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## Big molecule ejection—SIMS vs. MALDI

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### Abstract

Using the results of molecular dynamics (MD) simulations, we discuss the question of whether the observed difference in mass limits in secondary ion mass spectrometry (SIMS) and matrix assisted laser desorption ionization (MALDI) are inherently related to the underlying physics of ejection or rather insufficient experimentation. The simulations show clearly that the physics of large molecule emission in SIMS and MALDI is very different. Consequently, we conclude that larger molecules can be ejected in MALDI than in SIMS.

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### 1. Introduction

The ejection of large intact molecules underpins the applications of both secondary ion mass spectrometry (SIMS) and matrix assisted laser desorption ionization (MALDI). In some respects, the two processes appear quite similar as both are initiated by fast energy deposition events in the surface region. A high energy (5–25 keV) primary particle strikes the surface in SIMS, initiating a collision cascade that ultimately leads to the ejection of intact molecules. In MALDI, a laser irradiates the matrix and ultimately the large analyte molecules are ablated intact. In both experiments, ions are detected

although neutral species generally dominate the ejected material. There is a big difference, however, in the size of the molecules that have been detected. Currently the upper mass limit for organic molecules in SIMS is in the range of 10–12 kDa [1]. The mass limit for MALDI, on the other hand, may be as high as ~1 MDa [2].

The ultimate question is whether these mass limits are inherently related to the underlying physics of ejection or rather insufficient experimentation. We have modeled both the SIMS [3–5] and MALDI [6–8] processes with molecular dynamics (MD) simulations. It is our belief that the physics of ejection is sufficiently different such that MALDI can ablate larger molecules than can be sputtered in SIMS. We describe the ablation process in MALDI ablation first as it is probably less familiar to the readers of these proceedings.

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55 **2. MALDI**

56 The laser ablation process associated with MALDI  
 57 is modeled with a novel breathing sphere approach.  
 58 Each molecule in the system is represented by a  
 59 particle with the true translational degrees of freedom  
 60 but an approximate breathing mode that allows one to  
 61 obtain a reasonable rate of energy transfer from the  
 62 excited molecule to its neighbors [6]. This approx-  
 63 imation is necessitated by a collective character of the  
 64 ablation process that requires a large region of the  
 65 irradiated sample to be included in the simulation. The  
 66 properties of the laser including wavelength, pulse  
 67 width and fluence are input into the simulation. Using  
 68 a bead and spring representation of the analyte mole-  
 69 cule in conjunction with the breathing sphere model  
 70 we have observed in the simulation the ablation of  
 71 analyte molecules up to a mass of 30 kDa [7,8].

72 Two time snapshots of the ablation of an analyte  
 73 molecule with mass 11 kDa are shown in Fig. 1. At  
 74  $t = 0$ , the analyte molecule is beneath the surface. At  
 75  $t = 150$  ps (or immediately after the 150 ps laser pulse  
 76 has terminated), the plume containing the analyte  
 77 molecule is 200 Å above the surface. The analyte  
 78 molecule is entrained in the plume and is moving at  
 79 a velocity of 490 m/s or a kinetic energy of 14 eV. Of  
 80 note is that there is relatively little mass effect in the  
 81 velocity of analyte molecules so a heavier molecule  
 82 would be moving at a comparable velocity and thus an  
 83 even higher kinetic energy.

84 In ablation, the laser energy is rapidly deposited in  
 85 the sample. Depending on the laser pulse time, the  
 86 speed of sound in the material, the thermal diffusivity  
 87 and the penetration depth, the system can be in either  
 88 stress or thermal confinement [6]. In the thermal  
 89 confinement regime (UV MALDI), there is an over-

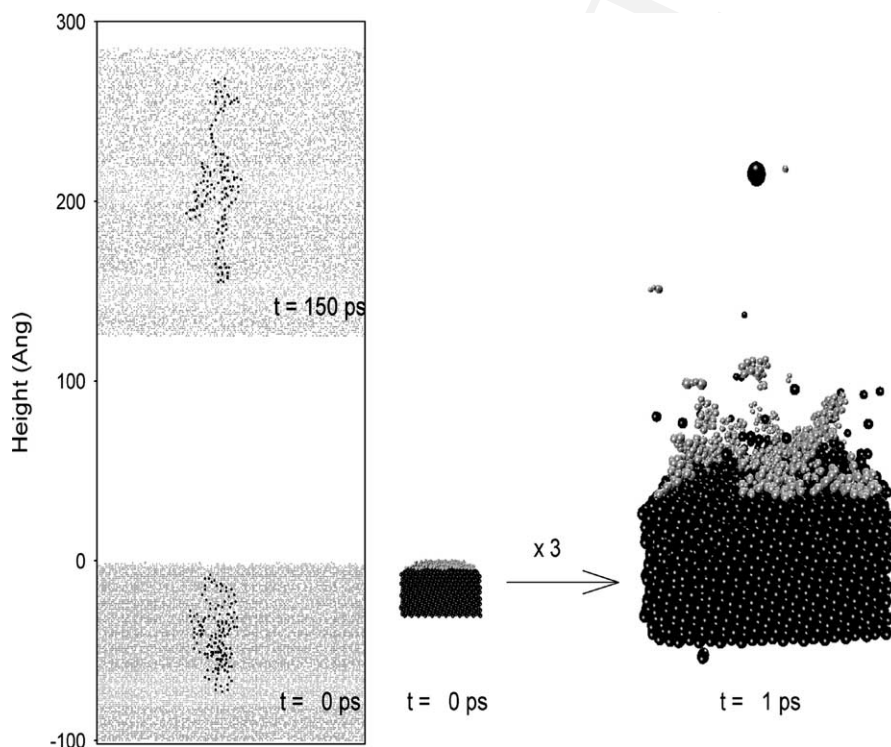


Fig. 1. Snapshots from the MALDI and SIMS MD simulations. The MALDI snapshots are on the left. Each matrix molecule is shown as a gray dot. The beads comprising the analyte molecule are shown as black dots. Only a portion of the simulation cell and plume are shown. The SIMS snapshots are shown on the right. The  $t = 0$  snapshot is at the same length scale as the MALDI snapshots. The Ag atoms are shown as black spheres and the atoms in the PS molecules as gray spheres.

90 heating of the material and a phase explosion occurs.  
91 In the stress confinement regime (perhaps IR  
92 MALDI), there is a spallation of the material. In both  
93 situations, the physics of the laser ablation process  
94 demands that there be a cooperative motion of mate-  
95 rial towards the vacuum.

### 96 3. SIMS

97 The Ar bombardment of *sec*-butyl terminated poly-  
98 styrene (PS) oligomers on a Ag{1 1 1} surface is  
99 modeled using atomistic MD computer simulations  
100 [4]. The sample consists of 13 PS tetramers (four  
101 styrene repeat units) placed on the Ag crystal. The  
102 mass of the PS tetramers using a tritium isotope of  
103 hydrogen in the simulations is 559 Da.

104 The MD simulations predict for sputtering that a  
105 diversity of actions can occur in the solid [4]. Some  
106 of the primary particle impacts result in very little  
107 material being removed from the surface. Other  
108 impacts give rise to tremendous motion, a phenom-  
109 enon termed megaevent [5]. Shown in the figure are  
110 two snapshots of an impact event in which a total  
111 mass of 10 kDa was ejected. The initial time frame is  
112 shown at approximately the same scale as the  
113 MALDI simulations. Our simulations show that there  
114 is a cooperative upward motion pushing the molecule  
115 towards the vacuum. The atoms involved in the  
116 cooperative uplifting arise, however, from only three  
117 to five atomic layers or  $\sim 10$  Å beneath the surface.  
118 Moreover, the most probable kinetic energies of the  
119 ejected molecules are typically on the order of  
120  $\sim 1$  eV. In another trajectory similar to the one shown  
121 in the figure, two PS hexadecamers (2001 Da each)  
122 are ejected.

### 123 4. Discussion and conclusions

124 The figure is designed to give a reasonable sense  
125 of perspective to the two experiments. We feel that  
126 our system sizes in the SIMS simulation are “rea-  
127 sonable” for modeling sputtering of 5 keV bom-  
128 bardment of an organic film on a metal surface.  
129 The system shown in the figure is  $\sim 60$  Å  $\times$  60 Å  
130 in width and  $\sim 25$  Å in depth. For the laser ablation  
131 calculations, we have chosen a laser penetration

132 depth of 400 Å. This value is about a factor of  
133 two to five smaller than penetration depths typically  
134 encountered in UV MALDI. The experimental sys-  
135 tems would have an even larger volume of material  
136 moving in a concerted manner than we have in our  
137 simulations.

138 The physics of large molecule emission in SIMS  
139 and MALDI is clearly very different. In SIMS there  
140 are high action events (megaevents) that lead to  
141 cooperative uplifting of the molecules from the  
142 surface. The upward motion occurs in only several  
143 Angstroms near the surface. Most importantly, the  
144 physics of the collision cascade does not demand  
145 that the atoms move in a concerted fashion. Rather,  
146 sometimes the atoms do move together. The physics  
147 of ablation requires that a rather large amount of  
148 material (tens of nanometer to microns in size)  
149 move in a concerted manner towards the vacuum.  
150 Because of the difference in the physics of material  
151 removal, we believe that the differences observed in  
152 maximum molecule size in SIMS and MALDI are  
153 real.

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161 More results including papers, graphics and anima-  
162 tions can be found on the group web page [http://  
163 galilei.chem.psu.edu/](http://galilei.chem.psu.edu/).  
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