

Microscopic Mechanisms of Laser Ablation of Organic Solids

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Molecular dynamics simulations are used to provide a microscopic view of the dynamics occurring during laser ablation and desorption of organic solids. A novel breathing sphere model has been developed to incorporate key aspects of laser irradiation of organic solids into molecular dynamics simulations [1]. The model significantly expands the length-scale (up to hundreds of nanometers) and the time-scale (up to nanoseconds) accessible for molecular-level computer simulation [2] and still provides a realistic description of energy relaxation of individual molecules internally excited by photon absorption. Parameters of the model are chosen to be appropriate for molecular solids and MALDI irradiation conditions.

Two series of simulations are discussed in the presentation. The first series of simulations is performed in the regime of thermal confinement that is characteristic for UV-MALDI conditions. The second series is performed under the conditions of stress confinement, a regime we speculate is comparable to IR-MALDI. The focus of this study is on the differences in the microscopic ejection mechanisms and the implications of these differences for MALDI.

The simulations show that for the conditions of thermal confinement (UV-MALDI) overheating of the surface region of the irradiated sample occurs and a phase explosion of the overheated material is responsible for the collective material ejection at laser fluences above the ablation threshold. This phase explosion leads to a homogeneous decomposition of the expanding plume into a mixture of liquid droplets and gas phase molecules. The decomposition proceeds through the formation of a transient structure of interconnected liquid clusters and individual molecules and leads to the fast cooling of the ejected plume.

For shorter laser pulses, in the regime of stress confinement (perhaps IR-MALDI), a lower threshold fluence for the onset of ablation is observed and attributed to photomechanical effects driven by the relaxation of the laser-induced pressure. Laser ablation in this case proceeds through the void nucleation and growth, which leads to disintegration and ejection of large relatively cold chunks of material. At laser fluences close to the ablation threshold, the mechanical fracture is localized at a certain depth under the surface. This depth is defined by the balance between the tensile stresses that are increasing with depth and the decreasing thermal softening due to the laser heating. At higher laser fluences material can lose its integrity over a larger surface region.

Under both thermal and stress confinement conditions, clusters are a natural part of the ablation process and are largest at fluences just above the ablation threshold. For UV-MALDI conditions, the fluence dependence of the particle ejection observed in the recent trapping plate experiments by Handschuh et al. [3], namely, no particle ejection below the ablation threshold, appearance of particles right above the threshold, and decreased particle ejection at higher fluences, is consistent with simulation results for the thermal confinement regime, Fig. 1a-c. Larger and more numerous clusters with higher ejection velocities are produced at the same laser fluences in

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the regime of stress confinement, Fig. 1d. For monomer molecules the ejection in the stress confinement regime result in broader velocity distributions in the direction normal to the irradiated surface, higher maximum velocities, and stronger forward peaking of the angular distributions.

Simulations predict that a well-defined threshold fluence separates two distinct regimes of molecular ejection, desorption at low fluences and ablation at high fluences. Experimental yield vs. fluence dependences measured by Dreisewerd et al. [4], however, do not exhibit thresholds. We resolve this discrepancy by analyzing for only the individual molecules that are ejected and omitting the clusters [2]. The fluence dependences of the total ablation yield in different irradiation regimes are related to the analytic descriptions for desorption and ablation discussed for MALDI by Johnson [5].

Simulations indicates that the amplitudes and the shape of the acoustic wave propagating from the absorption region are sensitive to the changes in the mechanisms of material ejection and can be used for tuning of the irradiation parameters to the desired ejection conditions in mass spectrometry experiments. Much stronger acoustic waves are generated in the regime of stress confinement. Moreover, the shapes of the pressure profiles recorded in the stress confinement regime for desorption and ablation are substantially different from one another. A characteristic bipolar thermoelastic pressure wave changes into a much stronger unimodal wave as the laser fluence exceeds the threshold for the ablation onset [6].

The simulations also predict entrainment of large molecules (analytes) in the plume of the ablated material, comparable axial velocities for both the matrix and analyte molecules, and highly forward peaked angular distributions for analytes. More information on the project can be found at <http://galilei.chem.psu.edu/~leo/Ablation.html>

References

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