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Phase transition at low fluences in laser desorption of organic solids: a molecular dynamics study

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Abstract

Molecular dynamics of a short pulse laser irradiation of a molecular crystal are performed to investigate the dependence of the mechanism of ejection on laser fluence. We find that at low laser fluences molecules are desorbed from a thin surface layer of solid sample. An increase in the laser fluence leads to the melting of the surface region and desorption occurs from an overheated melted state. An additional increase of the fluence leads to the ablation when the laser-induced pressure and phase explosion of the overheated liquid drives a collective ejection of a significant volume of irradiated material. © 1999 Elsevier Science B.V. All rights reserved.

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Investigations of the fundamental events occurring during laser desorption and ablation have received considerable attention in recent years as the applications of the process have become more popular and economically viable [1–3]. Despite the popularity of laser ablation, the understanding of the underlying mechanisms is rather poor. There have been attempts to establish a fundamental footing from both experimentalists [4–10] and theoreticians [11–14]. The complex nature of the process has, however, hindered the progress towards the complete understanding of the phenomena of laser desorption and ablation. It is also difficult to get a microscopic picture by observing the macroscopic quantities such as yields and kinetic energies.

Time-of-flight (TOF) measurements [15,16] of desorption yields and the kinetic energies of the ablated particles from C_6H_6/NaCl and C_6H_6/Au systems give insight into the process of laser desorption/ablation [17]. An intriguing mechanistic hypothesis has been made Braun and Hess. Namely, a solid–liquid phase transition occurring at laser fluences below the threshold for ablation have been proposed to be responsible for the plateau in the dependence of the mean kinetic energy of the desorbed particles from the laser fluence. Although their hypothesis of a phase transition is supported by their data and estimations of the temperature of irradiated molecular films, it is not possible to get a clear microscopic picture of the processes in the system from these experiments.

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The molecular dynamics (MD) technique is capable of providing a microscopic picture of laser ablation but simulations have been hampered by the long length and time scales of the process. We have developed a breathing sphere model aimed at overcoming the time and length scale limitations of MD simulations in studying the laser desorption/ablation process [18–20]. The novel feature of the breathing sphere model is an approximate representation of the internal motion which permits a significant expansion of the time and length scales of the model yet still allows one to reproduce a realistic rate of the vibrational relaxation of excited molecules. The initial verification of the model has been performed by simulating the laser ablation for molecular solids. The model identifies the processes that distinguish desorption from ablation, [18,19] explains a fluence threshold for ablation [19], and predicts the cluster distribution in the plume [21]. Below the fluence threshold for ablation there is desorption where the plume consists of clusters. This model also reveals the physics leading to the velocity distributions of ejected molecules [20,22], explains entrainment of heavy molecules in the plume [18,21] and predicts ablation processes as a function of laser properties such as laser fluence and pulse width [23,24].

The hypothesis by Braun and Hess of the melting that occurs below the ablation threshold and affects the kinetic energies of the ejected molecule can be tested by using the breathing sphere model. In molecular dynamics simulations not only various properties of the desorbed molecules but also the characteristics of the material remaining in the target after the ablation process is complete can be examined in detail. The main goal of this work is to provide insights into the processes leading to desorption at low fluences. In the following sections the details of the computational technique and the results from the simulations are presented.

The breathing sphere model presented elsewhere [18] has been used to study the laser desorption process. Briefly, the molecules in the system are treated as breathing spheres with true translational but approximate internal degrees of freedom. Even though the internal motion is represented in an approximate manner, it allows us to reproduce a realistic rate of conversion of the internal energy of the excited molecules to the translational motion. The parameters of the intermolecular interactions are chosen to represent the van der Waals interactions in a molecular solid. The parameters of the internal potential were chosen to provide a characteristic time of vibrational relaxation of an excited molecule to be on the order of 10 ps, a value typical for organic solids [25].

The system consists of a solid of $10\times10\times40$ nm^3 with 27 648 molecules of mass 100 daltons. A crystalline solid in which the molecules are close-packed is used. In order to obtain a relaxed starting configuration, the crystalline solid was heated to a temperature of 50 K and quenched using the generalized langevin equation (GLE) method [26]. The crystalline system, because of its perfect packing arrangement, gives a clear visual picture of the process and the effect of energy deposition on the system. Periodic boundary conditions parallel to the surface are imposed, thus the effects of the edges of the laser beam are neglected [18]. The bottom 8 Å of the crystal is given a mass of 1000 daltons and damping conditions are imposed on the bottom 40 Å of the crystal to reduce the effects of the reflected shockwave during the ablation process.

The laser irradiation is simulated by vibrational excitation of molecules that are randomly chosen during the laser pulse duration of 15 ps. In this case an implicit assumption is that the laser radiation is absorbed by the molecules and is internally converted to vibrational energy. The vibrational excitations are performed by depositing a quantum of energy equal to the photon energy into the kinetic energy of internal vibration of the molecules to be excited. The energy is deposited according to the Beer's law. A penetration depth of 7 nm is used to provide an absorption of 99% of the laser energy within the computational cell. The wavelength of the laser used is 337 nm (3.68 eV/photon).

The duration of the simulations was determined by running a few trajectories for longer times. The results presented here were calculated for the ejected particles after 100 ps of simulation. The desorption process slows down significantly after

100 ps and the number of desorbed particles did not change when the simulations were run for longer time.

We start by examining the total yield and the monomer yield as a function of fluence as shown in Fig. 1. The nature of the ablation threshold and the change in the plume composition from mostly monomers below the ablation threshold to a mixture of large molecular clusters and gas phase molecules is discussed in previous publications [18–21]. The same criteria have been used to define the ablation threshold in this case. For the discussion here, it suffers to say that for fluences below 0.7125 mJ/cm^2 there is desorption [1] and the ejected plume consists primarily of monomers, Fig. 1.

The proposal of Braun and Hess is that as the fluence increases the desorption from a solid gives a way to desorption from a liquid. In order to examine this proposal we have chosen four points labeled a, b, c and d in Fig. 1 to analyze in more detail. We have chosen to examine the density of molecules vs. distance from the surface into the solid, Fig. 2, after the desorption or ablation has occurred. The data in these plots have been averaged over 5 ps at the end of the simulation in order to account for the particle vibrations which are on the order of few tens of femtoseconds. These plots give us insight into the disorder in the system and a qualitative idea of the melting process. It can be seen from Fig. 2a that at point a, only the surface is disturbed and the order below the surface remains intact. As the fluence is increased to point b, melting of a thin surface layer ~3 monolayers in depth is observed. The surface melting is reflected in Fig. 2b as the deviation from the crystalline order in the top 10 Å. At the fluence of point c there is nearly a uniform density distribution in the top ~40 Å, an indication of the intense melting process. Fig. 2 shows that between fluences b and c part of the deposited energy is going into disordering of the system. Finally, 2d is representative

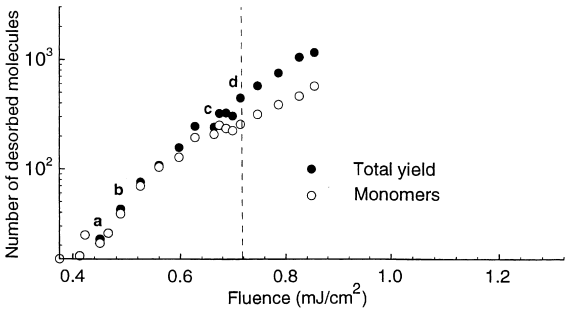

Fig. 1. Total and monomer yields vs. fluence. The dashed line indicates the threshold fluence for ablation.

of the ablation regime. In the ablation regime, more material is removed as noted by the lower intensity in Fig. 2d than in Fig. 2c.

The layer of origin of the desorbed molecules is consistent with the picture of desorption from a solid at fluences below point a in Fig. 1 and desorption from a melted region between points b and c. For all fluences below point a, the desorbed molecules originate from the top two layers. At the fluence corresponding to point c, just below the ablation threshold, some of the desorbed molecules come from as deep as layer 8 (~32 Å) even though a total of less than one layer of material is removed.

Simulations using the breathing sphere model have clearly delineated the phase transitions associated with laser desorption and ablation. At low fluences there is desorption of molecules from a solid. As the fluence increases we observe melting of the surface layer with gradual increase of the melted region with fluence. Above a certain threshold fluence ablation occurs.

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[1] The threshold for ablation is slightly higher in this crystalline system than what we found earlier for an amorphous system because the cohesive energy of the crystalline system is larger than the value for the amorphous system.

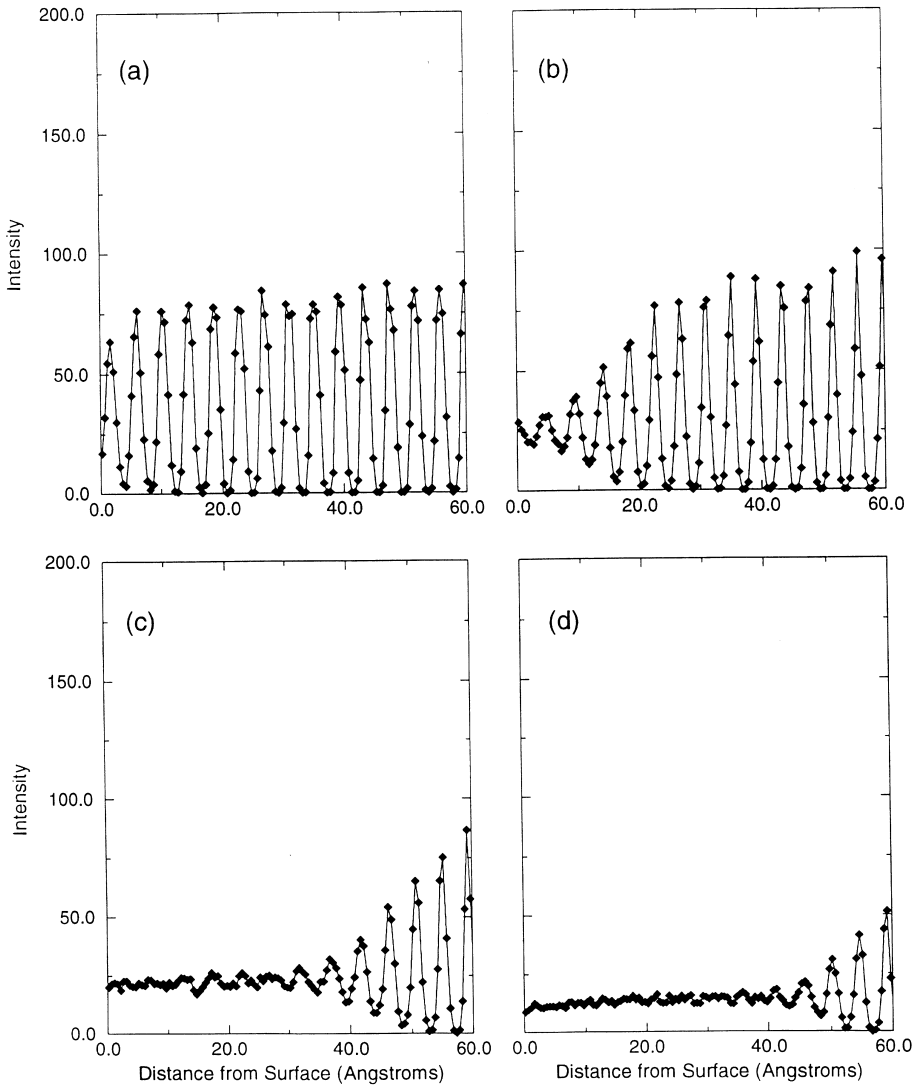

Fig. 2. Number density plots vs. depth from the surface. The fluences in plots a, b, c and d correspond to the points a, b, c and d in Fig. 1.

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References

[1] D.H. Lowndes, D.B. Geohegan, A. Puretzky, D.P. Norton, C.M. Rouleau, Science 273 (1996) 898.
[2] M. Karas, F. Hillenkamp, Anal. Chem. 60 (1988) 2299.
[3] F. Hillenkamp, M. Karas, R.C. Beavis, B.T. Chait, Anal. Chem. 63 (1991) 1193A.
[4] W. Ens, Y. Mao, F. Mayer, K.G. Standing, Rapid Comm. in Mass Spec. 5 (1991) 117.
[5] J. Zhou, W. Ens, K.G. Standing, A. Verentchikov, Rapid Comm. in Mass Spec. 6 (1992) 671.
[6] R.C. Beavis, B.T. Chait, Chem. Phys. Lett. 181 (1991) 479.
[7] B. Spengler, V. Bokelmann, Nucl. Instr. and Meth. B 82 (1993) 379.
[8] I. Noorbatcha, R.R. Lucchese, Y. Zeiri, Surf. Sci. 200 (1988) 113.
[9] G. Comsa, R. David, Surf. Sci. Rep. 5 (1985) 145.
[10] W. Zhang, B.T. Chait, Int. J. Mass Spec. and Ion Proc. 160 (1997) 259.

[11] B.J. Garrison, R. Srinivasan, Appl. Phys. Lett. 44 (1984) 849.
[12] B.J. Garrison, R. Srinivasan, J. Appl. Phys. 57 (1985) 2909.
[13] A. Vertes, R.D. Levine, Chem Phys. Lett. 171 (1990) 284.
[14] A. Bencsura, A. Vertes, Chem. Phys. Lett. 247 (1995) 142.
[15] P. Hess, Topics in Current Physics, Springer, Heidelberg, 1989, pp. 55.
[16] K. Domen, T.J. Chuang, J. Chem. Phys. 90 (1989) 3318.
[17] R. Braun, P. Hess, J. Chem. Phys. 99 (1993) 8330.
[18] L.V. Zhigilei, P.B.S. Kodali, B.J. Garrison, J. Phys. Chem. B 101 (1997) 2028.
[19] L.V. Zhigilei, P.B.S. Kodali, B.J. Garrison, Chem. Phys. Lett. 276 (1997) 269.
[20] L.V. Zhigilei, B.J. Garrison, Appl. Phys. Lett. 71 (1997) 551.
[21] L.V. Zhigilei, P.B.S. Kodali, B.J. Garrison, J. Phys. Chem. B 102 (1998) 2845.
[22] L.V. Zhigilei, B.J. Garrison, Rapid Commun. Mass Spectrom. 12 (1998) 1273.
[23] L.V. Zhigilei, B.J. Garrison, Appl. Surf. Sci. 127-129 (1998) 142.
[24] L.V. Zhigilei, B.J. Garrison, in Laser–Tissue Interaction IX, S.L. Jacques (Ed.), SPIE Proceedings Series, vol. 3254 (1998) 135.
[25] T.C. Chang, D.D. Dlott, J. Chem. Phys. 90 (1989) 3590.
[26] B.J. Garrison, P.B.S. Kodali, D. Srivastava, Chem. Rev. 96 (1996) 1327.