Molecular dynamics simulation study of the fluence dependence of particle yield and plume composition in laser desorption and ablation of organic solids

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Two distinct regimes of molecular ejection separated by a well-defined threshold fluence are observed in molecular dynamics simulation of pulsed laser irradiation of an organic solid. At fluences above the threshold a collective multilayer ejection or ablation occurs where large liquid droplets are ejected and the total yield of the ablated material follows a critical volume density of the deposited energy. Below threshold thermal desorption from the surface is observed and the desorption yield has an Arrhenius-type dependence on the laser fluence. The yield of monomers does not have a step increase at the threshold and thus deceptively does not give a straightforward interpretation of the ejection mechanisms. © *1999 American Institute of Physics.* [S0003-6951(99)01909-9]

The interaction of laser pulses with organic targets leading to the desorption of molecules or a massive material removal (ablation) is a practically important[1–3] but yet not fully understood phenomenon. In particular, there is still an ongoing discussion as to whether there is a difference between desorption and ablation and whether these two ejection regimes are separated by a threshold fluence. Models of material removal as a result of laser irradiation discussed in the literature can be divided into two major categories: ablation models based on the idea of a collective ejection of a volume of material due to a rapid nonequilibrium phase transition[1,4,5] or a critical pressure gradient,[1,2,6] and quasithermal desorption models that are based on different descriptions of the rapid surface vaporization process.[1,2,7] The ablation models predict the existence of the threshold laser fluence for the onset of ablation and are able to account for strongly forwarded emission and high maximum velocities of ablated particles.[4,6,8] A well-defined threshold fluence for ablation has been also observed in molecular dynamics simulations.[9] On the other hand, recent mass spectrometry data of Dreisewerd *et al.*[7] on the dependence of the number of desorbed molecules on laser fluence in matrix-assisted laser desorption/ionization (MALDI) are in accord with a quasithermal desorption model where there is a detection threshold rather than a real physical threshold. In polymer ablation, the threshold concept is commonly used to describe a steep increase of the ablated depth with laser fluence.[3] A detailed analysis in the low fluence regime reveals, however, that small, but finite amounts of material are removed at fluences below threshold[3,10] and the mass loss at low fluences can be well described by an Arrhenius-type dependence.[10] Apparently, more experimental and theoretical efforts are needed to resolve the controversy associated with the threshold behavior and, more generally, to gain a thorough understanding of the physical mechanisms of laser desorption/ablation.

Recent results of molecular dynamics (MD) simulations performed with the breathing sphere model have demonstrated the potential of this technique for the detailed investigation of the laser ablation phenomenon.[8,9,11] In the present work we extend our preliminary three-dimensional calculations by using a larger computational cell and a dynamic boundary condition so that irradiation parameters comparable to the experimental values can be used. Consequently, we can directly relate simulation results to experimental observations on the fluence dependence of the total desorption/ablation yield and plume composition. In doing this we, in effect, establish the appropriate analytical models to use in different irradiation regimes and address the controversy associated with the threshold behavior.

The MD simulations of laser ablation of a molecular solid are performed using the breathing sphere model which has been described in detail elsewhere.[11] Briefly, 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. A computational cell of dimensions $10\times10\times100$ nm (70,526 molecules) is used in this work. Periodic boundary conditions in the directions parallel to the surface are imposed. These conditions simulate the situation in which the laser spot diameter is large compared to the penetration depth so that the effects of the edges of the laser beam are neglected. At the bottom of the MD computational cell we apply a new dynamic boundary condition that accounts for the laser induced pressure wave propagation out of the MD computational cell as well as the direct laser energy deposition in the boundary region.[12] This boundary condition allows us to focus the computational effort of the MD simulation to the region where active processes of laser induced melting, desorption, and ablation occur.

The laser irradiation at a wavelength of 337 nm (3.68 eV) is simulated by vibrational excitation of molecules[11] that are randomly chosen during the laser pulse duration with an

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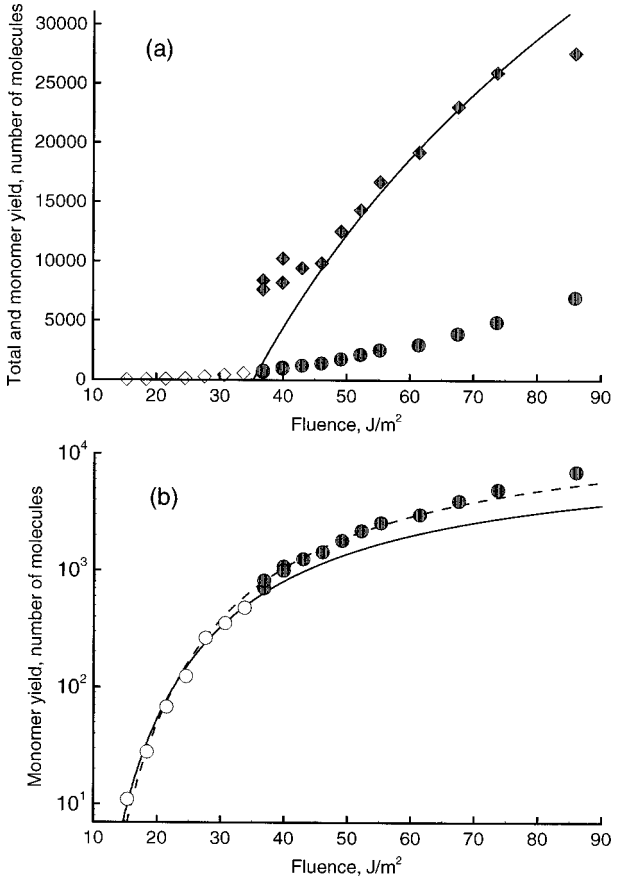

FIG. 1. Total yield (a) and monomer yield (a) and (b) vs laser fluence. The solid lines represent predictions of (a) the ablation model [Eq. (1)], with $E_v^* = 0.6$ eV and (b) the thermal desorption model [Eq. (2)], with $E_s^* = 0.46$ eV. The dashed line represents the best fit of all data points for the monomer yield (b) to Eq. (2), $E_s^* = 0.52$ eV. The rhombs and circles represent the total and monomer yields and the open and closed symbols show the data points below and above the threshold for ablation. A logarithmic scale is used in (b) for better presentation of low fluence data.

exponential decrease of the absorption probability with depth in accordance with Beer's law. The values of absorption depth (50 nm) and laser pulse width (150 ps) have been chosen in order to make sure we are in the same physical regime as MALDI experiments.[1,7] The pulse duration of 150 ps is short relative to the characteristic thermal diffusion time across the absorption depth (~10 ns) but longer than the time required for an acoustic wave to traverse the absorption depth (~20 ps). Thus, the simulations are performed in the regime of thermal confinement[7] but not thermo-elastic stress confinement.[9,13] This regime is also characteristic for ultraviolet (UV)-MALDI conditions.[7] It has been demonstrated recently by Dreisewerd *et al.*[14] that in the regime of thermal confinement the amount of energy deposited by the laser pulse rather than the pulse duration determines the desorption/ablation process. A comparison between the simulation results and UV-MALDI experimental data is therefore justified.

The discussions of laser desorption/ablation experimental data are often based on the dependence of the amount of material removed per pulse, i.e., the total yield, on the laser fluence. Thus, we also start the analysis of the simulation results from the yield–fluence dependence shown in Fig. 1(a). The lowest fluence at which a noticeable number of molecules desorb from the irradiated surface is 15 J/m^2. At this point 11 molecules are ejected from the 10 nm^2 surface of the computational cell during 400 ps of the simulation. The yield gradually rises to 579 molecules as fluence increases to 34 J/m^2. At 37 J/m^2 a nearly 15-fold stepwise increase of the total yield from 579 molecules (<1 nm layer of the original sample) to ~8000 molecules (~11 nm layer) is observed. This stepwise increase of the yield corresponds to the onset of ablation, a collective ejection in which the processes in the irradiated material at the mesoscopic rather than at the molecular length scale dominate.[9]

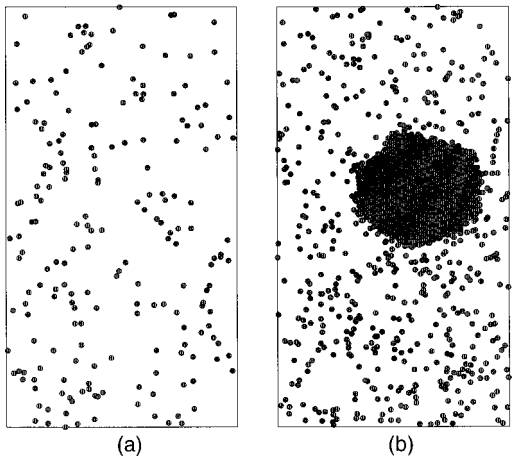

FIG. 2. Snapshots of the plume from the MD simulations at 400 ps after irradiation with 150 ps laser pulse at laser fluences of (a) 34 J/m^2 and (b) 40 J/m^2. The portion of the computational cell from 85 to 120 nm above the original sample surface is shown.

The fluence dependence of the yield of monomers (Fig. 1) that is presumably proportional to the yield of ions or postionized neutral molecules in mass spectrometry experiments,[1,2,4,6,7,14] is in a drastic contrast with the total yield curve. First, there is no step increase in the number of ejected monomers at the ablation threshold and one can hardly identify the threshold fluence from the plot. Second, while mostly monomers are ejected at fluences below the ablation threshold, they constitute a relatively small fraction of the ejected plume — from 9% at 37 J/m^2 up to 25% at 86 J/m^2 in the ablation regime. The drastic change in the plume composition is illustrated in Fig. 2, where snapshots of the plume are shown for laser fluences below and above threshold. Large liquid droplets constitute the bulk portion of the ejected plume above the ablation threshold, [Fig. 2(b)], whereas monomers dominate below [Fig. 2(a)].

In the ablation regime a cooperative ejection of a volume of material can be described by a simple model in which the ablation depth follows the laser energy deposition and all material that absorbs an energy density higher than a critical energy density E_v^* is ablated.[2,3] With an exponential decay of laser intensity given by Beer's law, the energy density E_v deposited at a depth z under the surface is $E_v = F/L_p \exp(-z/L_p)$, where F is the fluence at the surface, $z = 0$, and L_p is the laser penetration depth. The total number of molecules ejected per unit surface area is then given by

$$N_{\mathrm{tot}} = n_m L_p \ln\left(\frac{F}{L_p E_v^*}\right) \quad \text{for } F \geqslant L_p E_v^*, \tag{1}$$

where n_m is the molecular number density of the material. This expression predicts the existence of the threshold fluence $F^* = L_p E_v^*$ at which the critical energy density E_v^* is reached in the surface layer. As shown in Fig. 1(a), Eq. (1) with a value of the critical energy density E_v^* equal to 0.6 eV per molecule provides a good overall description of the yield–fluence dependence in the ablation regime, i.e., above 37 J/m^2.

Although E_v^* appears to have the same value as the cohesive energy, this does not imply that the material is all ejected as monomers. The deposited laser energy also goes into internal energy of molecules, flow energy of the ejected plume, and energy of the pressure wave propagating deeper into the sample. The remaining energy is insufficient to completely vaporize the ablated volume into monomers and clusters are a mandatory major integral part of the plume in the ablation regime [Fig. 2(b)]. Ablation in this case is driven by the explosive phase transition of the overheated material into the mixture of gas phase molecules and molecular clusters.[5,9]

Below the ablation threshold mostly monomers are ejected from the surface [Fig. 2(a)], and the yield has a distinctive Arrhenius-type dependence on the laser fluence, [Fig. 1(b)]. This suggests that thermal desorption from the surface is responsible for molecular ejection at low laser fluences. Assuming that the number of desorbed molecules is proportional to the desorption rate, the desorption yield can be approximated by[2,7,10]

$$N_m \approx N_{\mathrm{tot}} = A \exp\left(- \frac{E_s^*}{k_B (T_0 + BF)} \right) \quad \text{for } F < L_p E_v^* , \tag{2}$$

where N_m is the yield of monomers, E_s^* is an activation energy, A is a pre-exponential or frequency factor, B is a factor that describes the conversion of the deposited energy into an increase of temperature of the surface, T_0 is the initial temperature (zero in the simulations), and k_B is Boltzmann's constant. Taking into account that the internal motions of each molecule are approximated in our model by a single degree of freedom,[11] a specific heat capacity of the model molecular solid can be calculated as $C = 4 k_B n_m = 405 \times 10^3 \,\mathrm{J\,K^{-1}\,m^{-3}}$. With Beer's law for energy deposition the conversion factor B is $(C L_p)^{-1}$ or $49 \,\mathrm{K\,m^2\,J^{-1}}$. This conversion factor is an order of magnitude larger than the one estimated for the MALDI experimental conditions in Ref. 7, owing to two times longer penetration depth, three times higher specific heat capacity, and reflection losses in the experimental system as compared to the simulation. As shown in Fig. 1(b), Eq. (2) with activation energy E_s^* of 0.46 eV provides a good fit of the desorption yield below the ablation threshold.

A thermal desorption model was used in Ref. 7 to describe experimental results over the whole range of fluences. As shown in Fig. 1(b), an Arrhenius-type dependence of yield on fluence [Eq. (2)], appears to work over a larger fluence region in the present study as well, albeit with a somewhat higher best fit value of the activation energy, 0.52 eV. However, we know from the analysis of the simulation results that the physical processes leading to the ejection of the monomers are drastically different below and above the threshold fluence for ablation, 37 J/m^2. Below threshold we observe intensive desorption from the surface and application of Eq. (2) is justified. Above threshold the gas phase molecules result from the explosive phase transition of the volume of overheated material[5,9,11] and the fraction of monomers is determined by the degree of overheating.

In conclusion, the analysis of the results of simulations shows that different physical mechanisms are responsible for molecular ejection at low and high fluences. At low laser fluences thermal desorption from the surface is observed and the desorption yield has an Arrhenius-type dependence on the laser fluence. At the threshold fluence the ejection mechanism changes to ablation, in which a collective ejection of a volume of irradiated material due to a phase explosion of the overheated material occurs. Large clusters become a major constituent of the plume above threshold and the total amount of ejected material follows the critical volume energy density deposited by the laser pulse. The yield of monomers measured in mass spectrometry experiments does not reflect the total amount of material ejected in the ablation regime. Moreover, the drastic increase of the total yield at the ablation threshold is imperceptible in the fluence dependence of the monomer yield.

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