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Best Oral Paper Award

Frequency dependence in the initiation of ultrafast laser-induced damage

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ABSTRACT

Numerous studies have investigated the role of photoionization in ultrafast laser-induced damage of bulk dielectrics. This study examines the role of spectral width and instantaneous laser frequency in laser-induced damage using a frequency dependent multiphoton ionization model and numerical simulation of an 800 nm laser pulse propagating through fused silica. When the individual photon wavelengths are greater than 827 nm, an additional photon is required for photoionization, reducing the probability of the event by many orders of magnitude. Simulation results suggest that this frequency dependence may significantly affect the processes of laser-induced damage and filamentation.

Keywords: Ultrashort laser-pulse propagation, ultrafast laser-induced damage, SPIE Proceedings, fused silica

1. INTRODUCTION

The past two decades have witnessed the advent of the commercial femtosecond laser system as well as the use of ultrashort laser pulses to affect precise changes in a variety of materials.[1,2] Ultrashort laser pulses are increasingly used for micro-machining,[3,4] the writing of waveguides and other structures in bulk dielectrics,[5–7] and also in medical procedures.[8,9] One critical aspect common to all of these applications is the initiation of laser-induced damage (LID) processes that lead to permanent changes in the material structure. It is generally assumed that the initiation of LID begins with the process of photoionization, after which an optically significant plasma density can be generated giving rise to free-carrier absorption and impact ionization. The significance of impact ionization (or avalanching) in LID on the femtosecond time scale is still an open question in the literature, see for example the differing results from Refs. [10–13] and Refs. [14–18]. The necessity of photoionization, however, as at least a prerequisite to permanent LID stands in good agreement with nearly all models. Therefore, it is reasonable to assume that errors of many orders of magnitude in calculations of the photoionization rate threaten the validity numerical LID predictions.

This paper presents results of an investigation into one such source of error; that of the spectral variance found in ultrashort laser pulses. Photoionization calculations typically assume that a laser pulse is approximately monochromatic, that is $\Delta\omega/\omega_0 \ll 1$, where $\Delta\omega$ is the pulse's spectral width and ω_0 is a measure of the central frequency of the spectrum. However, one physical requirement of making a pulsewidth shorter is that the corresponding spectral width will generally grow larger. If the pulsewidth approaches a single optical cycle of the applied field, as with ultrashort pulses, then the monochromatic approximation becomes questionable. The spectra of ultrashort laser pulses may be further broadened by nonlinear optical effects during propagation, such as self-phase modulation, that not only widen the spectrum but can shift the central frequency away from its original value. Fig. (1) illustrates both of these situations by showing normalized spectra of an initially 140 fs, unchirped laser pulse at its spatial (beam) center both before and after 2.5 mm of simulated propagation in fused silica glass. Note that the initial spectrum is centered at 800 nm and has a width ranging approximately from 790 nm to 810 nm, while the final spectrum is much broader and reaches its peak value at 838 nm. The question that this paper seeks to address is whether spectral widths and shifts, such as those shown in Fig. (1), can alter the outcome of LID in a measurable way.

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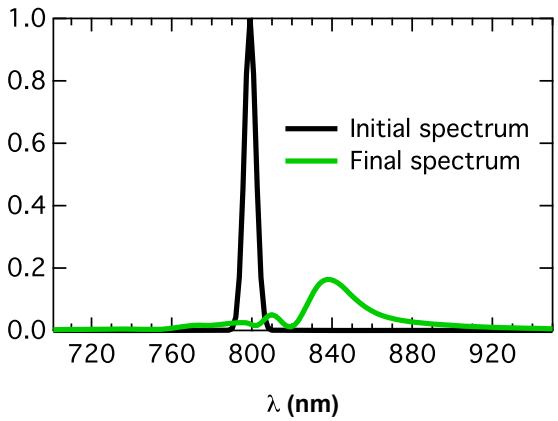

Figure 1. Initial spectrum (black line) and final spectrum (green line, grey in print) at the spatial center of an ultrashort laser pulse after propagation through a nonlinear medium in which LID is about to occur. The simulations giving rise to these plots are explained in detail in Sec. (3).

The results of this study suggest that the initial spectral variance found in laser pulses from a commercial femtosecond laser system can significantly affect the onset of LID by nonlinear optical changes to the instantaneous frequency at critical spatio-temporal locations within the pulse. To approximate these effects, simulations of ultrashort pulse propagation are performed in fused silica where the instantaneous frequency of the laser pulse is used in calculations of the photoionization rate. These results are compared to identical simulations of the kind ubiquitously performed in the literature, where the evolution of the electron plasma is calculated under the approximation that the pulse is monochromatic everywhere and at all times throughout the propagation.

2. THEORY

The most common models of photoionization used in ultrafast laser-induced damage calculations (the so called Keldysh[19] and PPT[20,21] models) include frequency dependence of the applied laser radiation. However, all of these models assume that the laser field is, at least approximately, monochromatic. When true, this condition ensures that the same number of photons must be absorbed for photoionization to occur anywhere in the multiphoton ionization (MPI) limit, regardless of the location in the material or the spatio-temporal position within the laser pulse. It could be argued that so long as a pulse's spectrogram were to remain symmetric about a central frequency, then violating the monochromatic assumption would not change the photoionization process significantly, as the absorption of lower energy photons would tend to be offset by the absorption of an equal number of correspondingly higher energy photons. Even in such a case, one must allow for the possibility of simultaneous absorption of photons with energies only lower (or higher) than those at the central frequency. In principle, such an event could result in an increase (or decrease) in the number of photons required for photoionization and thus alter the ionization rate accordingly.

At moderately high intensities between the MPI and tunneling limits, the issue is further complicated in the Keldysh model[19] by the need to absorb a total energy greater than the effective band gap

$$U_{\text{eff}} = U + \frac{e^2|\xi|^2}{4m_e\omega^2}, \tag{1}$$

where U is the standard band gap energy and the second term is the ponderomotive "wiggle" energy of the free carrier with charge e and effective mass m_e, $|\xi|$ is the laser field amplitude, and ω is the central optical frequency. In the multiphoton picture, the number of photons required for a photoionization event will be

$$n = \left\langle \frac{U_{\text{eff}}}{\hbar\omega} + 1 \right\rangle, \tag{2}$$

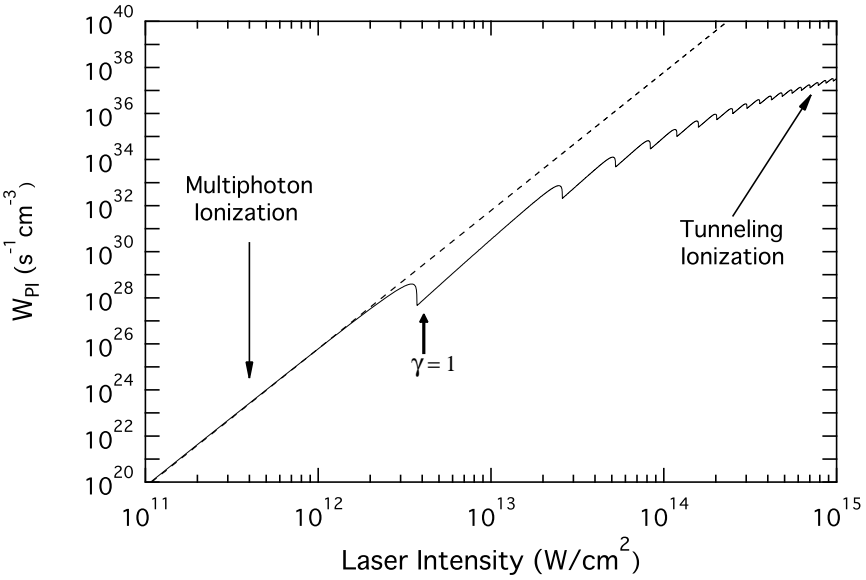

Figure 2. The Keldysh photoionization rate as a function of laser intensity for 800 nm light in fused silica with a band gap of 9 eV. The solid line shows the full Keldysh expression, while the dashed line shows the common multiphoton ionization rate that is valid at low intensities.

where the notation $\langle\cdot\rangle$ denotes the integer part. This condition ensures that the total number of photons required for photoionization will periodically increase as the laser intensity increases at a particular frequency. This further implies that, if the frequency of the field were to change, the MPI rate would change due both to changes in the ponderomotive energy of Eq. (1) and the photon energy in Eq. (2). The following subsections will demonstrate that such alterations may lead to changes of many orders of magnitude in the MPI rate.

2.1 The Keldysh Model of Photoionization

For the remainder of this work, the Keldysh photoionization rate for solids is used because in numerous studies it has provided good agreement with experiments of ultrashort laser pulse propagation in fused silica,[6, 11, 18, 22–28] and fused silica will be the material referenced in this work. The photoionization formula developed by Keldysh for solids is[19]

$$W_{\mathrm{PI}}(|\xi|,\omega;U,m)=\frac{2\omega}{9\pi}\left(\frac{m\omega}{\sqrt{\gamma_1}\,\hbar}\right)^{3/2}Q(\gamma,x)\exp\left(-\varpi\left\langle x+1\right\rangle\right). \tag{3}$$

Here the Keldysh parameter $\gamma=\omega\sqrt{mU/e}\,|\xi|$, $\gamma_1=\gamma^2/(1+\gamma^2)$, $\gamma_2=1-\gamma_1$, $\varpi=\pi\left(K(\gamma_1)-E(\gamma_2)\right)/E(\gamma_2)$, and $x=(2U/\pi\omega)(\sqrt{1-\gamma^2}/\gamma)E(\gamma_2)$. The functions $K(x)$ and $E(x)$ are complete elliptical integrals of the first and second kind, respectively, as defined in Ref. 29. The function $Q(\gamma,x)$ is given by

$$Q(\gamma,x)=\sqrt{\frac{\pi}{2K(\gamma_2)}}\sum_{n=0}^{\infty}\exp\left(-n\varpi\right)\Phi\left(\sqrt{\vartheta(n+2\nu)}\right),$$

where $\vartheta=\pi^2/4K(\gamma_2)E(\gamma_2)$, $\nu=\langle x+1\rangle-x$, and $\Phi(z)=\int_0^z\exp(y^2-z^2)dy$ is the Dawson function.

The solid line in Fig. (2) shows the Keldysh photoionization rate as a function of the optical intensity in fused silica with a band gap of 9 eV and an effective mass equal to the rest electron mass. The dashed line in Fig. (2) shows the Keldysh 6-photon (n=6) MPI rate; $W_{PI}=\sigma_6 I^6$, where $\sigma_6=6.04\times10^{-47}(\mathrm{cm}^2/\mathrm{W})^6\mathrm{s}^{-1}\mathrm{cm}^{-3}$ for the absorption of six 800 nm photons. Note that the Keldysh parameter γ is used to distinguish between the domains of MPI, $\gamma\gg1$, and tunneling ionization, $\gamma\ll1$. It is instructive to mention that the intensity at $\gamma=1$ in Fig. (2) marks the intensity at which MPI changes abruptly from a 6-photon process to a 7-photon

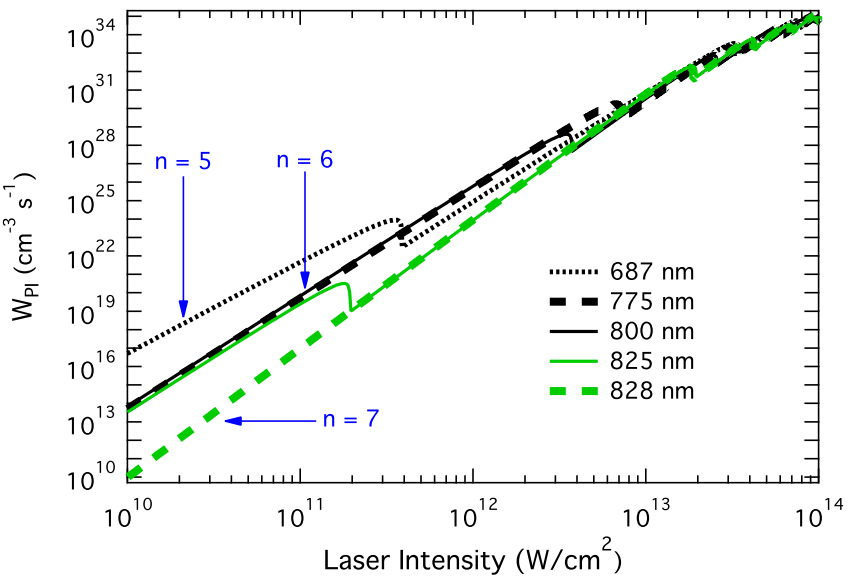

Figure 3. Photoionization rates as a function of laser intensity for various wavelengths around 800 nm in fused silica with a band gap of 9 eV. For this material the $n = 5$, $n = 6$, and $n = 7$ regions (as defined by Eq. (2)) are represented in the MPI (low intensity) regime.

process, hence the order of magnitude change from the dashed 6-photon MPI line. In the tunneling limit of high intensities for a particular frequency, the magnitude of these sudden periodic changes resulting from MPI decreases and the photoionization rate approaches that of a static field.

2.2 Photoionization Rates for Neighboring Wavelengths

To examine how different frequency components of an ultrashort laser pulse may affect the probability of photoionization, Fig. (3) shows the Keldysh photoionization rates for a field with a wavelength of 800 nm, as well as those for many neighboring wavelengths. Note that the 775 nm, 800 nm, and 825 nm wavelength rates are in good agreement for intensities in the MPI limit. This indicates that photoionization for the 140 fs laser pulse shown in Fig. (1), ranging spectrally from 790 nm to 810 nm, would be well approximated by simply using the rate for 800 nm in that limit. The same could be said for pulses as short as 50 fs that would still fit safely in the 775-825 nm spectral range. However, note the difference of 2–4 orders of magnitude between the 825 nm and 828 nm rates in the MPI limit. This is due to the fact that seven 828 nm photons are required to cross the band gap in the MPI limit, where as only six 825 nm photons are required. Note also that after crossing an intensity of 2×10^{11} W/cm^2 the 825 nm rate drops suddenly from a 6-photon rate to the 7-photon 828 nm rate. This is because an additional photon is required to cross the effective band gap at that intensity, as per Eq. (2). If significant portions of a pulse's spectrum were to lie on two different sides of such a transitional wavelength or intensity then it is unlikely the photoionization rate could be well approximated by the rate for a single wavelength. Nevertheless, ultrafast photoionization rates in the literature are almost exclusively calculated for a single wavelength.

Ultrashort laser pulses propagating through fused silica often experience bulk damage thresholds on the order of 10^{13} W/cm^2.[6,18,23] Figures (2) and (3) show that those intensities lie in the intermediate regime of the Keldysh photoionization rate where both MPI and tunneling ionization play significant roles, with the role of the former declining at high intensity and the role of the latter increasing. Therefore, at intermediate intensities Fig. (3) shows that all of the photoionization rates begin to converge to a single frequency-independent tunneling rate. If avalanching plays a significant role in ultrafast LID and photoionization rates for different frequencies begin to converge at and above the damage threshold intensity, then order-of-magnitude changes resulting from spectral variance in the photoionization rate should occur at the leading edge of the pulse where the intensity is lower

Table 1. A list of the variables and parameters used for all the simulations reported in this work. Material parameters are those for fused silica.

Symbol	*Description*	*Value*	*Units*
ξ	Electric field envelope		
r	Beam radius coodrinate		
z	Propagation axis coordinate		
τ	Retarded time coordinate		
$k(\omega)$	Wave vector		
ρ	Free-carrier number density		
σ	Free-carrier absorption cross section	$e^2\tau_c/n_0 c\epsilon_0 m_r(1+\omega_0^2\tau_c^2)$	
g	Free-carrier dispersion coefficient	$(-i\omega_0\tau_c)/(1-i\omega_0\tau_c)$	
I	Field intensity	$I=(1/2)n_0\epsilon_0 c\lvert\xi\rvert^2$	
k_m	m^{th} order dispersion coefficient	$\partial k/\partial\omega)_{\omega_0}$	
ω_0	Carrier frequency	$2\ \pi/\lambda$	
λ	Initial wavelength	800	nm
τ_0	Initial pulsewidth	140	fs
w_r	Initial beam waist	100	μm
E_0	Initial pulse energy	20	μJ
L_z	Sample length	2.5	mm
n_0	Linear refractive index	1.45	
n_2	Nonlinear refractive index	2.48×10^{-16}	$\mathrm{cm^2W^{-1}}$
f_r	Raman response fraction	0.18	
τ_1	Raman sinusoidal time	12.2	fs
τ_2	Raman decay time	32	fs
τ_r	Electron recombination time	150	fs
U	Material band gap	9	eV
m_r	Reduced electron-hole mass	0.5	m_{e0}
m_e	Effective electron mass	1.0	m_{e0}
τ_c	Free-carrier collision time	1.23	fs

and the precritical electron plasma is forming. Hence it is the initiation of laser-induced damage which should first be examined to find the influence of spectral variance.

3. SIMULATIONS

The effects of spectral variance on ultrafast LID are tested in this section by simulating the propagation of a 140 fs laser pulse through 2.5 mm of fused silica. A summary of all variables, initial pulse parameters, and material parameters for these calculations is provided in Table (1). During the course of this propagation the pulse undergoes catastrophic self-focusing and ends the propagation having generated a plasma density approaching, but not exceeding, the critical density of 10^{21} cm^{-3} often associated with permanent damage. This simulation is performed by solving for the complex envelope ξ of the linearly polarized, cylindrically symmetric electric field $\vec{E}$, defined by

$$\vec{E}(r,z,t)=\frac{1}{2}\left(\xi(r,z,t)\ e^{i(k_0 z-\omega_0 t)}+\text{c.c.}\right)\hat{x}\ .$$

The equation of propagation is derived in Ref. 30 and describes the evolution of ξ along the propagation axis z in the retarded time frame of the laser pulse, that is $\tau=t-z/v_g$, moving at the group velocity v_g.

$$\begin{aligned}\frac{\partial\xi}{\partial z} &= \frac{i}{2k_0}\hat{T}^{-1}\nabla_\perp^2\xi+i\hat{D}_b\xi+i\frac{k_0\epsilon_0 c n_2}{2}\hat{T}\left[\int_{-\infty}^{\tau}d\tau' R(\tau-\tau')|\xi(\tau')|^2\right]\xi \\ &\quad -\frac{\sigma}{2}\left(1+i\omega_0\tau_c\right)\hat{G}^{-1}\left[\rho\xi\right]-\frac{W_{\mathrm{PI}}U}{2\,I}\,\xi\end{aligned} \tag{4}$$

Here $\hat{D}_b$ is a bound charge linear dispersion operator, $\hat{G}$ is a free-carrier dispersion operator, and $\hat{T}$ is a steepening operator defined, respectively, as

$$\hat{D}_b = \sum_{m=2}^{\infty} \frac{k_m}{m!}(i\partial_\tau)^m,$$
$$\hat{G} = 1 + i\frac{g}{\omega_0}\partial_\tau,$$
$$\hat{T} = 1 + i\frac{1}{\omega_0}\partial_\tau,$$

where linear absorption due to bound charges is neglected. The first term on the right hand side of of Eq. (4) accounts for diffraction and linear shock, the second term accounts for dispersion due to bound charges, the third term represents contributions from the nonlinear polarization, the fourth term represents the contributions of free-carriers as calculated by the Drude model, and the fifth term accounts for absorption due to photoionization. The function $R(\tau)$ in the nonlinear term is the delayed nonlinear optical response function derived in Ref. 31 and is given by

$$R(\tau) = (1 - f_r)\delta(\tau) + f_r\frac{\tau_1^2 + \tau_2^2}{\tau_1\tau_2^2}\, e^{-\tau/\tau_2}\, \sin(\tau/\tau_1),$$

where the first term represents an instantaneous electronic response, f_r is the fraction of the Raman contribution to the nonlinear polarization, and the constants τ_1 and τ_2 are adjustable parameters chosen to provide an adequate fit with the Raman-gain spectrum. The nonlinear polarization term in Eq. (4) accounts for self-focusing, self-phase modulation, self-steepening (nonlinear shock), and stimulated Raman scattering.

Equation (4) must be solved simultaneously with an equation (or system of equations) describing the evolution of the free-carrier density ρ in the material. This paper uses a rate equation model for free-carriers in the conduction band:[6]

$$\frac{d\rho}{dt} = \left(W_{\mathrm{PI}} + \frac{\sigma I\rho}{(1 + m_r/m_{e0})U_{\mathrm{eff}}}\right)\left(1 - \frac{\rho}{\rho_{\max}}\right) - \frac{\rho}{\tau_r}. \tag{5}$$

This model includes contributions of photoionization, impact ionization (avalanching), and electron recombination. Equations (4) and (5) are solved simultaneously with the former being solved by a Crank-Nicholson finite difference method and the latter with a fourth-order Runge-Kutta method. To produce a qualitative indication of the importance of spectral variation in the laser pulse, the Keldysh photoionization rate W_{PI} in Eqs. (4) and (5) are calculated by Eq. (3) using the instantaneous frequency of the laser pulse, that is $\omega(\tau) = \omega_0 - \Im[(\partial_\tau\xi)/\xi]$, where the notation $\Im[\cdot]$ denotes the imaginary part. The plasma density generated by this simulation is then compared to that of an identical simulation where the frequency is assumed to be $\omega(\tau) = \omega_0$, *i.e.* monochromatic, for the entire laser pulse. The simulations begin by constructing the electric field envelope at the beginning of the propagation according to the formula

$$\xi(r, \tau, z = 0) = \sqrt{\frac{2I_0}{\epsilon_0 c}}\exp\left(-\frac{r^2}{w_r^2} - \frac{\tau^2}{\tau_0^2}\right),$$

where $I_0 = E_0/(\pi/2)^{3/2}\omega_r^2\tau_0$ is the initial peak intensity.

4. RESULTS

The evolution of the intensity and spectrum of the laser pulse during the 2.5 mm of propagation is shown in Figs. (4) and (5), respectively. Figure (4) shows the intensity of the pulse on the $r\tau$ plane. Figure (4,b-d) captures the process of catastrophic self-focusing as the pulse approaches $z = 2.5$ mm of propagation. At that point, shown in Fig.(4d), catastrophic self-focusing has occurred and LID is being initiated. If the influence of beam asymmetries and material defects were to be included, it is likely that the pulse as seen in Fig.(4d) would quickly undergo filamentation.[32] Note also that the peak intensity in Fig.(4d) of approximately 5×10^{13} W/cm^2, is significantly higher than that of the rest of the laser pulse. In other words, most of the energy of the laser pulse in Fig.(4d) appears in regions where the intensity is an order of magnitude lower than that found in the

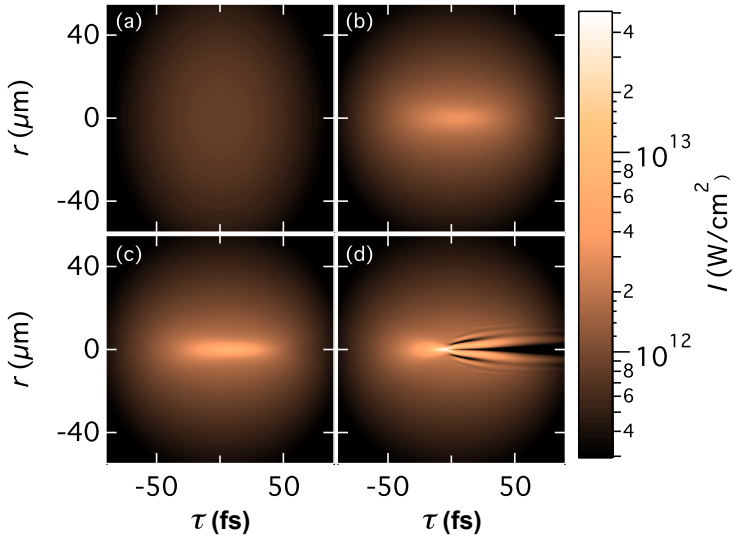

Figure 4. Laser pulse intensity as a function of the beam radius r and temporal position τ for propagation distances of (a) $z = 0$ mm, (b) $z = 2.3$ mm, (c) $z = 2.4$ mm, and (d) $z = 2.5$ mm in fused silica.

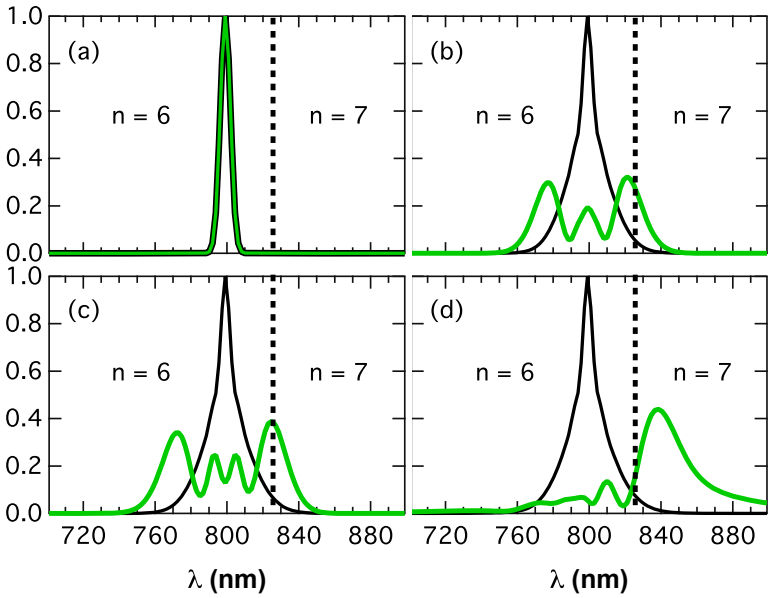

Figure 5. Normalized spectra of the complete laser pulse, shown in black, and the pulse at the beam center $r = 0$, shown in green (or grey in print), for propagation distances of (a) $z = 0$ mm, (b) $z = 2.3$ mm, (c) $z = 2.4$ mm, and (d) $z = 2.5$ mm in fused silica. The dashed black line marks the transition between ranges of $n = 6$ and $n = 7$ process for MPI, where n is defined by Eq.(2).

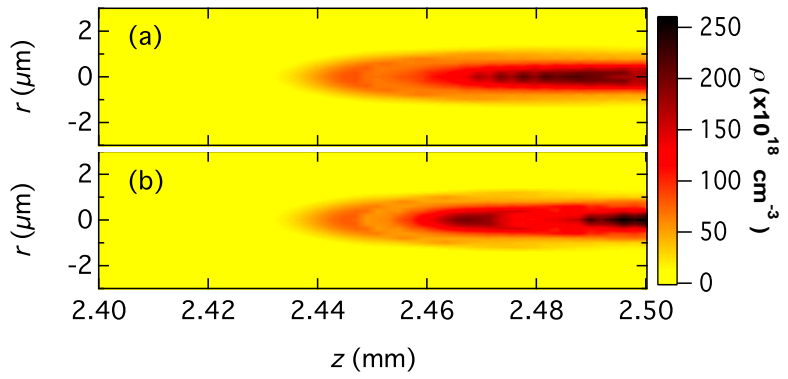

Figure 6. Maximum plasma densities generated between 2.4 mm and 2.5 mm of propagation in fused silica. A frequency corresponding to an 800 nm wavelength is used in the calculations of the Eq. (3) for (a), while (b) uses the instantaneous frequency of the laser pulse in calculations of Eq. (3).

spatio-temporal center region. Therefore, changes to the instantaneous frequency due to self-phase modulation will be an order magnitude greater at the center of the beam than on the wings. This is seen clearly in Fig. (5) which shows the normalized spectrum of the complete laser pulse (black line) and the spectrum at $r = 0$, or the beam center, (green line, or grey in print) at the same points during the propagation. Note that if laser-induced damage predictions are sought, it is the evolution of the plasma density at $r = 0$, or where ever the intensity is consistently high, that will ultimately make that determination because that is where damage is most likely to occur.

In Fig. (5a) the pulse spectrum and the $r = 0$ spectrum are identical because no nonlinear effects have occurred at the beginning of the propagation. However, at $z = 2.3$ mm Fig. (5b) shows significant deviation between the complete spectrum and the $r = 0$ spectrum due to the increased self-phase modulation at the beam center. In fact, the peak on the $r = 0$ spectrum does not even appear at 800 nm in Fig. (5b), nor will it for the remainder of the propagation. Despite these differences, most of the energy in the $r = 0$ spectrum in Fig. (5b), including the peaks of that spectrum, lie within the 6-photon (n=6) MPI range, and therefore the photoionization rate could be reasonably approximated by the 800 nm rate. In Fig. (5c), the peak of the $r = 0$ spectrum now lies on the transition region between the $n = 6$ and $n = 7$ MPI ranges. This spectral peak represents the "red-shifted" field on the front edge of the laser pulse, where the initial plasma density is being generated. It is therefore questionable whether a photoionization rate for an 800 nm field is a valid approximation on the leading edge of the pulse at this point in the propagation. At $z = 2.5$ mm, the overwhelming majority of the energy (as well as the spectral peak) for the $r = 0$ spectrum in Fig. (5d) is in the $n = 7$ MPI region. This would have the effect of reducing the photoionization rate on the front edge of the pulse by 2-4 orders of magnitude, as demonstrated by Fig. (3). The significantly red-shifted energy of the $r = 0$ spectrum in Fig. (5d) is that which remains at the front of the laser pulse after the blue-shifted light that formerly resided on the trailing edge was absorbed or dispersed by free-carrier optical effects (see the trailing edge of the pulse at $r = 0$ in Fig. (4d)).

Figure (6) shows the maximum plasma density generated in the material near the end of the propagation. Note that for the simulation where the instantaneous frequency is used in the Keldysh photoionization rate there is a range of about 20 μm from 2.47 mm to 2.49 mm where the plasma density is less than half the predicted value if the wavelength is assumed to be 800 nm throughout. It is also notable that the opposite is true at $z = 2.5$ mm where Fig. (6a) shows a maximum plasma density that is 40% smaller than that of Fig. (6b). These plasma densities do not exceed the frequently assumed value for permanent damage of 10^{21} cm^{-3}, but they are approaching this value within an order of magnitude. This range of plasma generation has previously been associated with reversible modifications to the material structure.[23] If one intends to use a commercial ultrashort laser system for the purpose of micromachining in bulk transparent materials, the above demonstrated 20 μm range of discrepant predictions for the generated plasma is not a trivial matter. A *post mortem* examination of this material region with a tightly focused laser pulse may be able to distinguish such differences.

5. DISCUSSION

Given these results it seems odd that this issue has not, to the author's knowledge, been addressed before current time. The consequences of spectral variance on LID initiation are demonstratively significant. There are perhaps two reasons why this may not have been addressed previously. The first is best demonstrated by a comparison of the complete spectra and the $r = 0$ spectra of Fig. (5). Note that from $z = 2.3$ mm to $z = 2.5$ mm, the complete pulse spectrum changes very little, despite the statio-temporal dynamics involved in catastrophic self-focusing as demonstrated in the corresponding plots of Fig. (4). Although the complete spectrum significantly broadens during the propagation, most of the pulse energy remains in the $n = 6$ MPI spectral region. If one relies only on the spectrum of the complete ultrashort laser pulse as a measure of chromatic integrity when calculating the plasma evolution, it is possible to significantly misrepresent the laser pulse in the material region where LID or filamentation will occur, especially if the pulse is chirped. Therefore, when calculating the plasma density, great care should be taken to account for the local spectrum in the region of concern.

The second reason this issue may not have been addressed previously is that, to the author's knowledge, there is no model of photoionization or avalanching that was derived specifically to account for pulses of arbitrary shape, temporal width, and phase. The Keldysh model, for example, was derived for a monochromatic CW field with a definite frequency;[19] as was the kinetic (Fokker-Planck) equation for the evolution of free-carriers in energy space[33,34] and the simplified rate equation that was derived from it,[12] (see Eq. (5) for a variation of this model). Even a more recently proposed multi-rate equation model for avalanching, developed by Rethfeld[16,17] specifically with ultrashort laser pulses in mind, still depends on the assumption of an approximately monochromatic field whose central frequency remains unchanged.

In this paper the author has attempted an *ad hoc* modification of the Keldysh photoionization rate for solids by performing calculations with the instantaneous frequency instead of the single frequency for which the model was derived. Such *ad hoc* modifications could also be extended to the models of avalanching. For example, one could use the instantaneous frequency when solving the kinetic (Fokker-Planck) equation for the electron energy distribution, or when calculating the Drude absorption cross-section in the rate equation. Additionally, one could "modify" Rethfeld's multi-rate equation model so that plasma electrons absorb photons of the instantaneous frequency. Doing that, however, would require the modeling of an effective energy continuum, in which case one may as well solve the Fokker-Planck equation. In any case, these *ad hoc* modifications should not be regarded as permanent substitutes for new comprehensive models of ultrafast photoionization and avalanching. The Keldysh model of photoionization was not derived with the assumption of a changing frequency, therefore the results of Fig. (6) are an admittedly *qualitative* demonstration. It has yet to be determined if a closed analytic formula, such as Eq. (3) or Eq. (5), can be derived for an ultrashort laser pulse of arbitrary shape and phase, but such a formula would be necessary for *quantitative predictions* of ultrafast LID and filamentation, as opposed to simply *qualitative descriptions*.

6. CONCLUSION

The validity of using photoionization rates derived for monochromatic fields to calculate ultrafast laser-induced damage has been investigated by inspection and simulation. In the multiphoton ionization limit, there are transitional wavelengths about which the number of photons required for photoionization changes by a single integer value, reducing or increasing the probability of the event by many orders of magnitude. If the spectrum of an ultrashort laser pulse straddles such a transitional wavelength, it is doubtful that a photoionization rate for a single frequency will accurately describe the initial generation of free-carriers. In the special case of fused silica with a band gap of 9 eV, the transitional wavelength from a 6-photon process to a 7-photon process occurs at approximately 827 nm. Given this condition, it was shown that MPI rates would be well approximated by simply using the rate for an 800 nm field in the case of an unchirped 800 nm laser pulse as short as 50 fs. However, 800 nm pulses shorter than 50 fs would straddle the 827 nm transition, as would longer but significantly chirped ultrashort pulses, such as the kind generated by self-phase modulation during self-focusing.

Simulations were performed to examine the influence of self-frequency shift in the initiation of laser-induced damage after propagating a 140 fs laser pulse through 2.5 mm of fused silica. The self-focusing of the laser pulse in the bulk material produced a local spectrum in the beam center with much greater variance than that of

the complete laser pulse. When pre-damage plasma absorption and defocusing became significant, the resulting spectrum at the beam center lay almost entirely in the 7-photon MPI region, as opposed to the 6-photon region near 800 nm in which it began the propagation and in which the wings of the pulse still resided. A simulation using the instantaneous frequency of the pulse to calculate photoionization rates was compared to a corresponding simulation using only the frequency of a constant 800 nm wavelength for calculating photoionization rates. The resulting differences in the generated plasma density were found to differ by as much as a factor of two, over distances as great as 20 μm. These results demonstrate the urgent need for new models of both photoionization and avalanching that account for the unique multi-frequency nature of ultrashort laser pulses.

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REFERENCES

[1] Boyd, R. W., [*Nonlinear Optics*], Academic Press, 3rd ed. (2008).

[2] Diels, J.-C. and Rudolf, W., [*Ultrashort Laser Pulse Phenomenon: Fundamentals, Techniques, and Applications on a Femtosecond Time Scale*], Academic Press, 2nd ed. (2006).

[3] Schaffer, C. B., Brodeur, A., Garcia, J. F., and Mazur, E., "Micromachining bulk glass by use of femtosecond laser pulses with nanojoule energy," *Opt. Lett.* **26**, 93–95 (Jan 2001).

[4] Schaffer, C. B. and Mazur, E., "Micromachining using ultrashort pulses from a laser oscillator," *Opt. and Phot. News* **12**, 20–23 (April 2001).

[5] Shimotsuma, Y., Kazansky, P. G., Qiu, J., and Hirao, K., "Self-organized nanogratings in glass irradiated by ultrashort light pulses," *Phys. Rev. Lett.* **91**, 247405 (Dec 2003).

[6] Winkler, S. W., Burakov, I. M., Stoian, R., Bulgakova, N. M., Husakou, A., Mermillod-Blondin, A., Rosenfeld, A., Ashkenasi, D., and Hertel, I. V., "Transient response of dielectric materials exposed to ultrafast laser radiation," *Appl. Phys. A* **V84**(4), 413–422 (2006).

[7] Zhu, X., Naumov, A. Y., Villeneuve, D. M., and Corkum, P. B., "Influence of laser parameters and material properties on micro drilling with femtosecond laser pulses," *Appl. Phys. A* **V69**(0), S367–S371 (1999).

[8] Vogel, A., Noack, J., Huttman, G., and Paltauf, G., "Mechanisms of femtosecond laser nanosurgery of cells and tissues," *Appl. Phys. B* **81**, 1015–1047 (Dec 2005).

[9] Giguère, D., Olivié, G., Vidal, F., Toetsch, S., Girard, G., Ozaki, T., Kieffer, J.-C., Nada, O., and Brunette, I., "Laser ablation threshold dependence on pulse duration for fused silica and corneal tissues: experiments and modeling," *J. Opt. Soc. Am. A* **24**(6), 1562–1568 (2007).

[10] Lenzner, M., Krüger, J., Sartania, S., Cheng, Z., Spielmann, C., Mourou, G., Kautek, W., and Krausz, F., "Femtosecond optical breakdown in dielectrics," *Phys. Rev. Lett.* **80**, 4076–4079 (May 1998).

[11] Mero, M., Liu, J., Rudolph, W., Ristau, D., and Starke, K., "Scaling laws of femtosecond laser pulse induced breakdown in oxide films," *Phys. Rev. B* **71**(11), 115109 (2005).

[12] Stuart, B. C., Feit, M. D., Herman, S., Rubenchik, A. M., Shore, B. W., and Perry, M. D., "Nanosecond-to-femtosecond laser-induced breakdown in dielectrics," *Phys. Rev. B* **53**, 1749–1761 (Jan 1996).

[13] Tien, A.-C., Backus, S., Kapteyn, H., Murnane, M., and Mourou, G., "Short-pulse laser damage in transparent materials as a function of pulse duration," *Phys. Rev. Lett.* **82**, 3883–3886 (May 1999).

[14] Jia, T. Q., Sun, H. Y., Li, X. X., Feng, D. H., Li, C. B., Xu, S. Z., Li, R. X., Xu, Z. Z., and Kuroda, H., "The ultrafast excitation processes in femtosecond laser-induced damage in dielectric omnidirectional reflectors," *J. Appl. Phys.* **100**, 023103 (Jul 2006).

[15] Quéré, F., Guizard, S., and Martin, P., "Time-resolved study of laser-induced breakdown in dielectrics," *Europhys. Lett.* **56**(1), 138 (2001).

[16] Rethfeld, B., "Free-electron generation in laser-irradiated dielectrics," *Phys. Rev. B* **73**(3), 035101 (2006).

[17] Rethfeld, B., "Unified model for the free-electron avalanche in laser-irradiated dielectrics," *Phys. Rev. Lett.* **92**(18), 187401 (2004).

[18] Wu, A. Q., Chowdhury, I. H., and Xu, X., "Femtosecond laser absorption in fused silica: Numerical and experimental investigation," *Phys. Rev. B* **72**(8), 085128 (2005).
[19] Keldysh, L. V., "Ionization in the field of a strong electromagnetic wave," *Sov. Phys. JETP* **20**(5), 1307 (1965).
[20] Perelomov, A. M., Popov, V. S., and Terent'ev, M. V., "Ionization of atoms in an alternating electric field: Ii," *Sov. Phys. JETP* **24**, 207 (1967).
[21] Perelomov, A. M., Popov, V. S., and Terent'ev, M. V., "Ionization of atoms in an alternating electric field: I," *Sov. Phys. JETP* **23**, 924 (1966).
[22] Berge, L., Skupin, S., and Steinmeyer, G., "Temporal self-restoration of compressed optical filaments," *Phys. Rev. Lett.* **101**(21), 213901 (2008).
[23] Couairon, A., Sudrie, L., Franco, M., Prade, B., and Mysyrowicz, A., "Filamentation and damage in fused silica induced by tightly focused femtosecond laser pulses," *Phys. Rev. B* **71**(12), 125435 (2005).
[24] Sudrie, L., Couairon, A., Franco, M., Lamouroux, B., Prade, B., Tzortzakis, S., and Mysyrowicz, A., "Femtosecond laser-induced damage and filamentary propagation in fused silica," *Phys. Rev. Lett.* **89**, 186601 (Oct 2002).
[25] Christensen, B. H. and Balling, P., "Modeling ultrashort-pulse laser ablation of dielectric materials," *Phys. Rev. B* **79**(15), 155424 (2009).
[26] Kaiser, A., Rethfeld, B., Vicanek, M., and Simon, G., "Microscopic processes in dielectrics under irradiation by subpicosecond laser pulses," *Phys. Rev. B* **61**, 11437–11450 (May 2000).
[27] Liu, J., Li, R., and Xu, Z., "Few-cycle spatiotemporal soliton wave excited by filamentation of a femtosecond laser pulse in materials with anomalous dispersion," *Phys. Rev. A* **74**(4), 043801 (2006).
[28] Polesana, P., Dubietis, A., Porras, M. A., Kucinskas, E., Faccio, D., Couairon, A., and Trapani, P. D., "Near-field dynamics of ultrashort pulsed bessel beams in media with kerr nonlinearity," *Phys. Rev. E* **73**(5), 056612 (2006).
[29] Abramowitz, M. and Stegun, I. A., [*Handbook of Mathematical Functions*], Dover, New York, tenth ed. (1964).
[30] Gulley, J. R. and Dennis, W. M., "Ultrashort-pulse propagation through free-carrier plasmas," *Phys. Rev. A* **81**, 033818 (Mar 2010).
[31] Blow, K. J. and Wood, D., "Theoretical description of transient stimulated raman scattering in optical fibers," *J. Quant. Electr.* **25**, 2665–2673 (Dec. 1989).
[32] Kandidov, V., Dormidonov, A. E., Kosareva, O. G., Chin, S. L., and Liu, W., [*Self-Focusing: Past and Present*], vol. 114 of *Topics in Applied Physics*, ch. 15, Springer (2009).
[33] Holway, L. H., "High-frequency breakdown in ionic crystals," *J. Appl. Phys.* **45**(2), 677–683 (1974).
[34] Holway, L. H., "Temporal behavior of electron distributions in an electric field," *Phys. Rev. Lett.* **28**, 280–283 (Jan 1972).

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Questions and Answers

Q. You talk of certain wavelengths that can cause problems in the region of interest, 700 – 900 nm. How many of them are there that are problematic and which ones are they?

A. Are you referring to the number of transitions in this region?

Q. I mean, the wavelengths that would cause problems because they are specifically at the border of a transition.

A. Fair enough. Let me go back in time a little bit here. Anytime you were to have a laser pulse that might be centered, say, at 827 nm, that would be a problem, or if you had a pulse that was centered around 690 nm, that would be a problem as well. These transition wavelengths can be calculated by just simply taking the regular bandgaps and dividing them by h-bar times the frequency in question. And, then you can get what these transition wavelengths are.

Q. Why don't you have anything about defocusing due to plasma in your model? As you have self-focusing, you also have plasma defocusing when you have this plasma. It has a different index of refraction which causes this effect.

A. There will be plasma defocusing and that is accounted for in the Drude model because it has both real and imaginary terms in it, and the plasma defocusing is in there but the self-focusing of the laser pulse is so strong that it has not yet stopped it. Eventually, it must stop it.

Q. In your model, you mention a 200 micron beam. Are you focusing ? Does your model focus the beam into the medium, or is it a parallel beam going through the medium?

A. It was assumed to have a flat phase going into the medium.

Q. Okay. You're aware, of course, that under certain conditions, certain intensities, one actually produces a white light continuum in materials and that continuum now has frequencies that go way into the bandgap and produces color centers and so forth and so on. Does what you are doing here only involve intensities below the continuum, is that what is going on?

A. There are, to my knowledge, parameters in the simulation that I could change if I wanted white light generation to come about. The way I designed the simulation, the critical power was so high and self-focusing was driven so strongly that laser-induced damage and free carrier generation essentially stopped white light generation before it could begin. It also stopped pulse splitting before it could begin. But, by lowering the intensity and allowing the self-focusing to continue over a much longer period, yes, you can get white light generation.

Q. I have a comment on the question from "The Ohio State University". Certainly, we've seen experiments with 3-photon absorption or less where the defocusing absolutely dominates the process, and no damage occurs.

Q. You said that the transition wavelength is very sensitive to the bandgap, of course, and you have chosen a 9 eV bandgap for fused silica, which, in my opinion, a very, very expensive fused silica than you need, a very dry fused silica, and maybe even a fluoride doped silica to get this. Typical fused silica from the stock for 900 nm would have a bandgap of 7 or 8 eV. This would certainly shift your transition. Have you checked this? Maybe it's not very dependent any more on your change of the wavelength because, you are settled right in the middle between the two transitions and maybe it's not very important for this kind of fused silica.

A. I have not checked it. I was doing these simulations with, in mind, the particular fused silica samples that I had available in my laboratory.

Q. You know that 9 eV is associated with no –OH in the glass and fluoride doping to get this. People know it from 157 nm experiments to get any light through fused silica. Maybe you can just consider this with a typical silica having a bandgap of 7.5 eV bandgap. And, just another question. If you go over the bandgap with fused silica, you definitely generate stable defects, e' and the –OH, which have certain energy levels in the bandgap. If you account for this, it may alter your multiphoton ionization process.

A. Yes. If I understand your question correctly, then no. If you're talking about energy levels located within the bandgap, then, no, I did not account for that. I assumed that the gap was clean.

Q. Thanks for your presentation. It's a very interesting presentation on a very interesting problem. But, that problem is extremely complicated because when you apply the Keldysh formula, you automatically assume that the multiphoton absorption happens because of simultaneous absorption of several similar photons of similar energy. When you have multifrequency electric field of the laser irradiation, definitely you have simultaneous absorption of several different photons with different energies. Do you have any ideas as to how to attack this problem?

A. At the moment, that's still under investigation, and that's why I emphasized on the conclusion slide that this kind of *ad hoc* approach of throwing in the instantaneous frequency is, a), meant to give a qualitative (not necessarily quantitative) estimate as to how significant these changes would be and b) it is not, not a substitute for a comprehensive formalism which is still a matter for open investigation. It's worth noting, though, that the Keldysh model has been modified in such a way for a gas in recent years (2008 by some Russian authors). It just hasn't been done for solids to my knowledge.

Q. What is the critical distance. Do we need to take this into account when dealing with optical coatings? I mean, very thin films? It's well known that over longer distances, pulses split into many filaments. Do you get the same solution in your model?

A. My simulations indicate that with propagation after the 2.5 mm that I showed here, that filamentation probably is going to occur, but I stopped it because the intensities… I actually reached a level where the approximation was no longer valid. So, I stopped it there. Now I can't remember the rest of your question.

Q. About the applicability of your model to the coatings…..

A. With regard to the distance it needs to propagate, that depends very greatly on what the peak intensities are at the start. You could alter the distance it needed to propagate in order to see these effects by changing what the intensities are, and then it's completely knows. The self-focusing distance will completely determine it and it's completely dependent on the intensities.

Q. I have a small comment on the previous question. The thing is that you need the TDSE (Time-Dependent Schrödinger Equation). Sorry, I was actually told by some other people that I should sy "The Ohio State University"; that's why I keep saying this as my institution. So anyway, it's been solved for gas, a single electron type model in the 90's and then for a 2-electron atom model in the late 90's and early 2000's but for solids, there is some work that has been done and is still going on. It's still going to be nonlinear TDSE. I presume that your model is just time-independent?

A. When you say the Schrödinger equation, are you referring to the propagation or the…

Q. No, no, both because basically you also have to model the ionization.

A. Yes.

Q. So, you're using the time-dependent Schrödinger equation for the ionization, because it's in a non-perturbative regime.

A. No. Strictly speaking, I'm just using the Keldysh formula to calculate photo-ionization and the rest of it is really quite classical.

Q. Okay. Yes. So, the approach you have to take the ionization as a non-perturbative Schrödinger equation.

A. Right. I can tell you what people in my position really want, iss that we want another Keldysh formula that we can put in place of the one currently used here, one that accounts for the shape and phase of an ultrashort laser pulse. It will require a bit more information, but if we could get an analytic approach, that would be nice. It might not be possible, we don't know.

Q. How difficult is it to actually measure that stuff and confirm or modify the model?

A. Do you mean, how would one perform an experiment to measure which aspect of the model?

Q. All of the aspects, the spectrum…

A. The spectrum, if you really wanted to verify what the spectrum was, well, measuring the spectrum of the entire laser pulse is pretty straightforward. If you want to just look at the spectrum at the center of the beam, then you would need to apply an appropriate aperture. But, as for actually looking at the actual damage tracks, that's a much trickier issue, I realize. But, I would say, my best advice on that would be to concentrate on the spectroscopy aspect of it first and see whether that matches and then if there are appropriate ways to look at the damage tracks to see the kinds of changes, then there may not be. I'm not as familiar with that part of the field. If there are, use them, and if not, then go with a pure spectroscopy approach.