Experimental Investigation of Ultrashort Pulse Laser-Induced Breakdown Thresholds in Aqueous Media

Daniel X. Hammer, Robert J. Thomas, Gary D. Noojin, Benjamin A. Rockwell, Paul K. Kennedy, and William P. Roach

***Abstract*—Laser-induced breakdown (LIB) thresholds are determined for pulse durations of 2.4 ps, 400 fs, and 100 fs at 580 nm in high purity water, saline and tap water. The dependence of LIB irradiance thresholds on pulse duration, optical wavelength, and focal volume is examined, and the experimental data obtained is compared with a theoretical model. The slopes of the probability curves calculated are compared with mechanisms for LIB, namely avalanche ionization, multiphoton initiated avalanche ionization, and multiphoton ionization. Lastly, the dependence of the peak breakdown electric field on pulse duration and focal volume is empirically determined and compared with previous work.**

I. Introduction

ALL matter exists in one of four states: solid, liquid, gas, or plasma. The plasma state occurs when matter is in the form of a charged mixture of positive ions and negative electrons. Laser-induced breakdown (LIB), one mechanism for creating plasmas, is a process that has been studied extensively in the previous 30 years since the discovery of the laser [1]–[3]. It has been studied predominately in gases and solids, driven by theory and applications pertaining to those states. Within the past fifteen years, LIB has been used in diversified applications extending from ophthalmic surgery to determination of hazardous waste contaminates [4], [5]. For example, LIB is used to puncture holes in ocular tissue in capsulotomies and iridotomies. Moreover, laser safety requires a thorough understanding of the mechanisms of optical radiation damage, which include LIB for ultrashort pulse exposures. In particular, the American National Standards Institute laser safety standards (ANSI Z136.1-1993) [6] have included only guidance but no definitive safety limit for pulses less than 1 ns due to lack of both biological data and a quantitative understanding of the damage processes induced by ultrashort pulses. LIB is believed to be one of the causes of ultrashort pulse lesions in the eye [7]. In fact, LIB has recently been observed in albino rabbit eye exposures to visible femtosecond pulses [8]. Attention has thus turned to LIB in liquids, particularly water and ocular media.

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D. X. Hammer, R. J. Thomas, B. A. Rockwell, and P. K. Kennedy are with Armstrong Laboratory, Brooks AFB TX 78235-5215 USA.

G. D. Noojin is with TASC, Inc., San Antonio, TX 78215 USA.

W. P. Roach was with Armstrong Laboratory, Brooks AFB TX 78235-5215 USA. He is now with the Air Force Office of Scientific Research (AFOSR), Washington, DC 20332-8080 USA.

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Many studies have documented the irradiance thresholds, the spatial and temporal dynamics, and various other characteristics of LIB for longer ($\tau_P > 30$ ps) pulse durations [9]–[17]. Herein we report observations of LIB made for various aqueous solutions that simulate ocular media at 580 nm and pulse durations of 100 fs, 400 fs, and 2.4 ps. To our knowledge, these are the first reported measurements of femtosecond pulse LIB thresholds in aqueous media.

This paper will concentrate on the experimental data and trends of ultrashort pulse LIB. In addition, we will make comparisons with past threshold data at longer pulse durations. We will examine data and trends for: a) LIB irradiance thresholds; b) the slope of the breakdown probability curve; and c) the amplitude of the electric field. Two papers from our laboratory [18], [19] outline the theoretical model of ultrashort pulse LIB and compare the theoretical model with the experimental data.

The measurement and characterization of LIB in ocular media for ultrashort ($\tau_P < 1$ ns) laser pulses is important in understanding eye damage mechanisms for both determination of detrimental laser exposure thresholds and application of beneficial ophthalmic techniques. Such studies are necessary for an understanding of the physics, for knowledge that may lead to future applications, and for laser safety related issues.

II. LIB Process

LIB is a complex process with many different thermal, acoustic, and mechanical effects. For brevity, this paper will highlight only the main points in the process. A laser pulse at high enough irradiance, directed into a cuvette of water or similar fluid, will break down the liquid, producing a plasma. A visible flash is emitted from the plasma and is usually used as an indicator of LIB. This broadband visible flash is a result of Bremsstrahlung emission and electron recombination. The plasma expands because of its high temperature and pressure. As it expands, it creates a shock wave traveling at supersonic speeds and a cavitation bubble. The plasma continues to expand and vaporize liquid. The cavitation bubble of vaporized gases expands from the breakdown site. The cavitation bubble then collapses, and may release a second shock wave depending on the pulse energy. The cavitation bubble may collapse and reexpand a number of times, ending when there is insufficient energy in the expansion to sustain bubble growth. A residual bubble is created from gas diffusion into the expanded cavity. The residual bubble is used in

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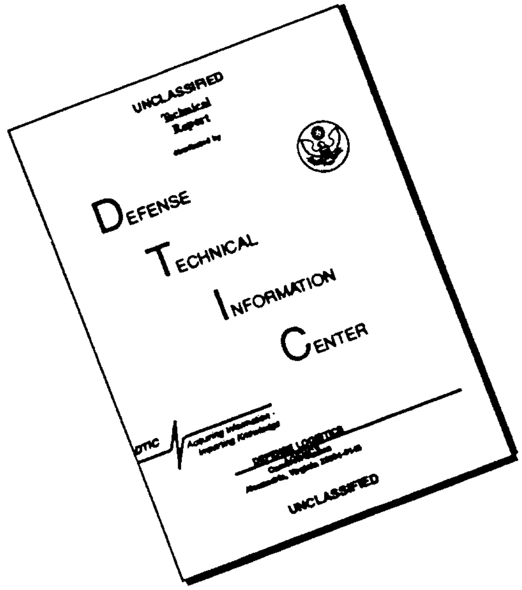

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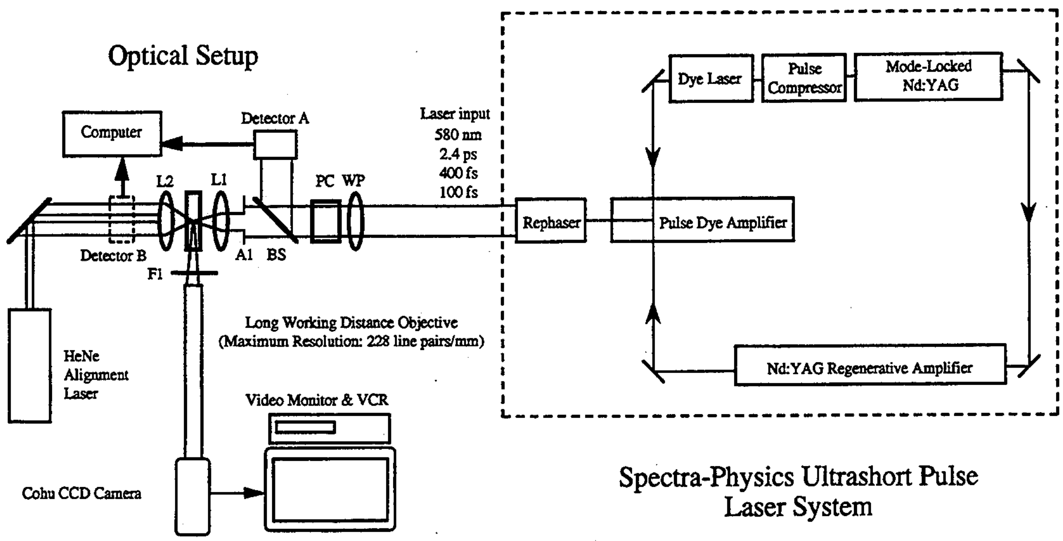


Fig. 1. Schematic of the optical setup used to measure LIB thresholds in ocular media. Components: $L1$ = 17 mm aspheric lens, $L2$ = 25 mm lens, PC = polarization cube, WP = 1/2 waveplate, $F1$ = 580 nm filter, $A1$ = aperture.

this study to quantify the LIB threshold for ultrashort pulse durations [9], [20], [21].

LIB is a stochastic event, usually defined by a threshold electron density in the focal volume estimated at 10^{18}–10^{20} cm^{-3} [18]. This electron density can be produced by three mechanisms: avalanche (or cascade) ionization initiated by seed electrons from impurities, avalanche ionization initiated by multiphoton absorption, and pure multiphoton ionization.

Avalanche ionization occurs if an initial quasi-free seed electron in the focal volume absorbs photons, accelerates and frees bound electrons by collisional ionization. These electrons in turn accelerate and free more electrons and an avalanche process occurs, forming a plasma. Avalanche ionization requires initial seed electrons and therefore tends to be impurity dependent. Impurity initiated avalanche ionization is the primary breakdown process for impure media at long pulse durations. For pure media, seed electrons must be provided by multiphoton ionization, which occurs when bound electrons are freed by absorption of multiple photons. Multiphoton-initiated avalanche ionization is the primary breakdown process for pure media at long pulse durations.

At intermediate pulsewidths, multiphoton initiation dominates any contribution of seed electrons from impurities. Thus, breakdown in both pure and impure media is by multiphoton initiated avalanche ionization. There is, however, a time constraint on avalanche breakdown due to the fact that the pulse must remain in the focal volume for a long time compared to the collisional ionization time. For pulsewidths of a picosecond or less, the pulse interaction time may be insufficient to support an avalanche from low initial densities to breakdown. In this transitional regime, multiphoton ionization must provide very high initial densities (multiphoton "jump start") before avalanche ionization can complete the breakdown process.

Pure multiphoton breakdown occurs in the low fs time regime where the pulse is present in the focal volume only long enough for instantaneous ionization to occur. Each atom is independently ionized by the field, so neither particle-particle interactions or seed electrons are necessary.

Most authors of previous LIB measurements have used visible flash as the endpoint for determining the threshold for LIB. These studies report the LIB threshold down to 30 ps. One study [13] used the cavitation bubble as the endpoint for LIB thresholds at 40 ps. We have found in our study that the residual bubble is a simple endpoint for measurement of the breakdown threshold due to the lack of visible flash for pulse durations of 3 ps and below. However, the LIB threshold may be determined by other endpoints, such as an acoustic shock wave signal from a hydrophone, or a cavitation bubble signal from a pump-probe or strobe light experiment.

III. Experimental Apparatus

The ultrashort pulse laser system used to produce visible wavelength (580 nm), gigawatt peak power pulses and the optical setup for measurement of laser-induced breakdown thresholds are shown in Fig. 1. The laser system was built by Spectra-Physics, Inc. The primary pulse comes from a mode-locked Nd:YAG laser that generates 80 ps pulses at 82 MHz pulse repetition frequency, 1064 nm wavelength, and approximately 11.5 W average power. The pulses are compressed to 5 ps with a fiber grating compressor and frequency doubled to 532 nm. A rhodamine dye laser is synchronously pumped by the compressed pulse and outputs 3 ps to 300 fs pulses at 580 ± 5 nm, 150 mW average power, and 82 MHz. The pulse is fiber chirped to 580 ± 15 nm. The pulse is amplified in a kiton red pulse dye amplifier. The pulse dye amplifier is pumped by a Nd:YAG regenerative amplifier, which is seeded by the mode-locked Nd:YAG. This also maintains the timing when the pulses are combined in the pulse dye amplifier. The pulse out of the pulse dye amplifier is then rephased with a prism pair. The output pulse is 580 nm at 100 μJ, and the pulse duration can be adjusted from approximately 100 fs to 3 ps.

The energy output from the laser was continuously controlled by 1/2 waveplate and polarization cube. Energy into the system was monitored by detector A. The pulses were

TABLE I-A
SUMMARY OF LIB THRESHOLD MEASUREMENTS FOR 2.4 ps PULSES

Medium	E (μJ) (variance)	d (μm)	F (J/cm²)	Slope	ε_B (V/cm)	I (W/cm²)
High Purity Water	4.08 (4.03-4.13)	21	1.18	57.24	1.67E+7	4.91E11
Saline (0.9% NaCl)	4.17 (4.12-4.22)	(±2.5)	1.20	68.96	1.69E+7	5.02E11
Tap Water	4.15 (4.10-4.20)		1.20	65.30	1.68E+7	4.99E11

TABLE I-B
SUMMARY OF LIB THRESHOLD MEASUREMENTS FOR 400 fs PULSES

Medium	E (μJ) (variance)	d (μm)	F (J/cm²)	Slope	ε_B (V/cm)	I (W/cm²)
High Purity Water	1.92 (1.59-2.31)	22	0.51	14.75	2.67E+7	1.26E12
Saline (0.9% NaCl)	1.99 (1.65-2.40)	(±2.5)	0.52	16.33	2.72E+7	1.31E12
Tap Water	1.92 (1.60-2.32)		0.51	14.80	2.67E+7	1.26E12

TABLE I-C
SUMMARY OF LIB THRESHOLD MEASUREMENTS FOR 100 fs PULSES

Medium	E (μJ) (variance)	d (μm)	F (J/cm²)	Slope	ε_B (V/cm)	I (W/cm²)
High Purity Water	1.31 (1.19-1.46)	17	0.58	9.90	5.72E+7	5.77E12
Saline (0.9% NaCl)	1.27 (1.15-1.41)	(±2.5)	0.56	11.62	5.63E+7	5.60E12
Tap Water	1.27 (1.14-1.40)		0.56	10.40	5.63E+7	5.60E12

focused into a cuvette by a 17 mm aspheric lens used to approximate the reduced focal length of the eye. Energy out of the cuvette was recollimated by a 25 mm spherical lens and monitored by detector B. Alignment of optics was made by transmission and back reflection of a He-Ne alignment laser. LIB was observed by imaging the bubble formation with a long working distance objective and CCD camera. Two observers were used to monitor video of the medium and determine if breakdown occurred.

Aberrations inherent within the 17 mm aspheric lens were measured with the knife-edge technique [20], [22] which gives the beam diameter in the focal volume of a lens. All beam diameter measurements were performed with the optical setup in Fig. 1, i.e., at the beam focus within the cuvette of water. From a fit of the beam diameter, we get a quantitative measure (the M^2 value) of all lens aberrations but no information of the degree to which a particular aberration distorts the beam. A measurement of the beam diameter is very important in specifying the LIB irradiance thresholds, but is rarely made. More often than not, the diffraction-limited spot sizes are used in irradiance calculations. This leads to erroneous calculations of the focal area and thus inflated irradiance calculations. Beam diameter measurements for each pulse duration are shown in Table I. The energies used in the knife-edge measurements made for this study were several orders of magnitude below the threshold for LIB and below the irradiance levels where appreciable self-focusing occurs. Some evidence [23] suggests that the beam diameter may decrease at higher irradiance levels, specifically at LIB irradiance levels. This has important implications for damage thresholds in the eye.

The dependence of LIB irradiance thresholds on spot size for long pulse durations is well documented [10]–[12]. Therefore, an optical system is desirable which closely approximates the eye in both focal length and degree of aberration. However, data on the beam diameter on the retina is limited [24], [25]. Moreover, the extent of aberration in a human eye varies widely from person to person. The 17 mm aspheric lens is a good first approximation of the eye and for comparison with past data. The ideal optical setup is one that can vary its performance from diffraction-limited to a high degree of aberration.

Three different aqueous media were used to model ocular media: high purity water, saline, and tap water. The high purity water was triply deionized, 18 MΩ-cm water from a water purification system made by Continental Water Systems Corporation. The saline was 0.9% sodium chloride irrigation saline made by Baxter Healthcare Corporation. The tap water was not tested for impurity content.

IV. RESULTS

Table I summarizes the LIB threshold (50% probability) measurements for each pulse duration. Fig. 2(a)–(c) shows the irradiance probability curves calculated from the energy probability curves. The energy probability curves were calculated by probit analysis of 200 single shot pulses taken over a single day. Energy probability curves were calculated for each medium for four days. Analysis of variance of the 50% probability threshold for all four days yielded the energy threshold measurements (E) with variance in parentheses. Analysis of variance was performed to quantify the day-to-day variations in the data that could not be eliminated from the laser system and optical setup. The fluence or energy density (F) and irradiance (I) calculations were made from the energy and the beam diameter (d) measurements. The slope of the energy probability curve between ED_{84} and ED_{50} is calculated by probit analysis. The peak electric field (ε_B) is related to the peak irradiance (I) by $\varepsilon_B = [2I/nc\varepsilon_0]^{1/2}$ where n is the refractive index of water, c is the velocity of light, and ε_0 is the permittivity constant.

V. DISCUSSION

The following remarks can be made from an examination of the data:

a) The irradiance thresholds increase while the energy thresholds decrease as the pulse duration is decreased from 2.4 ps to 100 fs. The fluence threshold decreases from 2.4 ps to 400 fs and then increases to 100 fs. Furthermore, the differences in threshold between different media are negligible (within the error bars of the data) for pulse durations less than 2.4 ps.

b) The slopes of the probability curves decrease as the pulse duration decreases from 2.4 ps to 100 fs.

c) The dependence of the peak breakdown electric field (ε_B) on pulse duration (τ_P) and focal volume (V) was empirically determined to be $\varepsilon_B = A/(\tau_P V)^{0.25} + C$ where A and C are constants.

Each of the observations above will be discussed in greater detail in the following sections.

A. Irradiance Threshold Trends

The irradiance threshold for pulse durations from 22 ns to 100 fs for different media is shown in Fig. 3(a)–(c). All

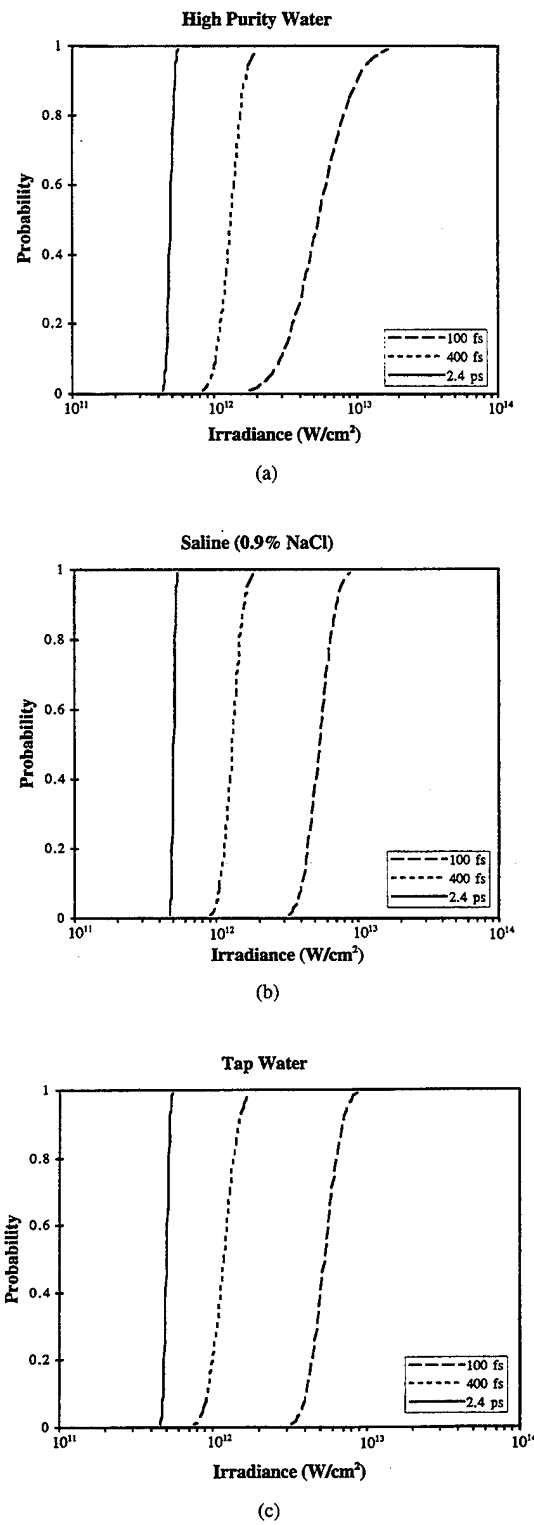


Fig. 2. Irradiance probability curves for LIB in (a) high purity water, (b) normal saline (0.9% NaCl), and (c) tap water at 580 nm and pulse duration of 100 fs, 400 fs, and 2.4 ps.

authors [10], [11], [13], [15], [19], [26], [27] used thresholds corresponding to 50% probability of breakdown. The legend in each figure shows each author with the wavelength and beam diameter at focus in parenthesis. Only recently have theories emerged that describe LIB for pulse durations less than 1 ps [18], [28]. The theory that relates irradiance with wavelength, focal volume, pulse duration, media characteristics, and the mechanism for breakdown (avalanche ionization or multiphoton ionization), is quite complex [18]. However, the trends in the data shown in Fig. 3 can be compared to a simplified model for insight into the dependence of irradiance on pulse parameters (wavelength, focal volume, and pulse duration). Differences in media parameters will generally be ignored because their influences are negligible in the ultrashort time regime.

The model for LIB detailed elsewhere [18] computes the irradiance threshold necessary for breakdown in three pulsewidth regimes: 1) For long pulses ($\tau_p > 200$ ps) breakdown is by avalanche ionization, which is initiated from impurities in impure media and through multiphoton absorption in pure media. 2) At shorter pulsewidths (200 ps $> \tau_p >$ 200 fs) breakdown in both pure and impure media is by multiphoton initiated avalanche ionization. As mentioned previously, for subpicosecond pulses multiphoton ionization must provide very high initial densities (multiphoton "jump start") before avalanche ionization can complete the breakdown process. 3) For ultrashort pulses ($\tau_p < 200$ fs) a transition occurs from multiphoton-assisted avalanche breakdown to pure multiphoton breakdown. The pulse durations corresponding to these regimes depend on wavelength and spot size. The values listed above are for our experimental values, $\lambda = 580$ nm and $d \approx 20$ μm.

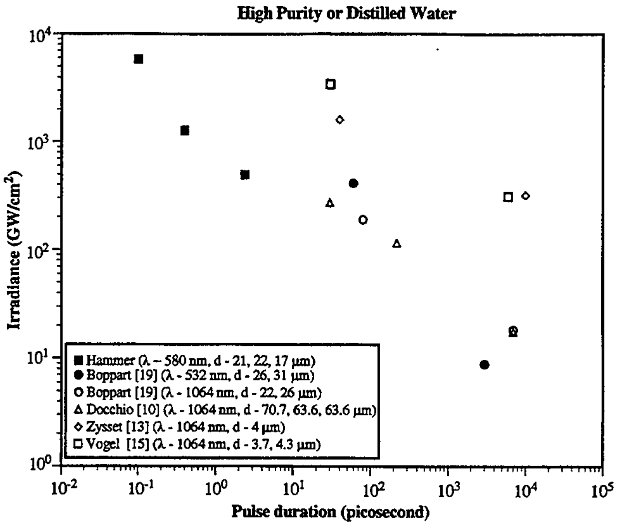
Only one data point from Fig. 3(a)–(c) corresponds to the multiphoton ionization regime so we will not discuss trends in this regime except to say that the model predicts the experimental threshold to within 5.4% [19]. Two equations give the thresholds for avalanche breakdown (I_{th}) and multiphoton initiation of avalanche breakdown (I_m),

$$I_{\text{th}} = A\left[g + 2(\tau_p)^{-1}\ln\left(\frac{\rho_{\text{cr}}}{\rho_0}\right)\right] + B \tag{1}$$

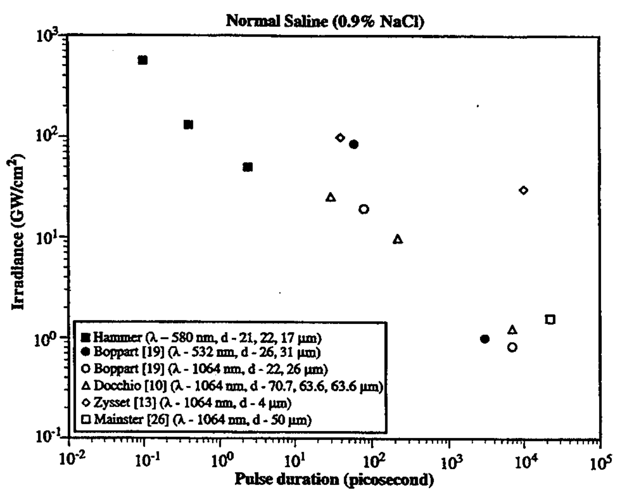
$$I_m = C[\rho_0 D(0.1\tau_p)^{-1}]^{1/K}, \tag{2}$$

where $A, B, C,$ and D depend on the optical frequency squared (ω^2), K depends on the optical frequency (ω), g describes the diffusion losses, ρ_{cr} is the critical electron density at breakdown, and ρ_0 is the minimum initial electron density, which depends on focal volume. Diffusion losses are significant only for pulses greater than 10 ns and can be ignored here. Equations (1) and (2) outline a dependence of the irradiance required for breakdown with pulse duration, optical frequency or wavelength, and focal volume. These equations can be compared to the experimental dependence of irradiance on pulse parameters.

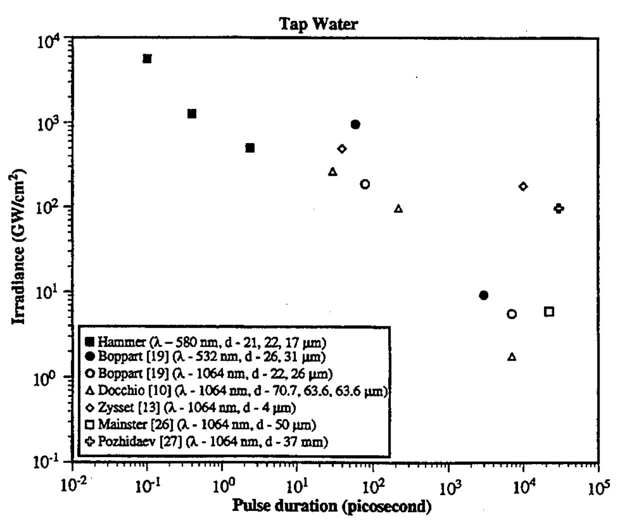
The wavelength dependence of the irradiance breakdown is included in the parameters $A, B, C, D,$ and K. This dependence tends to drive the breakdown threshold down as the wavelength is increased (or the optical frequency is decreased). Fig. 3 separates the data between visible (solid symbols) and infrared wavelengths (open symbols). From the figure, no experimental dependence is seen and thus any dependence on



(a)



(b)



(c)

Fig. 3. LIB threshold trends for (a) high purity water, (b) normal saline (0.9% NaCl, and (c) tap water. Open symbols indicate infrared wavelength data and closed symbols indicate visible wavelength data.

wavelength is masked by the dependence of irradiance on the other pulse parameters.

The focal volume dependence is included in calculations of the minimum electron density required to initiate breakdown (ρ_0). For $I_{\rm th}$ (avalanche breakdown), which dominates for very impure media or long pulses, a smaller focal volume will drive the threshold down, although only a slight amount due to the logarithmic dependence. For I_m (multiphoton initiation of avalanche ionization), the exact opposite is true, namely, that as the focal volume decreases the threshold will increase. This result can be understood qualitatively by the observation that as focal volume decreases the required minimum initial electron density will increase. Fig. 3 shows a focal volume dependence that corresponds to theory. Vogel and Zysset's data, taken at smaller spot sizes, have higher thresholds than the other data. The focal volume dependence will be discussed further in Section C.

Theory predicts an inverse relationship of pulse duration with irradiance. As seen in Fig. 3, this dependence agrees well with experiment. The pulse duration dependence will also be discussed further in Section C.

One additional comment regarding the irradiance threshold trends. There is a large variation of the data for tap water in the ns regime. Since seed electrons are provided by impurities, multiphoton initiation is not needed in tap water. A larger variation can therefore be expected in tap water where a wide variation in impurities from sample to sample can exist. For the shorter pulse durations examined in this paper, the differences in thresholds for different media are negligible. This indicates a breakdown process determined by multiple absorption of photons by the water molecules themselves; either to initiate the avalanche breakdown process by raising the initial free electron population or, when the width of the pulse is too short for avalanche breakdown to occur, to initiate pure multiphoton ionization. LIB caused by multiphoton absorption is impurity independent and thus the thresholds for different media will be the same.

Less energy is required to produce breakdown as pulse duration is decreased. This is an indication that the plasma temperature at threshold is cooler for ultrashort pulses than for longer duration pulses. This is seen qualitatively in the weaker acoustic and mechanical effects produced by the plasma. Both the sound of the plasma (a loud snap at ns durations) and the distance the residual bubble is ejected out of the focal volume are decreased. Quantitative measurements have indicated the same result [29]. Moreover, the cooler plasma at shorter pulse durations would explain the lack of visible broadband flash. The peak of the black body curve of the breakdown spectrum shifts to the infrared for cooler plasmas.

The trends in the irradiance threshold for LIB in saline and minimal visible lesions (MVL) in monkey eyes are shown in Fig. 4. Both irradiance trends exhibit an inverse relationship with pulse duration. Although the difference in thresholds at some points is more than an order of magnitude, the trends may indicate a relationship between the effects of LIB and the damage caused by retinal lesions, especially for pulse durations less than 1 ps. Furthermore, the irradiance thresholds for LIB indicate that catastrophic subretinal hemorrhagic lesions, that

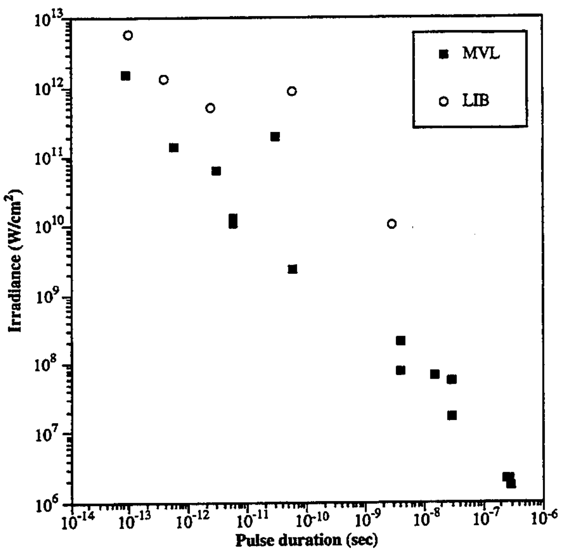


Fig. 4. Comparison of minimum visible lesion (MVL) irradiance thresholds in monkeys and LIB irradiance thresholds in saline. MVL irradiance is calculated with 10 μm spot size on retina. Visible wavelength was used for all data (480–580 nm).

occur at higher thresholds than LIB, may be accompanied by LIB in the vitreous and retinal layers causing rupture of Bruch's membrane and bleeding of the choroidal vessels.

B. Slopes of the Probability Curves

The average slopes of the probability curves across four days are listed in Table I. The trend observed is a decrease in average slope as the pulse duration decreases. This result is counterintuitive to the prevailing thought, namely, that as avalanche ionization gives way to multiphoton ionization, the slope of the probability curve should increase. This is due to a decreased dependence on impurities, and thus a more deterministic mechanism at the shorter pulse durations. This hypothesis has been experimentally confirmed by other authors who have seen increasing slopes as pulse duration decreases [10].

Past work, however, has resided exclusively in the long pulse, avalanche ionization regime, where impurities play a major role in the initiation of breakdown. For pulses less than 100–200 ps, the impurity dependence of the breakdown threshold vanishes, due to the fact that the threshold for multiphoton initiation of breakdown falls below the threshold for completion of breakdown by avalanche ionization [19]. All ultrashort pulse breakdown is thus initiated by multiphoton ionization, and a different explanation of the trends in the probability curves is required for ultrashort pulses.

For pulses less than approximately 5 ps, two events occur across the time width of the pulse. During the initial portion of the pulse, multiphoton ionization provides an initial electron density. During the final portion of the pulse, avalanche ionization completes the breakdown. As the pulse duration decreases, increasingly higher initial densities must be contributed by multiphoton ionization, in order for avalanche processes to have sufficient time to complete breakdown during the pulse. Avalanche ionization thus makes a decreasingly smaller contribution to the final electron density. Below about 150–200 fs, breakdown appears to be a purely multiphoton-dominated process, since the pulse is too fast for avalanche ionization [19].

For *initiation* of breakdown, multiphoton ionization is less probabilistic than ionization of impurities. Once breakdown has been initiated, however, the *completion* of breakdown by avalanche ionization is less probabilistic than completion of breakdown by multiphoton ionization. This may be due to the fact that the probability of multiphoton ionization is independent of electron density, whereas avalanche ionization becomes less probabilistic at higher densities. Thus, as pulse duration decreases and the contribution made by avalanche ionization decreases, the process will become more probabilistic, and the slope of the probability curve will decrease.

The trend in the slope of the probability curve from 10 ns to 100 fs can be summarized as follows. The slope indicates the degree to which impurities affect initiation of avalanche ionization for pulse durations down to approximately 5 ps (increasing slope), and it indicates the degree to which avalanche ionization contributes to breakdown for pulse durations less than 5 ps (decreasing slope). The slope of the probability curve, therefore, is an indication of the mechanisms initiating and completing breakdown.

C. Electric Field Intensity

The electric field intensity required to produce breakdown has been studied thoroughly in both solids and liquids for long pulse durations ($\tau_P > 30$ ps) where avalanche ionization mechanisms dominate. The electric field oscillating at optical frequency is responsible for imparting energy to initial free electrons necessary to ionize atoms by particle-to-particle interactions. Bass *et al.* [30] found a relationship between the probability of breakdown and the electric field in solid materials expressed as,

$$P(\varepsilon_B) = A \exp\left(-\frac{K}{\varepsilon_B}\right), \tag{3}$$

where A and K are constants that vary with material. Docchio *et al.* [10] used this relationship to further verify that avalanche ionization is the dominant mechanism in transparent liquids for pulse durations greater than 30 ps. The relationship for both studies can be expressed as a linear relationship between the logarithm of the probability and the inverse electric field. Docchio *et al.* have attributed the differences in the slope of the linear relationship to volumetric losses. Fig. 5 shows a logarithmic plot of the probability curves in Fig. 2(b) (saline) as a function of the inverse electric field. The curves display a form similar to Docchio's, namely a linear region up to about 75% and a parabolic region from 75–100%. The linear fit of the data up to 75% is also shown as solid lines. The shape of the curves in Fig. 5 indicate the relationship expressed in (3) is similar for ns, ps, and fs pulse durations and cannot be attributed to the specific breakdown mechanism predominant in each regime.

The dependence of the electric field required for breakdown on the volume and pulse duration in solid materials was

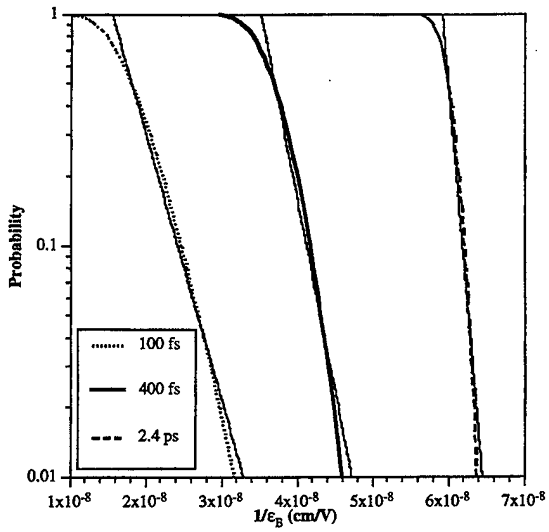


Fig. 5. Logarithmic plot of probability curves of Fig. 2(b) with respect to $1/\varepsilon_B$. The thin lines show a linear fit of the data up to a probability of 75%.

thoroughly discussed by Van Stryland *et al.* [14]. He found the following relationship for solids,

$$\varepsilon_{\rm rms} = \frac{A}{(\tau_P)^{0.25} V} + C, \tag{4}$$

where $\varepsilon_{\rm rms} = \varepsilon_B/\sqrt{2}$ and the volume V is proportional to the depth of focus times the focal area, i.e., $V \propto \omega_0^4/\lambda$, where ω_0 is the spot size (radius), and λ is the optical wavelength.

To determine the dependence of the electric field required for breakdown on the volume and pulse duration in transparent liquid materials, we plotted the electric field as a function of spot size (radius) and pulse duration in Fig. 6 for various authors (same as authors in Fig. 3(a)). We found a linear relationship, based upon the empirical results of Fig. 6, that can be expressed as follows:

$$\varepsilon_B = \frac{A}{(\tau_P V)^{0.25}} + C. \tag{5}$$

There has been debate, summarized by Van Stryland *et al.*, over the exact dependence of electric field on pulse duration and focal volume in solid materials . Bettis *et al.* [31] proposed a model in solid materials with the same dependence found in this paper. The differences in volumetric loss mechanisms between solids, liquids, and gases could determine the exact relationship between electric field and volume. In air, Van Stryland found the product $\tau_P^{0.25}\varepsilon_{\rm rms}$ to be linearly dependent on V^{-1}. One would expect liquid water to act more like an amorphous solid than a gas due to energy conduction across its tight-binding electronic states [32]. Moreover, the beam quality plays a major role in any electric field strength dependence. For a diffraction-limited beam, the electric field will be well characterized. However, aberrations lessen the strength of the electric field in the focal volume. This may account for the variability of the data seen in Fig. 6.

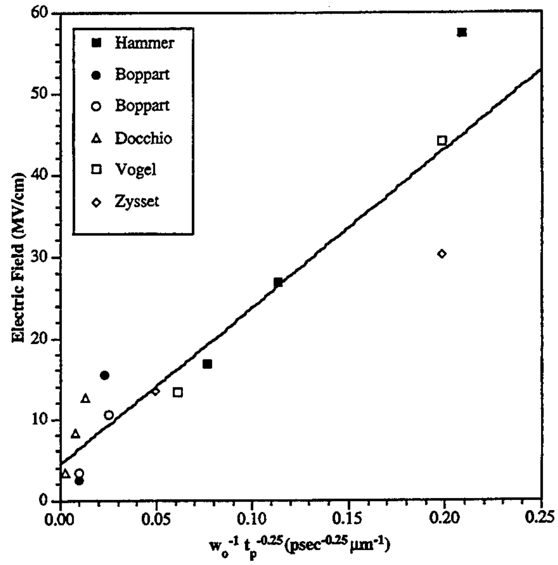


Fig. 6. Peak electric field ε_B necessary to cause breakdown in high purity or distilled water is plotted as a function of the spot size (radius), ω_0 and the pulse duration, τ_P. Beam and pulse parameters are the same as Fig. 3(a). The solid line is a linear least-squares fit of the data.

VI. Conclusion

We report the first measurements of LIB thresholds for pulse durations less than 30 ps using the residual bubble as the endpoint. We have found the irradiance threshold trends to be consistent with past data and theory. The slopes of the probability curves for ultrashort pulses give results that are counterintuitive to previous theoretical understanding but actually indicate a different mechanism for ultrashort breakdown, namely multiphoton ionization. Lastly, we have looked at the dependence of the electric field on probability, pulse duration, and focal volume for further insight into the breakdown threshold data. This threshold data may give a greater understanding of the eye damage mechanisms both for safety considerations and for various emerging ophthalmic applications.

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References

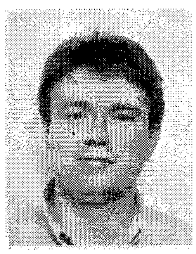
[1] L. V. Keldysh, "Ionization in the field of a strong electromagnetic wave," *Sov. Phys. JETP*, vol. 20, pp. 1307–1314, 1965.
[2] P. A. Barnes and K. E. Rieckhoff, "Laser induced underwater sparks," *Appl. Phys. Lett.*, vol. 13, pp. 282–284, 1968.
[3] N. Bloembergen, "Laser-induced electric breakdown in solids," *IEEE J. Quantum Electron.*, vol. QE-10, pp. 375–386, 1974.
[4] S. J. Gitomer and R. D. Jones, "Laser-produced plasmas in medicine," *IEEE Trans. Plasma Sci.*, vol. 19, pp. 1209–1219, 1991.
[5] R. Nordstrom, "Laser-induced plasma spectroscopy," *Lasers and Optronics*, pp. 23–24, Dec. 1993.
[6] ANSI Standard Z136.1-1993, *American National Standard for the Safe Use of Lasers*. New York: American National Standards Institute, Inc., 1993.
[7] C. P. Cain, C. A. Toth, C. D. DiCarlo, C. D. Stein, G. D. Noojin, D. J. Stolarski, and W. P. Roach, "Visible retinal lesions from ultrashort

laser pulses in the primate eye," *Inv. Ophthalmol. and Vis. Science*, vol. 36, pp. 879–888, 1995.
[8] C. P. Cain, C. D. DiCarlo, P. K. Kennedy, G. D. Noojin, R. E. Amnotte, and W. P. Roach, "In-vivo laser-induced breakdown in the rabbit eye," in *Laser Tissue Interaction VI, Proc. SPIE*, S. L. Jacques, Ed., vol. 2391A, pp. 41–47, 1995.
[9] M. P. Felix and A. T. Ellis, "Laser-induced liquid breakdown—A step-by-step account," *Appl. Phys. Lett.*, vol. 19, pp. 484–486, 1971.
[10] F. Docchio, C. A. Sacchi, and J. Marshall, "Experimental investigation of optical breakdown thresholds in ocular media under single pulse irradiation with different pulse durations," *Lasers in Ophthalmology*, vol. 1, pp. 83–93, 1986.
[11] F. Docchio, L. Dossi, and C. A. Sacchi, "Q-switched Nd:YAG laser irradiation of the eye and related phenomena: An experimental study. I. Optical breakdown determination for liquids and membranes," *Lasers in the Life Sciences*, vol. 1, pp. 87–103, 1986.
[12] C. A. Sacchi, "Laser-induced electric breakdown in water," *J. Opt. Soc. Am. B*, vol. 8, pp. 337–345, 1991.
[13] B. Zysset, J. G. Fujimoto, and T. F. Deutsch, "Time-resolved measurements of picosecond optical breakdown," *Appl. Phys. B*, vol. 48, pp. 139–147, 1989.
[14] E. W. Van Stryland, M. J. Soileau, A. L. Smirl, and W. E. Williams, "Pulse-width and focal-volume dependence of laser-induced breakdown," *Phys. Rev. B*, vol. 23, pp. 2144–2151, 1981.
[15] A. Vogel, S. Busch, K. Jungnickel, and R. Birngruber, "Mechanisms of intraocular photodisruption with picosecond and nanosecond laser pulses," *Laser in Surg. and Med.*, vol. 15, pp. 32–43, 1994.
[16] A. Vogel and W. Lauterborn, "Acoustic transient generation by laser-produced cavitation bubbles near solid boundaries," *J. Acoust. Soc. Am.*, vol. 84, pp. 719–731, 1988.
[17] W. L. Smith, J. H. Bechtel, and N. Bloembergen, "Dielectric-breakdown threshold and nonlinear-refractive-index measurements with picosecond laser pulses," *Phys. Rev. B*, vol. 12, pp. 706–714, 1975.
[18] P. K. Kennedy, "A first-order model for computation of laser-induced breakdown thresholds in ocular and aqueous media: Part I—Theory," *IEEE J. Quantum Electron.*, vol. 31, pp. 2241–2249, 1995.
[19] P. K. Kennedy, S. A. Boppart, D. X. Hammer, B. A. Rockwell, G. D. Noojin, and W. P. Roach, "A first-order model for computation of laser-induced breakdown thresholds in ocular and aqueous media: Part II—Code description and comparison to experiment," *IEEE J. Quantum Electron.*, vol. 31, pp. 2250–2257, 1995.
[20] D. X. Hammer, R. J. Thomas, G. D. Noojin, B. A. Rockwell, and A. Vogel, "Ultrashort pulse laser induced bubble creation thresholds in ocular media," in *Laser Tissue Interaction VI*, S. L. Jacques, Ed., Proc. SPIE, vol. 2391A, pp. 30–40, 1995.
[21] A. Vogel, P. Schweiger, A. Frieser, M. N. Asiyo, and R. Birngruber, "Intraocular Nd:YAG laser surgery: Light-tissue interaction, damage range, and reduction of colateral effects," *IEEE J. Quantum. Electron.*, vol. 26, pp. 2240–2259, 1990.
[22] A. E. Siegman, M. W. Sasnett, and T. F. Johnston, "Choice of clip levels for beam width measurements using knife-edge techniques," *IEEE J. Quantum Electron.*, vol. 27, pp. 1098–1104, 1991.
[23] B. A. Rockwell, P. K. Kennedy, R. J. Thomas, W. P. Roach, and M. E. Rogers, "The effect of nonlinear optical phenomena on retinal damage," in *Laser Tissue Interaction VI, Proc. SPIE*, S. L. Jacques, Ed., vol. 2391A, pp. 89–95, 1995.
[24] L. D. Forster, "Light intensity measurements with a fiber optic microprobe in the laser irradiated rhesus monkey eye," Ph.D. dissertation, The University of Texas, Austin, 1978.
[25] G. D. Polhamus, D. K. Cohoon, and R. G. Allen, "Measurement of the point spread function in the rhesus eye," USAF School of Aerospace Medicine, Tech. Paper, 1979.
[26] M. A. Mainster, D. H. Sliney, C. D. Belcher III, and S. M. Buzney, "Laser photodisruptors—Damage mechanisms, instrument design and safety," *Ophthalmology*, vol. 90, pp. 973–991, 1983.
[27] V. N. Pozhidaev and A. I. Fattevskii, "Optical breakdown thresholds in liquid water and micronsize water droplets exposed to single laser pulses," *Sov. J. Quant. Electron.*, vol. 11, pp. 65–68, 1981.
[28] M. H. Niemz, "Threshold dependence of laser-induced optical breakdown on pulse duration," *Appl. Phys. Lett.*, vol. 66, pp. 1181–1183, 1995.
[29] R. R. Krueger and T. Juhasz, "Comparative shock wave analysis during corneal ablation with an excimer laser, picosecond laser, and femtosecond laser," in *Ophthalmic Technologies V, Proc. SPIE*, J. Parel, Ed., vol. 2393, pp. 94–99, 1995.
[30] M. Bass and H. H. Barrett, "Avalanche breakdown and the probabilistic nature of laser-induced damage," *IEEE J. Quantum Electron.*, vol. QE-8, pp. 338–343, 1972.
[31] J. R. Bettis, R. A. House, and A. H. Guenther, "Spot size and pulse duration dependence of laser-induced damage," *Nat. Bur. Stand. Spec. Pub.*, vol. 462, pp. 338–345, 1976.
[32] F. Williams, S. P. Varma, and S. Hillenius, "Liquid water as a lone-pair amorphous semiconductor," *J. Chemical Physics*, vol. 64, pp. 1549–1554, 1976.

Daniel X. Hammer received the B.S. degree in electrical engineering from Rensselaer Polytechnic Institute in 1991.

He was commissioned in the Air Force in 1992 and is currently a Research Engineer in the Optical Radiation Division of Armstrong Laboratory at Brooks Air Force Base, Texas. His research interests include biomedical optics, laser-induced breakdown, and other biomedical effects of ultrashort laser pulses.

Mr. Hammer is a member of SPIE and OSA.



Robert J. Thomas received the B.S. degree in physics from Pittsburg State University, of Pittsburg, KS, in December, 1989, and the Ph.D. degree in physics from the University of Missouri at Columbia in August, 1994.

Currently, he is working with the Ultrashort Laser Pulse Effects Group in the Armstrong Labs at Brooks AFB, TX under a National Research Council Postdoctoral Fellowship. Research interests include experimental and theoretical studies of nonlinear optical phenomena in liquids, generation of ultrashort laser pulses, and applications of ultrashort laser pulse systems.

Gary D. Noojin received the AAS degree in 1986 in electronic engineering technology from the National Education Center and is pursuing the computer science degree from Texas Lutheran College.

He is an Electro-optics Technician for TASC Inc. He has 13 years of experience in electronics and related fields. Since 1990, he has operated and maintained the ultrashort pulse laser systems at the Air Force Armstrong Laboratory, Optical Radiation Division. He is currently the Chief Technician with a group of researchers studying the effects of ultrashort pulse damage mechanism and laser-induced beakdown.

Benjamin A. Rockwell received the B.S. degree in physics in 1986 from Central Missouri State University and the Ph.D. degree in physics in 1991 from the University of Missouri-Columbia.

He is a Research Biophysicist at the Air Force Armstrong Laboratory, Optical Radiation Division, Optical Biophysics Branch working in the field of laser tissue interactions on Brooks Air Force Base, Texas. He is currently the Technical Manager for an Air Force Office of Scientific Research-sponsored research effort entitled "Ultrashort Laser Pulse Effects in Biological and Related Media." His efforts include the study of the nonlinear optical properties of ocular media as part of an effort to understand the behavior of retinal damage for ultrashort laser pulses.

Dr. Rockwell is a member of SPIE, BiOS, APS, and OSA.

Paul K. Kennedy received the B.S., M.S., and Ph.D. degrees in physics from North Texas State University in 1976, 1980, and 1983, respectively.

In 1983, he joined the Rocketdyne Division of Rockwell International, where he served as a Theoretical Analyst and Scientific Programmer supporting research and development of high energy free-electron, excimer, and oxygen-iodine lasers. Since 1992, he has been a Research Biophysicist in the Optical Radiation Division of Armstrong Laboratory, characterizing and modeling the interaction of laser and other optical radiation with biological systems. His current area of interest is the physics of laser-induced breakdown in the eye and its relationship to observed ocular damage from ultrashort pulse exposures.

Dr. Kennedy is a member of APS and OSA.

William P. Roach received the B.A. degree in chemistry and mathematics from Avial College in 1983, and the M.S. and Ph.D. degree in physics from the University of Missouri-Columbia in 1986 and 1990, respectively.

He is the Chief, Optical Biophysics Branch, Optical Radiation Division, Armstrong Laboratory, Brooks AFB, TX. He is the consultant to the Air Force Surgeon General for laser application and use, and directs research for the United States Air Force designed to address issues involving ocular laser safety for National and Air Force interests.

Dr. Roach is a member of Sigma Pi Sigma, APS, OSA, and SPIE.

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Armstrong Laboratory
Occupational and Environmental Health Directorate
Optical Radiation Division
8111 18th St.
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Laser-induced breakdown (LIB) thresholds are determined for pulse durations of 2.4 ps, 400 fs, and 100 fs at 580 nm in high purity water, saline and tap water. The dependence of LIB irradiance thresholds on pulse duration, optical wavelength, and focal volume is examined, and the experimental data obtained is compared with a theoretical model. The slopes of the probability curves calculated are compared with mechanisms for LIB, namely avalanche ionization, muliphoton initiated avalanche ionization, and multiphoton ionization. Lastly, the dependence of the peak breakdown electric field on pulse duration and focal volume is empirically determined and compared with previous work.

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