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On the threshold behavior in laser ablation of organic solids

Leonid V. Zhigilei, Prasad B.S. Kodali, Barbara J. Garrison

Department of Chemistry, 152 Davey Laboratory, The Pennsylvania State University, University Park, PA 16802, USA

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Abstract

The microscopic mechanisms of the fluence threshold behavior in laser ablation of organic solids have been delineated using a breathing sphere model and molecular dynamics simulations. Below threshold, evaporation is identified to occur and primarily single molecules are desorbed. Above threshold, collective ejection or ablation occurs in which large molecular clusters constitute a significant portion of the ejected plume. The laser induced pressure buildup and the phase explosion due to overheating of the irradiated material are identified as the key processes that determine the dynamics of laser ablation.

The interaction of laser pulses with organic matter leading to massive material ablation from a target is a subject of scientific as well as applied interest. Important practical applications include laser surgery [1] and matrix-assisted laser desorption/ionization (MALDI) of biomolecules for mass-spectrometric investigations [2–4]. Despite the practical importance of laser ablation, the detailed understanding of the processes in the irradiated solid and the mechanisms of the ejection of molecules and molecular clusters is still lacking. In particular, the origin of the well-defined threshold fluence for surface damage and material ejection is not fully understood. The threshold behavior has been found in laser ablation of a wide variety of organic solids including technical polymers [5,6], biological tissue [7] and molecular systems [2,8,9]. The existence of this threshold fluence is regarded as a proof of a collective character of the ablation process. What is not fully understood is the relationship between the microscopic effects of molecular excitations by photon absorption and the processes in the irradiated material at the mesoscopic length scale that determine the nature of the threshold phenomenon [10].

The mesoscopic length scale of the collective processes in laser ablation represents a challenge for microscopic models. Recently molecular dynamics (MD) simulations using a breathing sphere model have laid the foundation for bridging the gap between the microscopic and mesoscopic aspects of laser ablation of organic films [11]. The novel feature of this model is that all vibrational modes of a given molecule are approximated by one internal breathing degree of freedom. This approximation permits a significant expansion of the time- and length-scales of the simulation yet still allows one to reproduce a realistic rate of energy relaxation of excited molecules. In agreement with experimental observations, the breathing sphere model reproduces the strongly forwarded emission and high (500–1500 m/s) maximum velocities of the ablated material. In addition, large analyte molecules (as in MALDI) have been found to ablate at nearly the same velocities as the matrix molecules. The foundation, thus, is

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established for elucidating the microscopic and mesoscopic physical mechanisms responsible for the onset of the collective effects of laser ablation. These mechanisms are addressed in the present Letter.

We have performed MD simulations of laser ablation of organic solids for two-dimensional (2D) and three-dimensional (3D) versions of the breathing sphere model [11]. The 2D simulation offers a clear visual picture of the ablation process and takes less computer time. The 3D model more closely maps to experimental conditions in which a quantitative comparison between the computed and experimental results can be made. Computational cells of dimensions 81×210 nm (58800 molecules) and $10 \times 10 \times 40$ nm (27648 molecules) are used in the 2D and 3D simulations, respectively. Periodic boundary conditions in the directions parallel to the surface are imposed, thus the effects of the edges of a laser spot are neglected. A mass of 100 dalton has been attributed to each particle and the parameters of the intermolecular potential are chosen to reproduce the density, cohesive energy, elastic and vibrational properties in the 3D model which are typical for molecular solids [11]. An internal degree of freedom is used to control the rate of energy transfer from an excited molecule to the rest of the system and the parameters of the internal potential determine the coupling between internal molecular motion and phonon modes of molecular solid. A characteristic time of the cooling of an excited molecule is set to be on the order of 10 ps.

The laser irradiation is simulated by vibrational excitation of molecules that are randomly chosen during the laser pulse duration. In this case an implicit assumption is that the UV laser radiation is absorbed by the molecules and internally converted to vibrational energy [1]. The vibrational excitations are created by depositing a quantum of energy equal to the photon energy into the kinetic energy of internal vibration of the molecules to be excited. Laser pulses of 15 ps in duration at a wavelength of 337 nm (3.68 eV) are used in the simulations. Since the ratio of cohesive energies in the 2D to 3D systems is 0.31–0.63 eV, the photon energy is lowered by factor of two for the 2D model. A series of simulations at different laser fluences is performed for the 2D and 3D models in order to reveal the physical processes leading to the onset of ablation.

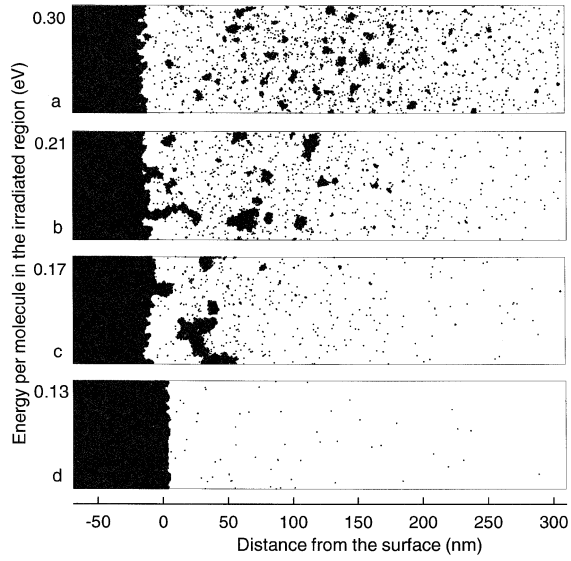

Fig. 1. Snapshots of the plume at 500 ps vs. deposited laser energy. The results are from the 2D simulation. A depth of 70 nm is depicted whereas the total depth in the simulation is 210 nm.

Snapshots of the plume in the 2D simulations at 500 ps for different laser fluences are shown in Fig. 1. Laser pulses with fluences that correspond to a total energy density of 0.17, 0.21 and 0.30 eV deposited per molecule within the penetration depth of 32 nm are sufficient to induce ablation. A significant part of irradiated volume is ejected as a plume consisting of molecular clusters of different sizes as well as individual molecules, Fig. 1a–c. There is a clear change in the structure of the ejected plume with laser fluence. At lower energies, bigger clusters are ejected and a rougher surface is left after the ablation, Fig. 1b, c. Below a certain energy, however, the amount of ejected material drops sharply and primarily single molecules are desorbed as shown in Fig. 1d. Thus the 2D simulations depict a fluence threshold for ablation and a strong dependence of the plume structure on the deposited laser energy.

A consistent physical picture emerges from the results of the 3D simulations shown in Fig. 2. At a

[1] An alternative result of absorption is for the molecules to photofragment, Ref. [5,6]. This absorption mode can be investigated with the breathing sphere model and is a subject of our current study.

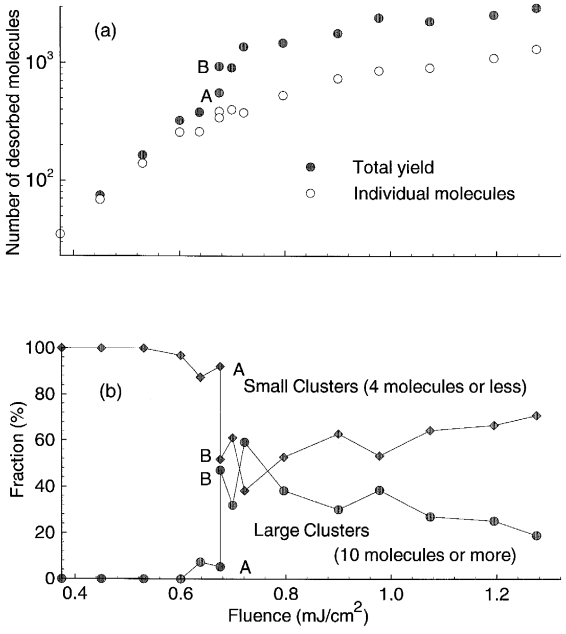

Fig. 2. Desorption yield (a) and plume composition (b) vs. fluence for the 3D simulation.

laser fluence of 0.4 mJ/cm^2 a noticeable number of molecules desorb from the surface, Fig. 2a. The yield gradually increases up to a fluence of 0.675 mJ/cm^2, point A in Fig. 2a, where a stepwise increase of the total yield occurs. We have repeated the simulation at 0.675 mJ/cm^2 four times and obtained a yield of ≈ 500 molecules two times and about 1000 molecules twice, points A and B in Fig. 2a, respectively. Increasing the irradiation dose beyond 0.675 mJ/cm^2 leads to the monotonic increase of the yield with clear indications of saturation at high fluences.

The most prominent feature of the calculated total yield curve is the stepwise increase at 0.675 mJ/cm^2 which also correlates with a change in plume structure, Fig. 2b. Primarily single molecules with a small number of molecular dimers and trimers are ejected at fluences lower than 0.675 mJ/cm^2. These molecules desorb from the surface due to thermal fluctuations in the kinetic energy indicating that an intensive evaporation is the mechanism causing desorption. Starting from point B the ejected plume is found to contain a substantial fraction of large molecular clusters. At this point there is a collective ejection process, namely, ablation. The results of the 2D simulations are in good agreement with these observations and the snapshots presented in Fig. 1 can be used as a vivid illustration of the plume structure even for the 3D model.

Comparing the simulation data with experimental mass spectrometry measurements [2,8,9,12] one should take into account the difference between the total yield and the yield of individual molecules as shown in Fig. 2a. The yield of individual molecules, the quantity commonly measured, is found to have no step increase at the ablation threshold. This suggests that the experimental threshold for matrix molecules in MALDI is likely to correspond to a detection threshold rather than the real physical threshold [12].

The next step is to correlate the picture of ablation described above with quantities such as temperature,

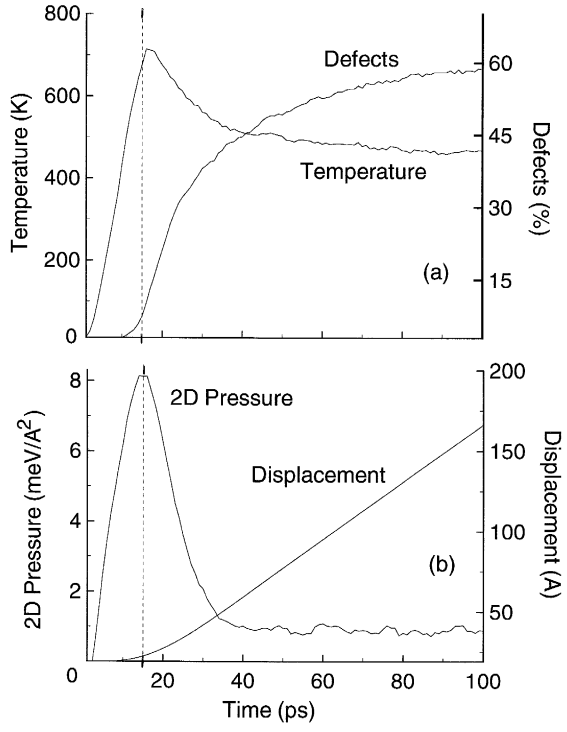

Fig. 3. Material characteristics vs. time. All quantities are averaged over the molecules in the original top 24 nm of the system. The results are for the 2D simulation shown in Fig. 1a. The end of the 15 ps laser pulse is denoted by a dashed line. (a) Temperature and defect density. As discussed in Ref. [13] the radial kinetic energy yields a reasonable indication of the temperature both in the solid and the plume. (b) 2D pressure and displacement.

pressure and defect density of the system. We choose to calculate these quantities for the 2D model since a more straightforward structural analysis can be made and also since a large number of ablated particles ensures better statistics. The concept of local atomic stresses is used in the pressure calculations and the number of non-sixfold coordinated molecules is used to define the defect density in 2D model [11].

The material characteristics calculated for the simulation with 0.30 eV deposited per matrix molecule are shown in Fig. 3. A rapid energy transfer from the vibrationally excited molecules occurs which results in intensive energy pumping into the thermal energy of the solid. Consequently, a sharp temperature rise occurs during the laser pulse duration, Fig. 3a. Since a hotter material has a larger equilibrium volume, heating is normally accompanied by thermal expansion. When the heating time is shorter than a characteristic time of mechanical relaxation, however, the material is inertially confined [7]. That is, it does not have time to expand, and locally, heating takes place at nearly constant volume. This constant volume heating inevitably leads to a high pressure buildup in the irradiated volume, as shown in Fig. 3b.

The high pressure formed within the penetration depth relaxes by expansion of the irradiated material. In the direction towards the bulk, this relaxation drives a strong compression wave into the cold part of the sample [11]. In the surface region, the pressure gradient leads to the forces driving the acceleration of the top layers in the direction normal to the surface. Ablation is initiated when these forces exceed the strength of the material and cause material fracture and ejection. The ablation of material is shown in Fig. 3b where the average displacement of the 24 nm thick surface layer is plotted vs. time. The acceleration of the region as a whole starts at ≈ 10 ps and is completed after ≈ 25 ps when the pressure drops. The displacement then increases linearly with time indicating that the whole region is ablated and moves away from the sample with an average velocity of ≈ 200 m/s. [2]

[2] The velocities of the ejected particles are nonuniformly distributed in the plume. Momentum transfer from the lower particles to the top particles results in high plume-front velocities of ≈ 700 m/s in the 2D model. See also Ref. [11,13].

The results from the simulation clearly demonstrate that an ablation process driven by the dynamics of the laser-induced pressure relaxation is energetically more efficient then vaporization. A relatively few interactions need to be broken in order for large chunks of material to spallate and the ablation can occur with energy densities significantly less than the cohesive energy, 0.31 eV for the 2D system shown in Fig. 1. It is not surprising that low thresholds are observed for ablation of organic matter [1,2,7,9]. A process that only involves a pressure driven spallation should primarily break off large pieces of the material. Many individual molecules, however, are observed above threshold in both the 2D (Fig. 1) and 3D (Fig. 2) models. In fact, concomitant with the pressure driven ablation there is also overheating of the material which induces a phase transition.

The defect density is used to monitor the phase changes in the 2D model, Fig. 3a. No defects are detected during most of the 15 ps laser pulse. Near the end of the laser pulse the defect density starts to rise sharply and nearly linearly with time. During the short time span between 15 and 30 ps the defect density increases to the level that far exceeds that of the liquid state. This increase starts simultaneously and proceeds with nearly the same rate in the entire depth of the irradiated part of the sample [11]. This points to a rapid homogeneous phase transition/explosion from a solid directly to a gaseous phase consisting of mixture of individual molecules and molecular clusters.

The explosive phase transition is attributed to the significant overheating of the material exposed to a short laser pulse. The energy deposited is sufficient not only to melt but to vaporize a fraction of the material. For reference, the melting temperature of the 2D system is ≈ 400 K. In this case the thermodynamic equilibration of the overheated matter proceeds in the form of explosive spontaneous decomposition of the ejected material into a mixture of gas phase molecules and molecular clusters with the fraction of molecules in the gas phase determined by the degree of overheating [14,15]. We find that the adiabatic expansion and intensive disintegration of the ejected material during the phase explosion lead to a fast temperature drop (Fig. 3a) when the kinetic energy of thermal motion is transferred into the

potential energy of material disintegration and the flow energy of the ejected plume.

The analysis given above for the highest fluence shown in Fig. 1a suggests that the laser-induced pressure buildup and the phase explosion due to the overheating are the two intertwined processes that control the dynamics of the laser ablation. This physical picture of the ablation provides an explanation for the fluence dependence of the plume structure shown in Figs. 1 and 2b. For smaller amounts of deposited energy there is a lower degree of overheating and a smaller pressure buildup in the irradiated material. The smaller pressure results in the lower ejection velocities. An estimate of the desorption velocities can be made from the extent of the plume in Fig. 1 where all four simulations are shown at 500 ps. The lower overheating leads to the less explosive phase transition and a smaller fraction of individual molecules in the ejected plume as shown in Fig. 1b, c and Fig. 2b. Below the certain level of the deposited laser energy the laser-induced pressure is not sufficient to rupture the material surface and ejection is limited to a small number of thermally evaporated molecules, Figs. 1 and 2b. In this case no explosive cooling and splitting of the axial and radial kinetic energies are observed.

In conclusion, molecular dynamics simulations using a newly developed model of breathing spheres have provided a microscopic picture of events leading to the threshold behavior in laser ablation of organic solids. Namely there is a laser induced pressure buildup and a phase explosion due to overheating of the irradiated material which are the key processes. Ablation driven by the dynamics of the laser-induced pressure relaxation provides an energetically efficient mechanism of material removal with large molecular clusters ejected just above the threshold. At higher laser fluences the explosive decomposition of the ejected plume into the mixture of individual molecules and molecular clusters results in a rapid cooling of the plume.

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