Strong-field ionization of molecules by few-cycle pulses.

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Abstract. Few-cycle pulses of 800 nm light cause ionization and dissociation of triatomic molecules like H₂O and CS₂ in the temporal regime where only electron rescattering dominates the laser-molecule interaction. In case of ionization of H₂O, significantly higher amounts of kinetic energy are released upon dissociation into atomic fragments. However, the case of CS₂ is somewhat special in that the wave packet of the rescattered electron destructively interferes with the antibonding π orbital of CS₂⁺ such that rescattering is also essentially turned off. Under such circumstances the dissociation channel is absent and long-lived singly, doubly, and triply charged molecular ions dominate the mass spectrum in the few-cycle regime. This brings to the fore the importance of molecular symmetry in strong-field ionization. Ultrafast atomic rearrangements are also observed: H atoms in H₂O are rearranged by strong optical fields generated by intense 9.3 fs laser pulses to form a new bond leading to H₂⁺; experiments show that this bond formation occurs within a single laser pulse.

1. Introduction

Molecular dynamics in intense optical fields is an area of contemporary research that continues to yield unexpected phenomena that serve to constantly invigorate the science that underpins the behaviour of matter in strong fields [1]. In the present context, strong fields are those where the magnitudes of the laser-generated optical field become comparable to the intramolecular Coulombic fields. The overall laser-molecule interaction is then dominated by ionization of one or more electrons and the consequent breaking of one or more bonds. Most studies of how molecules behave in strong fields have relied on ion yields measured with infrared pulses that are a few tens to a few hundred femtoseconds long [1-5], and it is established that enhanced ionization (EI), spatial alignment, and rescattering ionization are the main drivers of the overall dynamics [1]. Dynamic alignment of molecules like O₂ and N₂ does not occur in the few-cycle domain [2] as the duration of the optical field is far too short for polarization-induced torque to act on the molecular axis. Similarly, EI is effectively “switched off” as nuclei do not have enough time to move to the critical distance at which the ionization propensity is enhanced [3]. Hence, few-cycle dynamics is expected to be dominated only by electron rescattering. It may be possible to exercise some degree of control on the molecular dynamics by tuning the intensity and duration of the ultrashort optical field [6]. But is there any role of the quantal structure of the molecule itself? Does molecular symmetry, a consequence of the quantum-mechanically determined electronic structure have any role in the few-cycle, strong field regime? Does ultrafast chemistry, involving the formation new bonds, have any role in the few-cycle, strong field
regime? This Progress Report seeks to highlight recent experimental work that is concerned with these questions.

The two facets of our work that we focus on here are the following. i) Few-cycle pulses provides us with the ability to disentangle effects of different processes in strong-field molecular dynamics and of possibly being able to exercise some measure of control on the overall dynamics by tuning the intensity and duration of the ultrashort optical field. We have made measurements in which the quantum mechanical properties of the irradiated molecule also come into the reckoning: we show that non-bonding orbitals of the type encountered in the ground electronic state of CS$_2^+$ can affect the overall dynamics by destructively interfering with the rescattered electron wavepacket. ii) Exposing molecules to intense field from ultrashort laser inevitably results in field-induced ejection of electrons, leaving behind two or more ionic cores that experience strong Coulombic repulsion that, in turn, gives rise to the rupturing of one or more bonds. That fact that strong fields readily break bonds is well established. What we seek to address here is whether bonds can be 

2. Experimental details
Most of the measurements performed in the few-cycle ionization dynamics has, in the main, been conducted using the hollow-fiber pulse compression technique [6]. Due to simplicity in the generation of few-cycle pulses, filamentation in gas-filled tubes is demonstrated as an alternative [7] and it is this method that we have adopted to generate four-cycle pulses. Our experimental method (see Fig.1) has recently been presented in detail elsewhere [8]; in brief, we used 0.4 mJ, 50 fs laser pulses centered at 800 nm (1 kHz repetition rate) from a Ti:sapphire amplifier. After passing through an aperture we loosely focused laser beam using a metal-coated spherical mirror ($f$=1 m) inside a 1.5-m-long tube containing Ar gas at 1.2 atm. The central part of the resulting broadband light was compressed by a set of chirped dielectric mirrors (CDM) to produce 15 fs pulse (0.3 mJ energy). These pulses were then passed through another aperture and focused inside a second 1-m-long tube filled with Ar at 0.9 atm. The generated broadband light was then again compressed using a second pair of CDM to yield ~9-11 fs pulses (see Fig.1) with ~0.2 mJ energy. The few-cycle pulses were characterized using spectral phase interferometry for direct electric field reconstruction (SPIDER) and were then directed through a 300 μm fused silica window into an ultrahigh vacuum chamber (UHV) in which the laser-molecule interaction occurred at pressures of ~10$^{-9}$ Torr. The few-cycle pulses were precompensated for chirp and focused within the UHV chamber by a spherical mirror ($f$ =5 cm). Ion analysis was by conventional, linear time-of-flight (TOF) methods.

3. Results and Discussion
Fig. 2 shows a typical TOF spectrum obtained with few-cycle pulses at intensity 5×10$^{15}$ W cm$^{-2}$. Our measurement shows two striking features compared to long pulses (40 fs): i) the dominance of peaks corresponding to different charge states of molecular CS$_2$, and ii) the absence of fragment ion peaks that usually dominate spectra obtained with longer pulses [9]. The fragmentation pattern obtained with 40 fs pulses [9] are clearly very different, with energetic atomic fragments being produced up to charge state 4+ (S$^+$, S$^{2+}$ are measured to have ~4 eV energy), the precursors being excited electronic states of CS$_2$ $^g$+ ($q$>1) that Coulomb explode.
Long-lived molecular ions in high charge states, such as \( \text{CS}_2^{2+}, \text{CS}_2^{3+} \), are observed. The major difference between spectra for few cycle pulses and longer (40 fs) pulses lies in the remarkable suppression of fragmentation channels when few-cycle pulses are used. We have considered the possibility that the broad spectral bandwidth of few-cycle light might play a role by making separate measurements using broadband light covering the spectral range 500–900 nm. This supercontinuum was generated by irradiating 1-cm-thick BK-7 glass with 40 fs pulses of intense 800 nm light; the methodology adopted by us for such white light experiments on molecules, including estimation of the white light intensity, has been described recently [10]. The measurement using white light also shows fragments \( \text{S}^+ \) and \( \text{CS}^+ \), whose yields relative to, say, \( \text{CS}_2^{2+} \) are consistent with single-color 40 fs data. We believe that the broadband nature of our few-cycle pulses is not an important factor in suppressing \( \text{CS}_2 \) fragmentation. The other factor pointing to the importance of the quantal description of the irradiated molecule originates from observation of fragments like \( \text{S}^+ \) and \( \text{CS}^+ \) when we use single color 40 fs pulses.

The fragments \( \text{S}^+ \) and \( \text{CS}^+ \) cannot result from direct ionization of \( \text{CS}_2 \) since Franck-Condon factors preclude vertical access to the dissociation continua of the \( X, A \), and \( B \) electronic states of \( \text{CS}_2^+ \).
base this on the absence of any peak in the CS$_2$ photoelectron spectrum [11] near the appearance thresholds for S$^+$ and CS$^+$ fragments, and also from results of photoion-photoelectron coincidence measurements [12] that establish the equilibrium structure of CS$_2^+$ being close to that of CS$_2$. The next higher ionic state, C, lies above the dissociation limits S$^{++}$CS and S+CS$^+$ and is known to predissociate [11]. At intensities of 5×10$^{15}$ W cm$^{-2}$ used in our experiment the near absence of S$^+$ and CS$^+$ fragments appears to indicate that the optical field is not strong enough to allow direct, vertical access to the C-state for few-cycle pulses. In the case of longer-pulse (40 fs) experiments, however, the enhanced ionization process sets in, resulting in a lengthening of the C–S bond.

This has two effects. First, there is now an increased possibility of accessing the C state and higher excited states. Second, the bond lengthening gives rise to the possibilities for excitations in regions that lie outside the Franck-Condon region of CS$_2$. It is the population of higher excited electronic states of CS$_2^+$ that contribute in the long pulse regime and these states are precursors of the fragments that we observed in 40 fs experiments [9]. The absence of these fragments in few-cycle spectra is clear and direct signature that EI switches off in the few-cycle domain.

Electron rescattering is known to occur on ultrafast time scales and, as we discuss below, is another area where quantal considerations cannot be ignored. In recent experiments on double ionization of H$_2$ [6] induced by intense 15 fs pulses it was observed that the first return recollision essentially dominates the rescattering dynamics whereas for longer pulses, the third return recollision might assume importance. Recent experiments on methane [2] also draw attention to the importance of the first return recollision when 8 fs pulses are used: no dications were observed for 8 fs pulses but for longer pulses they started appearing. In the case of CS$_2$, even with EI being switched off in the few-cycle regime, if rescattering were to come into play, electron excitation from the ground state of neutral CS$_2$ to the C state and higher excited states would be energetically possible at intensities of 5×10$^{15}$ W cm$^{-2}$ and, consequently, S$^+$ and CS$^+$ fragments would be observed even with few-cycle pulses. However, Fig. 2 shows that long-lived dication and trication parent ions are formed in the

**Figure** 2. Time-of-flight spectrum of CS$_2$ measured at 5×10$^{15}$ W cm$^{-2}$ intensity with 11 fs pulses of 800 nm light [9]. Note the preponderance of molecular (as opposed to atomic) ions.
intensity range $10^{15}$ W cm$^{-2}$, presumably at the expense of fragmentation channels. This is an indication that rescattering might also be “switched off”. Intense field S-matrix calculations [13] have predicted suppression of ionization in homonuclear molecules with an antibonding valence orbital, like the outermost $\pi_g$ orbital in O$_2$, but not for molecules with a bonding valence orbital, like $\sigma_g$ in N$_2$. The shape of the $\pi_g$ orbital causes destructive interference by the two nuclei of the ionized electron’s wave packet; electron spectroscopy on molecules like N$_2$ and O$_2$ irradiated by strong laser fields of 100 fs duration has recently validated this predication [14].

The switching off of rescattering in our experiments is not because of the ultrashort duration of pulses that we use but because of the quantum mechanical nature of CS$_2$’s outermost $2\pi_g$ orbital that has a strikingly non-bonding character. The returning electron wave packet destructively interferes with the large spatial extent of this $\pi$-orbital, that leads to effective suppression of the rescattering process. The returning electron’s energy is hence not available for electronic excitation to highly excited CS$_2$ $^*$ states that allow dissociation into S$^+$CS and S+CS$^*$. The above discussion pertains to quantal interference affecting the rescattered electron wave packet while the S-matrix theory [13] treats interferences in the ejected electron channel. Theory predicts that such effects would be effective for short molecular bonds [13] while our measurements on CS$_2$ seem to indicate some measure of persistence of interference even for long bonds.

We now discuss results pertaining to H$_2$O (see Fig. 3.) when it is exposed to few cycles pulses of intensity in the range of $10^{15}$ W cm$^{-2}$ that bring to the fore the non-adiabatic nature of laser-molecule interactions in the few-cycle domain [13]. Non-adiabaticity gives rise to the ionized electron being exposed to higher amplitudes of the applied field, enabling recollision with the molecular core to occur with higher energies, resulting in ionization to H$_2$O$^{q+*}$ ($q>2$) states that are electronically ‘hotter’. The dissociation of such highly excited H$_2$O$^{q+*}$ states gives rise to protons that are more energetic than would be the case if they are generated by lower-energy states of H$_2$O$^q$. We note that quantum chemical studies of multiple-charged molecular states of diatomic molecules have shown that higher degrees of electronic excitation result in larger kinetic energy releases, asymptotically converging on the Coulomb repulsion energy.

**Figure 3.** a) TOF spectrum of H$_2$O measured at an intensity of $2\times10^{15}$ W cm$^{-2}$ with 10-fs pulses of 800-nm light; b) Typical yield of H$^+$ fragments [13].
The kinetic energy spectra of protons obtained using 10 fs and 100 fs pulses are shown in Fig. 4. It is clear that in the case of longer pulses the bulk of the H\(^+\) fragments possess kinetic energies of \(\sim 1.5\) eV, with the tail of the distribution extending to 7 eV. On the other hand, the spectrum obtained with 10-fs pulses indicates the formation of much more energetic protons, with the tail of the energy distribution now extending past 15 eV.

**Figure 4.** The distribution of kinetic energies of H\(^+\) produced during irradiation of water with a) 100 fs and b) 10 fs laser pulses [15]. The peak laser intensities were the same for both pulse durations.

Recent work on H\(_2\) and D\(_2\) molecules [3] have shown that it is convenient to distinguish strong-field dynamics in terms of sequential and recollision ionization. The former occurs when H\(_2\) is irradiated at laser intensities below \(\sim 10^{14}\) W cm\(^{-2}\) while the latter dominates at higher intensity values. As already discussed enhanced ionization that plays an effective role in sequential ionization is of little or no consequence in the few-cycle domain. If sequential ionization is assumed to dominate, time delay between the field-induced ejection of the first and second electrons would be observed in the energy spectrum. After ejection of the first electron, giving rise to the formation of H\(_2\)O\(^+\), nonlinear and non-resonant coupling between the \(^2B_1\) lowest-energy state of H\(_2\)O\(^+\) and the appropriate dissociative electronic state of the molecular ion would result in a nuclear wavepacket being launched such that, during the evolution of this nuclear wavepacket and the accompanying lengthening of the O-H bonds, a second electron would be field ionized. The O-H bond length at which double ionization occurs would give rise to H\(^+\) fragment with less kinetic energy than that which would result if there was an instantaneous nonsequential ejection of two electrons. The energy spectrum for the sequential ionization process would thus exhibit lower-energy features than in the case of recollision ionization. Our measurement show that for water, recollisions give rise to energetic proton formation when intense 10-fs pulses are used to irradiate water molecules at intensity levels in the \(10^{15}\) W cm\(^{-2}\) range and higher [15].

We discuss very recent results concerned with bond formation in strong and ultrashort fields. We have seen that molecular ionization totally dominates in the few-cycle regime[13], in contrast to the situation with 40–100 fs pulses wherein fragments like O\(^q\) (\(q=2–5\)) are obtained at 5%–10% yield levels (normalized to H\(_2\)O\(^+\)) at similar intensities \((2\times 10^{15}\) W cm\(^{-2}\)). Fragments such as OH\(^+\) and O\(^+\) have yield levels of \(\sim 2\%–5\%\). We would like to draw attention to the clear signatures that are obtained by us for formation of H\(_2\)\(^+\) ions at 1% yield levels [16]. We made measurements in the intensity range \(2–8 \times 10^{15}\) W cm\(^{-2}\) and at different operating pressures to confirm that the H\(_2\)\(^+\) signal does, indeed,
Figure 5 $\text{H}_2^+$ yield at an intensity of $4 \times 10^{15}$ W cm$^{-2}$ showing, in the lower panel, the dependence of the $\text{H}_2^+$ signal on the direction of incident laser intensity polarization [16].

originate from the laser-molecule interaction and from a unimolecular process [16]. We observed essentially linear pressure dependence of the $\text{H}_2^+$ signal was obtained at pressures below $\sim 1 \times 10^{-7}$ Torr, the deviation from linear dependence at higher pressures indicating the onset of bimolecular collisions. After prolonged baking of the UHV chamber, we did not detect background $\text{H}_2^+$ signal at pressures below $2 \times 10^{-8}$ Torr. The $\text{H}_2^+$ signals were obtained in TOF spectra measured at three pressures, each well above the background pressure which was almost two orders of magnitude lower. The most significant feature of the $\text{H}_2^+$ yield is the dependence it shows on the direction of incident laser polarization. This indicates clearly that the ion is being formed within a single laser pulse. A post-pulse interaction resulting in $\text{H}_2^+$ would, clearly, not be expected to be affected by the polarization change in the incident laser pulse [16]. We note that electron-ion momentum spectroscopy has also shown that isomerisation reactions can occur on timescales of $\sim 60$ fs [17]. Moreover, the equivalence of laser-induced and ion-induced strong fields [18, and references therein] has enabled reactions to be probed on even shorter timescales using fast charged projectiles [18,19].

From a basic perspective, our few-cycle results clearly indicate a richness of the dynamics that has some hitherto-hidden facets of strong-field physics. One is the necessity of properly incorporating quantal molecular structure effects in descriptions of ionization and fragmentation dynamics in strong fields. Another is the possibility that strong fields do not merely contribute to breaking of molecular bonds; they may even coax the formation of new bonds, thus paving the way for really ultrafast chemistry!
References

[1] Yamanouchi K, Chin S L, Agostini P, and Ferrante G 2007F Progress in Ultrafast Intense Laser Science, Vols. 1–3 (Berlin, Springer).

[2] Wu Z, Wu C, Liang Q, Wang S, Liu M, Deng Y and Gong Q, 2007 J. Chem. Phys. 126, 074311

[3] Tong X M, Zhao Z X, Alnaser A S, Voss S, Cocke C L and Lin C D, 2005 J. Phys. B 38, 333; Alnaser A S, Voss S, Tong X M, Maharjan C M, Ranitovic P, Ulrich B, Osipov T, Shan B, Chang Z and Cocke C L, 2004 Phys. Rev. Lett. 93, 113003.

[4] Feuerstein T, Egler Th, Rudenko A, Zrost K, Schröter CD, Moshammer R, Ullrich J, Niederhausen T and Thumm U, 2007 Phys. Rev. Lett. 99, 153002.

[5] Litvinyuk IV, Alnaser AS, Comtois D, Ray D, Hasan AT, Kieffer J-C and Villeneuve DM, 2008 New J. Phys. 10, 083011.

[6] Nisoli M, De Silvestri S and Svelto O, 1996 Appl. Phys. Lett. 68, 2793

[7] Hauri C P, Kornelis W, Helbing F W, Heinrich A, Couairon A, Mysyrowicz A, Biegert J and Keller U, 2004 Appl. Phys. B 79, 673.

[8] Dharmadhikari A K, Dharmadhikari J A, Rajgara F A and Mathur D 2008 Opt. Express 16, 7083.

[9] Mathur D, Dharmadhikari A K, Rajgara F A and Dharmadhikari J A, 2008 Phys. Rev. A. 78, 013405.

[10] Mathur D, Rajgara F A and Dharmadhikari A K, 2007 J. Phys. Chem. A 111, 9399.

[11] Brundle C R and Turner D W, 1969 Int. J. Mass Spectrom. Ion Phys. 2, 195.

[12] Brehm B, Eland J H D, Frey R and Kustler A, 1973 Int. J. Mass Spectrom. Ion Phys. 12, 213.

[13] Muth-Böhm J, Becker A and Faisal F H M, 2000 Phys. Rev. Lett. 85, 2280.

[14] Okunishi M, Shimada K, Prümper G, Mathur D and Ueda K, 2007 J. Chem. Phys. 127, 064310.

[15] Mathur D, Dharmadhikari A K, Rajgara F A and Dharmadhikari J A, 2008 Phys. Rev. A 78, 023414

[16] Rajgara F A, Mathur D, Dharmadhikari A K and Safvan C P, 2009 J. Chem. Phys. 130, 231104.

[17] Osipov T, Cocke CL, Prior MH, Landers A, Weber Th, Jagutzki O, Schmidt L, Schmidt-Böcking H and Dörner, 2003 Phys. Rev. Lett 90, 233002.

[18] Mathur D, 2001 Phys. Rev. A 63, 032502.

[19] Jochim B, Lucking A, Doehler L, Carey S, Wells E, Parke E, Leonard M, Carnes KD and Ben-Itzhak I, 2009 J. Phys. B 42, 091002.