White-Light-Induced Fragmentation of Methane†

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We experimentally probe molecular ionization and dissociation of methane molecules in the gas phase upon their irradiation by intense pulses of white light that spans the wavelength range 500−850 nm. White light pulses are generated upon irradiation of BK7 glass by 36-fs-long pulses of intense 820 nm laser light. Comparison is made of the molecular fragmentation patterns obtained using white light that is depolarized with those obtained using single-color (820 nm) light that is highly chirped. On the basis of such comparison, we make hitherto-unavailable estimates of the in situ intensity of white light pulses. Results obtained using white light also indicate that resonances apparently do not play any role in the ionization dynamics that ensue upon irradiation by intense, broadband light; neither are the dynamics affected by the polarization properties of the 820 nm light that is used to generate the white light.

Introduction

Optical manipulation and control of the macroscopic dynamics of atoms, molecules, and their aggregates is a manifestation of the interaction of radiation with matter and is a subject that continues to excite considerable contemporary interest. However, when the magnitudes of the optical fields that are used become very large, it is microscopic effects that start to assume importance. Indeed, when light intensities become large enough to give rise to optical fields whose magnitudes are a significant fraction of the Coulomb field that exists within the atomic and molecular constituents of matter, field-induced distortions of the potential energy surfaces occur that provide a proper quantum mechanical description of matter.[1] Under these strong-field circumstances, achieved using laser intensities of 1 TW cm^{-2} and above, optical field-induced ionization dominates the light−matter interaction.[2,3] At intensities in excess of about 10−100 TW cm^{-2}, multiple ionization readily occurs, and in the case of molecules, it is accompanied by Coulomb explosion of highly charged molecular entities. The study of molecular dynamics in such an intensity regime, which guarantees highly nonlinear behavior in a nonperturbative domain, has assumed considerable importance in the course of the past decade.[4−17] Experimental progress in the field has been both rapid and continuous and has been vigorously driven by advances in short-pulse technology, on the one hand, which have enabled high-intensity light pulses to be readily generated in individual laboratories using commercially available, table-top laser systems, and development of multiple coincidence methodologies, on the other, which enable simultaneous detection of charged fragments as a multiply charged molecule undergoes Coulomb explosion. Cogent reviews of this fast-growing subset of strong field science can be found in ref 17. As can be readily imagined, strong-field molecular ionization and dissociation dynamics occur on ultrafast (femtosecond) timescales. Quite counter-intuitively, recent experiments have yielded evidence that some molecular bond formation processes can also occur on similarly fast timescales.[11]

Almost all previous strong-field molecular dynamics work has been conducted using single color radiation. In recent times, the single color radiation has usually been infrared light from Ti:sapphire laser systems (wavelength in the vicinity of 820 nm); in the earliest strong-field experiments conducted in the late 1990s, Nd:YAG and similar lasers were the mainstay of experimental work, and consequently, the single color that was mostly used at that time was of either 1064 nm or 532 nm wavelength, with some work conducted using 10 μm wavelength light from CO_2 lasers.[18] Recent work has utilized wavelengths that are longer and shorter than 820 nm.[19,20]

How are the overall dynamics affected when the strong optical field is generated not by laser light with a single-valued wavelength, λ, but by multicolored light? What are the intensities of such multicolored light? Do resonances come into play in the overall ionization dynamics when white light is used? How do the polarization properties of white light affect the ionization and fragmentation dynamics in the strong field regime? The questions that we pose have not been addressed and constitute the subject matter of the experimental work that we report in the following. Before we describe our methodology and results, it is first necessary to make some general observations about the physics that determines how intense white light is produced and what is known about its properties.

White light generation, or supercontinuum production, is a consequence of the propagation dynamics of an ultrashort, intense infrared light pulse through an optical medium. The resulting broadband radiation arises from a plethora of light−matter interactions that are complex by themselves, and whose mutual interactions continue to be little understood. Among various effects that are observed in the course of propagation are group velocity dispersion (GVD), linear diffraction, self-phase modulation (SPM), self-focusing, multiphoton ionization (MPI), plasma defocusing, and self-steepening.[21−25] Supercontinuum, or white light, generation is a visually spectacular manifestation of these processes wherein the spectrum of the incident light becomes substantially broadened by additional wavelength components. 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

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for spectral broadening. Such broadening is found to be essentially symmetric around the incident laser wavelength. The leading part of the incident pulse generates red-shifted frequencies, whereas the trailing part generates the blue-shifted frequencies. The frequency chirp is essentially linear in the neighborhood of pulse center. For nonlinear index n_2, with positive sign, this gives rise to a positive chirp.[26] 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.[27−29] 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. Thus, at a simplistic level, one may regard the propagation of ultrashort laser pulses in optical media in terms of the dynamic 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.[27,28]

Although it is not difficult to unambiguously determine the spectral properties of the white light that is generated, knowledge of its temporal properties is difficult to come by. Indeed, it would not be an exaggeration to state that, at high power levels, temporal characterization of the pulses of white light that have been generated in numerous experiments remains a challenge. Consequently, information on the actual intensity of white light pulses also remains unknown in all hitherto-conducted experiments. In the present series of experiments, we make in situ measurements of white light intensity by making use of time-of-flight spectrometry to study the white-light-induced dissociative ionization of methane and comparing the spectral morphology with that obtained using only single-color (820 nm), highly chirped light of different intensities under otherwise identical conditions.

Apart from the intrinsic interest in experimental studies of white-light-induced dissociative ionization of molecules like methane, we also note one other motivation for our experiments. It is a fact that strong-field molecular dynamics has, by and large, had little use for concepts like resonance excitation and relaxation processes in rationalizing ionization and fragmentation patterns. However, recent work on polyatomics has yielded tantalizing data in which invocation of one-photon and multiphoton resonances to vibrationally and electronically excited states of either the neutral or the singly ionized molecule appears to rationalize the enhanced fragmentation that is observed at certain wavelengths in molecules,[30−36] including metal carbonyls (see the very comprehensive report by Fuss and co-workers).[30] On the basis of such results, one might anticipate that the use of intense white light might possibly induce a much higher degree of molecular fragmentation than would be obtained with single-colored light of the same intensity. This appears to be contrary to what is observed in our experiments that we describe.

There has been a very recent study in which resonant phenomena has been shown to play a possible role in strong-field ionization dynamics.[37] Strong nonresonant laser fields are known to cause spatial alignment of linear molecules along the optical field polarization direction. However, suppression of this effect has recently been achieved[37] by simultaneous application of two strong fields at two different colors, each of which, when applied individually, gives rise to spatial alignment of the molecule that is irradiated. It was shown that irradiation of CS_2 molecules with intense (in the range 1−100 TW cm^{-2}), 35 ps-long pulses of 512 nm or 355 nm light that is linearly polarized leads to spatial alignment of S−C−S bonds along the polarization vector, as experimentally exemplified by the anisotropic angular distributions of S^+ fragment ions. However, when both colors are simultaneously present, such spatial alignment disappears. This observation was taken to be somewhat akin to weak-field illumination of an atom by two colors wherein an electromagnetically induced transparency inhibits absorption by virtue of dipoles not being induced in two-color fields. As spatial alignment is also brought about by an induced dipole, disappearance of the latter ought to lead to vanishing of the former, as has, indeed, been observed in the case of one of the two colors being resonant with an electronic state of the irradiated molecule. Lack of such resonance does not give rise to EIT-like behavior.[37]

Experimental Method

In the present series of experiments, we generated white light using intense, ultrashort pulses of infra red light incident on BK7 glass. A schematic of the optical scheme that we adopted and our apparatus is shown in Figure 1. Specifically, we used 820 nm laser light (pulse duration of ∼36 fs, focused with f = 10 cm lens L_1) from an amplified 1 kHz repetition rate Ti:sapphire laser system with pulse energies of up to ∼0.8 mJ, incident on 12 mm thick glass. The spectral bandwidth of our 820 nm light was measured to be typically 30 nm in the course of our experiments. A large diameter (5 cm) achromatic lens L_2 (f = 10 cm) was kept downstream of BK7 glass to ensure optimum transmission of the white light into our laser-molecule interaction zone that was located within an ultrahigh vacuum (UHV) system pumped down to a base pressure of 2×10^{-9} Torr. The multicolored conical emission that accompanied supercontinuum production was apertured in our experiments such that only the central white light portion was focused using a lens L_3 (f = 5 cm) into an effusive molecular gaseous target (CH_4) inside our UHV system. Typical operating pressures with gas load were kept in the region of 10^{-8} Torr and below, ensuring absence of charge saturation effects. Molecular ionization that occurred within the system was probed by means of a linear, two-field time-of-flight (TOF) spectrometer.

Ions formed in the interaction of white light with methane were electrostatically extracted, with nearly unit efficiency, into our TOF spectrometer. TOF spectra were measured for each laser shot. A fast photodiode signal provided the start pulse of our TOF spectrum, whereas stop signals were from the channel electron multiplier ion detector used in pulse counting mode. TOF spectra were acquired with a 500 MHz-bandwidth digital oscilloscope, and data were recorded on a computer using a fast programmable bus. The results that we present in the following pertain to laser intensity fluctuations of ±5%.

In the context of how we shall put TOF spectra to use in our experiments, it is important to note that, in a high ion collection efficiency mode of operation that we adopted, we typically used ion extraction fields of ∼100 V cm^{-1}. The near unit collection efficiency that was ensured using such fields, even for fragment ions possessing several tens of eV of kinetic energy, came at the expense of temporal resolution with which we could measure our ion signals. A 3 mm aperture in front of the TOF spectrometer ensured that measurements were conducted in intensity-selective mode wherein only the central, most intense

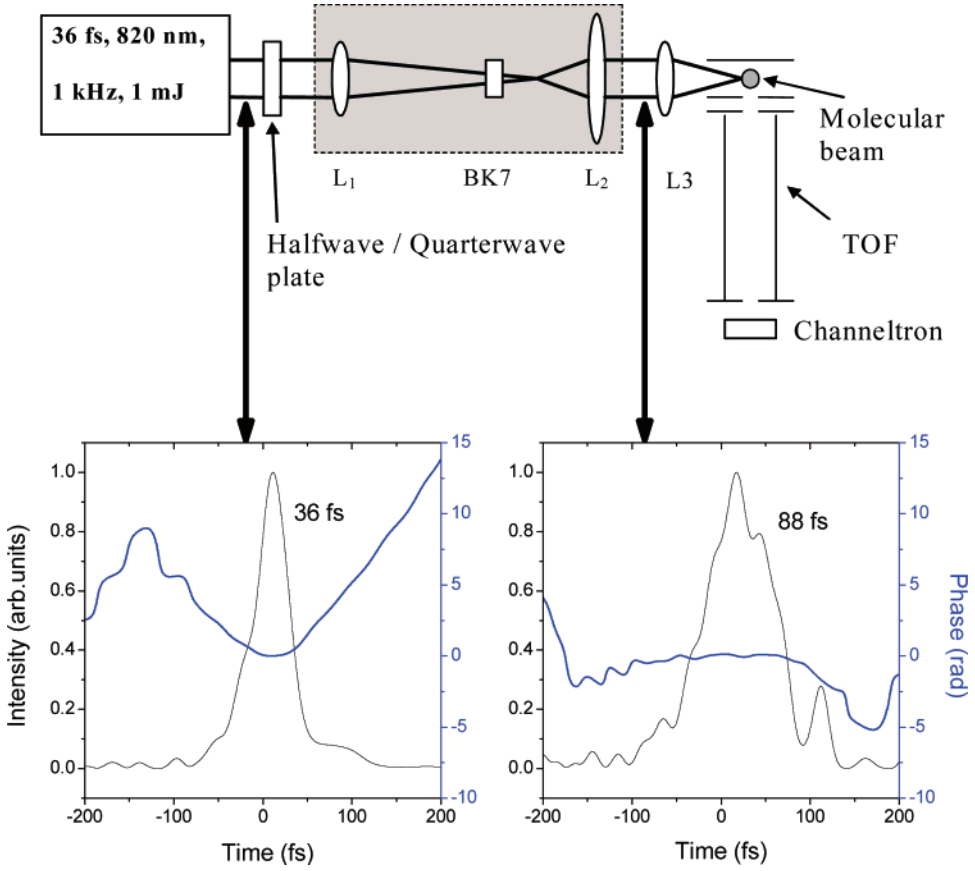

Figure 1. Optical scheme used to probe the intensity of white light produced using 36 fs, 820 nm wavelength light pulses incident on a 1 cm thick sample of BK7 glass. L1, L2, and L3 are lenses. TOF is a linear time-of-flight spectrometer used for probing molecular fragmentation patterns when methane was irradiated by chirped 820 nm light (gray portion of the apparatus removed) or by white light pulses (with the gray portion of the apparatus in position, as indicated). The lower panels show typical traces pertaining to temporal profile and spectral phase obtained from SPIDER (spectral phase interferometer for direct electric field reconstruction) measurements made at the locations in the apparatus indicated by the vertical arrows. The white light intensity is estimated to be 410 GW cm^{-2}.

part of the entire laser focal volume was sampled. Our optical system was such that the Rayleigh range for the incident 820 nm light was 6 mm. In the case of white light that was generated, each λ-component possessed its own Rayleigh range, giving rise to a line focus. The length of the line focus was determined to be 1 cm. The difference in effective focal length of our focusing lens was less than 0.3 cm over the wavelength range 500−850 nm. The use of large ion extraction fields in our TOF spectrometer also served the purpose of ensuring that ions produced along the entire line focus that is created by white light were effectively sampled by our TOF spectrometer. In all cases, CH_4 densities were kept low enough to ensure that space charge effects were not a concern in our measurements.

The temporal profiles and spectral phase information of laser light were monitored at locations indicated in Figure 1 using a single-shot autocorrelator and SPIDER (spectral phase interferometer for direct electric field reconstruction); some typical results obtained at lower incident intensity of 1 TW cm^{-2} are illustrated. For an incident 820 nm pulse of 36 fs duration, a SPIDER trace of the resulting white light is shown in the bottom left panel of Figure 1. The white light intensity is estimated to be 410 GW cm^{-2}. The white light pulse duration varied with intensity of the incident 820 nm laser light. Note the slight positive chirp in the incident pulse and the essentially constant optical phase within the 88 fs long white light pulse, corresponding to incident intensity of 2.2 TW cm^{-2} (the white light spectrum at this intensity is shown in Figure 2). A combination of halfwave plate and quarterwave plate was used to control the polarization of 820 nm light. Polarization analysis of both

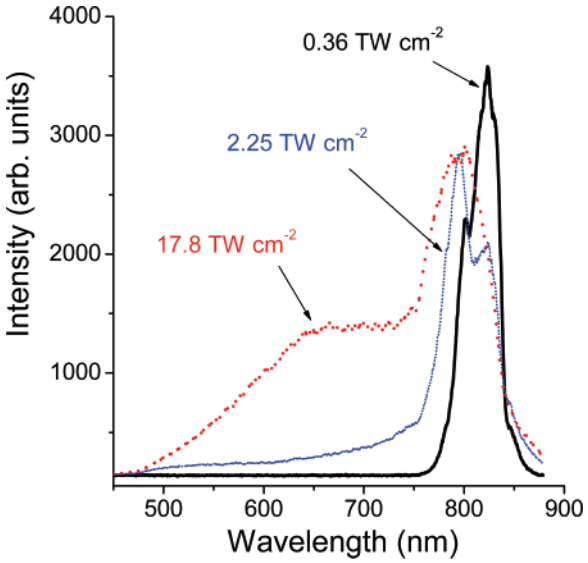

Figure 2. Typical spectra of white light pulses obtained when BK7 glass was irradiated by 36 fs long, 820 nm pulses of different intensities. Note the asymmetric broadening (toward the blue) that ensues upon increase of incident laser intensity.

the incident infrared light and the supercontinuum was by a Glan-Thompson polarizer. We quantified the linear polarization of the incident light in terms of the extinction ratio (ER), which is the ratio of intensity, $I_{\perp}$, that is transmitted when the analyzer is in the cross position to the intensity, $I_{\parallel}$,when it is in parallel

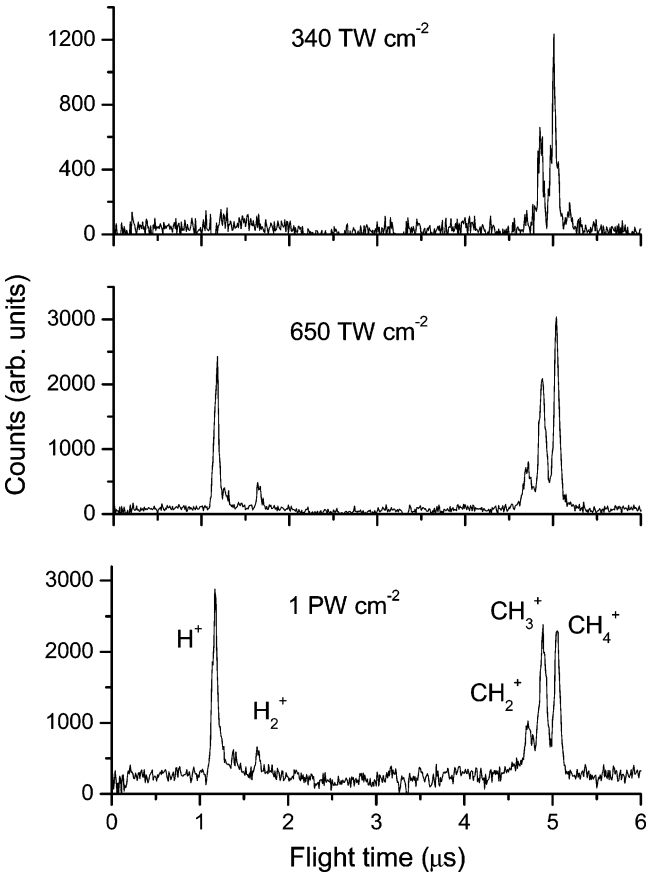

Figure 3. Time-of-flight spectra of methane measured using chirped pulses of 820 nm light covering the intensity range of 0.34−1.00 PW cm^{-2}.

position. ER values better than 3×10^{-3} were typical of what we measured, and were consistent with what is expected from pulses that are obtained from multipass amplifiers such as ours. The value of ER for our polarizer was 10^{-5} and its wavelength coverage spanned the region 350−2200 nm.

The spectrum of the white light that we generated using BK7 glass was characterized using an integrating sphere that was attached to a fiberoptic-coupled spectrometer (Ocean Optics, Model USB 2000 covering the range 200−900 nm). Some typical white light spectra that we measured at different values of incident 820 nm light are shown in Figure 2.

Results and Discussion

We first address the primary issue of white light intensity, and we do so with reference to the optical field induced dissociative ionization of CH_4 molecules. The dependence of the ionization dynamics on chirp has been discussed by us before.[10] In Figure 3, we show a subset of high collection efficiency TOF spectra of methane measured using chirped pulses of 820 nm light covering the intensity range of 0.34−1 PW cm^{-2}. At intensities in excess of about 0.5 PW cm^{-2}, multiply ionized methane undergoes Coulomb explosion, giving rise to energetic H^+ and H_2^+ fragments,[9] in addition to the low-energy fragmentation pathways leading to CH_n^+ ($n = 1-3$) fragments. In all these measurements, a halfwave plate placed in the location indicated in Figure l was used to ensure linear polarization, with the polarization vector along the axis of our TOF spectrometer. Light intensities were adjusted by using a polarizer in conjunction with the halfwave plate. We show in Figure 4 the corresponding ionization pattern obtained when white light (wavelength span 500−850 nm) interacts with CH_4.

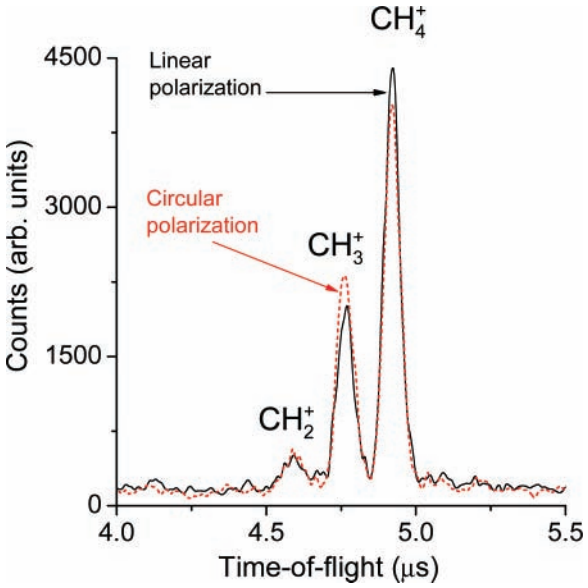

Figure 4. Ionization pattern obtained when white light (wavelength span 500−850 nm) interacts with CH_4. Comparison with corresponding measurements made using chirped 820 nm light enables us to deduce that the white light intensity in this case was ∼300 TW cm^{-2}. Note the similarity between spectra obtained using linearly and circularly polarized 820 nm light incident on BK7 glass (see text).

The white light time-of-flight (TOF) spectrum of methane was obtained with the shaded portion in Figure 1 introduced, when 900 μJ (1 PW cm^{-2}) of 820 nm light was focused using a lens of focal length ($f = 10$ cm) on BK7 glass kept 10−15 mm before the focus point. The white light that was generated had an energy of ∼540 μJ, and the accompanying conical emission was blocked by an aperture. This light was then focused on the CH_4 molecule using lens with $f = 5$ cm. We compared this pattern with the entire set of fragmentation patterns that we measured using chirped 820 nm light, and correspondence of the two sets of fragmentation patterns enables us to make an estimate of the in situ intensity of white light pulses.

In the case of the fragmentation pattern shown in Figure 4, we are able to estimate the white light peak intensity to be ∼300 TW cm^{-2}. The same procedure can be repeated with different values of intensity of 820 nm light incident on the BK7 glass, so that corresponding values of white light intensity may be estimated on the basis of the methane fragmentation pattern. We believe such estimates to be good to within a factor of 2.

Careful measurement of fragmentation patterns over a range of intensities failed to reveal any resonance like phenomena occurring in the strong-field ionization dynamics of methane.

We have also probed the effect that the polarization properties of white light have on methane ionization dynamics. Prevailing wisdom has long held that white light that is generated upon irradiation of an isotropic medium will have the same polarization property as the incident laser light.[21] To aid further discussion, we quantify the linear polarization of our incident 820 nm light by the factor ζ, where

$$\zeta = \frac{I_{\parallel}}{I_{\perp}} \tag{1}$$

The subscripts, parallel and perpendicular, refer to transmitted light intensity with a polarization analyzer in parallel and cross position, respectively. Linearly polarized laser pulses obtained from multipass amplifiers such as the one used in our experi-

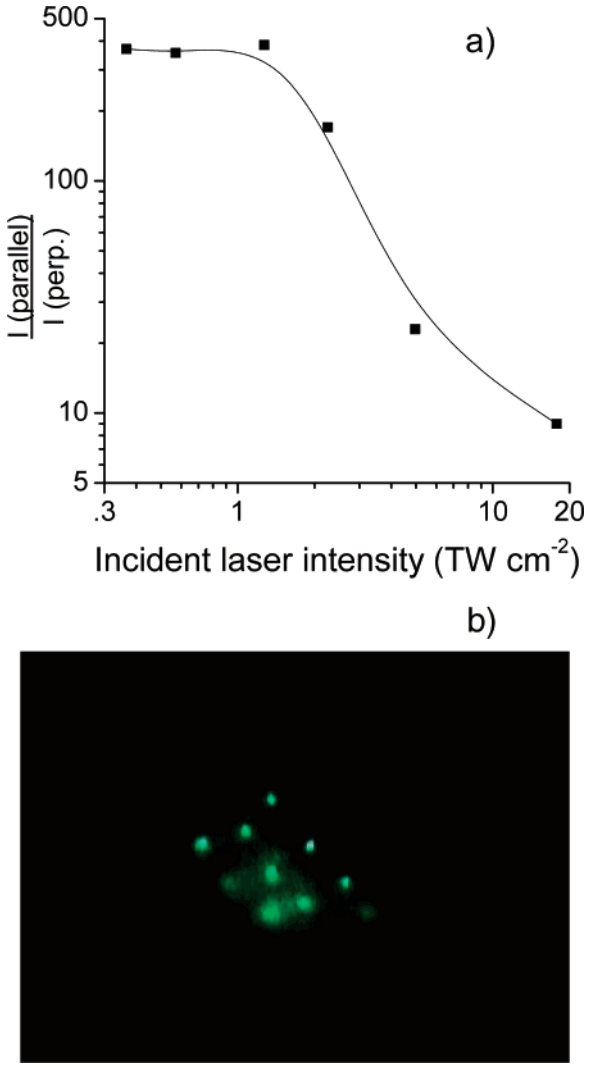

Figure 5. (a) Extent of depolarization of white light as the intensity of 820 nm light that is incident on BK7 glass increases. (b) Images of multiple filaments that give rise to this depolarization (see text).

ments are expected to have $\zeta \sim 500$. We have made measurements to confirm that for white light pulses, the value of ζ remains essentially intact for 820 nm intensities of $\sim$0.1−1 TW cm^{-2} incident on BK7. The pertinent result is depicted in Figure 5. In this intensity regime, the spectra shown in Figure 2 indicates that spectral broadening (750−850 nm) is reasonably symmetrical about 820 nm. Increasing the incident intensity of 820 nm light by an order of magnitude results in more extensive and asymmetrical broadening. The asymmetry becomes more pronounced toward the blue side of the wavelength spectrum as the incident laser power is increased and, as has been recently shown,[28] is related to the increasing importance of plasma effects that are brought about by multiphoton induced generation of free electrons in the supercontinuum production process. Asymmetric spectral broadening is accompanied by very significant degradation of the ζ value. As the bandwidth of the supercontinuum that we generate using BK7 glass becomes wider (and, correspondingly, as the white light spectrum becomes more asymmetric), the value of ζ degrades by more than an order of magnitude. In other words, the white light that is generated upon irradiation of BK7 glass at high incident intensities is essentially depolarized,[38] particularly in wavelength regions that are far removed from 820 nm.

The depolarization needs to be properly understood, but it is likely to be a consequence of the fact that multiple filamentation within the medium gives rise to complicated refractive index change, leading to local anisotropy that degrades the uniformity of polarization. Figure 5 also shows an image that we took using a CCD camera located at the exit plane of the BK7 glass and it establishes the existence of multiple filaments within BK7 at the intensities that were used in our experiments. It is clear that more work needs to be undertaken to clearly establish a causal link between multiple filamentation and the depolarization of white light. However, the immediate consequence on methane ionization dynamics of the depolarized nature of white light is exemplified by raw spectra depicted in Figure 4 where measurements were made using either linearly polarized or circularly polarized 820 nm light incident on BK7 glass. We note that the resulting white-light-generated fragmentation pattern of methane remains essentially unaltered, to within 30%, a number that is commensurate with accuracies that can reasonably be expected in experiments of this type.

Concluding Remarks

We have generated pulses of white light by irradiating BK7 glass with 36-fs-long pulses infrared light pulses from a Ti: Sapphire laser system, using intensities in the 10 TW cm^{-2} to 1 PW cm^{-2} range. In all hitherto conducted experiments on supercontinuum generation, although it has been possible to make reliable measurements of the spectral and polarization properties of the white light that is generated, direct measurement of the temporal properties have not been possible to make. Consequently, deductions of white light (supercontinuum) intensities have proved to be impossible to make. To overcome this important deficiency, we made use of strong-field molecular ionization dynamics. Specifically, we experimentally probed the molecular ionization and dissociation of methane upon their irradiation by pulses of white light.

White light generated fragmentation patterns were compared with those obtained using single-color (820 nm) near transform limited light pulses of different (relatively easy to measure) intensities and also using highly chirped pulses. The morphologies of the fragmentation patterns depend on incident intensity, and by making a comparison of the ionization spectra that we measure using chirped 820 nm light we are able to obtain estimates of the intensity of white light pulses generated in our experiments to be nearly 300 TW cm^{-2} when BK7 glass is used to generate the white light. Our experiments have provided a new perspective on the physics of white light generation in that molecular fragmentation patterns are shown to be useful diagnostics of white light intensity.

The depolarized nature of white light also results in almost identical fragmentation patterns (to within 30%) being obtained whether the seed (820 nm) light is linearly or circularly polarized.

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