Evidence of non collisional femtosecond laser electron heating in dielectric materials

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Electron dynamics in the bulk of large band gap dielectric crystals induced by intense femtosecond laser pulses at 800 nm is studied. With laser intensities under the ablation threshold (a few 10 TW/cm²), electrons with unexpected energies in excess of 40-50 eV are observed by using the photoemission spectroscopy. A theoretical approach based on the Boltzmann kinetic equation including state-of-the-art modeling for various particles interactions is developed to interpret these experimental observations. A direct comparison shows that both electron heating in the bulk and a further laser field acceleration after ejection from the material contribute equivalently to the final electron energy gain. The electron heating in the bulk is shown to be significantly driven by a non-collisional process, i.e. direct multiphoton transitions between sub-bands of the conduction band. This work also sheds light on the contribution of the standard electron excitation/relaxation collisional processes, providing a new baseline to study the electron dynamics in dielectric materials and associated applications as laser material structuring.

Developments of laser facilities delivering ultrashort and intense laser pulses with photon energy in the eV range have motivated studies in laser-solid interactions including metals [1, 2], semiconductors [3] and dielectrics [4, 5]. Focusing of a femtosecond laser pulse in a transparent dielectric material may induce modifications beneath the surface, which can be tailored to produce permanent three dimensional localized structural changes [6–10]. These nano-structurizations depend on the amount of laser energy deposited in the irradiated volume. A control of the amount and spatial shape of the deposited laser energy opens the way to a large variety of applications going from photonics, bulk microelectronics, nanofluidics, to medicine [11]. Together with advanced experimental setups, such a control can be achieved by an in-depth modeling description of the physical processes at play. An accurate prediction of the laser energy deposition may further support the development of these applications and improve the knowledge of the fundamental laws governing the laser-solid interaction. So there is a strong need to accurately describe the electron dynamics in dielectric materials irradiated by femtosecond laser pulses with intensities ranging from a few TW/cm² to the ablation threshold.

The admitted picture for the laser energy deposition into the dielectric material is as follows. The laser energy is first absorbed by electrons through the processes of both ionization and excitation/relaxation in the conduction band (CB). During the second stage, the absorbed laser energy is redistributed between the excited carriers which may reach higher energies while they undergo collisions with phonons, ions, and other electrons in the presence of the laser field. These processes eventually lead to the energy transfer to the lattice. This is a collisional picture theoretically described either by the Drude model, multiple rate equations [12], or the kinetic Boltzmann equation [4, 5, 13]. However, photoemission spectroscopy experiments [14–17], providing the energy distribution of electrons ejected from the sample surface have shown electrons with energies in excess of tens of eV for laser intensities below the breakdown threshold [17, 18], of which collisional heating is not able to account for. It has been suggested that it is due to direct multiphoton transitions between sub-bands of the CB, hereafter referred to as the interband process [15, 16]. The previous observations have been obtained for various dielectric materials including CsI, diamond, CeF₃, sapphire, and SiO₂ [17, 18], highlighting an universal behavior. A question then arises on the importance of the interband process relative to collision-assisted electron transitions, and on its contribution to the laser energy deposition in dielectric materials (which is related to the electron energy distribution).

Two main classes of models can address this question. (i) Collisional models as solving the state-of-the-art quantum Boltzmann equation, including all possible electronic excitation and relaxation processes, provide the electron energy distribution [4, 5, 12]. But the interband process has never been included except in [13]. (ii) Non collisional models based on a resolution of the time-dependent Schrödinger equation support the photoemission observation but the collisions are not included [15, 16]. Despite these studies, a direct comparison between theoretical and experimental electron energy distributions has never been performed while this is an indispensable step for validating any model [4, 5, 12, 15], leaving serious interrogations regarding the (non-equilibrium) electron dynamics in the conduction band of dielectric materials.

In the present work, the electron dynamics is studied both experimentally and theoretically for α-quartz (cristalline SiO₂) which is a representative example of large band gap dielectrics. The observed photoelec-
electron energy distributions are directly compared, within the challenging accuracy-demanding linear scale in the present context, to a model including the electron dynamics both inside the bulk and after ejection. It is described by a Boltzmann equation including all possible bulk excitation/relaxation processes coupled to a subsequent laser driven field acceleration (LDFA) of electrons after their ejection [19]. The model allows to predict photoelectron spectra which are in a good agreement with experimental results for various laser intensities. The non collisional direct multiphoton transitions between sub-bands of the CB make a significant heating of electrons in dielectric materials in contrast to the widely used assumption of a dominant role of collisional processes involving phonon-assisted photon absorption and inverse bremsstrahlung. Our model accounts in particular for the dielectric material property on a lengthscale \( v_b/\omega_{\text{ve}} \) where \( v_b \) is the velocity of bound valence electrons and \( \omega_{\text{ve}} \) is their plasma frequency. The order of magnitude of these quantities is \( 3 \times 10^6 \text{m.s}^{-1} \) and \( 10^{16} \text{s}^{-1} \), respectively, leading to \( v_b/\omega_{\text{ve}} \approx 3 \). The laser intensity is thus relatively constant a few nanometers beneath the surface, implying no spatial dependence in the electron distribution, \( f(\vec{k}, t) \), where \( \vec{k} \) is the momentum and the electron energy is \( E_k = \hbar^2 \vec{k}^2/2m_e \). The temporal evolution of \( f \) in the bulk is then given by:

\[
\frac{\partial}{\partial t} f(\vec{k}, t) = \frac{\partial f(\vec{k}, t)}{\partial t}_{\text{ioniz}} + \frac{\partial f(\vec{k}, t)}{\partial t}_{\text{relax}} + \frac{\partial f(\vec{k}, t)}{\partial t}_{\text{heat}},
\]

where the three collision integrals in the right hand side describe the ionization, the relaxation, and the laser excitation of conduction electrons, respectively. The electron distribution is assumed to be isotropic since it is due to electron collisions with acoustic phonons which characteristic timescale is \( 10 \text{ fs} \) [21].

The ionization processes consist of both the photoionization, which is evaluated through the complete Keldysh expression [22], and the impact ionization described as in [4]. The relaxation processes are related to electron-electron (e-e) [4] and electron-phonon (e-ph) [4, 21] collisions, which induce the energy exchange of electrons between themselves and to the lattice, respectively. These collision integrals are calculated with the Fermi’s golden rule. The electron recombination is also included with a characteristic time of \( 150 \text{ fs} \) [23] which is assumed not to depend on \( E_k \). The energy distribution of phonons is assumed not to evolve during this short interaction time and is set to the equilibrium Bose-Einstein distribution with a lattice temperature set to 800 K.

Two main processes are included for the laser-induced
excitation of conduction electrons. First, the electrons can absorb or emit simultaneously several photons during a collision with phonons or ions (inverse Bremsstrahlung) [4]. Second, electron excitation can also take place through a non-collisional process (no other particle as ion or phonon is involved to absorb photons) which is direct multiphoton interband transitions [13, 15, 17, 18, 25]. To include the latter process, the conduction band is described by multiple parabolic energy sub-bands. An illustration of this process is provided by Fig. 2. Note this mechanism departs from the Rethfeld’s approach [4, 12] and is expected to have a significant impact on the electron dynamics. The interband rate is evaluated according to the expression and parameters provided in [13]. Such an approach allows us to introduce explicitly the collisionless heating in a full kinetic treatment of the electron dynamics in laser-driven dielectrics [13].

Solution to the Boltzmann equation (1) provides the energy distribution of electrons in the material. Their ejection from the surface is possible if their energy is larger than the work function which is 0.9 eV for quartz [26, 27]. For low energy ejection, surface effects may modify the distribution [28]. However, this influence is negligible for the most energetic electrons which are considered here. Consequently, the distribution of ejected electrons near the surface is assumed to be the same as the one calculated in the bulk. To obtain a distribution directly comparable to the experimental data, \( f(E_k, t) \) is first weighted by the density of states \( g(E_k) \propto \sqrt{E_k} \) accounting for a three-dimensional free electron gas. Secondly, the influence of the laser electric field \( F(t) \), which may further accelerate or decelerate the ejected electrons depending on their instant of emission, is taken into account: it is a laser-driven field acceleration (LDFA) which can change the energy distribution [14, 19, 29]. The final energy of the ejected electron is obtained by integrating the classical equation of the electron motion in vacuum \( \frac{dv}{dt} = -eF(t)/m_e \) from the ejection moment \( t_e \) to the end of the laser pulse (160 fs in practice). The initial ejection velocity \( v_0 \) at \( t_e \) is evaluated from the calculated electron distribution in the bulk. Since electrons in the bulk undergo numerous collisions before ejection, they lose any coherence [30] with the laser electric field at the time of ejection. Consequently, the electrons are assumed to be ejected uniformly during the interaction: their ejection time is not related to any particular phase of the laser electric field. Since in experiments ejected electrons are collected over the whole laser pulse duration, the theoretical predictions are obtained by integrating the electron distribution over time. Note that the maximum energy gain corresponds to the classical energy of \( \frac{1}{2} \) an optical cycle. For an electron ejected at the optimal time, a simple calculation shows that the final energy is roughly 40 eV for an ejection energy \( E_{k0} = 20 \) eV and a laser intensity \( I = 50 \) TW/cm\(^2\).

Figure 3 shows, within a linear scale, the experimental distributions of ejected electrons from photoemission experiments (solid lines) and modeling (dashed lines) for various laser intensities.
Figure 4 provides the evolution of $E_{\text{max}}$ as a function of the laser intensity from experimental observations and as predicted by the modeling (the interband and LDFA processes are included or not). In the experiment, $E_{\text{max}}$ increases monotonically from 11 eV to roughly 40 eV. Without the interband and LDFA processes, $E_{\text{max}}$ cannot exceed 10 eV for the highest intensity, the heating being only due to e-ph-pt collisions in that case. By including the interband process, $E_{\text{max}}$ reaches about 23 eV, i.e. twice the energy of the previous configuration. Both e-ph-pt and interband contributions to the electron heating are thus comparable. A good agreement with the experimental data is obtained when the LDFA is included, providing an enhancement of the final electron energy of more than a factor of 2. These considerations clearly show that the observed photo-emission spectra result from three physical processes with comparable contributions. All the previous conclusions are expected to be similar for the above-mentioned other large band gap dielectric materials. A quantitative reproduction of other data being able by slightly adjusting a few modeling parameters as the value of the band gap and matrix elements.

We have shown the importance of the non collisional laser heating. For applicative purposes as laser structuring of materials, a simple expression to evaluate the laser energy deposition is desirable. It can be shown that the energy density absorbed per unit of time through the interband process, $dU_{nc}/dt$, reads:

$$\frac{dU_{nc}}{dt} = \frac{m\omega n_e(t)(\Delta k/(\pi/a))}{4\pi\hbar|p_f|} V_{1f}^2 \sum_n n J_n^2(B_{1f}) \left( \frac{\pi}{a} \right)^2 - k_n^2 \right)$$

(2)

with $B_{1f} = \frac{1}{\hbar^2} \frac{e\tilde{F}(t)\cdot\tilde{p}_f}{m\omega}$. All notations and values of parameters relative to the interband rate are defined in [13]. $n_e(t)$ is the electron density in the conduction band which here is evaluated by solving multiple rate equations [12]. $\Delta k/(\pi/a) = 2ma^2\hbar c/\pi^2\hbar^2$ is the relative part of the Brillouin zone participating to interband transition due to the collisional broadening (see Fig. 2). Setting the Drude averaged collision time to $\nu^{-1}_c = 10$ fs accounting mainly for electron-phonon collisions, the evolutions of the electron temperature ($= U/C_e$ with $C_e$ the classical heat capacity) as a function of the intensity including or not the non collisional laser heating are obtained (see Fig. 5). They exhibit similar trends as those provided by solving the quantum Boltzmann equation [13], and values consistent with the present electron energies (because $T_e \approx E_{\text{max}}/2$ [13]). This demonstrates the reliability of this simplified model (2) describing the additional contribution of non collisional heating to the Drude description.

To conclude, photo-emission experiments have been carried out with large band gap dielectric crystals irradiated by near infrared laser femtosecond pulses with intensities below the ablation threshold. The electron
energy spectra exhibit a long tail up to energies close to 40 eV for the highest intensities. The underlying electron dynamics has been analyzed through a state-of-the-art modeling based on the Boltzmann kinetic equation including the main excitation/relaxation processes, and the laser driven field acceleration of ejected electrons. A direct comparison of the theoretical predictions to the experimental data shows that both heating in the bulk and electric field acceleration in the vacuum make comparable contributions to the electron energy gain. The noncollisional direct multiphoton transitions between sub-bands of the conduction band is a major mechanism for electron heating in the bulk of dielectric materials which must be included for the evaluation of the energy deposition. For application purpose as laser structuring of materials, a simple expression to evaluate the energy deposition by non-collisional absorption can be derived [24].

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FIG. 5. Evolution of the electron temperature as a function of the maximum laser intensity as estimated with a simplified Drude-like modeling.

[1] B. Rethfeld, A. Kaiser, M. Vicanek, and G. Simon, Phys. Rev. B 65, 214303(1) (2002).
[2] B. Scharf, V. Perebeinos, J. Fabian, and P. Avouris, Phys. Rev. B 87, 035414(1) (2013).
[3] P. E. Selbmann, M. Gulia, F. Rossi, and E. Molinar, Phys. Rev. B 54, 4660 (1996).
[4] A. Kaiser, B. Rethefeld, M. Vicanek, and G. Simon, Phys. Rev. B 61, 11437 (2000).
[5] N. S. Shcheblanov and T. E. Itina, Appl. Phys. A 110, 579 (2013).
[6] E. N. Glezer, M. Milosavljevic, L. Huang, R. J. Finlay, T.-H. Her, J. P. Callan, and E. Mazur, Opt. Lett. 21, 2023 (1996).
[7] E.G. Gamaly, Physics Reports 508, 91.
[8] Andrius Marcinkevičius, Saulius Juodkazis, Mitsuru Watanabe, Masafumi Miwa, Shigeki Matsuo, Hiroaki Misawa, and Junji Nishii, Opt. Lett. 26, 277 (2001).
[9] Rafael R. Gattass and Eric Mazur, Nature Photonics 2, 219–225 (2008).
[10] J. Zhang, M. Gecevicius, M. Beresna, and P. G. Kazansky, Phys. Rev. Lett. 112, 033901 (2014).
[11] Ralf Menzel, Photonics: Linear and Nonlinear Interactions of Laser Light and Matter (Springer, 2001).
[12] B. Rethfeld, Phys. Rev. Lett. 92, 187401 (2004).
[13] L. Barilleau, G. Duchateau, B. Chimier, G. Geoffroy, and V. Tikhonchuk, Journal of Physics D: Applied Physics 49, 485103 (2016).
[14] P. Dombi, A. Horland, P. Racz, I. Marton, A. Trugler, J. R. Krenn, and U. Hohenester, Nano Lett. 13, 674 (2013).
[15] B. N. Yatsenko, H. Bachau, A. Belsky, J. Gaudin, G. Geoffroy, S. Guizard, P. Martin, G. Petite, A. Philippov, and A. N. Vasil’ev, Phys. Status. Solidi. C 2, 240 (2005).
[16] H. Bachau, A. N. Belsky, I. B. Bogatyrev, J. Gaudin, G. Geoffroy, S. Guizard, P. Martin, Yu. V. Popov, A. N. Vasil’ev, and B. N. Yatsenko, Appl. Phys. A 98, 679 (2009).
[17] A. Belsky, H. Bachau, J. Gaudin, G. Geoffroy, S. Guizard, P. Martin, G. Petite, A. Philippov, A. N. Vasil’ev, and B. N. Yatsenko, Appl. Phys. B 78, 989 (2004).
[18] A. Belsky, P. Martin, H. Bachau, A. N. Vasil’ev, B. N. Yatsenko, S. Guizard, G. Geoffroy, and G. Petite, Europhys. Lett. 67, 301 (2004).
[19] S. Zherebtsov, T. Fennel, J. Plenge, E. Antonsson, I. Znakovskaya, A. Wirth, O. Herwerth, F. Submann, C. Peltz, I. Ahmad, S. A. Trushin, V. Pervak, S. Karsch, M. J. J. Vrakking, B. Langer, C. Graf, M. I. Stokman, F. Krausz, E. Ruhl, and M. F. Kling, N. Phys. 7, 656 (2011).
[20] V. Bagnoun and F. Salin, Appl. Phys. B 70, S165 (2000).
[21] Ph. Daguzan, P. Martin, S. Guizard, and G. Petite, Phys. Rev. B 52, 17099 (1995).
[22] L. V. Keldysh, Sov. Phys. JETP 20, 1307 (1965).
[23] P. Martin, S. Guizard, Ph. Daguzan, and G. Petite, Phys. Rev. B 55, 5799 (1997).
[24] See Supplemental Material at [URL will be inserted by publisher] for an averaged expression of the non-collisional laser absorption.
[25] A. Belsky, A. N. Vasil’ev, B. N. Yatsenko, H. Bachau, P. Martin, G. Geoffroy, and S. Guizard, J. Phys. IV 108, 113 (2003).
[26] V. S. Kortov and S. V. Zvonarev, Journal of Surface Investigation. X-ray, Synchrotron and Neutron Techniques 5, 764 (2011).
[27] K. Ohya, K. Inai, H. Kuwada, T. Hayashi, and M. Saito, Surface and Coatings Technology 202, 5310 (2008).
[28] C. Mariani, Conf. Proc. Italian Phys. Soc. 82, 211 (2003).
[29] P. Mulser, S. M. Weng, and Tatyana Liseykina, Phys. Plasmas 19, 043301 (2012).
[30] A. Bourgeade and G. Duchateau, Phys. Rev. E 85, 056403 (2012).