Femtosecond laser pulse filamentation characterized by polymer gel dosimetry and Fricke dosimetry

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Abstract. A femtosecond laser pulse that can generate water radiolysis species was studied in view of its potential medical and biological applications. Intense ultra-short laser pulses can propagate in liquid water, leading to self-focusing and filamentation. Briefly, electrons produced by either multiphoton or tunnel ionization are further accelerated by the electric field of the pulse in an inverse Bremsstrahlung effect. If the electrons acquire enough kinetic energy, they will give rise to a second generation of electrons by impact ionization of other molecules in an avalanche-like process. The geometry and trajectory of femtosecond filaments were captured within a polymer gel dosimeter and imaged by magnetic resonance imaging (MRI) at high resolution. The results revealed that changing pulse duration modifies the penetration of the filament track in the medium. In addition, we used Fricke dosimetry to measure the absorbed dose and dose rate of the femtosecond laser pulse filamentation. A very high dose rate of $5.3 \times 10^{12}$ Gy/s was calculated in filaments having a diameter of ~600 µm.

1. Introduction

We used filamentation from a femtosecond laser pulse to generate avalanche low energy electrons that is called an inverse Bremsstrahlung process (1-3). The process can lead to the creation of molecular and radical species in liquid media. For conventional radiation sources (e.g., X-ray, γ-ray, accelerated electrons or heavier charge particle), the interaction with liquid water generates low-energy secondary electrons in large amounts ($\sim 5 \times 10^4$ electrons/MeV) from the absorption of the high-energy ionizing radiation. These electrons define the geometry of the radiation track (4) and their most probable kinetic energy is centered around $\sim 10$ eV (5). In this energy range, the penetration depth of electrons in water is ~10 nm (5). These low-energy electrons were shown to break plasmid DNA (6).

The physical origin of the formation of filaments from a femtosecond laser pulse is well understood (1-3). Briefly, self-focusing is an induced lens effect that results from the wavefront distortion inflicted on the beam by itself while traversing an optically nonlinear medium. Consequently, as the beam travels in the medium, the original plane wavefront of the beam gets progressively more distorted. The distortion is similar to that imposed on the beam by a positive lens. Since the direction of the optical ray propagation is perpendicular to the wavefront, the beam appears to focus by itself. This degenerative process is stabilized in the femtosecond regime by the generation of electrons forming a filament (1-3). Electrons produced by multiphoton or tunnel ionization are further accelerated by the electric field of the pulse in an inverse Bremsstrahlung effect. If they acquire
enough kinetic energy (~6.5 eV in the case of water), they give rise to a second generation of electrons by impact ionization of other molecules in an avalanche-like process. Those linearly distributed electrons (in the range of ~10^{18} cm^{-3} (1-2)) transfer their excess energy to the surrounding water molecules, generating in the self-focusing region chemically reactive species such as \(e_{aq}^-\), \(H^+\), \(\cdot\)O, and \(\cdot\)OH, and due to the recombination of the radicals, \(H_2\), \(O_2\), \(H_2O_2\) and \(O_2^\cdot\) (or \(HO_2^\cdot\), \(pK_a = 4.8\)). Filaments are analogue to conventional radiation tracks, having very small diameters in condensed matter (~100-250 \(\mu\)m) (1-3). Demonstration of the presence of \(H_2\) and \(H_2O_2\) has already been published (7). Although the stabilization of the filament is most probably due to the presence of electrons, no time-resolved measurement of this presence has been reported to date.

The dose deposition from laser filamentation was measured with the Fricke (ferrous sulfate) dosimeter, a well-known radiation chemical dosimeter. Comparison with \(^{137}\)Cs irradiation provided a dose rate for the filamentation process. The morphology of the filaments was evaluated using a polyacrylamide gel which is a 3D (8-9) and a tissue equivalent radiation dosimeter (10). The filaments were visualized and characterized in the dosimeter by magnetic resonance imaging (MRI).

2. Materials and methods

2.1. Laser instrument

A femtosecond Ti-sapphire laser beam (pulse duration 100 fs, 0.3 mJ/pulse and repetition rate 1 kHz, central wavelength 800 nm) was used in order to irradiate the sample contained in a quartz cuvette (1\(\times\)1\(\times\)5 cm\(^3\)) via a 3 cm focal length achromatic lens.

2.2. Fricke dosimeter

The chemicals used in the Fricke dosimeter solution are ferrous ammonium sulfate (hexahydrated salt, 99.99%, Sigma Aldrich), sulfuric acid (98%, Sigma Aldrich), and double-distilled water. The solutions were prepared from 0.342 g of \(Fe(NH_4)_2(SO_4)_2\cdot6H_2O\) dissolved in 0.4 \(M\) \(H_2SO_4\). The concentration of \(Fe^{2+}\) ions in the solution was 1 \(mM\) and the solution density 1.024 g/cm\(^3\). The solution was purged with oxygen for 2 h and protected from light by an aluminum foil. Special care was given to cleaning glassware according to the standard procedures used in radiation chemistry (11).

The Fricke solution was poured into 2 ml glass vials and the samples were irradiated up to 180 Gy at 25°C with \(^{137}\)Cs \(\gamma\)-rays in a Gammarcell (Atomic Energy of Canada Ltd.) with a dose rate of 0.2 Gy/s. For the filamentation laser irradiation, 2 ml of the Fricke solution was poured into the quartz cuvette and magnetically stirred during irradiation. The distance between the focus lens and the surface of the cell was 23 cm (Figure 1).

**Figure 1.** Schematic of the experimental setup to calculate the absorbed dose from the laser pulse using a Fricke dosimeter solution in a sample cell.
The concentration of ferric ions was calculated from the increase in the optical density at 304 nm using a molar extinction coefficient of Fe$^{3+}$ of 2207 M$^{-1}$ cm$^{-1}$. The radiation yield of Fe$^{3+}$ ions, $G$(Fe$^{3+}$), was calculated from the gradient of the linear curve between the Fe$^{3+}$ concentration and the absorbed dose. Normally, the yield of Fe$^{3+}$ depends on the linear energy transfer (LET) of the incident radiation. For low LET values such as for gamma photons from $^{137}$Cs (~0.9 keV/µm) (12), $G$(Fe$^{3+}$) is equal to 15.3 ± 0.3 molecules/100 eV (13).

2.3. Polymer gel dosimeter
The gel dosimeters were prepared from acrylamide (AA) and N,N'-methylene-bisacrylamide (BIS) (99+, electrophoresis grade, Aldrich), each at 3% w/w dissolved in gelatin (300 bloom, Aldrich) at 5% w/w, and water (de-ionized). In the manufacture process, gelatin was added to water at 25°C and left to soak for 10 min. The solution was then heated and maintained at a temperature of 45°C. AA and BIS were successively added and magnetically stirred for ~15 min until complete dissolution. The gels were prepared under a controlled N$_2$ atmosphere inside a glove box (8,14). The gel solution was poured into glass cells (diameter 2 cm × length 5 cm) (Fig. 2a) or in rectangular plastic container (Fig. 3a). In the latter case, the gel was prepared in the glove box with the same recipe but 5 mM of alkaline tetrakis (hydroxymethyl) phophonium chloride (THPC) (80%, Aldrich) was added to scavenge O$_2$. The samples were kept inside the glove box for 24 h after manufacture (15).

2.4. Magnetic resonance imaging
The samples were imaged using a 7 T small animal magnetic resonance imaging (MRI) scanner. A fast spin-echo protocol to acquire images in the axial (sagittal) planes with the following parameters: TR: 4 400 ms (2 000 ms), echo spacing: 13 ms, echo train length: 8, FOV: 25 × 25 mm$^2$ (60 × 30 mm$^2$), matrix: 256 × 256 (512 × 256), slice thickness: 1 mm (3.5 mm), number of slices: 40 (1), number of averages: 4. The in-plane spatial resolution of the axial images was thus ~ 100 µm.

3. Results and Discussion

3.1. Morphology of the filament tracks
Laser-induced water free radicals initiate polymerization in a polymer gel dosimeter such that the tracks caused by a femtosecond pulse are captured in the gel. The size of a single track was assessed by MRI (Fig. 2). The diameter and length of a track are estimated to be ~600 µm and 4 cm, respectively.

It is possible to create arbitrary irradiation patterns with laser filamentation. Figure 3 shows a photograph of a polymer gel dosimeter irradiated with several ultra-short laser pulses. Although difficult to appreciate with a photograph, visual inspection clearly revealed that changing the laser pulse duration leads to a change in the focus position (Fig. 3b). This indicates that the depth of the deposited dose profile can be adjusted.

3.2. Dose of the filament tracks
The Fricke dosimeter has found extensive use because of its ability to provide absolute dose results with a high accuracy. The estimated kinetic energy of the electrons in filamentation in water is ~6.5 eV such that the LET is expected to be ~1 keV/µm (5). The yield of Fe$^{3+}$ should then be 15.3 ± 0.3 molecules/100 eV (11). In other words, the same dose of gamma photons or of laser filamentation induced electrons is expected to lead to the same production of Fe$^{3+}$ in the Fricke dosimeter.

Initial calculations based on the power of the laser pulses, the energy of the electrons produced (1-3), the expected dimension of the filament tracks (diameter 100 µm and 1 cm long (1)), and the electron density $10^{18}$ per cm$^3$ (1), predicted a dose rate of $2.4 \times 10^{12}$ Gy/s for the filamentation process. The radiation absorbed dose of the laser filamentation and gamma radiation measured in a Fricke solution are plotted in Fig. 4. From this graph, the dose rate of the laser pulse was calculated to be 2.8
Gy/s. This is to be compared with the dose rate of the $\gamma$-rays (0.2 Gy/s). The sample cell is irradiated uniformly with gamma radiation, but only a small fraction of the cell is absorbing the dose from the femtosecond laser. When accounting for the pulse duration (~100 fs) and the volume irradiated, the calculated dose rate is $5.3 \times 10^{12}$ Gy/s, in close agreement with the predictions.

**Figure 2.** Femtosecond filamentation laser pulse in a polymer gel dosimeter. Photographs showing (a) the side view and (b) the top view of a glass cylinder irradiated from the top. The corresponding sagittal (c) and axial (d) magnetic resonance images were used to determine the length and the diameter of the laser filamentation tracks.

**Figure 3.** Photographs of containers filled with polymer gel dosimeter and irradiated with femtosecond laser pulses to draw the logo of the Université de Sherbrooke. (a) top view and (b) side view. Although not clearly visible on the photograph, the depth of the logo was modulated by changing the laser pulse duration.
Figure 4. Concentration of Fe$^{3+}$ calibrated in terms of an absorbed dose as a function of exposure time of a Fricke solution to (○) gamma radiation from $^{137}$Cs and (●) femtosecond laser pulses.

4. Conclusion

Laser light is not normally classified as an ionizing radiation. The self-focusing process of ultra-short laser pulses, which is called filamentation, leads to the production of an avalanche of low-energy electrons. These electrons can interact with surrounding molecules, resulting in the production of molecular and radical species. We characterized the physical properties of the laser filamentation track. The diameter was evaluated by polymer gel dosimetry and MRI at ~600 µm. Its penetration in a polymer gel dosimeter was around 4 cm. The dose rate in this volume was $\sim 10^{12}$ Gy/s as determined by Fricke and polymer gel dosimetry. Thus, nonlinear effects in the femtosecond laser pulse provide a convenient and effective radiation source with a very high dose rate. In view of such properties, this powerful tool could potentially be used in medical applications such as sterilization and radiotherapy.

References

[1] S L Chin, S A Hosseini, W Liu, Q Luo, F Théberge, N Aközbek, A Becker, V P Kandidov, O G Kosareva and H Schroeder 2005 Can. J. Phys. 83 863-905

[2] A Vogel J Noack, G Hüttman and G Paltauf 2005 Appl. Phys. B 81 1015-1047

[3] A Couairon and A Mysyrowicz 2007 Phys. Rep. 441 47-189

[4] D W Anderson 1984 Absorption of Ionization Radiation (Baltimore, MD:University Park Press)

[5] J Meesungnoen, J-P Jay-Gerin, A Filali-Mouhim and S Mankhetkorn 2002 Radiat. Res. 158 657-660

[6] B Boudaiffa, P Cloutier, D Hunting M A Huels and L Sanche 2000 Science 287 1658-1660

[7] S L Chin and S Lagace 1996 Appl. Optics 35 907-911

[8] M J Maryanski, J C Gore, R P Kennan and R J Schulz 1993 Magn. Reson. Imaging 11 253-258

[9] C Baldock, R P Burford, N Billingham, G S Wagner, S Patval and S F Keevil 1998 Phys. Med. Biol. 43 692-702

[10] A J Venning, K N Nitschke, P J Keall and C Baldock 2005 Med. Phys. 32 1047-53

[11] J W T Spinks and R J Woods 1990 An Introduction to Radiation Chemistry 3rd ed

[12] J Meesungnoen, M. Benrahmone, A Filali-Mouhim, S Mankhetkorn and J-P Jay-Gerin. Radiat. Res. 155, 269-278.

[13] ICRU Report 34, The Dosimetry of Pulsed Radiation. International Commission on Radiation Units and Measurements, Bethesda, MD, 1982.

[14] M Lepage, A K Whittaker, L Rintoul, S Å J Bäck and C Baldock 2001 Phys. Med. Biol. 46 1061-1074

[15] R Meesat, J-P Jay-Gerin, A Khalil and M Lepage 2009 Phys. Med. Biol. 54 5909-5917