast to single-photon ionization. Excitation can proceed through multiphoton absorption by bound electrons, or direct tunneling from lower lying electronic states [195]. In addition, light-induced inelastic rescattering, leading to the capture of an ionized electron by its parent ion into an excited state, has been identified as a major route to Rydberg state production [196]. Such a frustrated ionization has been predicted for the DI of molecular hydrogen with classical trajectory simulations [197–199]. However, so far, the experimental verification of frustrated ionization has been largely limited to atomic targets [200–203]. For molecular Rydberg state production, H_2^+ is not an ideal candidate due to the lack of stable excited states. However, neutral H_2 does have several bound excited states.

Recently, Mi *et al* [204] identified highly excited, auto-ionizing states in neutral H_2 caused by optical tunnel ionization. On the other hand, Palacios and co-workers have devised an XUV–pump–few-cycle IR probe scheme to probe doubly-excited, autoionizing states in H_2 [205].

Finally, the complex of questions about tunneling time and ionization delay which was first addressed in the helium atom [206] has only recently been applied to molecules like H_2 [207] and CO [208]. The ionization delay in H_2^+ has been addressed theoretically by Serov *et al* [209, 210]. The non-adiabatic

electron dynamics in H_2^+ however, make the interpretation of the photoelectron distribution very difficult [211, 212].

When studying the dynamics of more complex molecules, H_2 does not only show up as the chamber background contribution that we are trying to eliminate; its important role is played behind the scenes, as many of those experiments are only possible today because of research on H_2 in the past. The experimental and theoretical methods that were developed for hydrogen are ready to be transferred and applied to more complex molecular systems. Various ultrafast imaging techniques that have been successfully implemented and verified on the hydrogen molecule are now being transferred to polyatomic molecules; e.g., CEI has been applied to study the proton migration from the acetylene to the vinylidene isomer in the cation [213–215] and in the dication [216, 217]. The geometric structure of the acetylene dication at the moment of deprotonation has been recently imaged with the intra-molecular probing technique of LIED [218]. Similar to the molecular clock experiments discussed in section 3, in LIED, the electron undergoing diffraction originates from the ionized molecule itself. The ionizing laser wavelength determines the return time of the electron and thus the probe time [219, 220].

A recent study on the phenol photo-dissociation analyzes the difficulties one faces when adapting VMI to large molecules with more than 10 atoms, and how to suppress disturbing background signals from the parent ion [221]. Their study proposes a combination of VMI and multimag ion imaging [222] to obtain high velocity resolution together with a clean background-free signal.

The concept of molecular HHG that was developed on small molecules like H_2 [223] and N_2 [224] was extended to larger molecules [225], e.g., CS_2 and hexane [226], CO_2 [227, 228], or iodoacetylene [229].

Not only imaging approaches, but also the control mechanisms based on tailored light fields discussed in the last section are effectively transferred to more complex channels for molecular DI [230, 231]. The effects of BS which we have discussed in this review also played a major role in a single-pulse experiment by Xie *et al* where the bondbreaking of ethylene into two or three fragments was controlled with the pulse duration [232]. With a short pulse (5 fs) the molecular ion is prepared at high potential energies, since the molecule has almost no time to stretch, which favors the breaking of two bonds. At the longest pulse duration employed (25 fs), significant stretching occurs and the molecule most likely dissociates into two fragments due to the lowered barrier. As for the hydrogen molecule, also CEP control of few-cycle laser pulses is adapted to polyatomic molecules like N_2O [233], acetylene [234–236], ethylene and 1,3-butadiene [236], or allene [234]. Recently, those concepts have also been extended to the solid state, e.g., when controlling optical field-induced currents in dielectrics [237] or the photo-emission from metal nano-tips [238]. Also the isomerization in the acetylene dication, was controlled by using adaptively shaped fs laser [239]. The optimal pulse sequence consists of a series of three pulses where isomerization barriers are being lowered because of the right timing between the interaction of the pulse electric field with the molecular potential.

With those methods, whose accuracy has been verified with the simplest of all molecules, we have now a variety of tools at hand to image structural rearrangements in real time. In combination with high repetition rate, high energy laser sources of the future, these developments will further push imaging experiments with atomic temporal and spatial resolution of all kind of targets.

Due to its special energetic structure, research on H_2 moreover contributes to the development of quantum computers— H_2 acts on both sides, on the target side as the first real molecular system whose complete energy spectrum could be calculated based on quantum computations [240], but also on the computational side; vibrational wavepackets in D_2^+ were isolated to define superposition conditions required for quantum computations [241]. Furthermore, the special 2-electronic structure of H_2 leads to an important concept in quantum information, ‘entanglement’. Electron correlations occurring at large internuclear distances R can no longer be described by molecular orbitals, but rather become Heitler–London ‘entangled’ atomic configurations. This could lead a route to measuring electron entanglement via photo-ionization as a function of R [242].

However, H_2 does not only serve as a playground for fundamental science. Due to its truly unique properties it also finds broad applications outside of the laboratory, and we will briefly discuss two examples from laser technology and medicine here. (i) Possessing the highest of all vibrational frequencies, H_2 and D_2 are extraordinary Raman shifters for picosecond laser pulses. To give an example, using H_2 , e.g. an Nd:YAG beam of 1064 nm can be shifted to either 1907 nm (stokes) or 738 nm (anti-stokes), by just inserting a gas cell or a photonic crystal fiber into the beam [243, 244]. (ii) To slow down reaction times of drugs within the body, drugmakers aim to exploiting the extraordinary isotope effect when going from protonated to deuterated structures. A few month ago, the US Food and Drug Administration has released the first approval of deuterated drugs [245].

The show must go on.

ORCID iDs

Heide Ibrahim <https://orcid.org/0000-0001-6371-8501>

References

- [1] Posthumus J H 2004 The dynamics of small molecules in intense laser fields *Rep. Prog. Phys.* **67** 623–65
- [2] Bandrauk A D *et al* 1993 *Molecules in Laser Fields* ed A D Bandrauk (Boca Raton, FL: CRC Press)
- [3] Bandrauk A D and Légaré F 2012 Enhanced ionization of molecules in intense laser fields *Progress in Ultrafast Intense Laser Science VIII* ed K Yamanouchi *et al* (Berlin: Springer) pp 29–46
- [4] Giusti-Suzor A, Mies F H, DiMauro L F, Charron E and Yang B 1995 Dynamics of H_2^+ in intense laser fields *J. Phys. B: At. Mol. Opt. Phys.* **28** 309
- [5] Miller M R, Xia Y, Becker A and Jaroń-Becker A 2016 Laser-driven nonadiabatic electron dynamics in molecules *Optica* **3** 259
- [6] Lein M 2007 Molecular imaging using recolliding electrons *J. Phys. B: At. Mol. Opt. Phys.* **40** R135–73
- [7] Vrakking M J J 2014 Attosecond imaging *Phys. Chem. Chem. Phys.* **16** 2775–89
- [8] Niikura H and Corkum P B 2007 Attosecond and angstrom science *Adv. At. Mol. Opt. Phys.* **54** 511–48
- [9] Palacios A, Sanz-Vicario J L and Martín F 2015 Theoretical methods for attosecond electron and nuclear dynamics: applications to the H_2 molecule *J. Phys. B: At. Mol. Opt. Phys.* **48** 242001
- [10] Saenz A 2004 Molecular hydrogen in strong laser fields: bond softening, enhanced ionisation, and coherent control *Phys. Scr.* **T110** 126–31
- [11] Brannon P J J, Church C H H and Peters C W W 1968 Electric field induced spectra of molecular hydrogen, deuterium and deuterium hydride *J. Mol. Spectrosc.* **27** 44–54
- [12] Ramakrishna S and Seideman T 2006 Dissipative dynamics of laser induced nonadiabatic molecular alignment *J. Chem. Phys.* **124** 34101
- [13] Lee K F, Légaré F, Villeneuve D M and Corkum P B 2006 Measured field-free alignment of deuterium by few-cycle pulses *J. Phys. B: At. Mol. Opt. Phys.* **39** 4081
- [14] Niikura H, Légaré F, Hasbani R, Bandrauk A D, Ivanov M Y, Villeneuve D M and Corkum P B 2002 Sub-laser-cycle electron pulses for probing molecular dynamics *Nature* **417** 917–22
- [15] Niikura H, Legare F, Hasbani R, Ivanov M Y, Villeneuve D M and Corkum P B 2003 Probing molecular dynamics with attosecond resolution using correlated wave packet pairs *Nature* **421** 826–9
- [16] Huber K P and Herzberg G 2017 *Constants of Diatomic Molecules* ed P J Linstrom and W G Mallard (Gaithersburg, MD: National Institute of Standards and Technology) p 20899
- [17] Martín F *et al* 2007 Single photon-induced symmetry breaking of H_2 dissociation *Science* **315** 629
- [18] Urbain X *et al* 2004 Intense-laser-field ionization of molecular hydrogen in the tunneling regime and its effect on the vibrational excitation of H_2^+ *Phys. Rev. Lett.* **92** 163004
- [19] Goll E, Wunner G and Saenz A 2006 Formation of ground-state vibrational wave packets in intense ultrashort laser pulses *Phys. Rev. Lett.* **97** 103003
- [20] Ergler T, Feuerstein B, Rudenko A, Zrost K, Schröter C D, Moshhammer R and Ullrich J 2006 Quantum-phase resolved mapping of ground-state vibrational D_2 wave packets via selective depletion in intense laser pulses *Phys. Rev. Lett.* **97** 103004
- [21] Dietrich P, Ivanov M Y, Ilkov F A and Corkum P B 1996 Two-electron dissociative ionization of H_2 and D_2 in infrared laser fields weaker field transition happens at larger R , where potentials are closer together *Phys. Rev. Lett.* **77** 3–6
- [22] Alnaser A *et al* 2005 Simultaneous real-time tracking of wave packets evolving on two different potential curves in H_2^+ and D_2^+ *Phys. Rev. A* **72** 30702
- [23] Khosravi E, Abedi A and Maitra N T 2015 Exact potential driving the electron dynamics in enhanced ionization of H_2^+ *Phys. Rev. Lett.* **115** 263002
- [24] Dehghanian E, Bandrauk A D and Kamta G L 2010 Enhanced ionization of the H_2 molecule driven by intense ultrashort laser pulses *Phys. Rev. A* **81** 61403
- [25] Vanroose W, Martín F, Rescigno T N and McCurdy C W 2005 Complete photo-induced breakup of the H_2 molecule as a probe of molecular electron correlation *Science* **310** 1787–9

- [26] Lefebvre C, Nguyen-Dang T T, Dion F, Vrakking M J J, Serov V N and Atabek O 2013 Attosecond pump-probe transition-state spectroscopy of laser-induced molecular dissociative ionization: adiabatic versus nonadiabatic dressed-state dynamics *Phys. Rev. A* **88** 53416
- [27] Nguyen-Dang T T, Peters M, Wang S-M, Sinelnikov E and Dion F 2007 Nonvariational time-dependent multiconfiguration self-consistent field equations for electronic dynamics in laser-driven molecules *J. Chem. Phys.* **127** 174107
- [28] Lein M, Kreibich T, Gross E K U and Engel V 2002 Strong-field ionization dynamics of a model H_2 molecule *Phys. Rev. A* **65** 33403
- [29] Saenz A 2002 Behavior of molecular hydrogen exposed to strong dc, ac, or low-frequency laser fields: I. Bond softening and enhanced ionization *Phys. Rev. A* **66** 63407
- [30] Lein M, Hay N, Velotta R, Marangos J P and Knight P L 2002 Interference effects in high-order harmonic generation with molecules *Phys. Rev. A* **66** 23805
- [31] Bandrauk A D, Chelkowski S and Lu H 2009 Signatures of nuclear motion in molecular high-order harmonics and in the generation of attosecond pulse trains by ultrashort intense laser pulses *J. Phys. B: At. Mol. Opt. Phys.* **42** 75602
- [32] Bækhoj J E, Yue L and Madsen L B 2015 Nuclear-motion effects in attosecond transient-absorption spectroscopy of molecules *Phys. Rev. A* **91** 43408
- [33] Mulliken R S 1939 Intensities of electronic transitions in molecular spectra: II. Charge-transfer spectra *J. Chem. Phys.* **7** 20–34
- [34] Châteauneuf F, Nguyen-Dang T-T, Ouellet N and Atabek O 1998 Dynamical quenching of field-induced dissociation of H_2^+ in intense infrared lasers *J. Chem. Phys.* **108** 3974–86
- [35] Niikura H, Corkum P B and Villeneuve D M 2003 Controlling vibrational wave packet motion with intense modulated laser fields *Phys. Rev. Lett.* **90** 203601
- [36] Aubanel E E, Conjusteau A and Bandrauk A D 1993 Effect of rotations on stabilization in high-intensity photodissociation of H_2^+ *Phys. Rev. A* **48** R4011–4
- [37] Chu S-I and Telnov D A 2004 Beyond the Floquet theorem: generalized Floquet formalisms and quasienergy methods for atomic and molecular multiphoton processes in intense laser fields *Phys. Rep.* **390** 1–131
- [38] Floquet G 1883 Sur les équations différentielles linéaires à coefficients périodiques *Ann. Sci. l'école Norm. Supérieure* **12** 47–88
- [39] Bandrauk A D and Atabek O 1987 Semiclassical methods in multiphoton diatomic spectroscopy: beyond perturbation theory *J. Phys. Chem.* **91** 6469–78
- [40] Landau L 1932 Zur Theorie der Energieübertragung. II *Phys. Z. Sowjetunion* **2** 46–51
- [41] Zener C 1932 Non-adiabatic crossing of energy levels *Proc. R. Soc. A* **137** 696
- [42] Moiseyev N 1998 Quantum theory of resonances: calculating energies, widths and cross-sections by complex scaling *Phys. Rep.* **302** 212–93
- [43] Zavriyev A, Bucksbaum P H, Muller H G and Schumacher D W 1990 Ionization and dissociation of H_2 in intense laser fields at 1.064 μm , 532 nm, and 355 nm *Phys. Rev. A* **42** 5500–13
- [44] Giusti-Suzor A and Mies F H 1992 Vibrational trapping and suppression of dissociation in intense laser fields *Phys. Rev. Lett.* **68** 3869–72
- [45] Frasniski L J, Plumridge J, Posthumus J H, Codling K, Taday P F, Divall E J and Langley A J 2001 Counterintuitive alignment of H_2^+ in intense femtosecond laser fields *Phys. Rev. Lett.* **86** 2541–4
- [46] Bucksbaum P H, Zavriyev A, Muller H G and Schumacher D W 1990 Softening of the H_2^+ molecular bond in intense laser fields *Phys. Rev. Lett.* **64** 1883–6
- [47] Giusti-Suzor A, He X, Atabek O and Mies F H 1990 Above-threshold dissociation of H_2^+ in intense laser fields *Phys. Rev. Lett.* **64** 515–8
- [48] Wang P Q, Sayler A M, Carnes K D, Xia J F, Smith M A, Esry B D and Ben-Itzhak I 2006 Dissociation of H_2^+ in intense femtosecond laser fields studied by coincidence three-dimensional momentum imaging *Phys. Rev. A* **74** 43411
- [49] McKenna J *et al* 2008 Enhancing high-order above-threshold dissociation of H_2^+ beams with few-cycle laser pulses *Phys. Rev. Lett.* **100** 133001
- [50] McKenna J, Anis F, Sayler A M, Gaire B, Johnson N G, Parke E, Carnes K D, Esry B D and Ben-Itzhak I 2012 Controlling strong-field fragmentation of H_2^+ by temporal effects with few-cycle laser pulses *Phys. Rev. A* **85** 23405
- [51] Prabhudesai V S *et al* 2010 Tracing the photodissociation probability of H_2^+ in intense fields using chirped laser pulses *Phys. Rev. A* **81** 23401
- [52] Benis E P, Bakarezos M, Papadogiannis N A, Tatarakis M, Divanis S, Ö Broin C and Nikolopoulos L A 2012 Role of broadband-laser-pulse temporal extent in H_2^+ photodissociation *Phys. Rev. A* **86** 43428
- [53] Bavli R and Metiu H 1992 Laser-induced localization of an electron in a double-well quantum structure *Phys. Rev. Lett.* **69** 1986–8
- [54] Zuo T and Bandrauk A D 1995 Charge-resonance-enhanced ionization of diatomic molecular ions by intense lasers *Phys. Rev. A* **52** R2511–4
- [55] Seideman T, Ivanov M Y and Corkum P B 1995 Role of electron localization in intense-field molecular ionization *Phys. Rev. Lett.* **75** 2819–22
- [56] Bandrauk A D and Lu H 2001 Generalized space translation and new numerical methods for time-dependent Schrödinger equations of molecules in intense laser fields *J. Mol. Struct. Theochem.* **547** 97–111
- [57] Liang H, Xiao X-R, Gong Q and Peng L-Y 2017 Accurate computation of above threshold ionization spectra for stretched H_2^+ in strong laser fields *J. Phys. B: At. Mol. Opt. Phys.* **50** 174002
- [58] Codling K, Frasniski L J and Hatherly P A 1989 On the field ionisation of diatomic molecules by intense laser fields *J. Phys. B: At. Mol. Opt. Phys.* **22** L321
- [59] Corkum P B, Burnett N H and Brunel F 1989 Above-threshold ionization in the long-wavelength limit *Phys. Rev. Lett.* **62** 1259–62
- [60] Takemoto N and Becker A 2010 Multiple ionization bursts in laser-driven hydrogen molecular ion *Phys. Rev. Lett.* **105** 203004
- [61] Takemoto N and Becker A 2011 Time-resolved view on charge-resonance-enhanced ionization *Phys. Rev. A* **84** 023401
- [62] Takemoto N and Becker A 2011 Visualization and interpretation of attosecond electron dynamics in laser-driven hydrogen molecular ion using Bohmian trajectories *J. Chem. Phys.* **134** 74309
- [63] Odenweller M, Takemoto N, Vredenburg A, Cole K, Pahl K, Titze J, Schmidt L P H, Jahnke T, Dörner R and Becker A 2011 Strong field electron emission from fixed in space H_2^+ ions *Phys. Rev. Lett.* **107** 143004
- [64] Odenweller M *et al* 2014 Electron emission from H_2^+ in strong laser fields *Phys. Rev. A* **89** 13424
- [65] Spanner M *et al* 2012 Coulomb asymmetry and sub-cycle electron dynamics in multiphoton multiple ionization of H_2 *J. Phys. B: At. Mol. Opt. Phys.* **45** 194011
- [66] Doblhoff-Dier K, Dimitriou K I, Staudte A and Gräfe S 2013 Classical analysis of Coulomb effects in strong-field ionization of H_2^+ by intense circularly polarized laser fields *Phys. Rev. A* **88** 33411

- [67] Yuan K-J, Chelkowski S and Bandrauk A D 2015 Molecular photoelectron angular distribution rotations in multi-photon resonant ionization of H_2^+ by circularly polarized ultraviolet laser pulses *J. Chem. Phys.* **142** 144304
- [68] He P-L, Takemoto N and He F 2015 Photoelectron momentum distributions of atomic and molecular systems in strong circularly or elliptically polarized laser fields *Phys. Rev. A* **91** 63413
- [69] Murakami M and Chu S-I 2016 Photoelectron momentum distributions of the hydrogen molecular ion driven by multicycle near-infrared laser pulses *Phys. Rev. A* **94** 43425
- [70] Shao Y, He P, Liu M-M, Sun X, Li M, Deng Y, Wu C, He F, Gong Q and Liu Y 2017 Fully differential study on dissociative ionization dynamics of deuterium molecules in strong elliptical laser fields *Phys. Rev. A* **95** 31404
- [71] Yue L and Madsen L B 2016 Inter- and intracycle interference effects in strong-field dissociative ionization *Phys. Rev. A* **93** 31401
- [72] Li Y, Zhou Y, He M, Li M, Lan P and Lu P 2016 Time-resolved internal-electron-scattering effect of H_2^+ in enhanced ionization regions *Phys. Rev. A* **94** 13422
- [73] Alnaser A, Tong X, Osipov T, Voss S, Maharjan C, Shan B, Chang Z and Cocke C 2004 Laser-peak-intensity calibration using recoil-ion momentum imaging *Phys. Rev. A* **70** 23413
- [74] Spanner M, Smirnova O, Corkum P B and Ivanov M Y 2004 Reading diffraction images in strong field ionization of diatomic molecules *J. Phys. B: At. Mol. Opt. Phys.* **37** L243
- [75] Meckel M *et al* 2008 Laser-induced electron tunneling and diffraction *Science* **320** 1478–82
- [76] Wilbois T and Helm H 2011 Strong-field ionization of H_2 from ultraviolet to near-infrared wavelengths: photoelectron energy and angular identifications *Phys. Rev. A* **84** 53407
- [77] Haertelt M, Bian X B, Spanner M, Staudte A and Corkum P B 2016 Probing molecular dynamics by laser-induced backscattering holography *Phys. Rev. Lett.* **116** 1–6
- [78] Walker B, Sheehy B, DiMauro L F, Agostini P, Schafer K J and Kulander K C 1994 Precision measurement of strong field double ionization of helium *Phys. Rev. Lett.* **73** 1227–30
- [79] Weber T *et al* 2000 Kinematically complete investigation of momentum transfer for single ionization in fast proton–helium collisions *J. Phys. B: At. Mol. Opt. Phys.* **33** 3331–44
- [80] van der Hart H W 2000 Sequential versus non-sequential double ionization in strong laser fields *J. Phys. B: At. Mol. Opt. Phys.* **33** L699
- [81] Trump C, Rottke H and Sandner W 1999 Strong-field photoionization of vibrational ground-state H_2^+ and D_2^+ molecules *Phys. Rev. A* **60** 3924–8
- [82] Staudte A, Cocke C L, Prior M H, Belkacem A, Ray C, Chong H W, Glover T E, Schoenlein R W and Saalmann U 2002 Observation of a nearly isotropic, high-energy Coulomb explosion group in the fragmentation of D_2 by short laser pulses *Phys. Rev. A* **65** 20703
- [83] Sakai H, Larsen J J, Wendt-Larsen I, Olesen J, Corkum P B and Stapelfeldt H 2003 Nonsequential double ionization of D_2 molecules with intense 20 fs pulses *Phys. Rev. A* **67** 63404
- [84] Légaré F, Litvinyuk I, Dooley P, Quéré F, Bandrauk A, Villeneuve D and Corkum P 2003 Time-resolved double ionization with few cycle laser pulses *Phys. Rev. Lett.* **91** 93002
- [85] Alnaser A, Osipov T, Benis E, Wech A, Shan B, Cocke C, Tong X and Lin C 2003 Rescattering double ionization of D_2 and H_2 by intense laser pulses *Phys. Rev. Lett.* **91** 163002
- [86] Rudenko A, Feuerstein B, Zrost K, de Jesus V L B, Ergler T, Dimopoulou C, Schröter C D, Moshhammer R and Ullrich J 2005 Fragmentation dynamics of molecular hydrogen in strong ultrashort laser pulses *J. Phys. B: At. Mol. Opt. Phys.* **38** 487
- [87] Tong X M, Zhao Z X and Lin C D 2003 Correlation dynamics between electrons and ions in the fragmentation of D_2 molecules by short laser pulses *Phys. Rev. A* **68** 43412
- [88] Saugout S, Cornaggia C, Suzor-Weiner A and Charron E 2007 Ultrafast electronuclear dynamics of H_2 double ionization *Phys. Rev. Lett.* **98** 253003
- [89] Saugout S, Charron E and Cornaggia C 2008 H_2 double ionization with few-cycle laser pulses *Phys. Rev. A* **77** 23404
- [90] Tong A, Liao Q, Zhou Y and Lu P 2010 Internuclear-distance dependence of electron correlation in nonsequential double ionization of H_2 *Opt. Express* **18** 9064–70
- [91] Baier S, Ruiz C, Plaja L and Becker A 2006 Nonsequential double ionization of the hydrogen molecule in a few-cycle laser pulse *Phys. Rev. A* **74** 33405
- [92] Tong X M and Lin C D 2007 Carrier-envelope phase dependence of nonsequential double ionization of H_2 by few-cycle laser pulses *J. Phys. B: At. Mol. Opt. Phys.* **40** 641–9
- [93] Li Y, Chen J, Yang S P and Liu J 2007 Alignment effect in nonsequential double ionization of diatomic molecules in strong laser fields *Phys. Rev. A* **76** 23401
- [94] Baier S, Becker A and Plaja L 2008 Nonsequential double ionization of the hydrogen molecule: dependence on molecular alignment *Phys. Rev. A* **78** 13409
- [95] Yan L, Shi-Ping Y, Xin-Yan J and Jing C 2010 Nonsequential double ionization of the aligned hydrogen molecule in strong field *Chin. Phys. B* **19** 43303
- [96] Li Y-B, Wang X, Yu B-H, Tang Q-B, Wang G-H and Wan J-G 2016 Nonsequential double ionization with mid-infrared laser fields *Sci. Rep.* **6** 37413
- [97] Bandrauk A D, Barmaki S and Kamta G L 2007 Laser phase control of high-order harmonic generation at large internuclear distance: the H^+-H_2^+ system *Phys. Rev. Lett.* **98** 13001
- [98] Corkum P B 1993 Plasma perspective on strong field multiphoton ionization *Phys. Rev. Lett.* **71** 1994–7
- [99] Chelkowski S, Bredtmann T and Bandrauk A D 2012 High-order-harmonic generation from coherent electron wave packets in atoms and molecules as a tool for monitoring attosecond electrons *Phys. Rev. A* **85** 33404
- [100] Rosker M J, Dantus M and Zewail A H 1988 Femtosecond real-time probing of reaction: I. The technique *J. Chem. Phys.* **89** 6113
- [101] Zare R N 2012 My life with LIF: a personal account of developing laser-induced fluorescence *Annu. Rev. Anal. Chem.* **5** 1–14
- [102] Field G B, Somerville W B and Dressler K 1966 Hydrogen molecules in astronomy *Annu. Rev. Astron. Astrophys.* **4** 207–44
- [103] Ranitovic P *et al* 2014 Attosecond vacuum UV coherent control of molecular dynamics *Proc. Natl Acad. Sci.* **111** 912–7
- [104] Bainbridge A R, Harrington J, Kirrander A, Cacho C, Springate E, Bryan W A and Minns R S 2015 VUV excitation of a vibrational wavepacket in D_2 measured through strong-field dissociative ionization *New J. Phys.* **17** 103013
- [105] Sturm F P, Tong X M, Palacios A, Wright T W, Zalyubovskaya I, Ray D, Shivaram N, Mart F and Weber T 2017 Mapping and controlling ultrafast dynamics of highly excited H_2 molecules by VUV-IR pump-probe schemes *Phys. Rev. A* **95** 12501
- [106] González-Castrillo A, Palacios A, Bachau H and Martín F 2012 Clocking ultrafast wave packet dynamics in molecules through UV-induced symmetry breaking *Phys. Rev. Lett.* **108** 63009
- [107] Baker S, Robinson J S, Haworth C A, Teng H, Smith R A, Chirilă C C, Lein M, Tisch J W G and Marangos J P 2006 Probing proton dynamics in molecules on an attosecond time scale *Science* **312** 424–7

- [108] Krause J L, Schafer K J and Kulander K C 1992 High-order harmonic generation from atoms and ions in the high intensity regime *Phys. Rev. Lett.* **68** 3535–8
- [109] Drescher M, Hentschel M, Kienberger R, Tempea G, Spielmann C, Reider G A, Corkum P B and Krausz F 2001 X-ray pulses approaching the attosecond frontier *Science* **291** 1923–7
- [110] Popmintchev T *et al* 2012 Bright coherent ultrahigh harmonics in the keV x-ray regime from mid-infrared femtosecond lasers *Science* **336** 1287–91
- [111] Corkum P B and Krausz F 2007 Attosecond science *Nat. Phys.* **3** 381–7
- [112] Nabekawa Y, Furukawa Y, Okino T, Amani Eilanlou A, Takahashi E J, Yamanouchi K and Midorikawa K 2015 Settling time of a vibrational wavepacket in ionization *Nat. Commun.* **6** 8197
- [113] Rudenko A *et al* 2005 Fragmentation dynamics of molecular hydrogen in strong ultrashort laser pulses *J. Phys. B: At. Mol. Opt. Phys.* **38** 487–501
- [114] Bellini M, Lyngå C, Tozzi A, Gaarde M B, Hänsch T W, L'Huillier A and Wahlström C-G 1998 Temporal coherence of ultrashort high-order harmonic pulses *Phys. Rev. Lett.* **81** 297–300
- [115] Bian X B and Bandrauk A D 2014 Probing nuclear motion by frequency modulation of molecular high-order harmonic generation *Phys. Rev. Lett.* **113** 1–5
- [116] Yuan X, Wei P, Liu C, Ge X, Zheng Y, Zeng Z and Li R 2016 Effect of nuclear motion on spectral broadening of high-order harmonic generation *Opt. Express* **24** 8194–201
- [117] He L, Lan P, Zhai C, Wang F, Shi W, Zhang Q, Zhu X, Lu P and Lu Peixiang L 2016 Frequency shift in high order harmonic generation from isotopic molecules **21** 1–5 arXiv:1601.04835v2
- [118] Nisoli M, De Silvestri S and Svelto O 1996 Generation of high energy 10 fs pulses by a new pulse compression technique *Appl. Phys. Lett.* **68** 2793–5
- [119] Nisoli M, De Silvestri S, Svelto O, Szpöcs R, Ferencz K, Spielmann C, Sartania S and Krausz F 1997 Compression of high-energy laser pulses below 5 fs *Opt. Lett.* **22** 522–4
- [120] Légaré F, Lee K F, Litvinyuk I V, Dooley P W, Bandrauk A D, Villeneuve D M and Corkum P B 2005 Imaging the time-dependent structure of a molecule as it undergoes dynamics *Phys. Rev. A* **72** 1–4
- [121] Kanter E P, Cooney P J, Gemmell D S, Groeneveld K-O, Pietsch W J, Ratkowski A J, Vager Z and Zabransky B J 1979 Role of excited electronic states in the interactions of fast (MeV) molecular ions with solids and gases *Phys. Rev. A* **20** 834–54
- [122] Chelkowski S, Corkum P and Bandrauk A 1999 Femtosecond Coulomb explosion imaging of vibrational wave functions *Phys. Rev. Lett.* **82** 3416–9
- [123] Stapelfeldt H, Constant E and Corkum P B 1995 Wave packet structure and dynamics measured by Coulomb explosion *Phys. Rev. Lett.* **74** 3780–3
- [124] Ellert C, Stapelfeldt H, Constant E, Sakai H, Wright J, Rayner D M and Corkum P B 1998 Observing molecular dynamics with timed Coulomb explosion imaging *Phil. Trans. R. Soc. A* **356** 329–44
- [125] Dörner R, Mergel V, Jagutzki O, Spielberger L, Ullrich J, Moshhammer R and Schmidt-Böcking H 2000 Cold target recoil ion momentum spectroscopy: a 'momentum microscope' to view atomic collision dynamics *Phys. Rep.* **330** 95–192
- [126] Gerbig C, Senftleben A, Morgenstern S, Sarpe C and Baumert T 2015 Spatio-temporal resolution studies on a highly compact ultrafast electron diffractometer *New J. Phys.* **17** 43050
- [127] Otto M R, René de Cotret L P, Stern M J and Siwick B J 2017 Solving the jitter problem in microwave compressed ultrafast electron diffraction instruments: robust sub-50 fs cavity-laser phase stabilization *Struct. Dyn.* **4** 51101
- [128] Woerner M, Holtz M, Juve V, Elsaesser T and Borgschulte A 2014 Femtosecond x-ray diffraction maps field-driven charge dynamics in ionic crystals *Faraday Discuss.* **171** 373–92
- [129] Gardner D F *et al* 2017 Subwavelength coherent imaging of periodic samples using a 13.5 nm tabletop high-harmonic light source *Nat. Photon.* **11** 259–63
- [130] Matsuda A, Fushitani M, Takahashi E J and Hishikawa A 2011 Visualizing hydrogen atoms migrating in acetylene dication by time-resolved three-body and four-body Coulomb explosion imaging *Phys. Chem. Chem. Phys.* **13** 8697–704
- [131] Gagnon J, Lee K F, Rayner D M, Corkum P B and Bhardwaj V R 2008 Coincidence imaging of polyatomic molecules via laser-induced Coulomb explosion *J. Phys. B: At. Mol. Opt. Phys.* **41** 215104
- [132] Ullrich J, Moshhammer R, Dorn A, Dörner R, Schmidt L P H and Schmidt-Böcking H 2003 Recoil-ion and electron momentum spectroscopy: reaction-microscopes *Rep. Prog. Phys.* **66** 1463
- [133] Chandler D W and Houston P L 1987 Two-dimensional imaging of state-selected photodissociation products detected by multiphoton ionization *J. Chem. Phys.* **87** 1445
- [134] Eppink A T J B and Parker D H 1997 Velocity map imaging of ions and electrons using electrostatic lenses: application in photoelectron and photofragment ion imaging of molecular oxygen *Rev. Sci. Instrum.* **68** 3477
- [135] Vrakking M J J 2001 An iterative procedure for the inversion of two-dimensional ion/photoelectron imaging experiments *Rev. Sci. Instrum.* **72** 4084–9
- [136] Kelkensberg F *et al* 2009 Molecular dissociative ionization and wave-packet dynamics studied using two-color XUV and IR pump–probe spectroscopy *Phys. Rev. Lett.* **103** 16–9
- [137] Kling M F, Verhoef A J, Khan J I, Schultze M, Ni Y, Uiberacker M, Drescher M, Krausz F and Vrakking M J J 2006 Control of electron localization in molecular dissociation *Science* **312** 246–8
- [138] Ray D *et al* 2009 Ion-energy dependence of asymmetric dissociation of D₂ by a two-color laser field *Phys. Rev. Lett.* **103** 223201
- [139] Sansone G *et al* 2010 Electron localization following attosecond molecular photoionization *Nature* **465** 763–6
- [140] Li H *et al* 2014 Intensity dependence of the attosecond control of the dissociative ionization of D₂ *J. Phys. B: At. Mol. Opt. Phys.* **47** 124020
- [141] Nabekawa Y, Furukawa Y, Okino T, Amani Eilanlou A, Takahashi E J, Yamanouchi K and Midorikawa K 2016 Sub-10 fs control of dissociation pathways in the hydrogen molecular ion with a few-pulse attosecond pulse train *Nat. Commun.* **7** 12835
- [142] Niikura H, Villeneuve D M and Corkum P B 2006 Controlling vibrational wave packets with intense, few-cycle laser pulses *Phys. Rev. A* **73** 21402
- [143] Ergler T, Rudenko A, Feuerstein B, Zrost K, Schröter C D, Moshhammer R and Ullrich J 2006 Spatiotemporal imaging of ultrafast molecular motion: collapse and revival of the D₂ nuclear wave packet *Phys. Rev. Lett.* **97** 193001
- [144] Bocharova I, Mashiko H, Magrakvelidze M, Ray D, Ranitovic P, Cocke C and Litvinyuk I 2008 Direct Coulomb-explosion imaging of coherent nuclear dynamics induced by few-cycle laser pulses in light and heavy hydrogen *Phys. Rev. A* **77** 53407
- [145] Légaré F, Lee K F, Bandrauk A D, Villeneuve D M and Corkum P B 2006 Laser Coulomb explosion imaging for probing ultra-fast molecular dynamics *J. Phys. B: At. Mol. Opt. Phys.* **39** S503

- [146] Xu H, Li Z, He F, Wang X, Atia-Tul-Noor A, Kielpinski D, Sang R T and Litvinyuk I V 2017 Observing electron localization in a dissociating H_2^+ molecule in real time *Nat. Commun.* **8** 15849
- [147] Schmidt L P H, Jahnke T, Czasch A, Schöffler M, Schmidt-Böcking H and Dörner R 2012 Spatial imaging of the H_2^+ vibrational wave function at the quantum limit *Phys. Rev. Lett.* **108** 73202
- [148] Gong X *et al* 2016 Pathway-resolved photoelectron emission in dissociative ionization of molecules *Optica* **3** 643–6
- [149] Hu H, Xu H, Bai Y, Sang R T, Litvinyuk I V, Liu P and Li R 2016 Wavelength and intensity effects on the dissociation of H_2^+ in intense laser fields *Phys. Rev. A* **94** 53415
- [150] Xu H, He F, Kielpinski D, Sang R T and Litvinyuk I V 2015 Experimental observation of the elusive double-peak structure in R-dependent strong-field ionization rate of H_2^+ *Sci. Rep.* **5** 13527
- [151] Gibson G N, Li M, Guo C and Neira J 1997 Strong-field dissociation and ionization of H_2^+ using ultrashort laser pulses *Phys. Rev. Lett.* **79** 2022–5
- [152] Huismans Y *et al* 2011 Time-resolved holography with photoelectrons *Science* **331** 61–4
- [153] Staudte A *et al* 2009 Angular tunneling ionization probability of fixed-in-space H_2 molecules in intense laser pulses *Phys. Rev. Lett.* **102** 33004
- [154] Stapelfeldt H and Seideman T 2003 Colloquium: aligning molecules with strong laser pulses *Rev. Mod. Phys.* **75** 543
- [155] Magrakvelidze M, He F, De S, Bocharova I, Ray D, Thumm U and Litvinyuk I V 2009 Angular dependence of the strong-field ionization measured in randomly oriented hydrogen molecules *Phys. Rev. A* **79** 33408
- [156] Wu J *et al* 2013 Understanding the role of phase in chemical bond breaking with coincidence angular streaking *Nat. Commun.* **4** 2177
- [157] Palacios A, Gonzalez-Castrillo A and Martin F 2014 Molecular interferometer to decode attosecond electron-nuclear dynamics *Proc. Natl Acad. Sci.* **111** 3973–8
- [158] Xie X, Roither S, Kartashov D, Zhang L, Baltuška A and Kitzler M 2016 Channel-resolved subcycle interferences of electron wave packets emitted from H_2 in two-color laser fields *High Power Laser Sci. Eng.* **4** e40
- [159] Ergler T, Rudenko A, Feuerstein B, Zrost K, Schröter C D, Moshhammer R and Ullrich J 2005 Time-resolved imaging and manipulation of H_2 fragmentation in intense laser fields *Phys. Rev. Lett.* **95** 14–7
- [160] Alnaser A S and Litvinyuk I V 2017 Subfemtosecond directional control of chemical processes in molecules *J. Phys. B: At. Mol. Opt. Phys.* **50** 32002
- [161] Li H, Gong X, Lin K, de Vivie-Riedle R, Tong X M, Wu J and Kling M F 2017 Sub-cycle directional control of the dissociative ionization of H_2 in tailored femtosecond laser fields *J. Phys. B: At. Mol. Opt. Phys.* **50** 172001
- [162] Roudnev V and Esry B 2007 General theory of carrier-envelope phase effects *Phys. Rev. Lett.* **99** 220406
- [163] Staudte A *et al* 2007 Attosecond strobing of two-surface population dynamics in dissociating H_2^+ *Phys. Rev. Lett.* **98** 73003
- [164] Chelkowski S, Bandrauk A D, Staudte A and Corkum P B 2007 Dynamic nuclear interference structures in the Coulomb explosion spectra of a hydrogen molecule in intense laser fields: reexamination of molecular enhanced ionization *Phys. Rev. A* **76** 13405
- [165] Kelkensberg F, Sansone G, Ivanov M Y and Vrakking M 2011 A semi-classical model of attosecond electron localization in dissociative ionization of hydrogen *Phys. Chem. Chem. Phys.* **13** 8647–52
- [166] Hepburn J W and Brumer P 1988 Simplified laser control of unimolecular reactions: simultaneous (w1, 03) excitation moshe shapiro *Chem. Phys. Lett.* **149** 451
- [167] Charron E, Giusti-Suzor A and Mies F H 1993 Two-color coherent control of H_2^+ photodissociation in intense laser fields *Phys. Rev. Lett.* **71** 692–5
- [168] Charron E, Giusti-Suzor A and Mies F H 1994 Fragment angular distribution in one- and two-color photodissociation by strong laser fields *Phys. Rev. A* **49** 641–4
- [169] Charron E, Giusti-Suzor A and Meis F H 1995 Coherent control of photodissociation in intense laser fields *J. Chem. Phys.* **103** 7359
- [170] Chelkowski S, Zamojski M and Bandrauk A D 2001 Laser-phase directional control of photofragments in dissociative ionization of H_2^+ using two-color intense laser pulses *Phys. Rev. A* **63** 23409
- [171] Sheehy B, Walker B and DiMauro L F 1995 Phase control in the two-color photodissociation of HD^+ *Phys. Rev. Lett.* **74** 4799–802
- [172] Thompson M R, Thomas M K, Taday P F, Posthumus J H, Langley A J, Frasinski L J and Codling K 1997 One and two-colour studies of the dissociative ionization and Coulomb explosion of H_2 with intense Ti:sapphire laser pulses *J. Phys. B: At. Mol. Opt. Phys.* **30** 5755
- [173] Liu K, Hong W, Zhang Q and Lu P 2011 Wavelength dependence of electron localization in the laser-driven dissociation of H_2^+ *Opt. Express* **19** 26359–69
- [174] Liu K, Zhang Q and Lu P 2012 Enhancing electron localization in molecular dissociation by two-color mid- and near-infrared laser fields *Phys. Rev. A* **86** 33410
- [175] Znakovskaya I *et al* 2012 Subcycle controlled charge-directed reactivity with few-cycle midinfrared pulses *Phys. Rev. Lett.* **108** 63002
- [176] Wanie V, Ibrahim H, Beaulieu S, Thiré N, Schmidt B E, Deng Y, Alnaser A S, Litvinyuk I V, Tong X-M and Légaré F 2016 Coherent control of D_2/H_2 dissociative ionization by a mid-infrared two-color laser field *J. Phys. B: At. Mol. Opt. Phys.* **49** 25601
- [177] Kremer M *et al* 2009 Electron localization in molecular fragmentation of H_2 by carrier-envelope phase stabilized laser pulses *Phys. Rev. Lett.* **103** 213003
- [178] Xu H, Maclean J-P, Laban D E, Wallace W C, Kielpinski D, Sang R T and Litvinyuk I V 2013 Carrier-envelope-phase-dependent dissociation of hydrogen *New J. Phys.* **15** 23034
- [179] Gong X, He P, Song Q, Ji Q, Pan H, Ding J, He F, Zeng H and Wu J 2014 Two-dimensional directional proton emission in dissociative ionization of H_2 *Phys. Rev. Lett.* **113** 203001
- [180] Wang Z, Liu K, Lan P and Lu P 2015 Steering the electron in dissociating H_2^+ via manipulating two-state population dynamics by a weak low-frequency field *Phys. Rev. A* **91** 43419
- [181] Xu H, Hu H, Tong X-M, Liu P, Li R, Sang R T and Litvinyuk I V 2016 Coherent control of the dissociation probability of H_2^+ in w-3w two-color fields *Phys. Rev. A* **93** 63416
- [182] Sansone G, Kelkensberg F, Morales F, Mart F and Vrakking M J J 2012 Attosecond time-resolved electron dynamics in the hydrogen molecule *IEEE J. Sel. Top. Quantum Electron.* **18** 520–30
- [183] Singh K P *et al* 2010 Control of electron localization in deuterium molecular ions using an attosecond pulse train and a many-cycle infrared pulse *Phys. Rev. Lett.* **104** 23001
- [184] He F, Becker A and Thumm U 2008 Strong-field modulated diffraction effects in the correlated electron-nuclear motion in dissociating H_2^+ *Phys. Rev. Lett.* **101** 1–4
- [185] He F, Ruiz C and Becker A 2008 Coherent control of electron wave packets in dissociating H_2^+ *J. Phys. B: At. Mol. Opt. Phys.* **41** 81003

- [186] Kelkensberg F *et al* 2011 Attosecond control in photoionization of hydrogen molecules *Phys. Rev. Lett.* **107** 43002
- [187] Fischer A *et al* 2013 Electron localization involving doubly excited states in broadband extreme ultraviolet ionization of H₂ *Phys. Rev. Lett.* **110** 213002
- [188] Nguyen-Dang T T, Lefebvre C, Abou-Rachid H and Atabek O 2005 Floquet representation of absolute phase and pulse-shape effects on laser-driven molecular photodissociation *Phys. Rev. A* **71** 23403
- [189] Lafosse A, Lebech M, Brenot J C C, Guyon P M M, Spielberger L, Jagutzki O, Houver J C and Doweck D 2003 Molecular frame photoelectron angular distributions in dissociative photoionization of H₂ in the region of the Q_1 and Q_2 doubly excited states *J. Phys. B: At. Mol. Opt. Phys.* **36** 4683
- [190] Waitz M *et al* 2016 Electron localization in dissociating H₂⁺ by retroaction of a photoelectron onto its source *Phys. Rev. Lett.* **116** 43001
- [191] Serov V V and Kheifets A S 2014 p-H symmetry breaking in dissociative photoionization of H₂ due to the molecular ion interacting with the ejected electron *Phys. Rev. A* **89** 31402
- [192] Jiang S, Yu C, Yuan G, Wu T and Lu R 2017 Dissociation and ionization of quasi-periodically vibrating H₂⁺ in intense few-cycle mid-infrared laser fields *Sci. Rep.* **7** 42086
- [193] de Boer M P and Muller H G 1992 Observation of large populations in excited states after short-pulse multiphoton ionization *Phys. Rev. Lett.* **68** 2747–50
- [194] Jones R R, Schumacher D W and Bucksbaum P H 1993 Population trapping in Kr and Xe in intense laser fields *Phys. Rev. A* **47** R49–52
- [195] Akagi H, Otake T, Staudte A, Shiner A, Turner F, Dörner R, Villeneuve D M and Corkum P B 2009 Laser tunnel ionization from multiple orbitals in HCl *Science* **325** 1364–7
- [196] Nubbemeyer T, Gorling K, Saenz A, Eichmann U and Sandner W 2008 Strong-field tunneling without ionization *Phys. Rev. Lett.* **101** 233001
- [197] Emmanouilidou A, Lazarou C, Staudte A and Eichmann U 2012 Routes to formation of highly excited neutral atoms in the breakup of strongly driven H₂ *Phys. Rev. A* **85** 11402
- [198] Emmanouilidou A and Lazarou C 2012 Multiple electron trapping in the fragmentation of strongly driven molecules *New J. Phys.* **14** 115010
- [199] Price H, Lazarou C and Emmanouilidou A 2014 Toolkit for semiclassical computations for strongly driven molecules: frustrated ionization of H₂ driven by elliptical laser fields *Phys. Rev. A* **90** 53419
- [200] Eichmann U, Nubbemeyer T, Rottke H and Sandner W 2009 Acceleration of neutral atoms in strong short-pulse laser fields *Nature* **461** 1261–4
- [201] Eichmann U, Saenz A, Eilzer S, Nubbemeyer T and Sandner W 2013 Observing Rydberg atoms to survive intense laser fields *Phys. Rev. Lett.* **110** 203002
- [202] Larimian S, Erattupuzha S, Lemell C, Yoshida S, Nagele S, Maurer R, Baltuška A, Burgdörfer J, Kitzler M and Xie X 2016 Coincidence spectroscopy of high-lying Rydberg states produced in strong laser fields *Phys. Rev. A* **94** 33401
- [203] Larimian S *et al* 2017 Localizing high-lying Rydberg wave packets with two-color laser fields *Phys. Rev. A* **96** 21403
- [204] Mi Y, Camus N, Fechner L, Laux M, Moshhammer R and Pfeiffer T 2017 Electron-nuclear coupling through autoionizing states after strong-field excitation of H₂ molecules *Phys. Rev. Lett.* **118** 183201
- [205] Palacios A, González-Castrillo A and Martín F 2014 Electron streaking and dissociation in laser-assisted photoionization of molecular hydrogen *J. Phys. B: At. Mol. Opt. Phys.* **47** 124013
- [206] Eckle P, Pfeiffer A N, Cirelli C, Staudte A, Dörner R, Muller H G, Büttiker M and Keller U 2008 Attosecond ionization and tunneling delay time measurements in helium *Science* **322** 1525–9
- [207] Heuser S, Sabbar M, Boge R, Cirelli C and Keller U 2014 Photoionization time delay in molecular hydrogen *19th Int. Conf. Ultrafast Phenomena* 09.Wed.C.7 (<https://doi.org/10.1364/UP.2014.09.Wed.C.7>)
- [208] Cattaneo L, Vos J, Lucchini M, Cirelli C and Keller U 2016 Asymmetric Wigner time delay in CO photoionization *Int. Conf. on Ultrafast Phenomena OSA Technical Digest* (Santa Fe, New Mexico: Optical Society of America) p UM2B.3
- [209] Serov V V, Derbov V L and Sergeeva T A 2013 Interpretation of time delay in the ionization of two-center systems *Phys. Rev. A* **87** 63414
- [210] Serov V V and Kheifets A S 2016 Angular anisotropy of time delay in XUV + IR photoionization of H₂⁺ *Phys. Rev. A* **93** 63417
- [211] Abu-samha M and Madsen L B 2016 Alignment dependence of photoelectron momentum distributions of atomic and molecular targets probed by few-cycle circularly polarized laser pulses *Phys. Rev. A* **94** 23414
- [212] Abu-samha M and Madsen L B 2017 Interplay between pulse parameters and alignment of H₂⁺ in strong laser fields *J. Phys.: Conf. Ser.* **869** 12009
- [213] Jiang Y H *et al* 2010 Ultrafast extreme ultraviolet induced isomerization of acetylene cations *Phys. Rev. Lett.* **105** 263002
- [214] Jiang Y H *et al* 2013 Ultrafast dynamics in acetylene clocked in a femtosecond XUV stopwatch *J. Phys. B: At. Mol. Opt. Phys.* **46** 164027
- [215] Ibrahim H *et al* 2014 Tabletop imaging of structural evolutions in chemical reactions demonstrated for the acetylene cation *Nat. Commun.* **5** 4422
- [216] Hishikawa A, Matsuda A, Fushitani M and Takahashi E 2007 Visualizing recurrently migrating hydrogen in acetylene dication by intense ultrashort laser pulses *Phys. Rev. Lett.* **99** 258302
- [217] Liekhus-Schmaltz C E *et al* 2015 Ultrafast isomerization initiated by x-ray core ionization *Nat. Commun.* **6** 1–25
- [218] Wolter B *et al* 2016 Ultrafast electron diffraction imaging of bond breaking in di-ionized acetylene *Science* **354** 308–12
- [219] Blaga C I, Xu J, DiChiara A D, Sistrunk E, Zhang K, Agostini P, Miller T A, DiMauro L F and Lin C D 2012 Imaging ultrafast molecular dynamics with laser-induced electron diffraction *Nature* **483** 194–7
- [220] Pullen M G *et al* 2015 Imaging an aligned polyatomic molecule with laser-induced electron diffraction *Nat. Commun.* **6** 7262
- [221] Lee C, Lin Y-C, Lee S-H, Lee Y-Y, Tseng C-M, Lee Y-T and Ni C-K 2017 Advantage of spatial map ion imaging in the study of large molecule photodissociation *J. Chem. Phys.* **147** 13904
- [222] Tsai S-T, Lin C-K, Lee Y T and Ni C-K 2001 Multimass ion imaging detection: application to photodissociation *Rev. Sci. Instrum.* **72** 1963–9
- [223] Liang Y, Augst S, Chin S L, Beaudoin Y and Chaker M 1994 High harmonic generation in atomic and diatomic molecular gases using intense picosecond laser pulses—a comparison *J. Phys. B: At. Mol. Opt. Phys.* **27** 5119
- [224] Itatani J, Levesque J, Zeidler D, Niikura H, Pepin H, Kieffer J C, Corkum P B and Villeneuve D M 2004 Tomographic imaging of molecular orbitals *Nature* **432** 867–71
- [225] Marangos J P 2016 Development of high harmonic generation spectroscopy of organic molecules and biomolecules *J. Phys. B: At. Mol. Opt. Phys.* **49** 132001

- [226] Velotta R, Hay N, Mason M B, Castillejo M and Marangos J P 2001 High-order harmonic generation in aligned molecules *Phys. Rev. Lett.* **87** 183901
- [227] Kanai T, Minemoto S and Sakai H 2005 Quantum interference during high-order harmonic generation from aligned molecules *Nature* **435** 470–4
- [228] Vozzi C *et al* 2005 Controlling two-center interference in molecular high harmonic generation *Phys. Rev. Lett.* **95** 153902
- [229] Kraus P M *et al* 2015 Measurement and laser control of attosecond charge migration in ionized iodoacetylene *Science* **350** 790–5
- [230] von den Hoff P, Znakovskaya I, Kling M F and de Vivie-Riedle R 2009 Attosecond control of the dissociative ionization via electron localization: a comparison between D₂ and CO *Chem. Phys.* **366** 139–47
- [231] Kling M F, von den Hoff P, Znakovskaya I and de Vivie-Riedle R 2013 (Sub-)femtosecond control of molecular reactions via tailoring the electric field of light *Phys. Chem. Chem. Phys.* **15** 9448–67
- [232] Xie X *et al* 2014 Electronic predetermination of ethylene fragmentation dynamics *Phys. Rev. X* **4** 21005
- [233] Kübel M *et al* 2014 Strong-field control of the dissociative ionization of N₂O with near-single-cycle pulses *New J. Phys.* **16** 65017
- [234] Kübel M *et al* 2016 Steering proton migration in hydrocarbons using intense few-cycle laser fields *Phys. Rev. Lett.* **116** 193001
- [235] Miura S *et al* 2014 Carrier-envelope-phase dependence of asymmetric CD bond breaking in C₂D₂ in an intense few-cycle laser field *Chem. Phys. Lett.* **595–596** 61–6
- [236] Xie X *et al* 2012 Attosecond-recollision-controlled selective fragmentation of polyatomic molecules *Phys. Rev. Lett.* **109** 243001
- [237] Schiffrin A *et al* 2013 Optical-field-induced current in dielectrics *Nature* **493** 70–4
- [238] Ahn B *et al* 2017 Attosecond-controlled photoemission from metal nanowire tips in the few-electron regime *APL Photonics* **2** 36104
- [239] Wells E *et al* 2013 Adaptive strong-field control of chemical dynamics guided by three-dimensional momentum imaging *Nat. Commun.* **4** 2895
- [240] Lanyon B P *et al* 2010 Towards quantum chemistry on a quantum computer *Nat. Chem.* **2** 106–11
- [241] Bryan W *et al* 2007 Isolated vibrational wavepackets in H₂⁺: defining superposition conditions and wavepacket distinguishability *Phys. Rev. A* **76** 53402
- [242] Yuan K-J, Lu H and Bandrauk A D 2011 Linear- and circular-polarization photoionization angular distributions in H₂ and D₂⁺ by attosecond XUV laser pulses *Phys. Rev. A* **83** 43418
- [243] Benabid F, Knight J C, Antonopoulos G and Russell P S J 2002 Stimulated Raman scattering in hydrogen-filled hollow-core photonic crystal fiber *Science* **298** 399–402
- [244] Wang Z, Yu F, Wadsworth W J and Knight J C 2014 Efficient 1.9 μm emission in H₂-filled hollow core fiber by pure stimulated vibrational Raman scattering *Laser Phys. Lett.* **11** 105807
- [245] Mullard A 2017 FDA approves first deuterated drug *Nat. Rev. Drug Discov.* **16** 305