Near-invariance of femtosecond laser dielectric ablation spanning over three octaves

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Femtosecond lasers are today ubiquitous tools given their unique agility for achieving various material transformations in any transparent dielectrics. Here, we study single shot ablation in dielectrics using 200-fs pulses in a very broad spectral domain from deep-ultraviolet to mid-infrared. The measured fluence thresholds exhibit a plateau spanning over three octaves extending from the visible domain up to 3.5-µm wavelength. This is accompanied by a remarkable invariance of the observed ablation precision and efficiency. Only at the shortest tested wavelength of 258 nm, a twofold decrease of the ablation threshold and significant changes of the machining depths are detected. This defines a lower spectral limit of the wavelength-independence of the ablation process. By comparison with simulations, we quantify the apparent avalanche ionization rates varying with the wavelength. This can be directly beneficial to improve precision and robustness of predictive models and process engineering developments given the rapid developments of new ultrafast laser technologies emitting in various spectral domains.

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INTRODUCTION

A unique feature with the use of tightly focused ultrashort laser pulses is the ability to achieve localized energy deposition, down to the sub-micrometer scale at the surface or in the bulk of any materials, even those that are initially transparent to the laser wavelength [1]. This makes femtosecond (fs) lasers a key tool for inducing and controlling transformations of various materials with applications ranging from ultraprecision machining [2,3], nanosurgery [4] to warm dense matter physics [5].

Over decades, the efforts on both experimental and theoretical researches [6] have allowed to draw a general picture of ultrafast laser dielectric excitation and the resulting potentially extreme conditions accessible inside the matter. As reviewed in detail by Balling and Schou [7], and briefly summarized here, the process is triggered by the generation of free carriers induced by strong-field nonlinear ionization (SFI) mechanisms, as multiphoton (MPI) and tunneling ionization (TI), and subsequently increased by impact ionization (IMP). If the excitation is high enough, the transferred energy from the free electron sub-system to the lattice induces high local temperature and pressure conditions, responsible for material transformations. If the irradiation is performed at the surface, material expansion and ablation can occur [8,9]. This is the basis of industrial micro-machining [10] process solutions or high-precision surgery applications [4,11].

The constantly growing interest on this flexible technology is today accompanied by the advent of new source technologies, opening an enormous palette of accessible parameters, as pulse duration, repetition rate or wavelength that are all supposed to influence the strongly nonlinear material responses and so the experimental outcomes. Therefore, the influence of each parameter remains a question of topical interest for fundamental and industrial perspectives.

On one hand, the role of the repetition rate and pulse duration has been widely explored. For example, studies focusing on repetition rate influence have found benefits on the optimization of waveguide writing at MHz repetition rates [12] and ablation efficiency and cleanliness by using ultrafast pulse trains at GHz repetition rate [13]. Experiments focusing on the pulse duration have revealed that conventional longer femtosecond pulses (> 100 fs) leads to significant IMP contributions responsible for plasma absorption assisting laser energy deposition [14–16], whereas energy deposition with the shortest pulses takes more profit from MPI [17,18] and even TI when few-cycles pulses are applied [19,20].

On the other hand, the wavelength has been the subject of less investigations. Most probably this is because the fundamental wavelength of most available ultrafast laser technologies remained confined until recently in a relatively
narrow spectral domain in the near infrared (typ. 800 nm or 1.03 µm for resp. Ti:Sapphire or Yb-doped-crystals technologies). With the recent advent of new compact technologies delivering increased power in new spectral regions and in particular the mid-infrared domain (incl. fiber technologies), one should reasonably expect the possibility to cause drastic changes in the balance between the above described physical processes. By affecting the relative role of MPI, TI and AI, one can look for optimization on the drivers for energy deposition. This introduces the timeliness for a debate of the achievable performance for precision processing considering the full spectrum covered with the newly available sources.

From a fundamental perspective, one can refer to the Keldysh theories that directly account for the wavelength dependence of nonlinear ionization [21,22]. For the experimental works (including ours), one usually relies on studies with optical parametric amplifiers (OPA). These become routinely available in laboratories and allow a continuous tuning of radiations for assessing the detailed spectral dependencies of material responses.

The literature on this subject remains scarce but it is important to refer to the pioneering works of Simanovskii et al. [23] and Jia et al. [24], measuring the breakdown fluence thresholds at the surface of several dielectrics with varying wavelength conditions. Despite the gap separating the spectral domains which were investigated on this two works, one can already extrapolate from their combination a relative invariance of the apparent nonlinear absorption rates (within experimental uncertainty) in a broad spectral region. It is only at the tested spectral limits that a significant change could be observed. In their study concentrating in the mid-infrared, Simanovskii et al. [23] measured a drop for the breakdown threshold fluence when increasing the wavelength above 5µm. According to the electronic transition picture described above, this was attributed to a breakdown process that becomes seeded by TI, a wavelength-independent process [25] but driven by IMP with efficiency scaling with the wavelength according to a simple Drude model. However, the investigated spectral domain up to 7.8 µm is at the edge of the vibrational absorption bands, an aspect that raises question on an interpretation solely based on the ionization yield. A similar increase of absorption efficiency is also reported approaching the UV part of the spectrum by Jia et al. [24]. While this can be directly interpreted by increased ionisation rates with a pure MPI picture, the authors had also to introduce significant contributions from sub-conduction band transitions to quantitatively describe the measured process efficiency at short wavelengths.

It is only recently that more experimental investigations have been added on these questions. Gallais and coauthors [26] measured femtosecond laser induced damage thresholds of various bandgap materials (1 to 10 eV) in a spectral region from 310 to 1030 nm. While the paper was concentrating on thin-film materials, the measured thresholds for silica substrates and the reported wavelength dependence compares reasonably well with Jia et al. [24]. For recent investigations turned toward the mid-infrared part of the spectrum, one can turn to Migal et al. [27] who investigated the breakdown response of SiO2 and MgF2. The reported thresholds were strongly deviating from those in the pioneer’s paper of Simanovskii et al. [23]. However, this and another work conducted by Austin et al. [28] on narrow gap material as Germanium concluded that the conventional nonlinear ionization models fail in describing the mid-infrared response. Multi-band and/or intra-conduction band effects were then considered to discuss the obtained results. Among the other related works, it has been studied the laser wavelength influence on the direct writing of optical waveguides or other buried structures in glasses [29] and in silicon [30]. Additionally in silicon surface, we reported the optimization of amorphization by tuning the laser wavelength (258-nm to 4-µm) [31] and Otobe theoretically studied the wavelength dependence (800-nm to 3-µm) of laser-excitation [32]. We can also mention the study of laser-induced breakdown in water [33] or on ablation of corneal stroma [11]. While all are relevant for fundamental and technological considerations, the results obtained in these specific configurations are more hardly comparable to the previously mentioned papers focused on material dielectric ablation.

In this paper, we bridge the gap between these previous reports by investigating the femtosecond laser ablation response in an unprecedented spectral range from 258 nm to 3500 nm. We find a nearly-invariant observables including ablation fluence thresholds, thermally affected zones or maximum crater depths on a very large spectral domain from the visible to the mid-infrared part of the spectrum. Supported by simulations, we concentrate the analyses on sapphire and fused silica, dielectric materials of reference both in applications and in the fundamental study of laser-matter interaction. Simple nonlinear absorption rate considerations lead to the report of apparent avalanche rates deviating from those that can be derived by a Drude model. The gained knowledge on the spectral dependence of femtosecond laser machining is discussed in terms of potential optimizations in model and application developments.

METHODS

A. Laser system and optical set-up

The multiwavelength study is performed by using a commercial femtosecond amplifier (Pharos, Light Conversion) emitting at 1030 nm with pulse energies up to 500 µJ and 180±10 fs pulse duration at full-width at half maximum (FWHM), characterized by single-shot autocorrelation (TiPA, Light conversion). Tunable near-infrared (NIR) and mid-infrared (MIR) radiation is accessible through optical parametric amplification (Orpheus, Light Conversion), designed for efficient conversion on a large infrared range (signal: 1.5 µm -2.06 µm, idler: 2.06 – 5 µm). In this work, we performed
experiments up to 3.5 μm (MIR), due to the limited pulse energy on longer wavelengths. Indeed, the use of tight focusing conditions is avoided in order to maintain the same ex-situ characterization methodology (as explained later on) for all the analyses. Visible (VIS) and ultraviolet (UV) radiation (515 and 258 nm) are obtained through harmonic generation (Hiro, Light Conversion). For all the wavelengths, the beam irradiates the targets at normal incidence with linear polarization. Using the already mentioned autocorrelator device, we measured pulse durations of 190±10 fs FWHM on the range from 1.55-μm to 2-μm and 160±10 fs FWHM at 515-nm. Temporal characterization on the idler spectral range could not be performed with the employed instrument. However, a direct correspondence of the pulse duration is expected between signal and idler, given the optical parametric amplification process generating both beams together. For the deep ultraviolet, we also expect a pulse duration very close to the one measured at 515-nm according to the design (thickness) of the last doubling crystal for generating the 258-nm radiation.

**Figure 1.** Sketch of the experimental set-up. On the top part is represented the beams of different wavelengths obtained from the same master femtosecond laser through harmonic generation (HG), for ultraviolet and visible radiation, and optical parametric amplification (OPA), for infrared radiation. On the bottom part, it is represented the main optical elements of the irradiation configuration including an in situ microscopy system for precise positioning of the focal spot on the surface. The OPA beams are directed toward the irradiation setup using gold mirrors. A selection of dielectric mirrors is used for the other wavelengths (removable mirrors shown by empty volumes).

A sketch of the experimental set-up is shown in Figure 1. Experiments are performed on the basis of single-shot irradiations, by making use of a pulse-picker at the output of femtosecond amplifier. For each selected wavelength, the beam is directed toward the same irradiation beam line. Gold mirrors are used for the beams in the mid-infrared domain covered by the OPA. For the other beams, these are systematically replaced by specific high-reflectivity dielectric mirrors to reduce energy losses and assure excellent spectral filtering at the considered wavelength. The selected beam is then focused normally onto the sample surface by means of an uncoated UV-fused silica aspheric lens (nominal \( f = 50 \text{ mm} \)) for the spectral range between 248 nm to 2 μm, and a calcium fluoride plano-convex lens (nominal \( f = 25 \text{ mm} \)) from 2.2 μm to 3.5 μm. These choices of materials and focal distances were made because of two reasons: the loss of transparency of UV-fused silica in the infrared range and the reduction of accessible energy in the infrared range. A ring-actuated iris diaphragm is situated as close as possible to the lens to truncate all beams (transmitted power ~75%) and so we always irradiate the samples with well-defined profiles. This is of importance to suppress potential biases in the analyses caused by some of the OPA beam profiles exhibiting pedestals [34].

On the beam path, a motorized wheel with neutral density metallic filters (1 mm UV-fused silica substrate with nickel coating) is placed. The broadband response of the filters allows to control the pulse energy on the full spectral region of interest in this work. For all experiments, the applied power is measured at 1 kHz repetition rate with a thermal powermeter (3A, Ophir), which is calibrated for the spectral range of interest. Peak-to-peak pulse energy stability is measured a pyroelectric energy meter (PE9, Ophir) to be less than 4% for all the considered wavelengths, being sufficiently low for making unnecessary a measurement of the energy of each applied pulse. Since the powermeter is placed just before the lens, the energy at the sample position is obtained by simply accounting for the Fresnel reflection losses expected on the lens surfaces.

The sample is mounted on a XYZ motorized stages and aligned perpendicular to the irradiation axis. Precise parallelism of the sample with respect to motion axes is achieved by using a 2-axis kinematic sample holder. Motion in the XY plane, perpendicular to the axis of laser incidence, allows to position the sample on a fresh surface before each irradiation. Optimal focusing position is determined empirically by a Z-scanning and surface imaging with an in-situ microscopy (10x microscope objective, tube lens and CCD-camera) placed at 45° as shown in Figure 1. Repositioning of the different samples at the best focal position is guaranteed by exploiting the ≈10-μm depth of field of the microscopy system.

**B. Samples and metrology**

In this work we study four different samples of three dielectric materials widely used in optics and photonics applications: sapphire, soda-lime glass and fused silica (amorphous, a-SiO₂). The sapphire sample is a sapphire window from Meller Optics, Inc. (2 mm thick). The soda-lime glass sample is a microscope slide from Corning (1 mm thick). Two different samples of fused silica were studied. First a sample of synthetic fused silica (Suprasil 2) from Heraeus of 3-mm thickness, being superpolished by Thales-SESO (with measured Ra = 0.2 nm). The same sample was used for some other studies conducted by our group [15]. For this work, it is named as “UV-fused silica”. Second is a
sample of fused quartz provided by Thuet-France (1 mm thick), named on here as “IR-fused silica”. The transmittivity in the ultraviolet region of the spectrum differs on these two samples, being observed by spectrophotometry measurements (UV-2600, Shimadzu, range 190-1500 nm). Measurable absorption is found at 250-nm (~5 eV) for IR-fused silica. In contrary, the full transparency in this UV domain for UV-fused silica is consistent with the expected absorption edge according to the bandgaps considered in the literature from 7.75 to 9.9 eV (7.75 eV used by Gallais et al. [35], 9.6 eV reported by Ravindra et al. [36], 8.9 eV indirect or 9.9 eV direct bandgap reported by Tan et al. [37]). The same measurements performed for the other samples reveal absorption under ~350 nm in soda-lime glass corresponding to an apparent optical bandgap of ~3.5 eV. The absence of measurable absorption in sapphire for the entire measured spectral range is consistent with the band gap of 8.8 eV from the literature [38]. For characterizing the laser induced modifications on the different samples, we use confocal microscopy (Leica DCM3D). Under monochromatic illumination (460 nm) and using a 150x objective lens (NA 0.95) the laser induced modifications are characterized with transverse submicrometre spatial resolution and nanometric vertical resolution. This technique allows to characterize the ablated area on different samples under a removal depth-based criterion suppressing any potential subjectivity in the analyses. This is a major advantage in comparison to methods relying on conventional optical microscopy where the interpretation based on an apparent optical contrast which can be dependent on the nature of modifications and material responses. Another advantage of the confocal microscopy method compatible with a well-defined and fixed threshold criterion is the possibility to achieve automated crater analyses using a software-solution (Mountains 8, Digital Surf) as demonstrated in previous works [39,40]. In Figure 2 (a), we show examples of craters produced on each of the mentioned samples, after irradiation by a single pulse at 1.7-µm wavelength. The grey scale of the images is set to show in black the surface depressions and in white the surface elevations. Subsequent analyses of the images allow to obtain the total ablated area (depression region taken under -10-nm level) and the crater profile (see Supplemental figures S1, S2 and S3).

As part also of the metrology, firstly, each irradiation condition (each energy on each material) was repeated three time in order to add statistics to our analysis. Secondly, the fluence threshold in this work is obtained by following the Liu’s method [41]. However, this is rigorously valid for perfect Gaussian beams. This deviated from some of our OPA beam profiles exhibiting a pedestal (e.g. see in ref. [39] the profile at 1.55 µm) and it is the reason of the truncation of all our beams by using a circular aperture (see before). In this way, we do not irradiate with Gaussian spots but systematically with well-defined Airy-like beam shapes that allow to calculate for correction factors to the threshold determination. The details corresponding to this applied procedure extending the Liu’s method to imperfect beams is described and demonstrated in ref. [42].

In Figure 2 (b) is shown the representation following the Liu’s methodology, where the ablated area of craters shown in Figure 2(a) are represented as a function of the pulse energy (in logarithmic scale). A linear regression enables to extract an energy threshold ($E_{th}$) and an equivalent Gaussian beam waist ($w_{0,Liu}$). The fluence threshold value is then obtained as $F_{th} = (2E_{th}/\pi w_{0,Liu}^2) \eta_{E_th} \eta_F$, with $\eta_{E_th}$ and $\eta_F$ the corrections factors to apply for a truncated beam (Airy-like beam on target) [42]. Rigorously, those corrections factors depend on the power transfer of the aperture ($P_T$) and the maximum excitation energy considered for the linear fitting procedure (M.E.) [42]. $P_T$, M.E. and values of the retrieved $w_{0,Liu}$ can be found in the Supplemental Note 1.

C. Modelling

For evaluation of the relative roles of the ionization mechanisms depending on tested radiations, we perform calculations of the temporal evolution of the electron density on the conduction band, $n_e(t)$ according to the standard electron density rate equation,
\[
\frac{dn_e(t)}{dt} = \frac{n_T - n_e}{n_T} \left( W_{\text{SFI}}(I(t)) + \alpha \cdot I(t) \cdot n_e(t) \right) \quad \text{Eq. 1}
\]

where \( n_T \) is total density of accessible electrons (valence electron density) in the medium as described by Christensen and Balling [43] and fixed at \( n_T = 1 \cdot 10^{23} \text{ cm}^{-3} \). The first term, \( W_{\text{SFI}} \), is the photoionization rate by SFI (MPI or/and TI) and the second term represents the contribution of IMP, where \( \alpha \) is the avalanche coefficient and \( I(t) \) is the instantaneous laser intensity. For simplification, here we neglect all the relaxation sources (incl. electron trapping mechanisms).

On the same graph, we append several iso-contour lines representing the Keldysh adiabatic parameter \( \gamma = \omega/\sqrt{m^* \cdot BG/(e \cdot E)} \), \( (m^*, E, \text{ and } BG) \) are respectively the reduced mass of the electron-hole pair, the laser electric field, and the band gap of the material). This parameter is usually referred when discussing the relative importance of MPI and TI. When \( \gamma \gg 1 \) MPI is expected to dominate, corresponding for the calculated example to irradiations in the UV-visible range or when irradiating on the NIR with intensities well under the modest TW/cm² level. When \( \gamma \ll 1 \) TI dominates, corresponding to extremely strong laser fields or long wavelengths regimes (MIR) with intensities exceeding 10 TW/cm².

An example of application of equation 1 when accounting only its first term (only SFI) is shown in figure 3 (b). Plotted in blue is represented the temporal profile in intensity for a 190-fs pulse. The integration over time leads to a fluence value of 4.9 J/cm², which, as shown later on, corresponds to the ablation fluence threshold of sapphire at a wavelength of \( \lambda = 2 \mu \text{m} \). Additionally, the free electron generation by SFI in sapphire is calculated according to Eq. 1 using this pulse characteristics. Under these conditions, we note that the photoionization channel leads to the creation of a free-electron density with a maximum predicted at around \( 8 \cdot 10^{18} \text{ cm}^{-3} \).

The second term on the right side of equation 1 accounts for the contribution of AI. In this work, a simplified way to account for a wavelength dependence of this coefficient can be to rely on the semi-classical Drude formalism, where the avalanche coefficient is expressed as,

\[
\alpha = \frac{\sigma}{BG} = \frac{1}{BG \cdot n(\omega) \cdot m^* \cdot c \cdot \varepsilon_0} \cdot \frac{\tau_e}{1 + \omega^2 \cdot \tau_e^2} \quad \text{Eq. 2}
\]

Where \( \sigma \) is the inverse Bremsstrahlung absorption cross section, \( n(\omega) \) the refractive index of the irradiated material at the excitation wavelength, \( c \) the speed of light, \( \varepsilon_0 \) the vacuum permittivity and \( \tau_e \) the free electron scattering time.

However, this last term depends on the free electron density and electron temperature and is therefore a dynamic parameter during the pulse [44,45]. As we will see later on, this makes hard to derive a robust description by taking a constant for this parameter when a large range of laser conditions, as those in this work are explored.

Another striking example of the limitations of the Drude model is a study of Rajeev et al. [14] where a field dependence of the apparent avalanche coefficient was revealed by irradiating dielectrics with different pulse durations. This interestingly introduced the concept of field-assisted impact ionization. Inspired by this work, we decided to extract from our ablation threshold measurements, apparent avalanche coefficients by fixing an absorbed energy density target to be reached at the end of the irradiation pulse for ablation. While this approach will not permit to describe the detailed aspect of the underlying physics, it leads to the interesting possibility for a phenomenological modelling of

**Figure 3.** (a) Numerical calculation of the strong-field photoionization rate \( W_{\text{SFI}} \) as a function of the wavelength and intensity (ranges investigated in this work) following the Keldysh formulation for sapphire (bandgap equal to 8.8 eV) and considering \( m^* = m_e \). To assess the transition from TI \( (\gamma < 1) \) to MPI \( (\gamma \gg 1) \), contour lines for given adiabatic coefficients \( (\gamma = 2, \gamma = 1, \gamma = 0.5 ) \) are appended. (b) (Blue line) Intensity temporal profile of a pulse of 190 fs (FWHM) for a fluence of 4.9 J/cm² corresponding to the measured fluence threshold for ablation of sapphire at \( \lambda = 2 \mu \text{m} \). (Red line) Corresponding build-up of the free electron population expected form the strong field ionization (time integral).

The term \( W_{\text{SFI}} \) is calculated from Keldysh formalism [21], dependent on the conditions of irradiation (laser intensity and wavelength) and on the material properties (material band gap). In this work, we perform calculations for sapphire and UV-fused silica assuming bandgaps of 8.8 eV [38] and 8.9 eV [37] respectively. As an example, the figure 3 (a) shows the calculated \( W_{\text{SFI}} \) values for sapphire on the range of laser wavelengths and laser intensities investigated in this work.
the wavelength dependence of femtosecond laser ablation using the usual electron density rate equation (Eq. 1).

RESULTS AND DISCUSSION
A. Fluence ablation threshold as a function of the wavelength
The measured ablation fluence thresholds as a function of the wavelength are represented in figure 4 (a) for the four different samples. Tables containing the values ($w_{0,li}$, $F_{th}$ and errors) and further information can be found in the supplemental material.

As a first general observation, one can note that despite an exploration over more than five octaves the relative changes of the fluence threshold does not exceed a factor of 3. This and the positions for the minimum (ultraviolet) and the maximum threshold values (near infrared) are common features for all the considered dielectric materials. Concentrating on fused silica, we report on a maximum relative change of only 1.9, marking a significant difference with the study of Jia et al. [24] where threshold changes exceeding a factor 3 are reported. While the pulse duration (150 fs pulse duration) and the investigated spectral range (260 nm to 1.7 µm) are comparable, one can however attribute this difference to a material incubation response. We make this comment in regard to our single shot study in comparison to Jia’s work [24] considering the effect of 3 applied pulses. This is also supported by a more comparable result reported by Gallais et al. [26] where a factor of difference of approximately 2.5 was reported for single-pulse irradiations for fused silica (310 nm – 1030 nm, pulse duration approx. 100 fs).

A second important and general tendency for all materials is a near-invariance of the measured thresholds all over the infrared range (from 1.03 to 3.5 µm). After a steep increase on the fluence ablation threshold from the UV to the near-infrared (258 to 1030 nm), a very moderate increase on the short-wave infrared regime followed by a stabilization up to 3.5 µm is noted. This result reproduces the observation reported by Jia et al. up to 1.7 µm [21] in fused silica and calcium fluoride, and confirms the constancy of the ablation response deeper to the infrared (up to 3.5 µm). For an interpretation of this characteristic response, calculations and discussions about the relative role of the different ionization processes will be pursued in section B.

Looking now in more detail at the response of each material, the results obtained on the two fused silica samples deserve particular attention. As mentioned on the sample description, the linear optical response of the two samples is different, with absorption observed in the IR-fused silica at wavelengths around 250 nm (aprox. 5 eV). This indicates a different optical material bandgap, which should be reflected by different nonlinear absorption response and finally different fluence thresholds for modification. Nevertheless, figure 4 (b) does not confirm this point by showing very similar thresholds found for both materials independently of the wavelength. Accordingly, the discussion on the relative change of the fluence threshold values between materials cannot be reduced to the simple bandgap difference.

Expanding on the comparison between samples, figure 4 (b) reveals also an almost constant ratio between measured thresholds $\sim \times 1.2$, between fused silica and sapphire. Interestingly, some previous studies irradiating those two materials with different conditions found similar relative differences. Puerto et al. [46], (120 fs, 800 nm and angle of incidence of 53°) reported an ablation fluence thresholds of 5.4 J/cm² for fused silica and 7.0 J/cm² for sapphire, that is a relative difference of 1.30. Garcia-Lechuga et al. [47] (120 fs, 800 nm) reported fluence thresholds at 3.7 J/cm² for fused silica and 4.6 J/cm² for sapphire. These values and the corresponding difference factor of 1.24 compare remarkably well with our measurements for $\lambda=1030$ nm. Overall, the figure 4 (b) tends to confirm more a material-dependent differences than a wavelength-dependent response. This holds very well for all studied cases at the exception of the UV-domain.
This difference in material responses is again not directly related with the material bandgaps (sapphire: 8.8 eV and UV-fused silica: 8.9 eV), leading to a conclusion which deviates from the one extracted from the work by Gallais and coworkers [26]. Looking at the other material properties that could be associated with the observed differences between the two materials, one can refer to the findings of Grehn and coauthors [48] and compare the ratio difference between the dissociation energies of two materials:

\[
\frac{e_{\text{dist}}(\text{Sapp})}{e_{\text{dist}}(\text{FS})} = \frac{78 \text{ kJ/cm}^3}{65 \text{ kJ/cm}^3} = 1.2
\]

Eq. 3

This ratio compares very favourably with the measured fluence thresholds for ablation. Therefore, the dissociation energy could be hypothesized as the parameter of major importance for understanding the relatively modest differences between the fluence threshold for ablation observed between dielectrics. This leads to the hypothesis of nonlinear energy deposition with femtosecond pulses nearly independent of the considered dielectric material and of threshold values mainly related to a critical dissociation energy to be reached and depending on materials. This appears to hold true when comparing fused silica and sapphire but it should be extended to other materials and configurations to reinforce our observation. Nevertheless, this view is also supported by the identical response for the two fused silica samples. For these two materials, the different linear absorption response is attributed to the material purity level (defect absorption). According to the very deterministic ablation response in the ultrafast regime, it is commonly accepted that the nonlinear ionization response becomes independent to defects because the number of produced carriers during the pulse largely exceeds the material defect densities. Also, we expect the dissociation energy to be a macroscopic material property that will not depend on low-density defects. Overall, the identical ablation thresholds found for these samples is then interpreted as a direct consequence of these retained considerations for our analysis.

B. Relatives roles of ionization processes at fluence threshold levels.

From now, we will concentrate only on fused silica and sapphire, being two of the most studied and widely used dielectrics for applications. For the particular case of fused silica, modelling will only consider the experimental data and bandgap of UV-fused silica.

In Figure 5, we represent the Keldysh adiabatic parameter calculated considering the peak intensity at fluence threshold conditions (values on fig. 4) for sapphire and fused silica. It can be observed on both cases that values well above unity are only occurring for 258 nm and 515 nm. Therefore, only for the UV-VIS spectral region, MPI is expected as the dominant photoionization mechanism. From 1.55-µm wavelength (NIR and MIR radiation) the Keldysh parameter becomes significantly smaller than one, which corresponds to a dominance of TI. It is striking to note that the most commonly studied ablation conditions near 1-µm actually correspond to the apparently most complex situation with a mix between the two processes (γ−1).

On a first attempt to explain the threshold tendency observed in Fig. 4, we can reasonably attribute the increasing values of fluence threshold for ablation from UV to VIS to an increase on the multiphoton order and so a corresponding decrease of the MPI yield. The near invariant ablation fluence threshold values in NIR and MIR is respectively consistent with the expected wavelength-independent response when TI becomes the dominant ionization mechanism [25]. This leads to an overall qualitatively consistent picture but with a validity obviously limited due to an absence of consideration of the collision-assisted ionization processes.

In order to enlarge the information that can be extracted from experimental data, we have performed calculations of the free electrons generated by SFI for each experimentally determined threshold conditions, as shown as the example in figure 3 (b). The calculated values of \( n_e / \text{SFI} \) for fused silica and for sapphire are plotted on figure 6 (a). Under UV radiation electron densities generated by SFI exceeds \( 10^{21} \text{ cm}^{-3} \), corresponding to high excitation values above 1% of the total valence electron density \( n_T = 1 \cdot 10^{23} \text{ cm}^{-3} \). However, for VIS, NIR and MIR regimes, the percentage of generated free electrons by SFI shown in figure 6 varies between 0.1% and 0.001% of the valence density. This low percentages are far below the physical conditions expected for the occurrence of ablation (e.g. 2% set by Christensen and Balling [43]), and thus directly indicates a largely increasing importance of impact ionization mechanism (IMP) in energy deposition.

After showing in section A a correlation between ablation fluence threshold and dissociation energy in a similar way that it was also stated by Grehn and coauthors [48], we propose in this work a simplified expression to evaluate the level of energy deposition and to establish a direct
comparison with the dissociation energy. Ignoring the potential energy stored by acceleration of free electrons in the conduction (absence of hot electrons), we convert the created free-carrier density directly in deposited energy density, $E_{dep}$, according to:

$$E_{dep} [kJ/cm^3] = BG [kJ] \times n_e [cm^{-3}] \quad \text{Eq. 4}$$

With this conversion, we simply consider that each electron promoted from the valence to the conduction band has required the absorption of sufficient energy from the laser pulse to span the material band gap of energy $BG$. Those estimates at threshold conditions for sapphire and fused silica are plotted on Figure 6 (b). The values obtained for the full spectral range are largely below the dissociation energy of the considered materials.

![Graph](image)

**Figure 6.** (a) Numerical calculations of the maximum free electron density obtained by SFI in UV-fused silica and in sapphire at the fluence threshold level. (b) Estimations of the corresponding minimal deposited energy to create the calculated free-carrier population. Dash lines represent the dissociation energy of both materials for comparisons.

In order to account for the potential contribution of IMP, we calculate the apparent avalanche coefficient values for each considered wavelength ($\alpha(\lambda)$), so that the deposited energy equals the dissociation energy. In practice, we implement a calculation procedure based on eq.1 and eq.4, which iteratively tests different avalanche coefficient values until a match is obtained between energy densities. The obtained avalanche coefficients for both materials are plotted in Figure 7. As shown in the figure, higher values are obtained for fused silica than for sapphire. This is a direct consequence of a deposited energy by SFI which is less efficient than for sapphire (figure 6 (b)) while dissociation energies are not differing much. Additionally, both materials show a similar tendency with low variations in NIR-MIR spectral range and an increase of typically a factor 2 from the shortest considered wavelength in UV to the end of the VIS region. Therefore, observing the tendencies on Figure 6 (a) and Figure 7, we conclude on nearly invariant SFI and IMP contributions in the NIR-MIR for the studied dielectric materials. It is worth noting that this picture differs from the interpretation of Jia and co-workers [24]. A plateau on the ablation fluence threshold in the infrared was also observed in their study but this trend was interpreted based on an increasing importance of IMP compensating an expected decrease of the SFI yield towards the infrared.

![Graph](image)

**Figure 7.** (Symbols) Estimated wavelength-dependent avalanche coefficients for deposition of an energy density equal to the dissociation energy of the material (eq.1 and 5) at fluence threshold conditions for ablation (measured). (Dashed lines) Calculated avalanche coefficients following the Drude model (eq. 2) for fused silica (considering two different collision rates).

As stated before, a simple way to calculate avalanche coefficients without the presented comparison between simulation and measurement results is to use the Drude model (eq.2). For comparison, we present in figure 7 (dashed lines) calculations taking the electron mass for $m^*$, the physical properties of fused silica (band gap and refractive index [49]) and two different values for the carrier scattering time ($\tau_c = 1$ fs and $\tau_c = 0.1$ fs). In comparison to our analysis, the Drude model calculations with $\tau_c = 1$ fs lead to values that underestimate the contribution of IMP in the UV and strongly overestimate it at NIR and MIR. However, the calculation $\tau_c = 0.1$ fs reproduces much better the general trend even if a constant overestimation is observed all over the spectrum. As reported in works exploring femtosecond excitation dynamics of dielectrics, $\tau_c$ is not rigorously a constant and is expected to depend on the free-
 electron density among other parameters. For instance, simulations on the reflectivity response of sapphire [47] (pulses of 120 fs at 800 nm) reveal a scattering time (inverse of the scattering rate showed on the reference) varying from 1 fs at the beginning of the pulse to values under 0.1 fs from the time at peak intensity for material modification conditions. Accordingly, the relatively good qualitative correspondence obtained with an “averaged” fixed value of 0.1 fs can appear reasonable. For quantitative analyses, it remains important to note the significantly different avalanche coefficients derived from our simulations and measurements in comparison to those that can be predicted using the Drude model. While the underlying physical processes behind the determined wavelength-dependence of the avalanche coefficient will require more investigations, the obtained data can already serve (with extrapolation) to improve the predictivity precision of models based on the standard electron density rate equation. This holds for instance for recent modelling efforts considering a modified electron density rate equation accounting for the potential influence of ultrafast carrier trapping processes (modified version of Eq. 1). The aim of such developments is to assess the expected specificities of the modification response of dielectric materials with the advent of new ultrafast MIR laser technologies [50].

C. Crater topography as a function of the wavelength

In previous sections, we have concentrated on the measured ablation fluence threshold for the analyses. However, more experimental observables become available above threshold conditions to enrich the discussion on the wavelength-dependence of the material responses. In particular, we focus here on the changes of the superficial and volumetric aspects of the produced modifications.

As reported in a previous publication [39] but with a data set limited to two wavelengths (515 nm and 1550 nm), we confirm here (fig. 2 and Supplemental Figure S1) that sapphire exhibits always neat craters, without noticeable elevations on the crater borders. In contrary, as can be seen on fig. 2 (a) ($\lambda =1.7 \mu m$), sodalime glass presents notorious elevations at the edges, which has been associated previously to the flow and resolidification of molten material [51]. This observation in sodalime glass independent on the laser wavelengths (see also Supplemental Figure S2) together by similar observations on fused silica samples (Supplemental Figure S3) confirm that the superficial morphology of the modifications, and therefore the quality of the laser machining depends more on the material characteristics than the applied laser wavelength. Indirectly, this also confirms that the drastic changes of contributions from SFI (MPI or TI) and IMP expected from UV to MIR do not have a clear influence on the processing quality.

Another interesting observable in this context is the obtained crater depths revealing the ability of the different wavelengths to penetrate in the excited transparent materials. This provides both access to more understanding of the physics of interaction and to the ablation efficiency of interest for the potential industrial applications. For clarity of the presentation, we present and discuss here the results obtained on sapphire and provide similar data sets obtained for the other dielectrics (Supplemental Figures S4 and S5).

In figure 8 (b-c) we report the maximum crater depth found in craters (at centre) produced in sapphire as a function of the irradiation peak fluence ($F_0$). For the ease of comparisons between wavelengths, the x-axis is represented normalized with respect to the fluence threshold of ablation ($F_0/F_{th}$).

![Figure 8](image)

**Figure 8.** (a-b) Maximum crater depth produced sapphire under a single-shot irradiation at different excitation levels ($F_0/F_{th}$). The inset in (a) shows a zoom of the data close to the fluence threshold.

A first observation is a systematic saturation behaviour on the achievable ablation depth. It is also striking to note a near identical saturation depth for all the considered wavelength at $\approx 500$ nm here for sapphire ($\approx 450$ nm for fused silica, shown in Supplemental Figures S4). Despite the good precision in focus positioning ($< 10 \mu m$ that is significantly smaller than the confocal parameters of all beams), the small differences of the observed plateau levels can be attributed to this question. We make this comment after verifying the sensitivity of this measurement to relative changes of the focusing depth with micrometre precision (Supplementary Note 2).

Interestingly, this measured invariance of maximum ablation depth deviates significantly from the predictions of the
modelling work of Christensen and Balling [43] where the change of the apparent nonlinearity of interaction by varying the material bandgap (3 to 9 eV) or the wavelength in a spectral range much smaller than the one studied here (between 400 and 1060 nm) was leading to more significant variations (deeper machining at longer wavelength). While such experimental quantities are not accessible by our current model which does not describe pulse propagation into the excited dielectrics, this shows a possibility for improved and more robust simulations by implementing the wavelength-dependent avalanche coefficients derived from our work. 

Looking at the details of the ablation depths near threshold conditions, one can note slightly different slopes as a function of the normalized fluence between 1030 nm and 515 nm and significantly reduced ablation rates at 258 nm (see inset in Fig. 8(a)). This variation of the energy dependence can be directly attributed to the dominating role of MPI (few photons) expected for UV. This causes a nonlinear Beer-Lambert law that requires more energy increase to see the ablation front penetrating deep inside the matter. Again, given the modest wavelength-dependence of nonlinear absorption in the NIR-MIR domain and the exponential growth of carrier-density based on the dominating avalanche mechanism, one can qualitatively understand the more abrupt depth rise before saturation as observed with near invariant measurements in this spectral domain (Fig. 8).

SUMMARY AND CONCLUSIONS

From this work aiming at a broadband study of single shot ablation with 200-fs pulses, we report on near-invariant responses over more than 3 octaves in a domain ranging from VIS to MIR up to 3.5 µm. This holds for the measured fluence thresholds for ablation, the observed machining qualities (crater morphologies) and efficiency (ablation depths) and complements our previous findings on the nonlinearity invariance of machining resolution due to the deterministic threshold-nature of ablation in ultrafast regimes [39].

For technological considerations, these conclusions open a wide range of possibilities for processing system optimizations with the advent of new ultrafast laser technologies emitting in different spectral domains and giving access to different performance advantages. For instance, one can refer to the kW power level demonstrated with compact fiber laser technologies in the mid-IR (mainly Thulium-Based fiber lasers) [52]. This can offer solutions for high-throughput production capabilities without compromising machining qualities. On the precision aspects (repeatability and resolutions), the observed invariance on the energy dependencies found in all this spectral domain tend also to confirm that the most critical parameter remains the laser energy stability (pulse-to-pulse) [40,53], another laser technology-dependent parameter. Finally, the only modest variations observed in the UV make this spectral domain remain probably the most promising one for accessing even higher processing performances. As shown with typical two-fold decrease of the ablation thresholds, this part of the spectrum is highly favourable for efficient energy coupling to materials, but it is obviously also an optimum in dealing with diffraction limits and thus achieving high-lateral processing resolutions. Interestingly, we also show in this work a more modest sensitivity of machining depth to the applied energy and material for near threshold conditions (in comparison to VIS-NIR-MIR). This reveals a situation beneficial for reliable material removal with extreme longitudinal resolution. Recently, impressive demonstrations have been made on reliable matter removal with nanometric precision (depth) at the surface of dielectrics materials using NIR femtosecond pulses [54]. On the basis of our findings, even higher precision can be expected using similar pulses (same stability) in the UV domain.

Overall, we expect the general report made on the wavelength-dependence of ablation can be beneficial for improved simulations (accounting for instance the reported avalanche coefficients) and understanding on a scientific question that remains a matter of debate. However, we also believe that there is a timeliness for such a report for advanced process engineering developments given the continuously growing diversity of ultrafast laser technologies emitting today in various spectral domains.

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