Matter in strong fields: from molecules to living cells

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Abstract. Strong optical fields induce multiple ionization in irradiated molecules. The ionization dynamics are governed by optical-field-induced distortions of molecular potential energy surfaces and molecular dissociation is the expected by-product. Recent experiments have even shown, quite counter-intuitively, that strong optical fields may even induce bond formation processes in molecules. All such processes are all manifestations of how intense light affects matter. In turn, matter also affects intense light. A visually dramatic manifestation of matter affecting light is obtained when ultrashort pulses of intense light propagate through condensed matter. The temporal and spatial properties of the incident light pulse are modified, and such modifications manifest themselves in an enlarged optical frequency sweep, resulting in the generation of broadband radiation (white light) known as supercontinuum production. Although the physics that governs supercontinuum generation is not properly understood, some recent progress is summarized. Novel applications of strong field phenomena are reported that are of relevance in the biomedical and life sciences.

1. Introduction
The commercial availability of table-top, high-intensity femtosecond lasers has enabled many laboratories to have ready access to light pulses with peak amplitudes that lie in the range of TW cm$^{-2}$ and more. Such light intensities are large enough to generate fields whose magnitudes are comparable to those of Coulombic fields within atoms and molecules. Irradiation of matter by such intense optical fields inevitably leads to a host of nonlinear phenomena that can only be treated in non-perturbative fashion [1]. This Progress Report will highlight two facets of light-matter interactions in the strong field regime by considering (i) how strong light affects matter and, (ii) how matter, in turn, affects strong light.

One experimental manifestation of the interaction of strong optical fields with isolated atoms and molecules is ionization: ionization of one or more electrons is inevitable in such strong fields (Fig. 1). Experimental probes of the field-matter interaction can, therefore, involve measurement of the energy spectra of electrons or ions. In the case of atoms, the strong-field ionization dynamics are adequately described by the oft-used Keldysh-Faisal-Reiss theory that has, as its foundation, consideration of a simple zero-range potential and of a single active electron in such a potential. Experiments on electrons ionized from atoms in strong fields have established the efficacy of this simple theory in rationalizing observations. Quite unexpectedly, recent experimental work is beginning to demonstrate that such an atomic description also appears quite apt for large molecules as well where one would have expected a zero-range potential to be of limited utility [2].

In the case of molecules, conventional wisdom would have it that such strong fields would only give rise to ionization and dissociation phenomena. Experimental probes of the optical-field-induced...
bond breaking process usually involve measurement of mass and energy spectra of ions that are produced. Recent experiments have also shown, quite counter-intuitively, that very strong optical fields may even induced bond formation processes in molecules [3,4]. Such processes occur on ultrafast timescales that compete with the time taken for a multiply charged molecule to Coulomb-explode [3]; bond-formation actually occurs in some molecules as a consequence of the optical-field-induced distortions of molecular potential energy surfaces! Illustrative examples in relation to the interaction of intense fields with alcohol molecules are presented in Section 2.

Ionization, molecular fragmentation and molecular bond formations are all manifestations of how intense light affects matter. In turn, matter also affects intense light. When gas-phase atoms and molecules are irradiated by intense laser light, the resulting generation of high harmonics constitutes an indirect manifestation of this reverse process. A visually more dramatic manifestation of matter affecting light is obtained when ultrashort pulses of intense light propagate through condensed matter. The temporal and spatial properties of the incident light pulse are modified, and such modifications manifest themselves in an enlarged optical frequency sweep, resulting in the generation of broadband radiation known as supercontinuum, or white light, production [5]. Much remains to be elucidated about the physics that governs the generation of broadband radiation as a result of propagation effects. However, the absence of a proper, all-encompassing theoretical understanding of the physics that governs propagation effects in the ultrafast and high intensity regime has not precluded the development of new methodologies and applications [6], and some of these are discussed in Section 3 in the context of a novel application of strong field phenomena to biomedical engineering and the life sciences [7].

2. Breaking and forming bonds in strong optical fields

Strong optical fields are generated when photon densities become very large, of the order of $10^{36}$ photons s$^{-1}$ cm$^{-2}$ and more. As indicated in Fig. 1, such fields lead to gross distortions of atomic radial potential functions such that ionization becomes inevitable, either by tunnelling or, with much higher
light intensities, by over-the-barrier ionization. In the case of molecules, ejection of two or more electrons due to optical-field-induced distortion of potential energy surfaces inevitably leads to the breakage of one or more molecular bond. Examples of optical-field-induced bond breakages in methanol, ethanol and dodecanol molecules, all linear alcohols, are shown in Fig. 2. The individual bars denote the propensity for fragmentation into specific channels that lead to the ions indicated on the horizontal axes in the figure; the hatched bars denote the situation when linearly polarized light is used and the solid bars the corresponding situation obtained with circularly polarized light. The differences between the two sets of bars bring to the fore a special facet of molecular ionization in strong optical fields: electrons that are field ionized continue to ‘feel’ the effect of the optical field. The wavepacket that describes the ejected electron initially moves away from the vicinity of the molecule. In the case of optical fields that are linearly polarized, the electronic wavepacket is pulled back towards the molecular core half a cycle after it was initially formed. For an optical field \( E \), of angular frequency \( \omega \), the ponderomotive potential that acts on the electron is given by \( V = (eE)/(m\omega) \).

For 800 nm photons at an intensity of \( 10^{16} \) W cm\(^{-2} \), the mean amplitude of oscillation, which can be expressed as \( (eE)/(m\omega^2) \), is as large as 7 nm. The probability that the electron will rescatter off the molecular core depends on the laser phase, and on the initial velocity and phase of the electron wavepacket. In the case of circularly polarized light, there is no obvious direction that can be attributed to the optical field and, consequently, electron rescattering does not occur.

Figure 2 shows typical fragment ion yields that are obtained when three different alcohol molecules are irradiated by linearly- and circularly-polarized, 806 nm light at intensities in the \( 10^{16} \) W cm\(^{-2} \) range. These spectra were measured using intensity values that ensured that the optical fields experienced by the molecules were the same for both polarization states. Circular polarization results in a distinct suppression of fragment ion yields in all the alcohols. This observation also holds for the doubly-charged molecular ions like, for instance, \( \text{CH}_3\text{OH}^{2+} \). The observation of dications in time-of-flight spectra indicates that their lifetimes against unimolecular dissociation lie at least in the microsecond range. Figure 2 also shows \( \text{C}^q \) (\( q=1-3 \)), \( \text{O}^{2+} \) atomic fragments as well as \( \text{CH}^+ \) and \( \text{CH}_3^+ \) molecular fragment ions obtained from ethanol. As in the case of methanol, suppression of fragment ion yields with circular polarization is clearly observed. The spectrum for a larger alcohol, dodecanol, also confirms that ion yield suppression occurs with circular polarization. This dependence of the fragmentation dynamics on polarization has been rationalized using a simple electron rescattering model. Circular polarization switches “off” electron rescattering and leads to suppression of multiple ionization and molecular fragmentation. The degree of suppression depends upon the amount of energy transfer from the optical field to the molecule [8]: the larger the energy transfer that is required
for a particular fragmentation channel, the more marked is its suppression when circular polarization is used. The maximum kinetic energy that is released upon fragmentation appears to be more or less independent of the polarization state of the incident light. The observation that the actual values of kinetic energy released are less than Coulombic confirms that the enhanced ionization mechanism also holds for circularly polarized light.

On the basis of such results, it might, a priori, be thought legitimate to suppose that bond formation is likely to be of little or no concern to molecular dynamics under such strong field conditions, and this has indeed been the prevailing wisdom. However, recent experiments on the ionization of alcohol molecules by 800 nm light of intensity in the $10^{15}$ to $10^{16}$ W cm$^{-2}$ range have demonstrated bond formation involving proton migration on ultrafast timescales [3]. The light intensities are strong enough to induce double and triple ionization of alcohol molecules, leaving the multiply charged alcohol molecular ions susceptible to Coulomb explosion. Proton migration, which appears to occur much before the Coulomb repulsion makes the fragment ions fly apart, leads to formation of H$_2^+$ ions. These molecular fragment ions are formed with substantial kinetic energy in the molecular center-of-mass frame. The short-duration, intense light field actually coaxes molecular rearrangement in addition to causing molecules to undergo fragmentation into ions.

Figure 3. Dissociation pattern of C$_2$H$_5$OH (left panel, solid bars: linear polarization, hatched bars: circular polarization) and time-of-flight spectrum of fragments obtained at low values of m/q (right panel a). Note the unexpected formation of H$_2^+$ whose spectral shape depends on the polarization direction of the laser light (right panel b), indicating that H$_2^+$ formation occurs within one laser pulse (100 fs duration).

Figure 3 shows part of a typical time-of-flight (TOF) spectrum obtained when ethanol molecules were irradiated with pulses of peak intensity $8 \times 10^{15}$ W cm$^{-2}$. Note that along with the multiply charged molecular ion peaks the TOF spectrum offers evidence for multiply charged fragment ion peaks, like C$^{2+}$. In the case of multiply charged atomic fragments, the large kinetic energy release (KER) in the fragmentation event manifests itself in TOF spectra as splitting in the arrival times of ions. The splitting indicates that fragments that are initially scattered in a direction towards the
detector in the TOF spectrometer reach early, and are labelled as forward scattered ions (marked $f$ in Fig. 3), while those that are initially formed in the opposite direction reach the detector later, and are denoted backward scattered ions (marked $b$ in Fig. 3). The time difference between the forward and backward ions provides a measure of the kinetic energy release (in the centre-of-mass frame) that accompanies a particular ion formation channel [9] and tells us that the rearrangement process not only gives rise to an unusual ionic fragment, $H_2^+$, but that it is also formed with a substantial amount of kinetic energy (a most probable value of about 5 eV in the centre-of-mass frame). That the $H_2^+$ fragment is formed by a unimolecular reaction is established by gas pressure measurements [3]; results of polarization dependence measurements (Fig. 3b) indicate that the rearrangement occurs within the 100 fs duration of the laser pulse and is driven by the strong light field [3]. Subsequent work by Yamanouchi and coworkers [9] and by De et al. [10] has also observed rearrangements involving not just two but of three H-atoms from alcohol precursors, although no temporal quantification of the process has been possible in these studies.

3. Matter affects light in the strong field regime

When gas-phase matter is irradiated by intense laser light, the resulting generation of high harmonics may be regarded as constituting one well-studied, albeit indirect, manifestation of matter affecting light. A visually dramatic manifestation of matter affecting light is obtained when ultrashort pulses of intense light propagate through condensed matter. The temporal and spatial properties of the incident light pulse are modified, and such modifications manifest themselves in an enlarged optical frequency sweep, resulting in the generation of broadband radiation known as the production of a supercontinuum, or white light generation [5,11,12].

White light generation, or supercontinuum production, arises from a plethora of light-matter interactions that are complex by themselves, and whose mutual interactions continue to be little understood and subject to continuing, vigorous study. Among various effects that are observed in the course of propagation of ultrafast pulses of intense light through condensed media are group velocity dispersion (GVD), linear diffraction, self-phase modulation (SPM), self-focusing, multi-photon ionization (MPI), plasma defocusing and self steepening (for references to original works, see [11,12]). At relatively low values of incident laser power, it now appears established that it is mainly self-phase modulation due to the Kerr nonlinearity that is responsible for spectral broadening. Such broadening is found to be essentially symmetric around the incident laser wavelength. At very high power levels, other mechanisms come into play, like self steepening and free electron generation due to multiphoton excitation. These give rise to only blue-side frequency components, resulting in an asymmetry in the spectral broadening [11]. Self-focusing of the incident, ultrashort laser beam usually precedes white light generation and gives rise to the formation of filaments within the optical medium. The collapse of laser energy into filaments in condensed media is curtailed by multiphoton ionization (MPI) and plasma formation, the combined effects of which serve to defocus the laser beam, limiting its further collapse. The consequent limiting of intensity within the medium is believed to be an important factor that determines the spectral extent of supercontinuum generation [12]. Thus, at a simplistic level, one may regard the dynamics of ultrashort laser pulse propagation in optical media in terms of the interplay of two processes: self-focusing in the medium and plasma-induced defocusing brought about by multiphoton processes that depend on the incident laser power [11].

Typical white light spectra measured using 45 fs long pulses of 820 nm light from a high-intensity Ti:sapphire laser system that is incident on BK-7 glass are shown in Fig. 4. The incident laser wavelength was 820 nm, with an initial spread of ~30 nm. As the incident laser intensity is enhanced, the white light spectrum becomes broadened such that, at intensities that lie in the region of $10^{13}$ W cm$^{-2}$, the broadening extends over a very considerable wavelength range. It is also noteworthy that the broadening at higher intensities is dramatically asymmetric, extending preferentially into the blue part of the spectrum. As noted above, purely SPM-induced processes would lead to broadening that is essentially symmetric around the incident wavelength; in the ultrafast, high-intensity regime, the observed asymmetry has been ascribed to plasma effects that arise when multiphoton ionization within
Figure 4. Experimental manifestation of BK-7 glass affecting intense light: 820 nm light is converted into broad-band radiation. Note how the spectrum broadens as the incident laser intensity is increased from $5 \times 10^{11}$ W cm$^{-2}$ to $1.8 \times 10^{13}$ W cm$^{-2}$. The broadening at higher intensities is noticeably asymmetric vis-à-vis the incident wavelength of 820 nm.

The irradiated material produces free electrons that alter the nonlinear, intensity-dependent refractive index in such manner that asymmetric broadening results [11].

The basic underlying physics of how matter affects light in the high-intensity, ultrashort-pulse domain still continues to be the subject of intense inquiry. Nevertheless, numerous and diverse applications have been discovered for such effects, ranging from control of atmospheric lightning, to remote sensing and broadband spectroscopy of atmospheric constituents (see [11] for original references). In transparent condensed media, propagation effects present even richer potential, like bulk modification, laser writing, laser-driven microexplosions, modification of refractive index and the formation of color centers. Formation of optical waveguides, photonic crystals and 3-D optical memories are some applications that constitute a major driver in this area of contemporary research (see [6] for original references). The propagation of ultrashort, intense laser pulses through medium containing biological material has not been investigated so extensively and has constituted the subject matter of a recent study that we have conducted. By way of illustration we present in the following results of experimental studies that have been conducted on supercontinuum generation in water that contains different concentrations of salivary proteins, such as $\alpha$-amylase and various amino acids. The specific interest in $\alpha$-amylase stems from the importance of this enzyme as a potential marker of stress experienced by humans. Figure 5 shows typical spectra that depict the spectral broadening that is obtained upon irradiation of water and water mixed with a tiny concentration of $\alpha$-amylase. Note that over and above the prominent asymmetric broadening that is observed in pure water, there is also a marked dip at 630 nm. We attribute this feature to an inverse Raman effect wherein upon irradiation of a sample by intense monochromatic light of frequency $\nu_0$ and, simultaneously, with an intense continuum, molecules within the sample are stimulated to emit radiation at frequency $\nu_0$ and, at the same time, absorb radiation at frequencies corresponding to $(\nu_0 + \nu_m)$ and $(\nu_0 - \nu_m)$. $h\nu_m$ denotes the...
Figure 5. Spectrum of white light that is transmitted upon irradiation of pure water and of water doped with α-amylase by <45 fs long pulses of 820 nm light of intensity 8 TW cm$^{-2}$. Note the suppression of asymmetric broadening. Note also the suppression of the inverse Raman feature [7].

separation between different quantal states. The relatively sharp and distinct dip that is observed in Fig. 5 is due to absorption on the higher frequency side, and corresponds to the well measured ~3500 cm$^{-1}$ Raman shift in water. Upon addition of α-amylase to water there is a distinct change in the spectrum of transmitted light: at molar concentration of >60 μM, the extent of broadening markedly decreases even though the incident laser power is kept constant. Below this concentration there is gradual reduction in generated white light, particularly in the blue side of the spectrum. The extent to which white light production appears to be suppressed with enzyme concentration is also reflected in the extinction of the inverse Raman feature. At 60 μM concentration of α-amylase in water, the remnant broadening that is observed is almost symmetrical about the incident 820 nm wavelength and represents supercontinuum production of the type that is expected purely on consideration of self-phase modulation effects. This brings to the fore the question: wherefore the white light suppression by α-amylase?

As noted above, the asymmetry towards the blue region in the spectral broadening that is observed has contributions from plasma effects arising from free electrons generated by multiphoton ionization (MPI) of water. The symmetric broadening that is observed upon addition of α-amylase (Fig. 5) indicates almost total extinguishing of plasma-induced effects. In other words, addition of α-amylase to water appears to result in efficient electron scavenging action involving a dissociative attachment process [7]. The resultant disappearance of MPI-generated free electrons is what leads to suppression of asymmetric (plasma-induced) broadening and leaves behind the remnant SPM-induced supercontinuum that is essentially symmetrically broadened around the incident 820 nm wavelength.

This electron scavenging action is not understood at present but may be instigated by the action of free radicals that are generated. The role of free radicals, like atomic oxygen, in physiological functions and malfunctions has been cogently reviewed recently [13]. In the case of water+α-amylase, it seems to be the case that no sooner are free electrons generated by multiphoton processes, they are efficiently scavenged by α-amylase and an essentially symmetrically broadened spectral distribution results. This symmetric broadening is rationalized in terms of SPM brought about by the instantaneous
Kerr nonlinearity. Upon entering water, the leading part of the incident 820 nm pulse experiences change in refractive index due to the Kerr effect that increases with time; this gives rise to the generation of frequencies that are lower than the incident frequency (the Stokes region). The situation is reversed during the trailing part of the pulse, giving rise to the generation of higher frequencies (the anti-Stokes region). The net result is spectral broadening that is symmetric around 820 nm. If α-amylase was not scavenging electrons, the MPI-generated free electrons would also contribute to spectral broadening: the frequency deviation would become positive because of the negative contribution to the time-varying refractive index. Under these situations, spectral broadening would be asymmetric, with a higher propensity for generation of frequencies that are higher relative to 820 nm (anti-Stokes broadening).

Do other proteins in human saliva also display contribute to suppression of the supercontinuum? In excess of 300 proteins have presently been detected in human saliva, and there may be many more. The role played by each of these is also not clearly established, although it is fair to state that, at present, it is only α-amylase amongst these that appears to be linked to questions of physiological and psychological stress in humans, and to white light suppression.

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