Wavelength dependence of femtosecond laser-induced breakdown in water and implications for laser surgery

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The wavelength dependence of the threshold for femtosecond optical breakdown in water provides information on the interplay of multiphoton, tunneling, and avalanche ionization and is of interest for parameter selection in laser surgery. We measured the bubble threshold from ultraviolet to near-infrared wavelengths and found a continuous decrease of the irradiance threshold with increasing wavelength λ. Results are compared to the predictions of a numerical model that assumes a band gap of 9.5 eV and considers the existence of a separate initiation channel via excitation of valence band electrons into a solvated state followed by rapid upconversion into the conduction band. Fits to experimental data yield an electron collision time of ≈1 fs and an estimate for the capacity of the initiation channel. Using that collision time, the breakdown dynamics were explored up to $\lambda = 2\,\mu$m. The irradiance threshold first continues to decrease but levels out for wavelengths longer than 1.3 μm. This opens promising perspectives for laser surgery at wavelengths around 1.3 and 1.7 μm, which are attractive because of their large penetration depth into scattering tissues.

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I. INTRODUCTION

Focused femtosecond laser pulses offer the potential of precisely tunable nonlinear energy deposition in nominally transparent dielectrics. More specifically, femtosecond laser-induced optical breakdown in water and aqueous media enables one to perform highly precise surgery on cells [1–3] and within transparent biological tissues [4–8]. The dependence of optical breakdown thresholds on laser parameters provides information about breakdown mechanisms, such as the interplay of strong-field ionization (SFI) and avalanche ionization (AI) [9–14], as well as about the band structure of the breakdown medium and the mechanisms of breakdown initiation [15,16]. Detailed knowledge of the parameter dependence of breakdown thresholds is, furthermore, important for material processing and laser surgery.

Strong-field ionization consists of multiphoton ionization (MPI) and tunneling ionization (TI). The relative significance of AI compared to SFI is still a matter of debate. This question has been experimentally addressed by studying the pulse duration dependence of the breakdown threshold I_{th} [11–13,17–21] or of focal transmittance [22], by investigating the temporal dynamics of free electron density at individual laser parameters via spectral interferometry [23–28] or time-resolved reflectivity measurements [29–31], or by exploring nonlinear absorption associated with femtosecond filamentation [32]. The interplay of AI and SFI was then assessed by comparing model predictions with the experimental data. However, the results were contradictory, as recently reviewed by Balling and Schou [14]. Positions reach from refuting the importance of AI in femtosecond breakdown [23,33,34] through acknowledgements of their moderate importance [35,36] to emphasizing their large importance [2,11,20–22,29,37–39] or even dominance [19,40–43]. The ongoing controversy defines a need for an extension of the experimental data base accompanied by further refinements of breakdown modeling.

Besides the pulse duration dependence, also the wavelength dependence of the breakdown threshold $I_{\mathrm{th}}(\lambda)$ contains valuable information on the breakdown dynamics [44]. Studies on $I_{\mathrm{th}}(\lambda)$ for infrared (IR) nanosecond breakdown confirmed MPI initiation of AI [15,16]. In femtosecond breakdown, seed electrons for AI are abundant, and SFI can contribute significantly to the free electron density reached at the end of the laser pulse. While TI exhibits no wavelength dependence because it depends on the laser field strength [34,45], the rate of MPI decreases with increasing wavelength, since the simultaneous absorption of an increasing number of photons is required to overcome the band gap. A leading role of MPI should, therefore, be reflected in an increase of I_{th} with increasing wavelength (λ). By contrast, the AI rate increases with λ, and I_{th} should decrease if AI dominates. Variations of the relative importance of MPI versus AI at wavelengths at which the order k of the multiphoton process increases could also result in a more complex shape of the $I_{\mathrm{th}}(\lambda)$ curve, such as steps whenever one more photon is needed for MPI [15,16,46]. Therefore, it is not sufficient to probe $I_{\mathrm{th}}(\lambda)$ at a few individual wavelengths, but a dense grid of data points needs to be collected over a large wavelength range to allow for meaningful conclusions.

The wavelength dependence of femtosecond breakdown in band-gap solids has been investigated in several studies [29,34,46–48], but no detailed paper on the wavelength dependence of femtosecond breakdown in water is yet available, to our knowledge. Olivié *et al.* measured I_{th} at the surface of corneal tissue at eight wavelengths between 800 and 1400 nm and interpreted the $I_{\mathrm{th}}(\lambda)$ trend using a breakdown model for water [49]. Consideration of the potential influence of biomolecules on the breakdown threshold is challenging and was not attempted in that paper. Interpretation of $I_{\mathrm{th}}(\lambda)$ data for pure water would be more straightforward. In this paper, we determine the femtosecond breakdown threshold in bulk

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water at 50 wavelengths between 335 and 1085 nm under diffraction-limited focusing conditions. Focusing at a large numerical aperture (NA $\geqslant$ 0.8) avoids nonlinear beam propagation effects that could distort the threshold determination [50,51].

The experimental data are compared to model predictions based on the Keldysh theory of SFI and a modified Drude model for AI together with Rethfeld's multiple-rate-equation approach that accounts for the time constraints of AI in femtosecond breakdown [35]. Our model adopts recently gained insights about the band structure of water relevant for optical breakdown processes by assuming a band gap of water of 9.5 eV together with a separate initiation channel via excitation of a valence band electron into a solvated state, followed by rapid excitation into the conduction band [16]. In the conduction band, the electron is quasifree, and we will thus use the term "free electron" synonymously with "conduction band electron." Fitting model predictions to experimental data yields the Drude electron collision time τ_{coll} and the capacity of the initiation channel. Literature values for τ_{coll} used in previous papers on optical breakdown in transparent dielectrics vary by two orders of magnitude (from 0.11 fs in Ref. [49] to 23.3 fs in Ref. [52]). This paper will narrow the range of reasonable values for the effective Drude collision time in water, which is of great importance for future breakdown modeling.

Besides providing information on the breakdown mechanisms, knowledge of $I_{\text{th}}(\lambda)$ can guide parameter selection for femtosecond laser surgery on cells and tissues. Cell surgery has mostly been performed using Ti:sapphire lasers emitting at 800 nm [2,53] but can be even more precise with ultraviolet (UV)-A wavelengths [51]. Femtosecond laser dissection in transparent tissues is already well established for creating corneal flaps in refractive laser surgery. Usually Ytterbium-based laser materials emitting at wavelengths around 1040 nm are employed [54], but UV wavelengths are also being tested to increase the cutting precision [55–58]. Great efforts have also been undertaken to perform plasma-mediated surgery in scattering tissues such as skin, vocal cords, sclera, and brain [8,59–62]. Here, IR wavelengths around 1300 and 1700 nm seem to be optimally suited because they feature a large penetration depth due to a favorable combination of low scattering and moderate water absorption [49,59,63–65]. We use the Drude electron collision time obtained from fits in the range between 335 and 1085 nm to derive predictions for nonlinear energy deposition up to a wavelength of 2000 nm.

II. EXPERIMENTAL METHODS

The experimental setup for investigating the wavelength dependence of femtosecond optical breakdown is presented in Fig. 1. Laser pulses are focused at high NA through long-distance water-immersion objectives (Leica, HCX APO L U-V-I, 63×, NA = 0.9 and 40×,NA = 0.8) into deionized and filtered (0.2 μm) water. The objectives are inserted into the wall of the water cell to enable aberration-free focusing of the laser pulses. The rear entrance pupil of each objective is slightly overfilled to create a uniform irradiance distribution corresponding to an Airy pattern in the focal plane. Breakdown is identified with the occurrence of bubble formation that is detected using the scattering of a continuous probe laser beam

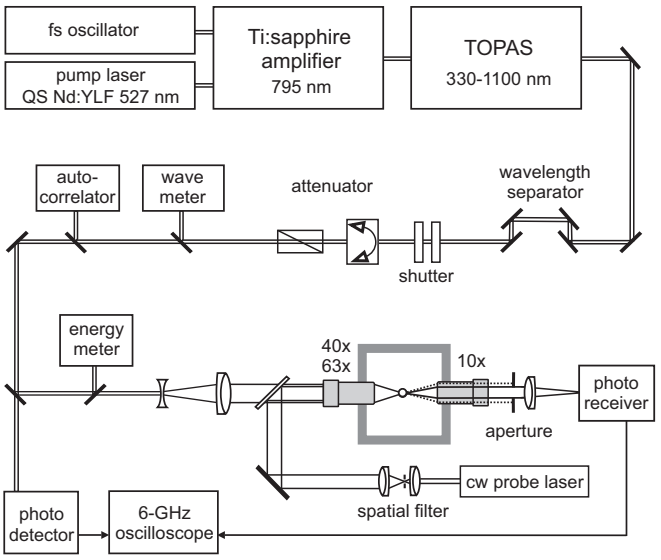

FIG. 1. Experimental setup for investigating the wavelength dependence of femtosecond laser-induced breakdown in water. For details see text.

adjusted collinear and confocal with the pulsed laser beam. The scattering signal is detected by means of a fast photoreceiver (FEMTO, AC coupled, 25 kHz–200 MHz bandwidth) and a digital oscilloscope (Tektronix, DPO 70604). The scattering signal yields information on the timescale of the bubble oscillations, which is used to determine the maximum bubble radius R_{max} [51]. This method provides a clear threshold criterion, since bubbles can be detected down to $R_{\text{max}} \approx 150$ nm.

Laser pulses with tunable wavelength (335–1085 nm) are generated by a traveling-wave optical parametric amplifier of superfluorescence (TOPAS; Light Conversion, TOPAS 4/800). The TOPAS is pumped by a Ti:sapphire femtosecond laser (Spectra Physics Spitfire) emitting 460 μJ pulses of 120 fs duration at 795 nm wavelength and 1 kHz repetition rate. Coverage of a large wavelength range from UV to IR is achieved by generation of signal, idler, second-harmonic signal, second-harmonic idler, sum-frequency of pump and signal, sum-frequency of pump and idler, fourth-harmonic signal, and fourth-harmonic idler [66]. Maximum pulse energies vary between 3 and 50 μJ in the investigated wavelength range. This is sufficient for a reliable breakdown threshold determination, since all threshold energies remain below 25 nJ due to the tight focusing of the laser beam. The TOPAS output is a mixture of the target wavelength and other contributions such as pump and idler. Six sets of dichroic mirrors are employed to separate the respective target wavelength from the other wavelengths over the entire tuning range.

For $\lambda > 450$ nm, spectra and pulse duration of the laser pulses are determined using a wave meter (Ocean Optics, HR 2000), and an autocorrelator (APE, pulseCheck), respectively. Examples of spectra and autocorrelation traces are provided in Supplemental Material Fig. S1 [67]. Wavelengths below 450 nm are outside the autocorrelator's measurement range. Here, the pulse duration is set equal to the average pulse duration for $\lambda > 450$ nm, which is 250 fs. The duration of the TOPAS output fluctuates with wavelength, as shown in

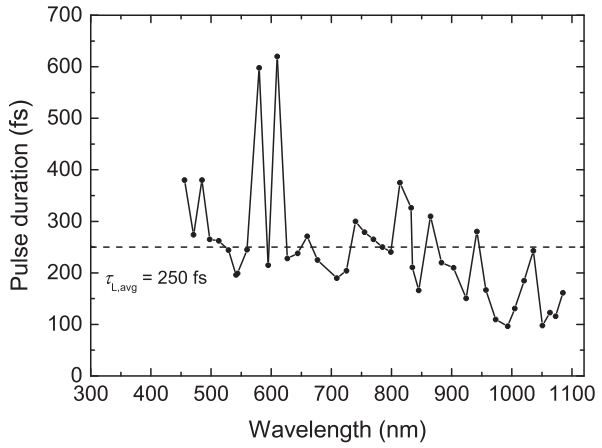

FIG. 2. Pulse durations $\tau_L(\lambda)$ of the TOPAS system in the wavelength range between 450 and 1085 nm. Wavelengths below 450 nm were outside the autocorrelator's measurement range. The averaged pulse duration above 450 nm is $\tau_{L,avg} = 250$ fs.

Fig. 2. To account for these variations, breakdown thresholds are normalized to the average over the whole range of measured pulse durations, as described further below.

A combination of two mechanical shutters (Uniblitz electronics, LS6) selects single pulses out of the 1 kHz pulse train. Wavelength-independent beam attenuation is achieved by a Fresnel-rhomb retarder in front of a Glan laser prism (both Karl Lambrecht Corporation). The energy in front of the microscope objectives is calibrated by a reference measurement for each wavelength, and the transmittance of the objectives is considered using data provided by the manufacturer. Breakdown energy thresholds (E_{th}) are determined by counting how frequently bubble formation occurs as the energy is increased from subthreshold to superthreshold values. To eliminate the influence of energy fluctuations of the TOPAS output, the energy of each individual laser pulse is measured. Data are then binned into small energy intervals ($n \geqslant 15$) with >20 events per interval and fitted using the Gaussian error function. Here, E_{th} corresponds to 50% breakdown probability. The threshold irradiance I_{th} is then calculated using the equation

$$I_{th} = \frac{E_{th}}{\tau_L \pi \left(\frac{M^2 d}{2}\right)^2} \times 3.73. \quad (1)$$

Here, τ_L denotes the laser pulse duration, M^2 is the beam quality parameter ($M^2 = 1.4$ according to manufacturer data for the TOPAS), and d is the diffraction-limited diameter of the Airy pattern arising from focusing a beam with top-hat profile, which is given by $d = 1.22\,\lambda/\mathrm{NA}$. The factor 3.73 relates the average irradiance values within the pulse duration and focal spot diameter to the respective peak values that determine the onset of optical breakdown phenomena.

Measured threshold data are normalized to the average pulse duration (250 fs) via the experimentally determined pulse duration dependence of I_{th} for ultrashort-pulsed optical breakdown, which is $I_{th} \propto {\tau_L}^{-0.75}$ for pulse durations between 100 fs and 3 ps [20,68].

III. MODEL OF FEMTOSECOND LASER-INDUCED PLASMA FORMATION

Since bubble formation defines the experimental breakdown threshold in aqueous media, the same threshold criterion must be used for modeling. This is comparatively easy for femtosecond breakdown. Here, only one set of free electrons is generated during the pulse because the recombination time is on the order of a few picoseconds [25,69], which is considerably longer than the laser pulse duration. Correspondingly, the thermalization of energy carried by the free electrons through recombination and collisional energy transfer occurs mainly after the laser pulse. Therefore, the resulting temperature rise resulting in a phase transition can be assessed from the number density and average kinetic energy of free electrons at the end of the pulse [2,70].

As established previously, free electron generation is described using the full Keldysh model for SFI together with a Drude model for AI [2]. However, this approach is now used in conjunction with Rethfeld's multiple-rate-equation approach that considers the time constraints on AI in femtosecond breakdown [35,36,38]. Furthermore, we consider recent insights about band structure and ionization pathways of water relevant for the optical breakdown.

A. Band structure and ionization pathways of water

Spectroscopic findings collected during the last two decades suggest that the band gap E_{gap} of liquid water is considerably larger than the value of 6.5 eV that has often been assumed in optical breakdown models for water. A band gap energy $E_{gap} = 9.5$ eV seems appropriate to consider both vertical and autoionization [16,71–74]. What was thought to be the band gap is actually an intermediate energy level between valence and conduction band, which plays a role mainly for breakdown initiation. Optical breakdown threshold spectroscopy of IR nanosecond breakdown in water revealed two pronounced steps in the $I_{th}(\lambda)$ spectrum located at wavelengths for which an additional photon is required to provide the excitation energy E_{ini} for seed electron generation [9]. From the separation of these steps, E_{ini} can be deduced and was found to be on average 6.6 eV [16]. This value lies slightly above the threshold E_{thsolv} for the generation of solvated electrons e^-_{aq}, which is 6.4 eV [75–78]. That led to the conclusion that breakdown initiation proceeds via excitation of valence band electrons into the $\widetilde{A}1^1B_1$ absorption band, followed by their hydration and subsequent upconversion of e^-_{aq} into the conduction band as shown in Fig. 3(a).

Formation of e^-_{aq} at energies far below the conduction band requires the existence of preexisting trap sites consisting of favorable local arrangements of water molecules that can accommodate the electron [78,79]. When an excited water molecule is located close to a trap site, an excess electron can be abstracted, prehydrate within ≈50 fs [80], and hydrate completely within less than 300 fs [74,80–82]. This process involves proton transfer to a neighboring water molecule resulting in the formation of a OH_{aq} radical and a hydronium ion $H_3O^+_{aq}$ [83–85]. An ideal trap corresponds to a tetrahedral conformation of four to six water molecules with their OH bonds directed towards the center [86,87] [Figs. 3(b) and 3(c)]. With increasing excitation energy E_{exc}, electrons can be

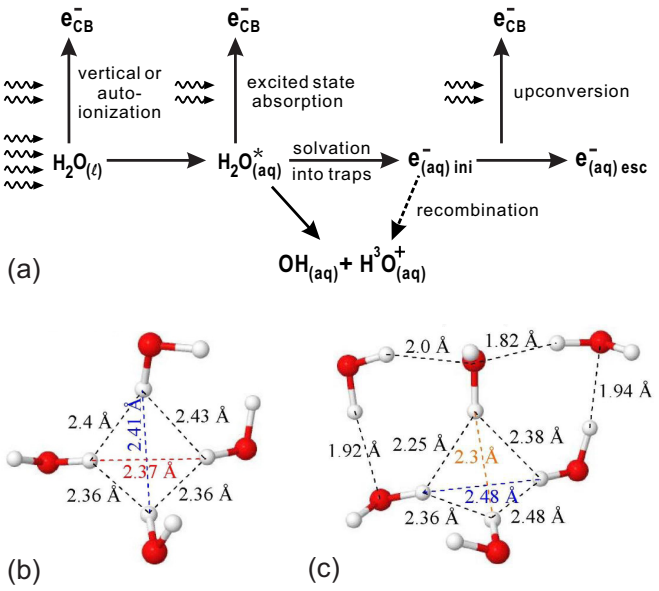

FIG. 3. (a) Ionization and geminate recombination pathways in liquid water as proposed in Ref. [16]. For large excitation energies, ionization proceeds via vertical ionization ($E_{exc} \geqslant 11$ eV) or autoionization ($E_{exc} \geqslant 9.5$ eV), while for $E_{exc} < 9.5$ eV, ionization is possible only as a two-step process involving solvated electron creation followed by upconversion of e^-_{aq} into the conduction band. The latter process competes with geminate recombination, especially at pulse durations longer than $\tau_{gemrec} \approx 60$ ps. (b) and (c) Tetrahedral conformations of water molecules hosting a solvated electron. Reprinted with permission from Ref. [87], supporting information Fig. S7.1 [67]. Copyright (2015), American Chemical Society. The constellation with lowest potential energy is that in (b). Randomly formed cavitylike molecular conformations like that in (b) and (c) can act as traps promoting the abstraction of an electron from an excited water molecule. Deviations from these constellations require higher excitation energies for trap occupation, since part of E_{exc} is now required for conformation changes.

accommodated also by initially less perfect configurations of water molecules, since part of E_{exc} is now available for rearranging the molecules in the process of electron abstraction.

The ultrafast hydration dynamics [80] and the long lifetime of solvated electrons [77] suggests that the breakdown initiation path via formation and upconversion of e^-_{aq} into the conduction band is favored compared to the path via light absorption by excited water molecules. This is because H_2O^* exhibits a very short lifetime and a small absorption coefficient [88], whereas both ground state and excited states (p states) of the solvated electron absorb well in a broad wavelength range from below 500 to above 1100 nm [77,81,89,90]. Therefore, only upconversion of e^-_{aq} is considered in the model, and light absorption by excited water molecules is neglected.

Geminate recombination of e^-_{aq} with their $H_3O^+_{aq}$ hydronium counter-ions occurs on a timescale of tens of picoseconds [83] and plays no role for femtosecond breakdown dynamics. Solvation of conduction band electrons becomes manifest only toward and after the end of the laser pulse [91,92], whereas during the pulse, solvated electrons will be rapidly reexcited. Therefore, solvation of conduction band electrons has been neglected in the model.

B. Parameters governing breakdown initiation

When seed electrons produced by SFI are available, "local" avalanches arise around these electrons, which then merge into a "global" avalanche encompassing the entire focal volume [16,42,48]. The possible range of the seed avalanches decreases when the pulse duration is reduced and fewer doubling sequences can occur during a pulse. Correspondingly, the seed electron density ρ_{seed} necessary for the development of a homogeneous breakdown process must increase. While the exact choice of the ρ_{seed} value is crucial for IR nanosecond breakdown, where it critically influences I_{th}, it is less decisive for the modeling of femtosecond breakdown, where seed electrons produced by SFI are abundant. Thus, ρ_{seed} is generally neglected in modeling femtosecond breakdown, and we do the same in this paper.

The possible capacity of the initiation channel via formation and upconversion of e^-_{aq} into the conduction band is given by the density and stability of preexisting traps that can accommodate solvated electrons. The trap density χ_{trap} in liquid water at room temperature has been estimated to be 0.73×10^{19} cm^{-3} for $E_{ini} = 6.42$ eV [16]. It remains on the order of 10^{19} cm^{-3} up to 7.8 eV excitation energy and increases rapidly thereafter. The trap density is 4–7 orders of magnitude higher than the critical seed electron density required for AI initiation in IR nanosecond breakdown [16]. For nanosecond breakdown, seed electrons will, therefore, not act back on the initiation channel. However, for ultrashort pulse durations at which seed electrons produced by SFI are abundant, the influence of free electrons on the initiation channel must be taken into account. Changes of the potential landscape induced by free electrons will likely disturb the local conformations of water molecules constituting the traps. Slight distortions of the trap sites will probably just increase the excitation energy required for e^-_{aq} formation, but for sufficiently high free-electron density, the distortions will likely become so strong that the initiation channel vanishes. In our model, we assume that the initiation channel progressively decays while the free-electron density increases. The maximum number of free electrons that can be produced via the initiation channel is denoted $\rho_{ini,max}$.

For UV wavelengths, many free electrons are produced via SFI already early during the laser pulse, as will be shown further below in Sec. IV B. Therefore, traps are distorted earlier during the pulse than at longer wavelengths, and E_{ini} must be higher to sustain the initiation pathway via preexisting traps. For IR nanosecond breakdown, Linz *et al.* obtained a good fit between measured and calculated $I_{th}(\lambda)$ curves assuming $E_{ini}(\lambda) = -(27/22400) \times \lambda + 7.59$ (with λ in nanometers and E_{ini} in electronvolts) [16]. In this paper, we use the same $E_{ini}(\lambda)$ dependence and extrapolate it towards shorter wavelengths. For wavelengths >990 nm, the fitting formula cannot be used because it yields E_{ini} values below the excitation threshold into the solvated state. Here, a constant value $E_{ini} = E_{thsolv} = 6.4$ eV is assumed.

C. Description of the breakdown dynamics

The dynamics of femtosecond breakdown is mainly determined by SFI and AI, whereas recombination and diffusion play little or no role for ultrashort laser pulses. Strong-field ionization can either proceed through the initiation channel

via excitation of valence band electrons into an intermediate level E_{ini} followed by subsequent upconversion, or it can occur as one-step ionization across the entire band gap. The total SFI rate is given by

$$\left(\frac{d\rho_{\mathrm{SFI}}}{dt}\right) = \left(\frac{d\rho_{\mathrm{ini}}}{dt}\right) + \left(\frac{d\rho_{E\mathrm{gap}}}{dt}\right), \tag{2}$$

with

$$\left(\frac{d\rho_{\mathrm{ini}}}{dt}\right) = \eta_{\mathrm{SFI}}(E_{\mathrm{ini}}) \times \left(1 - \frac{\rho_{\mathrm{ini}}}{\rho_{\mathrm{ini,max}}}\right), \tag{3}$$

$$\left(\frac{d\rho_{E\mathrm{gap}}}{dt}\right) = \eta_{\mathrm{SFI}}(\tilde{\Delta}). \tag{4}$$

Here, the expressions $\eta_{\mathrm{SFI}}()$ represent the full Keldysh formulas (including multiphoton and tunneling effects) for photoexcitation into the intermediate E_{ini} level and direct photoionization, respectively [2,93]. Also, $\tilde{\Delta}$ denotes the effective ionization potential across the band gap that accounts for the oscillation energy of free electrons in strong electromagnetic fields, which is given by [93]

$$\tilde{\Delta} = \frac{2}{\pi} E_{\mathrm{gap}} \frac{\sqrt{1+\gamma^2}}{\gamma} E\left(\frac{1}{\sqrt{1+\gamma^2}}\right),$$

with

$$\gamma = \frac{\omega}{e}\sqrt{\frac{m' c\, n\, \varepsilon_0\, E_{\mathrm{gap}}}{I}}. \tag{5}$$

The symbols ω and I denote the circular frequency and peak intensity of the electric laser field, e and m' are electron charge and reduced effective exciton mass, c is the vacuum speed of light, ε_0 the vacuum dielectric permittivity, and n is the refractive index of the medium at frequency ω. The reduced exciton mass m' is approximated by half of the mass m_{c} of conduction band electrons [10,33,35]. The term $E()$ denotes an elliptic integral of the second kind. The Keldysh parameter γ distinguishes SFI regimes: for $\gamma \ll 1$ tunneling dominates, while for $\gamma \gg 1$, MPI prevails; the transition occurs around $\gamma = 1.5$ (see Fig. 2 in Ref. [2]).

Equation (3) is based on the assumption that the rate at which free electrons are produced via the initiation channel is fully determined by the rate at which excited water molecules at level E_{ini} are created. This simplification is justified by the fact that usually a high-order multiphoton process is needed to provide $E_{\mathrm{ini}} \approx 6.6\,\mathrm{eV}$, whereas subsequent excitation of hydrated or solvated electrons into the conduction band is much easier. The second energy gap is smaller (3 eV) and contains intermediate energy levels (p states of e^-_{aq}) that, like the ground state of the solvated electron, have a large absorption cross-section even for low-energy photons [81,90,94]. Therefore, we neglect details of the upconversion and assume that all excess electrons are immediately elevated into the conduction band [16]. The depletion factor containing $\rho_{\mathrm{ini,max}}$ considers the finite capacity of the initiation channel that has been discussed in Sec. III B. It should be noted that the initiation channel plays a significant role only for $\tau_{\mathrm{L}} \geqslant 50\,\mathrm{fs}$ when a substantial amount of hydrated and solvated electrons is available [80]. For shorter pulse durations, SFI must overcome the entire band gap of 9.5 eV because of the small absorption cross-section of H_2O^*.

When conduction band electrons have become available through SFI, they gain kinetic energy through inverse Bremsstrahlung absorption of photons and can generate further free electrons when their energy exceeds the critical energy required to cause impact ionization. To satisfy the conservation laws for energy and momentum, the kinetic energy of the impacting electron must be larger than the effective ionization potential $\tilde{\Delta}$ [95,96]. For a parabolic band gap, the minimum required energy is $E_{\mathrm{crit}} = (3/2)\ \tilde{\Delta}$ [2,33,35,39]. The excess energy remaining after impact ionization is distributed among the collision partners. Thus, each quasifree electron produced by impact ionization has to gain less energy than $1.5\ \tilde{\Delta}$ to reach E_{crit}. However, the average energy leading to an impact ionization event is likely somewhat larger than E_{crit} because the impact ionization rate increases with kinetic energy [33,97]. Therefore, we assume that the average energy gain required for a free electron to cause impact ionization is $1.5\ \tilde{\Delta}$ during the entire breakdown process. Impact ionization will follow shortly after an electron has gained $1.5\ \tilde{\Delta}$ [33,97].

If all conduction band electrons could take part in impact ionization, the average AI rate would be given by [35]

$$\eta_{\mathrm{AI}} = W_{1\mathrm{pt}} \frac{\hbar\omega}{E_{\mathrm{crit}}}, \tag{6}$$

where $W_{1\mathrm{pt}}$ is the intraband one-photon excitation rate that relates to the intraband one-photon absorption cross-section $\sigma_{1\mathrm{pt}}$ by

$$W_{1\mathrm{pt}} = \sigma_{1\mathrm{pt}} \frac{I}{\hbar\omega}. \tag{7}$$

However, only energetic electrons with $E > E_{\mathrm{crit}}$ are able to induce impact ionization. Therefore, impact ionization must be preceded by several collisions between electrons and heavy particles or phonons, during which the energy gain through inverse Bremsstrahlung absorption occurs [2,10,35]. The minimum number of collisional absorption events is

$$k' = \left\langle \frac{E_{\mathrm{crit}}}{\hbar\omega} + 1 \right\rangle. \tag{8}$$

By fitting Eqs. (7) and (8) into Eq. (6), one can express η_{AI} in terms of $\sigma_{1\mathrm{pt}}$, k' and photon flux $I/\hbar\omega$

$$\eta_{\mathrm{AI}} \approx \sigma_{1\mathrm{pt}} \frac{1}{k'} \frac{I}{\hbar\omega}. \tag{9}$$

However, the fact that excitation to E_{crit} requires a finite number of collisions imposes temporal constraints to AI, which are not yet considered in Eq. (9). The microscopic processes involved have been followed in detail for crystalline solids by solving Boltzmann equations for the electrons and its collision partners [33,97–99], but this kinetic approach is numerically very intensive. Furthermore, the necessary material parameters are not yet known for water. Fortunately, Rethfeld has introduced a simplified model based on a set of rate equations, which keeps the essentials of the full kinetic approach but turns it into a more practical way [35]. The multiple-rate-equation model describes the excitation of the "free" electrons using $k' + 1$ discrete energy levels to represent the conduction band. Free electrons in lower energy levels are excited into higher energy levels in one-photon excitation steps occurring at rate $W_{1\mathrm{pt}}$. Impact ionization occurs only when they

have reached the k'th energy level. For a detailed description of the model composed of $k'+1$ ordinary differential equations, the reader is referred to Refs. [35,36,38].

The full set of rate equations is needed to describe the nonstationary electron distribution evolving in the course of very short laser pulses. At longer times, a transition to an asymptotic regime takes place for which the model can be simplified into a single-rate equation with a stationary AI rate similar to Eq. (9). The asymptotic avalanche regime governs the breakdown dynamics during laser pulses that are longer than the transition time [35,36]

$$t_{\mathrm{MRE}} = \frac{1}{(\sqrt[k']{2}-1)W_{1\mathrm{pt}}}. \tag{10}$$

The transition time t_{MRE} depends on irradiance, wavelength and on material parameters such as the band gap, and $\sigma_{1\mathrm{pt}}$. The AI rate predicted by the asymptotic limit of the multiple-rate-equation model is

$$\eta_{\mathrm{AI,\,asymp}} = (\sqrt[k']{2}-1)W_{1\mathrm{pt}}. \tag{11}$$

By applying the Laurent series to $\sqrt[k']{2}$, Eq. (11) can be approximated by [35]

$$\eta_{\mathrm{AI,\,asymp}} \approx \ln 2\,\eta_{\mathrm{AI}}. \tag{12}$$

Based on the Drude model, the intraband one-photon absorption cross-section can be expressed as [10]

$$\sigma_{1\mathrm{PA}} = \frac{\tau_{\mathrm{coll}}}{\omega^2\tau_{\mathrm{coll}}^2+1}\cdot\frac{e^2}{cn_0\varepsilon_0 m_c}, \tag{13}$$

with τ_{coll} denoting the time between momentum transfer collisions.

Combining Eqs. (6), (7), (11), and (13), we obtain the asymptotic AI rate as

$$\eta_{\mathrm{AI,asymp}} \approx \ln 2\,\frac{\tau_{\mathrm{coll}}}{\omega^2\,\tau_{\mathrm{coll}}^2+1}\left[\frac{e^2\,I}{cn\varepsilon_0 m_c\left(\frac{3}{2}\right)\tilde{\Delta}}\right]. \tag{14}$$

Momentum transfer collisions entering the Drude model are collisions of electrons with phonons and heavy particles such as neutrals and ions [10,14,33,97–103]. Electron-electron collisions cannot contribute to τ_{coll} as both particles have the same effective mass. Therefore, their interaction conserves the total carrier momentum, which renders inverse Bremsstrahlung absorption impossible because the photon's momentum cannot be accommodated [99,100].

Theoretical investigations of the respective collision rates for water are still lacking, and experimental investigations cannot easily distinguish between the individual contributions. Therefore, we treat τ_{coll} as a free parameter in our model and use fits of the model to experimental results to determine the effective average τ_{coll} value for a free-electron density corresponding to the bubble threshold. Similar approaches have previously been followed by other researchers [19,26,32,104]. Reasonable fits can be expected for τ_{coll} values for which the one-photon absorption cross-section is approximately proportional to the collision frequency. According to Eq. (13), this is the case if $\omega^2\tau_{\mathrm{coll}}^2 \gg 1$, with $\omega^2\tau_{\mathrm{coll}}^2 = 1$ defining a lower limit. The latter condition is fulfilled for $\tau_{\mathrm{coll}} = 0.19$ fs at $\lambda = 350$ nm, and for $\tau_{\mathrm{coll}} = 0.56$ fs at 1050 nm.

The growth of free-electron density may be affected by diffusion and recombination losses. Diffusion out of the focal volume must be considered for picosecond and nanosecond pulse durations but can be neglected in the description of femtosecond breakdown. Possible recombination pathways include radiative electron-ion recombination [105], Auger recombination [96,105], nonradiative electron-ion recombination, electron neutral attachment with vibrational redistribution of the electron's energy [106], and electron solvation with subsequent decay of e_{aq}^- [77]. How important are these recombination pathways for the optical breakdown dynamics in water? Electron solvation becomes relevant only after the end of the laser pulse and will hardly influence the breakdown threshold [91]. Radiative recombination is pronounced in semiconductors [105] but plays little role in water breakdown. In femtosecond breakdown, plasma radiation is faintly discernible only at pulse energies well above the bubble threshold, and even for nanosecond breakdown, which is associated with bright blackbodylike plasma luminescence, the radiation was found to contain less than 10^{-3}% of the absorbed laser energy [68]. Auger recombination describes an energy-conserving interaction between two low-energy electrons and a hole upon which one electron recombines with the hole, and the other is excited onto a higher energy level. Its role for breakdown processes in silicon and SiO_2 has recently been investigated [98,99], but Auger processes have not yet been reported for water breakdown, to the best of our knowledge. By contrast, nonradiative recombination of excess electrons with $H_3O_{\mathrm{aq}}^+$ ions and electron attachment to neutral OH fragments are well known [72,77,85,107]. Nonradiative recombination involves rapid dissipation of a large quantum of energy via vibrational relaxation and breakage of hydrogen bonds that is favored by the tight hydrogen bond network characteristic for liquid water [108–112]. At small excitation rates, ionization events are well separated from each other, and recombination progresses mainly as geminate recombination within isolated ensembles of the three reaction partners e^-, $H_3O_{\mathrm{aq}}^+$, and OH produced during ionization [Fig. 3(a)]. Geminate recombination has a fixed time constant, the value of which depends on the excitation energy that determines the ejection length of the excess electron [16,72]. However, at irradiance values leading to optical breakdown, ionization events are no longer isolated from each other, and cross-recombination processes between photoproducts from independent ionization events dominate [84]. Under these circumstances, recombination is proportional to the square of free-carrier density because two types of free carriers are involved in each event [10,106]. Therefore, we assume that recombination is proportional to ρ_c^2 and use an experimentally determined value for the recombination constant η_{rec}

$$\left(\frac{d\rho_c}{dt}\right)_{\mathrm{rec}} = -\eta_{\mathrm{rec}}\times\rho_c^2,$$

with

$$\eta_{\mathrm{rec}} = 1.8\times10^{-9}\ \mathrm{cm^3\ s^{-1}}\ . \tag{15}$$

The η_{rec} value is the average of results obtained by inspecting the decay of plasma luminescence [106]

($\eta_{rec} = 2.0\times10^{-9}\,cm^3\,s^{-1}$) and by spectrally resolved reflection spectroscopy [25] ($\eta_{rec} = 1.6\times10^{-9}\,cm^3\,s^{-1}$).

We shall see below in Sec. III D that the electron density at the bubble threshold amounts to $\rho_{th} = 1.8\times10^{20}\,cm^{-3}$. The corresponding recombination time obtained based on Eq. (15) is 2.8 ps. Thus, recombination during the laser pulse plays no significant role at the bubble threshold of femtosecond breakdown. However, this changes above threshold. For example, at $\rho_c > 5\times10^{20}\,cm^{-3}$, the time constant has dropped below 1 ps, and recombination will start to influence the breakdown dynamics.

The overall temporal evolution of conduction band electron density is given by

$$\left(\frac{d\rho_c}{dt}\right) = \left(\frac{d\rho_{SFI}}{dt}\right) + \eta_{AI,asymp}\times\rho_c - \eta_{rec}\times\rho_c^2, \qquad (16)$$

when using the asymptotic model. For comparison, we also calculate the results predicted by the full multiple-rate-equation model. In the latter case, the full set of rate equations described in Ref. [35] is used instead of the term $\eta_{AI,asymp}$ from Eq. (14). The rate Eq. (16) is solved numerically for a Gaussian laser pulse using a Runge-Kutta method with adaptive step size control. The pulse duration τ_L is identified with the full width at half maximum. In order to evaluate the influence of MPI and AI, separate bookkeeping is used for temporal evolution of ρ_{SFI} (total contribution from SFI), ρ_{ini} (excitation into an intermediate level followed by upconversion into the conduction band), and ρ_{Egap} (excitation across the entire band gap) as given by Eqs. (2)–(4), respectively. The contribution of AI is $\rho_{AI} = \rho_c - \rho_{SFI}$.

D. Breakdown threshold criterion

The breakdown threshold is identified with bubble formation, i.e. with the temperature T_{th} that produces a phase transition at the focus center [2]. In femtosecond breakdown, energy deposition is stress confined, and the phase transition is facilitated by thermoelastic tensile stress [2]. For near-IR laser pulses focused at NA = 0.8, a threshold temperature $T_{th} = 440.7\,K$ has been determined [51], corresponding to a temperature rise $\Delta T_{th} = 147.7\,K$ above room temperature (293 K). For femtosecond breakdown, ΔT_{th} can be connected to ρ_{th} by considering that the plasma energy density ε_{th} corresponds to the product of free-electron density and average energy of a free electron. For electrons produced by AI, the latter is given by the sum of ionization potential $\tilde{\Delta}$ and average kinetic energy. Thus, we have

$$\varepsilon_{th} = \rho_{th}(\tilde{\Delta} + \bar{E}_{kin}). \qquad (17)$$

For estimating $\bar{E}_{kin}$, we assume that the energy distribution of electrons up to the impact ionization level is approximately flat. An average gain of 1.5 $\tilde{\Delta}$ required for impact ionization is consistent with a start energy of 0.5 $\tilde{\Delta}$ and an impact ionization level of 2 $\tilde{\Delta}$ [2], leading to $\bar{E}_{kin} = (5/4)\tilde{\Delta}$. The temperature rise after the laser pulse is

$$\Delta T = \frac{\varepsilon_{th}}{\rho_0\, C_p}, \qquad (18)$$

where C_p is the heat capacity and ρ_0 the mass density of the medium. By combining Eqs. (17) and (18), we obtain

$$\rho_{th} = \frac{\rho_0\, C_p\, \Delta T}{\left(\frac{9}{4}\right)\tilde{\Delta}}. \qquad (19)$$

For $T_{th} = 440.7\,K$, the threshold electron density is $\rho_{th} = 1.8\times10^{20}\,cm^{-3}$, corresponding to an ionization degree of 0.27% (the number density of bound electrons that can be ionized is $6.68\times10^{22}\,cm^{-3}$ [10]).

The electron density at the bubble threshold is considerably smaller than the critical electron density $\rho_{crit} = \omega_L^2\, m_c\, \varepsilon_0/e^2$ at which the plasma frequency equals the laser frequency ω_L [2,24] (ρ_{crit} amounts to $\approx10^{22}\,cm^{-3}$ at $\lambda = 335\,nm$ and to $\approx10^{21}\,cm^{-3}$ at 1085 nm). Since $\rho_{th} < \rho_{crit}$ for all wavelengths investigated, the optical properties are sufficiently well described by Eq. (13), and changes in laser plasma coupling associated with the transition to electron densities $> \rho_{crit}$ [38,39,104] must not be considered. In bulk breakdown, that simplification remains valid even above threshold because the free-carrier density is limited by an upstream movement of the breakdown front during the laser pulse [18,106,113].

IV. RESULTS AND DISCUSSION

A. Wavelength dependence of breakdown thresholds

Figure 4(a) shows the experimental results on $I_{th}(\lambda)$ for NA = 0.8 and 0.9 together with bars marking the range between 10 and 90% breakdown probability. Experimental threshold data have been normalized to the average pulse duration $\tau_{L,avg} = 250\,fs$ as described at the end of Sec. II. Tabulated data from the threshold measurements before and after normalization are presented in Supplemental Material Table S1 [67]. Figures 4(b) and 4(c) present a comparison of experimental data averaged over both NAs with predictions of the full and asymptotic multiple-rate-equation model. The effective Drude collision time τ_{coll} and the capacity of the initiation channel $\rho_{ini,max}$ are used as free parameters.

Although the experimental data in Fig. 4(a) fluctuate by about ±20%, they clearly show a decrease of I_{th} with increasing wavelength. The modeling results in Fig. 4(b) reproduce this trend. However, the steps in the $I_{th}(\lambda)$ curve predicted for wavelengths at which the order of multiphoton excitation increases are not discernible in the experimental data. We attribute this to shortcomings of the complex TOPAS system rather than to inadequacies of the breakdown model, as will be discussed in the following.

The full Keldysh model employed for modeling SFI is widely accepted in the scientific community and used in most studies on femtosecond breakdown. In agreement with this model, steps in the $I_{th}(\lambda)$ curve have experimentally been observed for nanosecond breakdown, where SFI initiation determines I_{th} [15,16]. They were found also for femtosecond breakdown in a low-band-gap material (TiO_2, with $E_{gap} = 3.6\,eV$) at the transition from $k = 2$ to $k = 3$ [46]. The band gap in water is larger than for TiO_2. Therefore, the corresponding step size at equal wavelengths is smaller since the step size decreases with increasing k. As a consequence, the steps in water are more easily obscured by I_{th} fluctuations.

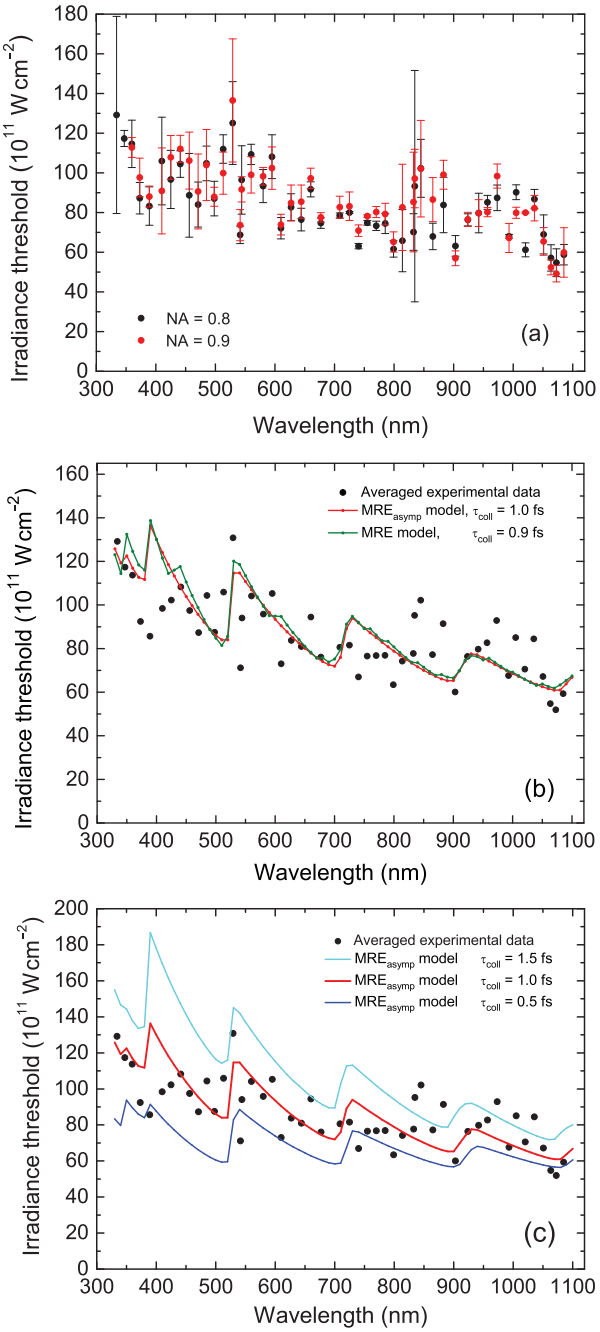

FIG. 4. Wavelength dependence of the optical breakdown threshold $I_{th}(\lambda)$ for femtosecond laser pulses. (a) Experimental data normalized to the average pulse duration of $\tau_L = 250$ fs for both investigated numerical apertures, NA = 0.8 and 0.9. The bars mark the irradiance range between 10 and 90% breakdown probability. (b) Best fit of model predictions for $I_{th}(\lambda)$ to the experimental data averaged over both NAs. Parameters used for the calculations are: $\tau_L = 250$ fs, $E_{gap} = 9.5$ eV, $\rho_{ini,max} = 10^{19}$ cm^{-3}, and $E_{ini}(\lambda)$ as described in Sec. III B. The effective collision time was $\tau_{coll} = 0.9$ fs with the full multiple-rate-equation model, and $\tau_{coll} = 1.0$ fs with the asymptotic limit of the model (MRE$_{asymp}$). (c) Plots of results obtained with the asymptotic model for collision times between 0.5 and 1.5 fs show that the fit depends critically on τ_{coll}.

The $I_{th}(\lambda)$ fluctuations in Fig. 4(a) are at most wavelengths very similar for both NAs. This indicates that they are more likely related to variations of the laser emission rather than to imperfections of the technique for threshold determination. The laser beam quality (M^2) will differ between individual wavelength settings due to the complexity of the TOPAS system and the need for readjustment after wavelength tuning. Variations of M^2 by $\pm 10\%$ will already change I_{th} by $\pm 20\%$. Threshold fluctuations may also originate from hot spots in the laser beam if the distribution of these intensity peaks varies for different wavelengths.

In principle, variable positive or negative chirps of the pulse could also affect the threshold determination [114]. Such influence has been observed when positive or negative chirps where imposed intentionally on 35 fs pulses with 18.7 nm transform-limited bandwidth [114]. However, in our case, the average pulse duration is 250 fs, corresponding to a transform-limited bandwidth of only 2.6 nm. The small bandwidth limits the possible effect of chirping, and randomly arising chirps will usually be smaller than the outcome of intentional pulse shaping that prolonged the 35 fs pulse to 960 fs in Ref. [114]. Therefore, randomly arising chirps will probably have little influence on I_{th}.

The sharpness of the breakdown threshold will be affected by pulse-to-pulse variations of the transverse beam profile. Threshold sharpness is defined as $S = E_{th}/\Delta E_L$, where ΔE_L is the energy interval between 10 and 90% breakdown probability. For the TOPAS measurements, S is not as good as with fixed wavelengths, where values $S > 20$ are common. Only in 7% of the cases, $S > 20$, but in 16.3% of the cases ($n = 16$), $S < 3$ (Supplemental Material Table S1 [67]). Low threshold sharpness indicated by large bars in Fig. 4(a) was observed mainly at the edge of individual functioning regimes of the TOPAS, as already reported in previous studies [49].

Good agreement between model predictions and experimental results was obtained with an effective collision time $\tau_{coll} = 0.9$ fs for the full multiple-rate-equation model and $\tau_{coll} = 1.0$ fs for the asymptotic limit of the model [Fig. 4(b)]. A comparison of the best fit with the asymptotic model at $\tau_{coll} = 1.0$ fs to results obtained with collision times of 0.5 and 1.5 fs shows that the fit depends critically on τ_{coll} [Fig. 4(c)]. A collision time of 1 fs is still within the validity limits for the Drude model discussed in Sec. III C, which reaches down to $\tau_{coll} \approx 0.5$ fs for $\lambda = 1050$ nm. With both modeling approaches, the best fit was obtained for $\rho_{ini,max} = 10^{19}$ cm^{-3}, as will be further discussed in Sec. IV C.

To further substantiate the appropriateness of our modeling approach, we tested also another approach that predicts no steps in the $I_{th}(\lambda)$ curve. Some researchers argued that MPI is quenched by collisions such that femtosecond breakdown is driven by tunneling-initiated AI [40–43]. In that case, $I_{th}(\lambda)$ should exhibit no discontinuities since the TI rate is wavelength independent. The electron density produced by tunneling alone can be estimated from the result of the full Keldysh model at long wavelengths where MPI plays a negligible role. We used $\rho_{SFI} = 10^{15}$ cm^{-3} predicted for $\lambda = 2000$ nm (see Sec. IV D) as a start value for modeling a breakdown process driven by tunneling-initiated AI. Concretely we used Eq. (16) without the SFI term, assuming that a seed electron density $\rho_{TI} = 10^{15}$ cm^{-3} is present already at the beginning of the laser pulse. The results are presented in Fig. 5. With $\tau_{coll} = 1$ fs, reasonable agreement with experimental data is observed for

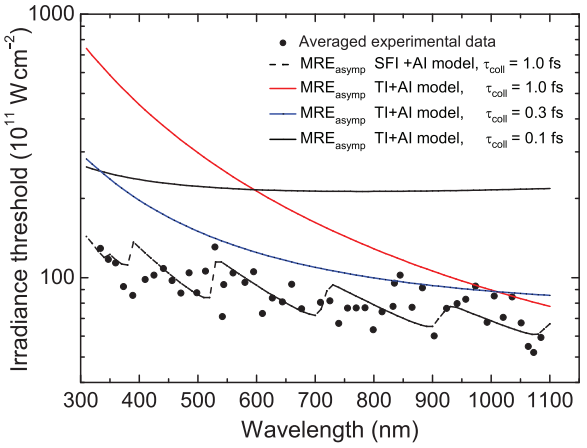

FIG. 5. Simulations of $I_{th}(\lambda)$ for a breakdown process driven by tunneling-initiated AI (TI+AI model). Breakdown thresholds are calculated by means of Eq. (16) without SFI term, assuming that TI produces an electron density $\rho_{TI} = 10^{15}\,\mathrm{cm}^{-3}$, which is present from the beginning of the laser pulse. The electron collision time is varied in the range $0.1\,\mathrm{fs} < \tau_{coll} < 1.0\,\mathrm{fs}$. Results are compared to experimental data averaged over both NAs and to the fit obtained using Eq. (16) with SFI term, representing the full Keldysh theory (SFI+AI model).

$\lambda > 900\,\mathrm{nm}$, but for UV wavelengths the threshold values are about six times too high. Thus, the $I_{th}(\lambda)$ dependence is much too steep. With shorter collision time ($\tau_{coll} = 0.3\,\mathrm{fs}$), a better match seems to be possible, but this "improvement" is deceiving because now the condition $\omega^2\tau_{coll}^2 \geqslant 1$ is no longer fulfilled at long wavelengths. With $\tau_{coll} = 0.1\,\mathrm{fs}$, the above condition is violated in the entire wavelength range, and the results become completely nonphysical. Thus, the full Keldysh theory provides significantly better fitting results than the alternative approach that would be consistent with a smooth $I_{th}(\lambda)$ dependence. This supports our interpretation that imperfections of the tunable laser system employed in this paper have precluded the experimental observation of steps in the $I_{th}(\lambda)$ curve.

The overall agreement between the predictions of the full and asymptotic multiple-rate-equation models is very good because t_{MRE} is considerably shorter than the laser pulse duration in the entire wavelength range (t_{MRE} is 174 fs at 350 nm, and 22 fs at 1050 nm). The shape of the $I_{th}(\lambda)$ curves differs slightly. Both models predict steps whenever the order k of the multiphoton process needed for excitation into the E_{ini} level or across the band gap changes. However, the full model predicts additional steps for changes of the number k' of one-photon excitation events that are needed to reach the impact ionization level. As mentioned above, such details cannot be resolved with the tunable laser system that was available for this paper.

The τ_{coll} value obtained in the fitting procedure is linked to the model assumptions on the electronic band structure of water. For a given threshold value, the assumption of a smaller band gap results in longer collision times because a slow avalanche will suffice to complete breakdown. Use of a simple rate equation without consideration of AI time constraints will also prolong τ_{coll}. Feit *et al.* obtained $\tau_{coll} \approx 3.3\,\mathrm{fs}$ for 140 fs pulses using $E_{gap} = 6.5\,\mathrm{eV}$ and a smaller critical energy for impact ionization than in this paper ($E_{crit} = E_{gap}$ instead of $E_{crit} = (3/2)\,\tilde{\Delta}$) [104]. Dubietis *et al.* found $\tau_{coll} \approx 3\,\mathrm{fs}$ using $E_{gap} = 6.5\,\mathrm{eV}$ and a reduced cross-section for MPI [32]. In both studies, a simple rate equation based on the Drude model was used to assess AI. Sarpe *et al.* and Winkler *et al.* evaluated time-resolved spectral interferometry data obtained at $\lambda = 785\,\mathrm{nm}$ with the help of a Drude model using ionization coefficients and collision time as fitting parameters [26,28]. They obtained $\tau_{coll} \approx 1.6 \pm 0.3\,\mathrm{fs}$ using $E_{gap} = 6.5\,\mathrm{eV}$ [26], but the value of the effective collision time dropped to 0.18 fs (outside of the validity range of the Drude model) when they adjusted the band gap value to 8.3 eV without considering interband energy states [28]. Thus, it should be emphasized that the value $\tau_{coll} \approx 1\,\mathrm{fs}$ obtained in this paper relates to the use of a band gap value of 9.5 eV in the breakdown model, the consideration of an initiation path via excitation into preexisting traps at $E_{ini} \geqslant 6.4\,\mathrm{eV}$, and the employment of a multirate equation approach accounting for the time constraints of AI.

The procedure used for determining the effective collision time does not allow for a direct distinction between electron-phonon, electron-neutral, and electron-ion collisions. However, different collision mechanisms will dominate at different free-carrier densities [14]. Up to the bubble threshold, the free-electron density corresponds to an ionization degree of $\leqslant 0.27\%$ (Sec. III D), and molecules in liquid water behave like those in a solid for vibrations above the Frenkel frequency [115]. Thus, electron-phonon collisions will prevail, and $\tau_{coll} \approx 1\,\mathrm{fs}$ obtained by fitting model predictions to experimental bubble threshold data largely represents the electron-phonon collision time.

B. Interplay of SFI and AI

The observed decrease of I_{th} with increasing λ indicates that AI plays an ever more important role for longer wavelengths. This becomes obvious by looking at the wavelength dependencies of MPI and AI rates presented in Fig. 6. All rates are calculated for the mean threshold irradiance $\overline{I}_{th} = 8.25\times10^{16}\,\mathrm{Wm}^{-2}$ obtained experimentally (Fig. 4). While the MPI rate decreases with increasing number of photons required for the multiphoton process, the AI rate increases for longer wavelengths. The tunneling rate exhibits no significant wavelength dependence [34,45]. Thus, I_{th} will drop with increasing λ if AI dominates.

The interplay of SFI and AI is portrayed in more detail by the temporal evolution of free-electron density shown in Fig. 7 for UV, visible, and IR wavelengths. At 347 nm [Fig. 7(a)], the initiation pathway is saturated, visible by the fact that ρ_{ini} rapidly reaches the maximum possible capacity of this channel, which for $\rho_{ini,max} = 10^{19}\,\mathrm{cm}^{-3}$ equals χ_{trap}. The contribution from SFI crossing the entire band gap is large ($\rho_{Egap} \approx 2.5 \times \rho_{Eini}$). Avalanche ionization starts to play a role at the peak of the laser pulse when already a large number of free electrons have been generated. Since the AI rate is small at short wavelengths, the free electron density created by AI at the end of the pulse is just 3.6 times larger than the contribution from SFI. At 520 nm, the initiation pathway is still saturated, but the SFI contribution from crossing the

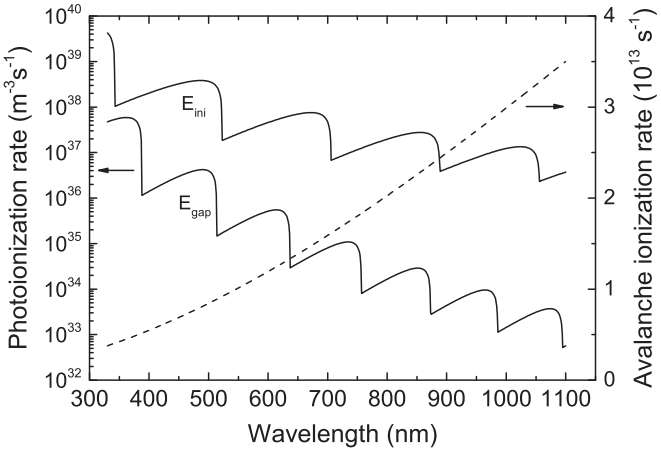

FIG. 6. Wavelength dependence of AI and MPI rates needed to reach E_{ini} and to cross E_{gap}. All rates are calculated for the mean threshold irradiance $\bar{I}_{\mathrm{th}} = 8.25\times10^{16}\,\mathrm{W\,m^{-2}}$ obtained experimentally (see Fig. 4).

entire band gap is now small compared to stepwise excitation via solvated states [Fig. 7(b)]. The relative importance of AI increases to $\rho_{\mathrm{AI}}/\rho_{\mathrm{SFI}} = 17$. Finally, at 1040 nm, AI clearly dominates the breakdown process [Fig. 7(c)]. Although seed electrons are still abundant, with $\rho_{\mathrm{ini}} = 3.5\times10^{17}\,\mathrm{cm^{-3}}$, the initiation channel is not saturated any more (only 11.5% of its maximum capacity is used), and AI provides 265 times more free electrons than SFI. At 1040 nm, AI starts to dominate the breakdown process already when ρ_c has exceeded a level of $10^{16}\,\mathrm{cm^{-3}}$, whereas at 347 nm, AI prevails only for $\rho_c > 10^{19}\,\mathrm{cm^{-3}}$.

Figure 8 presents the simulated wavelength dependence of the ratio $\rho_{\mathrm{AI}}/\rho_{\mathrm{SFI}}$. The ratio increases stepwise whenever one more photon is needed for MPI, which is correlated also with a stepwise increase of I_{th} [Fig. 4(b)]. The reduced MPI contribution is compensated by an increased contribution of AI, which becomes possible through the increase of threshold irradiance at each step. Below 380 nm, E_{ini} can be reached by a two- or three-photon process, and the entire band gap can also be crossed by a three-photon process, which corresponds to a small $\rho_{\mathrm{AI}}/\rho_{\mathrm{SFI}}$ ratio. The step at 380 nm is due to an increase of the photon number required to cross E_{gap} from 3 to 4, as seen in Fig. 6. For $\lambda > 400\,\mathrm{nm}$, all steps in the $\rho_{\mathrm{AI}}/\rho_{\mathrm{SFI}}$ ratio are caused by an increase of the photon number needed to reach E_{ini} because MPI across the entire band gap plays now only a negligible role [Figs. 7(b) and 7(c)]. Below 350 nm, $\rho_{\mathrm{AI}}/\rho_{\mathrm{SFI}}$ is higher than between 350 and 380 nm. This is because, for $\lambda < 350\,\mathrm{nm}$, a two-photon process suffices to reach E_{ini}, which leads to early saturation of the initiation channel and provides a long time window for AI. Therefore, I_{th} drops [Fig. 4(b)], and the relative importance of AI increases.

Altogether, the breakdown process in water at 250 fs pulse duration can be well characterized as multiphoton-seeded AI, with AI largely determining the bubble threshold I_{th}. It is interesting to note that this characterization still applies for pulse durations well below 100 fs. For $\lambda = 800\,\mathrm{nm}$, Sarpe *et al.* found that, even at 35 fs pulse duration, AI accounts for more than 85% of the final free-electron density, which corresponds

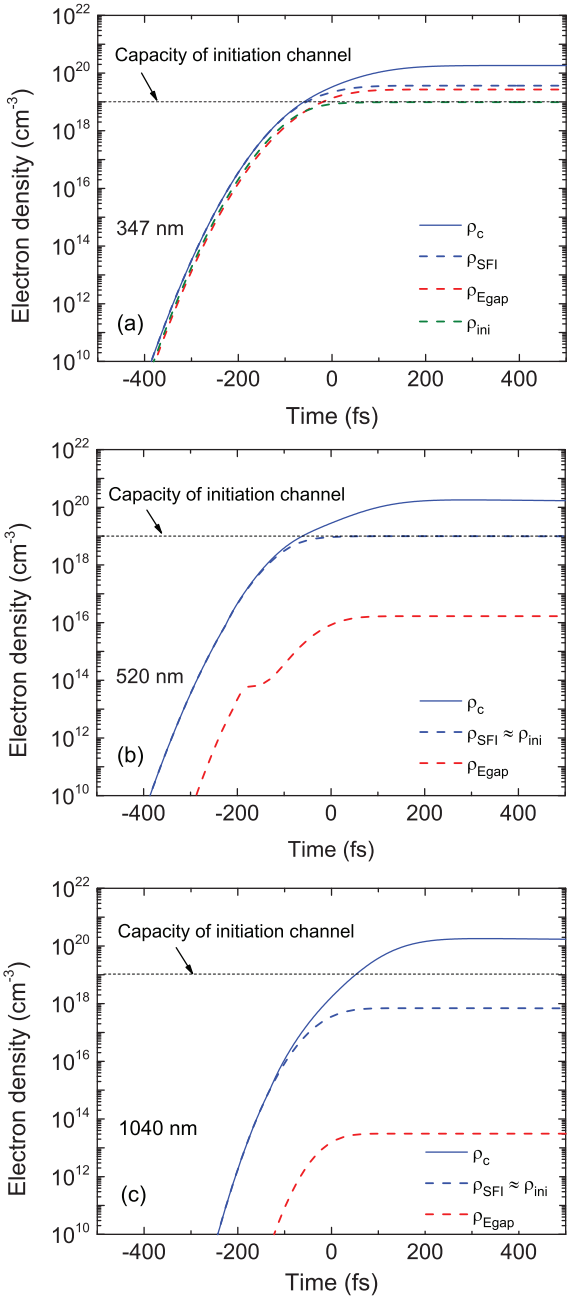

FIG. 7. Temporal evolution of optical breakdown by 250 fs pulses of different wavelengths as predicted by the full multiple-rate-equation model for (a) 347 nm, (b) 520 nm, and (c) 1040 nm. Each graph shows the total conduction band electron density ρ_c (all nonlinear absorption pathways including AI), the total contribution by ρ_{SFI} (plasma dynamics without AI arising from SFI), and the components constituting SFI. The contribution of AI to ρ_c is given by $\rho_{\mathrm{AI}} = \rho_c - \rho_{\mathrm{SFI}}$. Strong-field ionization includes a contribution ρ_{ini} from the initiation pathway (excitation into an intermediate level at E_{ini} followed by upconversion into the conduction band), and a contribution $\rho_{E\mathrm{gap}}$ from excitation across the entire band gap. They are linked by $\rho_{\mathrm{ini}} = \rho_{\mathrm{SFI}} - \rho_{E\mathrm{gap}}$. In (b) and (c), ρ_{ini} is almost identical with ρ_{SFI} because $\rho_{E\mathrm{gap}}$ is very small. Therefore, $\rho_{\mathrm{ini}} \approx \rho_{\mathrm{SFI}}$ is not displayed separately. The free-electron density at the bubble threshold is two orders of magnitude lower than the density $\rho_c = 6.68\times10^{22}\,\mathrm{cm^{-3}}$ corresponding to full ionization [2,10].

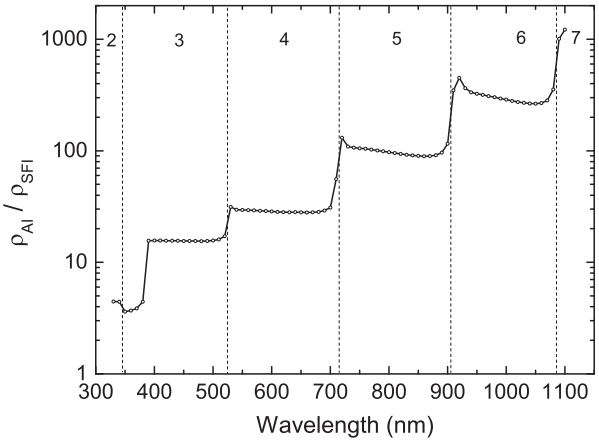

FIG. 8. Ratio of free-electron density produced by AI to that created by SFI ρ_{AI}/ρ_{SFI} plotted as a function of wavelength for 250 fs laser pulse duration. Calculations were performed using the asymptotic limit of the multiple-rate-equation model. For $\lambda > 400$ nm, steps in the $\rho_{AI}/\rho_{SFI}(\lambda)$ curve correspond to changes of the order of the multiphoton process required to reach E_{ini} (the respective orders are indicated by the numbers in the figure). For $\lambda < 400$ nm, changes in the order of MPI excitation across the entire band gap also play a role.

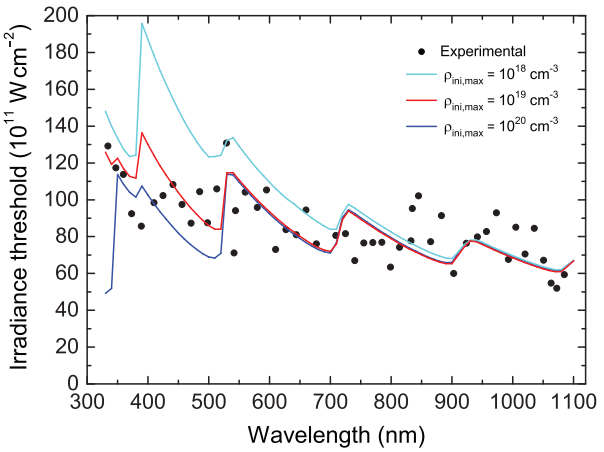

FIG. 9. Predictions of the asymptotic model for $I_{th}(\lambda)$ assuming different capacities of the initiation channel in the range $10^{18}\,\mathrm{cm}^{-3} < \rho_{ini,max} < 10^{20}\,\mathrm{cm}^{-3}$. The pulse duration is $\tau_L = 250$ fs.

to $\rho_{AI}/\rho_{SFI} = 5.6$ [14,26]. At the same wavelength and $\tau_L = 250$ fs, the ratio is $\rho_{AI}/\rho_{SFI} = 97$ (Fig. 8).

Assumptions on collision processes made in optical breakdown models strongly influence the outcomes on the relative importance of AI and SFI. In some classical theoretical studies on breakdown in SiO_2, attention was focused only on electron-phonon scattering, and electron-ion collisions, which become ever more relevant with increasing free-carrier density, were neglected [33,35,97]. As a consequence, the rate of free-carrier absorption in fused silica ablation and the role of AI were underestimated. For example, the W_{1pt} value for free-carrier absorption in fused silica employed originally by Rethfeld [35] corresponds to $\tau_{coll} = 14.3$ fs in the Drude model, as can be seen by comparing Eqs. (7) and (13). This resulted in a much smaller contribution of AI than found in the present paper on breakdown in water, which has a similar band gap (9.5 eV) as fused silica (9 eV). For breakdown in fused silica at $\lambda = 500$ nm, $\tau_L = 250$ fs, it was predicted that less than 5% of the free electrons are generated by AI [35]. By contrast, with $\tau_{coll} = 0.9$ fs that provides the best fit to our present experimental results, the multiple-rate-equation model predicts for the same wavelength and pulse duration that 15.7 times more electrons are produced by AI than by SFI. This picture is consistent with a later paper by the Rethfeld group [38] in which electron-ion collisions were included and an effective electron collision time in the order of 1 fs was assumed, in accordance with experimental studies [19,100,102,116]. Now an avalanchelike behavior was found for irradiance conditions above the ablation threshold, both with the multiple-rate-equation model and the kinetic approach [38]. In several recent studies on optical breakdown in large-band-gap solids, effective collision times $\leqslant 1$ fs were used, and the results consistently revealed a large influence of AI, in agreement with our results on water [27,29,31,39,47].

C. Interband energy states and breakdown initiation

The interplay between SFI and AI is determined by the laser pulse duration, the band gap, and material parameters governing collisional interactions. Furthermore, intermediate energy states between valence and conduction band that exist in many types of transparent dielectrics also play an important role. If such states act as centers of reduced excitation energy as in water, they will facilitate breakdown, but if they arise from self-trapping of excitons, the breakdown dynamics will, at least transiently, be slowed [27,38].

In water, the intermediate states consist of specific geometric arrangements of water molecules that are stabilized by relatively weak hydrogen bonds (see Sec. III A). Therefore, they are labile and may be destroyed by the electric fields of conduction band electrons once their density exceeds a certain level (Sec. III B). In order to assess the capacity of the initiation channel in water, we varied the parameter $\rho_{ini,max}$ of the breakdown model and compared the predicted wavelength dependence with the experimental $I_{th}(\lambda)$ curve (Fig. 9). We see that, for $\rho_{ini,max} = 10^{18}\,\mathrm{cm}^{-3}$, UV thresholds are too high, and the slope of the $I_{th}(\lambda)$ curve is too steep. For $\rho_{ini,max} = 10^{20}\,\mathrm{cm}^{-3}$, the UV thresholds at wavelengths $\leqslant 340$ nm are much too low. Thus, $\rho_{ini,max} = 10^{19}\,\mathrm{cm}^{-3}$, equal to the trap density in liquid water, provides a good fit to experimental data. We conclude that about 10^{19} electrons per centimeter cubed can reach the conduction band through the initiation channel before it decays. Future studies will need to provide more data points at $\lambda < 340$ nm to consolidate this finding.

The free-electron density coming from the initiation channel drops with increasing wavelength, when the MPI rate decreases (Fig. 7). According to our model, the initiation channel is saturated for $\lambda < 530$ nm. For $\lambda > 530$ nm, the order of the multiphoton process necessary for reaching E_{ini} changes from $k = 3$ to $k = 4$, and $\rho_{ini,max}/\chi_{trap}$ drops below 60%. With each increase of k, saturation drops further until it reaches values around 10% for $\lambda > 910$ nm, $k = 6$. The decrease of the seed electron density at longer wavelengths is compensated by an increasing strength of AI, as discussed in the previous section.

A decay of the initiation channel during the breakdown process, as hypothesized for water in this paper, is rather exceptional. It is a key factor in explaining the drop of breakdown thresholds with increasing λ in the short-wavelength range, which differs from the behavior in crystalline solids [29,47,48] and corneal tissue [49], where I_{th} increases with λ for $\lambda < 1000$ nm. The discrepancy may be partially linked to differences in band gaps and pulse durations, but we attribute it mainly to differences in number density, stability, and excitation kinetics of interband energy levels. The breakdown threshold at UV wavelengths will generally be reduced by conditions favoring MPI, such as a small band gap, short pulse durations, and interband energy levels. Correspondingly, the UV threshold was found to be smaller than at visible or IR wavelengths in simulations for a relatively small band gap $E_{gap} = 5$ eV and $\tau_L = 100$ fs [39]. In our investigations, the band gap is larger (9.5 eV for water) and the pulse duration longer (250 fs), which already lessens the relative importance of MPI. It will be further quenched by a decay of the initiation channel during the breakdown process, as indicated by the simulations in Fig. 9.

In crystalline solids, interband energy states are more stable than in water, and their number increases during breakdown. For example, during breakdown in SiO_2, which has a band gap of ≈9 eV [117], color centers are formed via rapid self-trapping of excitons occurring with a time constant of 150 fs [117–120]. Self-trapped excitons constitute an energy state ≈5.7 eV below the conduction band edge [38,117,120]. Although self-trapping will initially slow AI because it drains electrons from the conduction band, the situation changes when the STE density becomes saturated later during the pulse or at higher irradiance [27]. Avalanche ionization is then no longer inhibited, and the interband energy states formed by the laser irradiation facilitate not only MPI but also boost AI [29,121]. The influence of interband energy levels is largest for $\lambda < 1000$ nm. At longer wavelengths, tunneling becomes increasingly important for seeding AI, and differences between different breakdown media are less significant. Therefore, the wavelength dependencies of breakdown threshold for water and crystalline solids start to resemble each other for $\lambda > 1300$ nm (Sec. IV D).

In transparent or semitransparent tissues, centers of reduced excitation energy consist of biomolecules acting as electron donors. Electrons can be abstracted from certain aminoacides with energies similar or even smaller than those needed in pure water [122–124]. Such centers of reduced excitation energy are more stable than the preexisting traps in water and exist in large numbers. These features explain why the $I_{th}(\lambda)$ dependency for cornea shows a similar threshold drop at shorter wavelengths as observed for crystalline solids [49].

Excess electrons originating from biomolecules may lower I_{th} in two ways: after upconversion into the conduction band, they can either directly seed AI, or their interaction with biomolecules can create reaction products exhibiting enhanced one- or multiphoton absorption. Several studies provided evidence that ultrashort pulsed laser-induced modification of biomolecules produces intermediates with different optical or electronic properties that accelerate further linear or nonlinear modification processes once their concentration is sufficiently high [125–130]. Thus, abstraction of excess electrons from biomolecules will either directly or indirectly enhance the photoionization channel of breakdown, which will lower the modification thresholds in biological media compared to the bubble formation threshold in pure water [2].

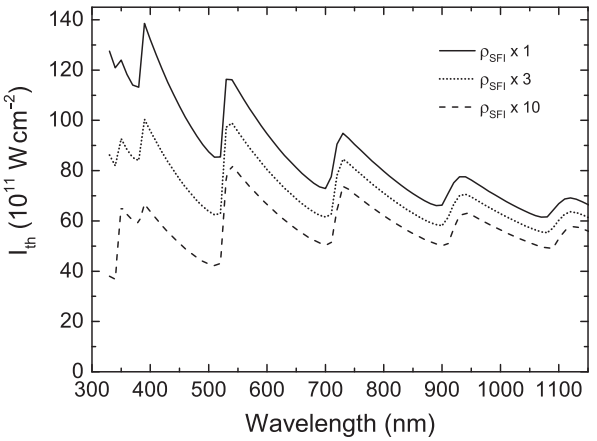

FIG. 10. Simulation of $I_{th}(\lambda)$ assuming different strengths of the photoionization channel. The curve for $\rho_{SFI} = 1$ represents the situation in pure water, whereas the 3- and 10-fold enhancement of the photoionization channel serves as simple model for the possible influence of additional interband states facilitating MPI. The enhancement is simulated by multiplying the term $(d\rho_{SFI}/dt)$ in Eq. (16) by a factor of 3 or 10, respectively.

The possible amount of the threshold reduction by the presence of biomolecules is estimated in Fig. 10, where $I_{th}(\lambda)$ dependencies for pure water are compared with curves corresponding to a 3- and 10-fold enhanced photoionization channel. Threshold changes are relatively small in the IR region where AI provides three or four orders of magnitude more free electrons than SFI, but increase considerably for shorter wavelengths. At 330 nm, a 10-fold enhancement of ρ_{SFI} results in a threefold reduction of I_{th}. This trend is confirmed by experimental observations. For example, the threshold energy for bubble formation in mouse intestine by 355 nm, 500 ps pulses focused at NA = 1.2 amounts to only one third of the respective value in water (33 vs 103 nJ) [131]. Threshold measurements with IR and UV femtosecond laser pulses in water with increasing concentration of bovine serum albumin showed that, at a concentration of 10 mgml^{-1}, the bubble threshold decreased by 40% for 400 nm pulses, compared to only 7% at 800 nm [57,132].

Local variations in the concentration or composition of biomolecules that can provide excess electrons will be reflected in variations of the bubble threshold. According to the simulations in Fig. 10, such fluctuations will be more pronounced at short wavelengths than for IR breakdown. As a consequence, the size of laser effects produced by IR pulses of constant laser energy that are scanned across the tissue will likely be more uniform than effects produced at visible or UV wavelengths.

D. Consequences for femtosecond laser tissue surgery

Femtosecond laser surgery has been explored for various tissues such as cornea, lens, sclera, skin, vocal folds, and brain [4–8,62,133,134]. To date, surgery has mostly been performed at 800 and 1040 nm, the wavelengths of Ti:sapphire lasers

and ytterbium-based lasers [6,8,54]. Recently UV-A pulses have been employed for flap cutting in corneal refractive surgery because the shorter wavelengths provide a better cutting precision due to the shorter plasma length [55–58,135]. Furthermore, the collagen molecules in corneal tissue act as stable centers of reduced excitation energy in UV breakdown that lower the breakdown threshold and minimize mechanical side effects [58]. On the other hand, wavelengths considerably longer than 1040 nm have been tested for plasma-mediated surgery in strongly scattering tissues, such as sclera, skin, and brain [59–61,63], and in edematous corneas [64].

Scattering decreases with increasing wavelengths, but for $\lambda > 1\ \mu$m, light penetration is increasingly affected by water absorption [136]. Xu and Wise determined the effective penetration depth for brain tissue given by the wavelength-dependent interplay of absorption and scattering, and found peaks around 1.3 and 1.7 μm [65]. Here, the optical penetration depth amounts to 330 and 480 μm, respectively, compared to only 130 μm at 800 nm. Thus, wavelengths of 1.3 and 1.7 μm are of great interest for laser surgery. Therefore, we use our model to derive predictions for nonlinear energy deposition in this parameter regime. For this purpose, the fit obtained in the wavelength region between 335 and 1085 nm was extrapolated up to 2000 nm using the same values for $\tau_{\rm coll}$ and $\rho_{\rm ini,max}$ as for the shorter wavelengths. In this context, it is interesting to note that the choice of $\rho_{\rm ini,max}$ is relevant only for UV breakdown (as shown in Sec. IV C) and has no influence on the modeling results in the extrapolation range. The results are presented in Fig. 11.

For $\lambda > 1\ \mu$m, the bubble threshold $I_{\rm th}$ first continues to decrease with increasing λ due to the growing efficiency of AI, but it levels out for $\lambda > 1200$ nm [Fig. 11(a)]. These model predictions for water are in good agreement with the experimental observation of a constant damage threshold in SiO_2 in the wavelength range between 1200 and 2200 nm reported by Grojo *et al.* [34]. For $\lambda > 1200$ nm, TI becomes increasingly important for the creation of seed electrons as indicated by the drop of the Keldysh parameter γ with wavelength that is presented in Fig. 11(b). The influence of tunneling is the reason why SFI-produced seed electrons are abundant even at wavelengths around 2 μm [Fig. 11(c)]. Experimental evidence for the role of TI in initiating dielectric breakdown at mid-IR wavelengths has been provided in Ref. [48]. The $\rho_{\rm SFI}(\lambda)$ curve in Fig. 11(c) does not distinguish between TI and MPI. Nevertheless, we can roughly assess their respective contributions by assuming that at $\lambda = 2\ \mu$m ($\gamma \approx 1$) $\rho_{\rm SFI}$ is largely provided by TI. Since tunneling is wavelength independent [34,45], the contribution from TI at shorter wavelengths is approximately the same as at 2 μm. This yields ratios $\rho_{\rm MPI}/\rho_{\rm TI}$ of about 8000 at 347 nm, 275 at 800 nm, and $\rho_{\rm MPI}/\rho_{\rm TI} > 10$ for all wavelengths up to 1300 nm. Only at wavelengths $> 2\ \mu$m, TI starts to dominate over MPI (for $\tau_{\rm L} = 250$ fs).

The initial electron density predicted for 1050 nm, $\rho_{\rm SFI} = 3.5\times10^{17}\ {\rm cm}^{-3}$, is in good agreement with an estimate for the seed electron density in large band-gap materials that was derived from the surface roughness of laser-produced nanofeatures produced at this wavelength [42]. However, while in Ref. [42] seed electrons are attributed to TI, our modeling results indicate that at 1050 nm $\rho_{\rm SFI}$ is produced mainly by MPI.

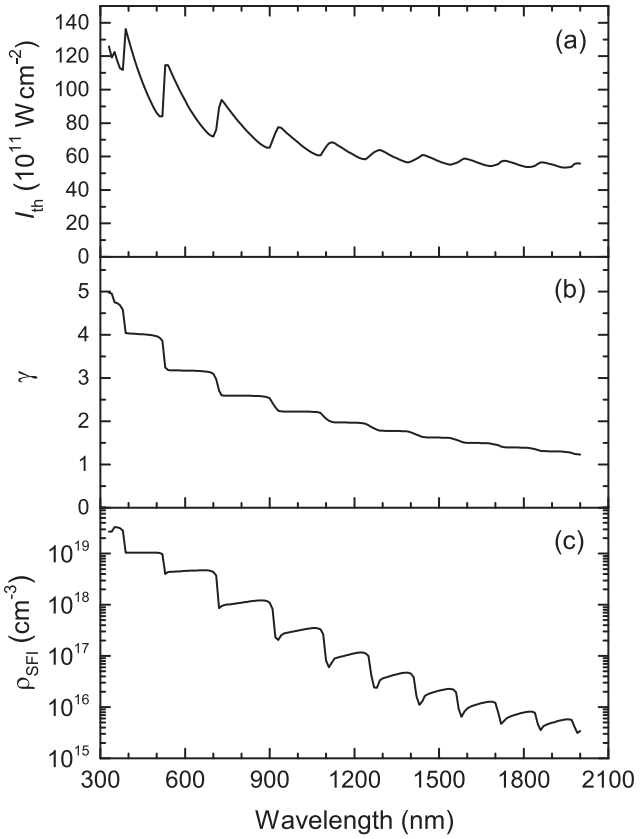

FIG. 11. Predictions for the wavelength dependence of femtosecond laser breakdown in water up to $\lambda = 2\ \mu$m, for $\tau_{\rm L} = 250$ fs. (a) Irradiance threshold for bubble formation, (b) Keldysh parameter at the bubble threshold, and (c) free-electron density created by SFI.

Grojo *et al.* concluded from the observation of a constant $I_{\rm th}$ value between 1200 and 2200 nm that the entire breakdown process in this wavelength region is dominated by TI, and AI plays no role [34]. However, our modeling results show that TI alone does not suffice to produce breakdown and that the observed $I_{\rm th}(\lambda)$ behavior is well compatible with a prominent role of AI. The larger number k' of inverse Bremsstrahlung absorption events needed to produce impact ionization at longer wavelengths is compensated by an increase of the photon flux, as becomes obvious from Eq. (9), together with a slight increase of the one-photon absorption cross-section [Eq. (13)]. Therefore, the influence of AI first continues to increase with wavelength: we obtain $\rho_{\rm AI}/\rho_{\rm SFI}$ values of 1.48×10^4 at $\lambda = 1.7\ \mu$m, and 5.29×10^4 at $\lambda = 2.0\ \mu$m. Since AI gains strength with increasing λ, a smaller seed electron density suffices to initiate homogeneous plasma formation, and $\rho_{\rm seed}$ can readily be provided by SFI. Finally, for wavelengths $> 2\ \mu$m, $\rho_{\rm seed}$ converges against a constant value produced by TI, and the increase of the one-photon cross-section with wavelength saturates because $\omega^2\tau_{\rm coll}^2$ drops well below 1 [Eq. (13)]. Since also the AI strength remains constant due to the balance between changes in k' and photon flux, $I_{\rm th}$ remains constant too.

For IR breakdown in biological tissues, similar trends should apply as for water because the relatively small seed electron density sufficient for initiating AI at IR wavelengths

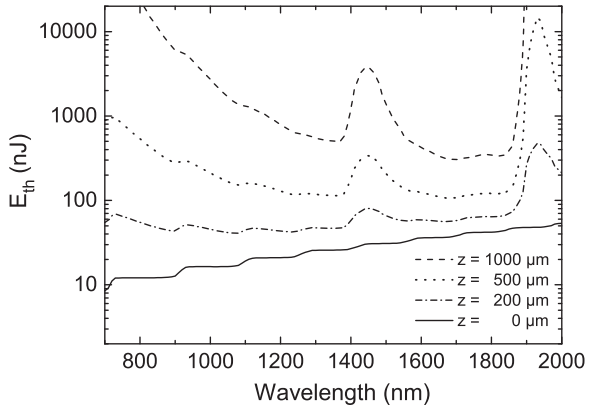

FIG. 12. Calculated wavelength dependence of the pulse energy threshold E_{th} for femtosecond laser breakdown in brain tissue at the tissue surface ($z = 0$) and different focusing depths. Calculations were performed for $\tau_{\text{L}} = 250\,\text{fs}$, NA $= 0.8$, and $M^2 = 1.4$ using the $I_{\text{th}}(\lambda)$ data of Fig. 10 and data on optical penetration depth from Ref. [65]. Breakdown dynamics and threshold temperature were assumed to be the same as for bubble formation in water.

implies that biomolecules providing additional seed electrons have little influence on I_{th} (Fig. 10). The low optical breakdown threshold in water at wavelengths >1 μm thus offers good prospects for femtosecond laser surgery deep within scattering tissues. Figure 12 presents the wavelength dependence of the energy threshold for bubble formation $E_{\text{th}}(\lambda)$, both at the tissue surface and at various focusing depths z within the tissue. All data are calculated using Eq. (1) for $\tau_{\text{L}} = 250\,\text{fs}$, NA $= 0.8$, and $M^2 = 1.4$, assuming the same breakdown dynamics and thresholds as for water. Here, $E_{\text{th}}(\lambda)$ at the tissue surface relates directly to the $I_{\text{th}}(\lambda)$ curve in Fig. 11(a) but considers the increase of spot size with growing wavelength. Estimates of E_{th} values at 200, 500, and 1000 μm focusing depth are obtained using data on the optical penetration length for brain tissue taken from Ref. [65]. The difference in optical path lengths inside the tissue between central and peripheral rays of the tightly focused laser beams are neglected in this simple estimate.

For small focusing depths up to 200 μm, pulse energies required for surgery are smallest at wavelengths around 800 nm (emission of the Ti:sapphire laser). However, the energy minimum shifts to wavelengths around 1350 nm for $z = 500\,\mu$m, and to the wavelength range around 1700 nm for $z = 1\,$mm. For $z = 500\,\mu$m, pulse energies between 0.2 and 0.3 μJ will probably suffice to perform surgery, but for $z = 1$mm, pulse energies around 1 μJ may be needed even at the optimum laser wavelengths to achieve breakdown within cortical tissue. Cutting depths and cutting energies for tissues other than brain will vary depending on their scattering coefficients, vascularization, and pigmentation [136], but the values obtained in this paper can serve as a landmark for parameter selection.

V. CONCLUSIONS

The wavelength dependence of the threshold for femtosecond optical breakdown in water at ≈250 fs pulse duration was investigated by measuring the threshold for bubble formation at 50 wavelengths between 335 and 1085 nm under diffraction-limited focusing conditions. We found a continuous decrease of I_{th} with increasing wavelength. Experimental results were compared to model predictions based on the Keldysh theory of SFI and a modified Drude model for AI together with a multiple-rate-equation approach that accounts for the time constraints of AI in femtosecond breakdown [35]. The model assumes a band gap of water of 9.5 eV and the existence of a separate initiation channel via a solvated electron state that is quenched at high conduction band electron densities when the local conformations of water molecules constituting the traps are disturbed.

Good agreement between model predictions and experimental $I_{\text{th}}(\lambda)$ data was obtained with an effective Drude collision time of $\tau_{\text{coll}} = 0.9\,$fs when the full multiple-rate-equation model was used, and $\tau_{\text{coll}} = 1\,$fs when the computationally less intensive asymptotic limit of the model for fully developed AI was employed. The value of τ_{coll} is of major importance for obtaining a realistic picture of the interplay between SFI and AI. Furthermore, together with wavelength and irradiance, it determines the transition time t_{MRE} to the asymptotic regime in which AI can be described by a single rate equation. A value of $\tau_{\text{coll}} = 1\,$fs implies that, for breakdown in water by 250 fs pulses, the asymptotic model can be used in the entire wavelength range investigated in this paper.

The decrease of I_{th} with increasing λ indicates that AI plays a dominant role in the optical breakdown process because the AI rate becomes more effective for longer wavelengths, whereas the MPI rate decreases with increasing number of photons required for MPI, and tunneling exhibits no significant wavelength dependence. According to the model calculations, the ratio of the free-electron densities provided by AI and SFI increases from $\rho_{\text{AI}}/\rho_{\text{SFI}} = 3.6$ at 350 nm to $\rho_{\text{AI}}/\rho_{\text{SFI}} = 265$ at 1050 nm and 5.3×10^4 at 2000 nm. Thus, breakdown proceeds as multiphoton-seeded AI, with AI determining I_{th}.

Steps in the $I_{\text{th}}(\lambda)$ dependence predicted by the breakdown model at wavelengths where one more photon is needed for MPI could not be discerned experimentally because the scattering of the $I_{\text{th}}(\lambda)$ data exceeded the predicted height of the steps. This scatter and the small threshold sharpness at some wavelengths were caused by imperfections of the tunable laser system. Exploration of the fine structure of the $I_{\text{th}}(\lambda)$ dependence remains a challenge that can be met only with improved laser technology.

The large value of the bubble threshold at UV wavelengths is indicative of a decay of the initiation channel in the course of the optical breakdown process. At short wavelengths, the free-electron density grows initially very fast by MPI, but that induces changes of the potential landscape, which progressively distort the traps constituting an intraband energy level at E_{ini}. The best fit to experimental $I_{\text{th}}(\lambda)$ data was achieved for $\rho_{\text{ini,max}} \approx \chi_{\text{trap}}$, i.e. by assuming that the maximum number density of electrons which can reach the conduction band through the initiation channel approximately resembles the density of preexisting traps in liquid water under normal conditions, $\chi_{\text{trap}} \approx 10^{19}\,\text{cm}^{-3}$.

The $I_{\text{th}}(\lambda)$ dependence observed for water differs from that in crystalline solids, where I_{th} increases with wavelength for $\lambda < 1000$ nm. This discrepancy can be explained by differences in the kinetics of interband energy states. While

centers of reduced excitation energy fade away during the breakdown process in water, new centers are created by self-trapping of excitons in dielectric solids. Also in cells and tissues, biomolecules constitute fairly stable centers of reduced excitation energy. Therefore, the UV breakdown threshold in tissue is considerably lower than in water.

In UV-A breakdown, MPI contributes a considerable fraction of the final free-electron density both in water and biological tissues. Therefore, local variations of the density of centers of reduced excitation energy caused by inhomogeneities can strongly influence the breakdown threshold. By contrast, in IR breakdown, AI provides three or four orders of magnitude more free electrons than SFI. As a consequence, additional seed electrons from biomolecules have little influence on the breakdown dynamics, and the breakdown threshold fluctuates less.

Infrared wavelengths around 1300 and 1700 nm are of great interest for laser surgery within scattering tissues due to a favorable combination of low scattering and moderate water absorption. Therefore, we used the model parameters obtained from fitting our experimental $I_{\mathrm{th}}(\lambda)$ data to derive predictions for nonlinear energy deposition up to a wavelength of 2000 nm. Up to $\lambda = 1300$ nm, MPI provides at least 10 times more seed electrons than tunneling. However, while the influence of MPI ceases for longer wavelengths, the contribution of tunneling remains approximately constant and guarantees the availability of seed electrons even at $\lambda = 2\,\mu$m or larger. The strength of AI first continues to increase with wavelength and then remains approximately constant for $\lambda > 2\,\mu$m, where the influence of increasing k' and photon flux balance each other. Since with increasing λ the strength of both SFI (in the form of TI) and AI converge against constant levels, the bubble threshold assumes an approximately constant and low level for $\lambda > 1.3\,\mu$m. This model prediction offers good prospects for femtosecond laser surgery deep within scattering tissues.

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