Velocity distribution of neutral particles ejected from biological material under ultra short laser radiation

Wolfgang Husinsky and Hatem Dachraoui

Institut für Allgemeine Physik, Vienna University of Technology, Wiedner Hauptstrasse 8-10, A-1040 Wien, Austria

Abstract

Neutral particles ejected from biological material under ultra short laser ablation have been investigated by laser post-ionization time-of-flight mass spectrometry. It could be shown, that beside ionized species, a substantial amount of neutral particles is ejected. A temporal study of the ablation plume is carried out by recording neutral particle time-of-flight mass spectra as a function of delay time between the ablation and post-ionization pulse. Close the ablation threshold, the mechanism of ejection is found to be of predominantly mechanical nature, driven by the relaxation of the laser-induced pressure. In this regime of stress confinement, the ejection results in very broad velocity distributions and extremely low velocities.

PACS numbers: 79.20.Ds, 79.20.Eb, 42.65.Re, 42.65.Sf.
I. INTRODUCTION

The interaction of ultra short laser light with biological tissue is the basis for an immense and still expanding number of medical applications of lasers. Tissue processing with ultra short laser pulses has been of growing interest due to the high precision achieved. Refractive surgery inside the human eye or ‘nano-surgery’ of single biological cells are striking examples. The potential of ultra short laser radiation for surgical applications can be considered as established.

While the nature of the mechanisms behind ultrafast laser ablation of biological targets has been studied theoretically quite extensively, mostly using molecular-dynamics (MD) simulations, the number of detailed experimental investigations is very limited. For example, molecular dynamics (MD) ablation studies of organic solids have suggested two principal classes of ablation mechanisms based on the laser parameters such as fluences and pulse widths: (i) photochemical processes in which the breakup of the material is the result of strong tensile stresses (spallation). (ii) photothermal ablation, where laser energy absorption is followed by its conversion into heat, which finally results in high temperatures; possible consequences include homogeneous nucleation, phase explosion and vaporization.

For femtosecond laser pulse irradiation, the exact dynamics of the ablation process is not well understood as it appears to be a complex combination of these different mechanisms and also a function of the material properties which may change during the course of ablation.

In this paper we analyze the mechanisms of material ejection from biological tissue under ultra short laser radiation, as well as their pulse width dependence. Using laser postionization mass spectrometry techniques we follow the temporal evolution of the plume composition. The measured velocity distributions of the ejected neutral particles are extremely broad and cannot be described by a Maxwell Boltzmann distribution. For fluences close to the ablation threshold but below that for plasma formation, laser induced pressure due to overheating of the irradiated material is identified as the key processes that determine the dynamics of laser ablation.
II. EXPERIMENTAL SETUP

The experiments have been performed in an UHV chamber equipped with a reflectron-type time-of-flight (TOF) mass spectrometer for detecting laser ablated particles. Laser-Post-Ionization is used for neutral particle detection. Ablation and post ionization is performed with ultra short laser radiation by a system which consists of two multipass CPA Ti: Sapphire amplifiers (Femtopower) seeded from a common mode locked Ti:Sapphire oscillator (Femtosource). The system, operating at a repetition rate of 1 kHz, provides laser pulses at a center wavelength around 800 nm (1.5 eV photons) with a typical duration of 25 fs. The ablation beam was incident on the surface at an angle of 45 measured from the surface normal and was focused to a spot size of typically 100-500 µm in diameter. The ablation- and post-ionizing laser beam can be delayed with respect to each other (ablation and post-ionizing beam). The post-ionizing laser beam was crossing 2.5 mm normal in front of the target. The base pressure in the UHV chamber was approximately $10^{-7}$ mbar, since baking the chamber is not possible with biological samples. In addition, one of the two amplifiers was equipped with an opto-acoustic dazzler, which allowed pulse shaping of the laser beam. This measurement can be achieved despite the many experimental complexities that result from the not ideal vacuum conditions. Soft tissues (i.e. cornea), in particular, pose problems in vacuum environments. We have chosen hard human tissues (bone, tooth) material for our investigations. The main components of human teeth are enamel and dentin. Enamel contains 95% hydroxyl-apatite (Ca10 (PO4)6 (OH)2), 4% water and 1% organic material. Furthermore, it contains impurities like Cl, Na, K, F or Mg. Dentin contains about 70% (Ca10 (PO4)6 (OH)2), 20% organic components (collagen fibers) and 10% water. Human bone is made up of 50-60% hydroxyl-apatite, 15-20% water, 1% phosphates (inorganic components), 20% collagen and 2% proteins (organic components).

III. RESULTS AND DISCUSSION

Under ultra short laser irradiation, neutrals as well as ions are ejected from bone- and tooth-material. The detection and measurement of ablated ions is relatively simple and has been reported previously. The mass spectra of particles ablated from tooth material and bone material are very similar and have the basic features in common. Therefore it is sufficient
to display and to discuss the experimental results of one example, and we have chosen the data of tooth. A typical mass spectrum measured at laser fluence $F = 200 \text{ mJ/cm}^2$ is shown in Figure 1. The dominant signal (highest yield) arises for $m/z = 40$, with $m$ ion mass and $z$ the ion charge. In addition, the ion spectrum shows the presence of many weak peaks attributable to the presence of organic $C_mH_n$ ions. The observation of relatively large particles is a characteristic signature that photomechanical effects induced by pressure relaxation play a crucial role in the ablation of biological tissue. Further analysis was focused on the detection of the neutral particles. Typical mass spectra of the photoionized neutral particles obtained with fresh and etched ablated surfaces are shown in Figure 2. The spectra were measured for an ablation laser fluence of about $200 \text{ mJ/cm}^2$ and at time delay $\Delta t = 5 \mu s$ between the ablation and the post ionization laser pulses. As can easily be seen, the mass spectrum is significantly modified. In addition to the large two peaks at $m/z = 26$ and $m/z = 28$, organics $C_mH_n$ are observed. Only with the fresh surface, the organics $C_mH_n$ are observed in relatively high abundance. In contrast to the cation spectrum the neutral mass spectrum shows no intensity at the mass $/z (39, 96, 103$ and $112)$. This observation suggests that many parent clusters undergo non linear dissociation during the post-ionisation event. Thus, the neutral spectrum consists essentially of fragment particles rather than direct ejected particles. Furthermore, comparison with the ion spectrum reveals, that close to the ablation threshold neutral and ions are ejected with a majority of neutrals.

Given the large number of clusters found in the plume in this regime, ablation exhibits a mechanical rather than thermal character.

Laser ablation in the short-pulse regime involves different processes which are effective at different deposited laser energies. In order to investigate the mechanisms of the ejection close to the ablation threshold we have measured the time-of-flight (TOF) distributions of several neutral particles. Contrary to measurements of the velocity of ejected ions, the measurement of neutrals is more informative due to the physical ablation process itself, since neutrals are not influenced by potentials in the surface (the surface-space-charge effect), which can obscure the results quite substantially and have led to different interpretations and velocities reported ($\text{eV-keV}$). The measurements are performed with etched surfaces when no signal change with the number of laser pulses occurred. Here it is important to note that the system relaxes within a few hundreds picoseconds after the excitation ($<<$ the laser repetition period). Figure 3 shows the integration over the 28/z and 54/z peaks as a
function of the flight time between target and ionizing laser. The TOF spectra can be directly converted into a velocity or energy distribution. Both $m/z = 28$ and $m/z = 54$ distribution are maximized at 5 µs time delay that corresponds to 600 m/s velocity. This velocity of 600 m/s, observed for most particles, seem to be rather low at first sight, but similar slow velocity distributions have been predicted in earlier MD simulations of laser ablation of organic solids in the stress confinement irradiation regimes$^9$. For all TOF data of biological samples measured, there is a clear discrepancy between the data and a best fit according to the Maxwell-Boltzmann (MB) distribution. The experimental TOF distributions are broader than a MB distribution. For comparison, we also include in figure 3 the TOF distribution of the emitted neutral Fe ($m/z=56$) from a steel target. In contrast to the biological TOF distributions, the measured Fe distribution can satisfactorily be described by a MB distribution. As we have clearly demonstrated previously in$^{10-12}$, in the case of a metal, matter removal can be attributed to phase explosion (photothermal effect). Based on these facts, photothermal effects are, under these conditions, not responsible for the ejection of material from biological tissue.

For longer time delays $\Delta t > 20$ µs, neutral particles are observed in the mass spectra. Moreover within the experimental repetition period of 1 ms, the TOF distribution not recovers to the initial state. This feature was confirmed by observing neutral particles in the mass spectra recorded at negative delay time. Negative time delay corresponds to the post-ionization pulse preceding the ablation pulse. These extremely slow particles explain the observed background in the TOF distributions. This brings us to an obvious question: what is the origin of these particles?

It is evident from the low temperature of the ejected particles that the physical processes leading to material ejection have predominantly mechanical character. Two observations support photomechanical mechanisms: (i) the neutral TOF distributions do not follow the MB distribution. (ii) the $28/z$ and $54/z$ peaks show the same temporal evolution; this constitutes a strong indication that the origin of the particles with low velocities (600 m/s) could be due to the ejection of larger clusters, which are fragmented by the postionization pulse into relatively small $C_mH_n$ fragments. Our data is consistent with experimental$^{13,14}$ and MD simulation$^9,15$ results of laser ablation of biological tissue, where photomechanical effects has been identified as the main mechanisms responsible for the ablation in the regime of stress confinement. Furthermore, a plausible explanation of the observed neutrals particles
at time delay around 1 ms is the separation of a large surface layer from the sample with a velocity of 30 m/s. This behavior is very similar to that observed in simulations of ablation of organic solids\textsuperscript{16}. In this theoretical modelling the authors demonstrated that irradiation under conditions of stress confinement can lead to the ejection of complete layers of the material.

The origin of the broad distributions can be related primarily to layer (depth) effects. Confirmation can be found in the literature. Earlier molecular-dynamics simulations of ablation in organic solids have shown that different regions form in the sample during the ablation process. These regions differ in their expansion dynamics and in the pressure relaxation they follow. This suggests that different ejection conditions for molecules, depending upon their original depth in the substrate. This means that the total TOF distribution might be a superposition of Maxwell-Boltzmann distributions with different stream velocities. Moreover, subsequent collisions in the expanding plume can lead to further broadening of the distribution. The experimental TOF distribution ($m/z = 28$) can satisfactorily be described by a shifted Maxwell-Boltzmann distribution\textsuperscript{17}. So, a fit of the TOF distributions ($m/z = 28$) to a modified Maxwell-Boltzmann distribution results in temperatures of 1300 K.

We can derive from the data a basic conclusion: the relevance of stress confinement as an important contribution to the ablation mechanism. In this scenario, the thermal expansion of the volume heated by a laser pulse generates compressive stresses. The subsequent propagation of these stresses from the free surface can transform them into tensile stresses of sufficient strength to cause mechanical fractures parallel to the surface of the sample and ejection of the upper layers. The spallation proceeds through nucleation, growth and coalescence of voids within the spallation region\textsuperscript{18,19}.

As already demonstrated in previous experimental and molecular dynamics simulation studies\textsuperscript{10,20}, the ablation mechanisms, and the parameters of the ejected plume have a strong dependence on the laser pulse duration. Figure 4 shows the measured TOF distribution of the ablated neutral ($m/z = 28$) for two different additional laser pulse widths $\Delta \tau = 350$ and 500 fs (in addition to the data for the regular 25 fs pulses). The energy per pulse was kept constant. In this regime of stress confinement, pulse width variation allows us to obtain important information about the dependence of the material ejection on the laser peak intensity as a function of $\Delta \tau$. It is well known that the photomechanical fracture
is determined by the interplay between the tensile pressure and the thermal softening due to the laser heating: higher tensile pressure (up to -150 MPa) does not cause mechanical fracture\textsuperscript{19,21}.

Much broader TOF distributions with slow velocities are observed in Figure 4a, which can not be described by a Maxwell-Boltzmann distribution. For a pulse width $\Delta \tau = 500$ fs, the velocity distributions can be roughly described by a modified Maxwell-Boltzmann distribution. Simulations demonstrate that a broader distribution is characteristic for the plume ejected in the stress confinement regime\textsuperscript{9}. Furthermore, a comparison with figure 3 (TOF distribution at 25 fs, circles ) reveals two interesting features in this measurement: (i) a clear shift of the TOF distributions to lower velocities. A similar effect of temperature-decrease has been observed earlier in MD simulations of laser ablation of molecular samples. The authors have related the decrease in the temperature of the plume to enhanced ejection and rapid material disintegration\textsuperscript{9}, even though here a comparison between our results and the simulations has to be regarded with care (these MD simulations were performed for 15 and 150 ps duration pulses). We will return to this point below. (ii) Increase in the background value with increasing the pulse duration from 25 to 350 fs. This observation reflects the increase in the abundance of large cluster in the plume.

The dependence of the amount of $m/z = 28$ material removed in the time window of about 1 ms versus laser pulse width is shown in figure 4b. The total ablated yield increases with increasing the laser pulse width. This observation can explain the observed decrease in the temperature of the plume (figure 4c). Our interpretation of the increase in the total amount of the ejected material takes into account two main effects: (1) An enhancement in the amplitude of the pressure wave and (2) under these radiation conditions, the balance between the amplitude of the tensile component and the thermal softening is more favourable for photomechanical effects (such as spallation).

In the first scenario, in spite of the dominance of photomechanical ablation in the first case (short pulse $\Delta \tau = 25$ fs, high peak intensity), one can imagine that this regime is characterised by the occurrence of photothermal effects in addition to the photomechanical effects. Because laser-induced spallation can be initiated at energy densities much lower than those required for phase explosion and vaporization, we believe that the increase in the pulse duration leads to an irradiation regime below the thermal ablation threshold and thus phase explosion cannot occur and account for material ejection in this regime. So,
more laser energy is converted to mechanical energy of the thermoelastic stress wave. This is probably the reason why spallation becomes more dominant. Second, The etch depth is determined not only by the amplitude of the tensile component of the pressure wave, but also the temperature gradient produced within the irradiated surface region. Close to the ablation threshold a decrease of the peak intensity leads to an increase in the tensile pressure. This means that tensile-wave-mediated effects become more dominant for longer pulses (350 − 500 fs).

IV. CONCLUSIONS

In summary, we have investigated the mechanisms of the femtosecond laser ablation of biological material. At laser fluences above the ablation threshold, our results indicate that photomechanical effects, driven by the relaxation of high thermoelastic pressure, are responsible for the collective material ejection. The velocity distributions are broader than a Boltzmann distribution and exhibit an offset (extremely slow particles), presumably fragmentation products of larger clusters or surface layer. A comparison of the results the velocities obtained with 25 and 350 fs laser pulses also reveals a number of differences that can have important implications for practical applications of laser ablation. Larger ablated volume and broader velocity distributions are produced at the same laser fluences for pulse longer Δτ = 350 fs than for τ = 25 fs. The experiments presented demonstrate the potential for further investigations to identify the ablation mechanisms of biological material at high laser fluences. Experiments with soft tissues should follow.

V. ACKNOWLEDGMENTS

This work has been partly supported by the Austrian Science Foundation FW under project numbers P13756-N02 and P15937-N02.

* husinsky@iap.tuwien.ac.at
† Present address: Molecular and Surface Physics, Faculty of Physics, Bielefeld University, Germany

1 H. Lubatschowski, A. Heisterkamp, F. Will, A. I. Singh, J. Serbin, A. Ostendorf, O. Kermani, R. Heermann, H. Welling, and W. Ertmer, RIKEN Review 50, 113 (2002).

2 W. Sekundo and e. al., J Cat. Refract. Surg. 34, 1513 (2008).

3 H. Lubatschowski and A. Heisterkamp, in Femtosecond Technology for Technical and Medical Applications, Vol. 96 of Topics in Applied Physics, edited by H. L. F. Dausinger, F. Lichtner (Springer Verlag, Berlin, 2004), p. 91.

4 E. Leveugle, D. S. Ivanov, and L. V. Zhigilei, Applied Physics A 79, 1643 (2004).

5 E. Leveugle and L. V. Zhigilei, Applied Physics A: Materials Science & Processing 79, 753 (2004).

6 P. Lorazo, L. J. Lewis, and M. Meunier, Physical Review B 73, 134108 (2006).

7 D. Perez and L. J. Lewis, Physical Review Letters 89, 255504 (2002).

8 O. Kreitschitz, W. Husinsky, G. Betz, and N. H. Tolk, Applied Physics A: Materials Science & Processing 58, 563 (1994).

9 L. V. Zhigilei and B. J. Garrison, Journal of applied physics 88, 1281 (2000).

10 H. Dachraoui, W. Husinsky, and G. Betz, Applied Physics A: Materials Science & Processing 83, 333 (2006).

11 H. Dachraoui and W. Husinsky, Applied Physics Letters 89, 4102 (2006).

12 S. Bashir, M. S. Rafique, and W. Husinsky, Applied Surface Science 255, 8372 (2009).

13 I. Itzkan, Proc.Natl Acad.Sci.USA 92, 1960 (1995).

14 D. Albagli, Opt.Lett. 19, 1684 (1994).

15 A. G. Zhidkov, L. V. Zhigilei, A. Sasaki, and T. Tajima, Applied Physics A: Materials Science & Processing 73, 741 (2001).

16 L. V. Zhigilei and B. J. Garrison, Applied Physics A: Materials Science & Processing 69, S75 (1999).

17 L. V. Zhigilei and B. J. Garrison, Applied Physics Letters 71, 551 (1997).

18 G. Paltauf and P. E. Dyer, Chemical Reviews 103, 487 (2003).

19 L. V. Zhigilei, E. Leveugle, B. J. Garrison, Y. G. Yingling, and M. I. Zeifman, Chemical Reviews 103, 321 (2003).

20 P. Lorazo, L. J. Lewis, and M. Meunier, Physical Review Letters 91, 225502 (2003).
21 D. Perez and L. J. Lewis, Physical Review B 67, 184102 (2003).
VI. FIGURECAPTIONS

Fig.1: Typical mass spectrum of ions emitted from tooth sample under ultra short laser radiation (25 fs, 800nm F= 200 mJ/cm²).

Fig. 2: Mass spectra of neutral particles of tooth sample produced at F= 200 mJ/cm² and detected at ∆t = 5 µs with relatively fresh (a) and etched (b) surfaces.

Fig. 3: Measured TOF distribution of m/z=28 and 54 neutral particles ablated from tooth material with 25 fs ablation laser pulse and fluence 200 mJ/cm² (Triangles and circles). TOF distribution of ablated neutral Fe from steel for 400 fs laser pulse width and 100 mJ/cm² laser fluence (squares). The red and green solid lines represent fits to a Maxwell-Boltzmann distribution. Blue line is a fit to shifted Maxwell-Boltzmann distribution. A 10-points moving average has been applied to the raw data. Error bars indicate the reproducibility of the data.

Fig. 4: (A) Measured TOF distribution of m/z=28 for ablation laser pulse width τ= 350 and 500 fs and fluence 200 mJ/cm². The lines represent fits to a modified-MB distribution. For comparison, we also include the modified-MB fit of the m/z=28 TOF distribution (blue line, figure 3)(B) Surface temperature, determined from modified MBD, as a function of the laser pulse width. (C) The total yields, derived from the area of the modified MBD, as a function of the laser pulse width.
