# Surface-Induced Dissociation Kinetics

The research is designed to improve measurement of fast fragmentation kinetics of surface activated ions, to improve our understanding of how ions fragment and how energy transfers in collisions of ions with surfaces. A new technique, silicon nano-particle assisted laser desorption/ionization (SPALDI), was developed recently[1] and allowed investigation of the kinetics of surface-induced dissociation (SID) of small molecules. A Bruker Proflex MALDI TOF[2] and peak shape analysis model are used to investigate fast fragmentation of ions.

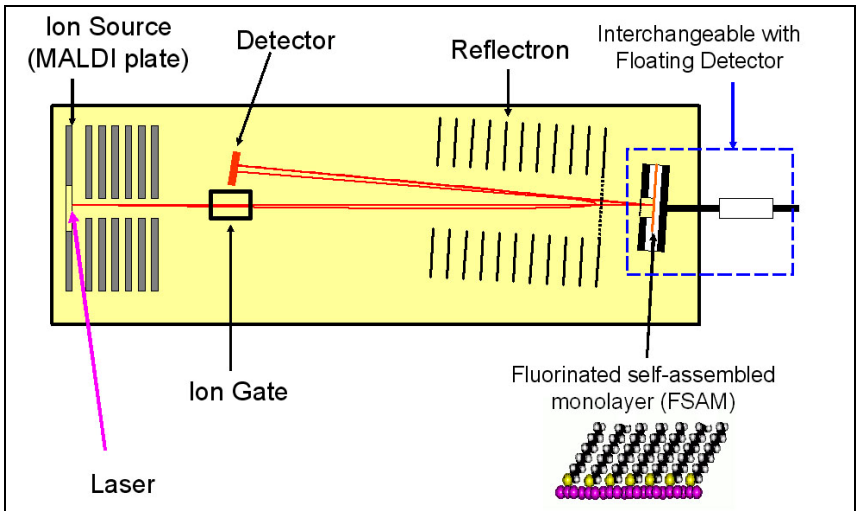


Figure 1. MALDI-TOF-SID-TOF mass spectrometer

The ability of structural characterization of molecules and surfaces is critical to numerous fields. Tandem mass spectrometry (MS/MS) experiments, in which fragment ions are generated from a selected parent ion and used to determine parent structure, provide a key technology in characterization. The success of MS/MS depends on many factors, including the type of activation that is applied to cause ion dissociation. Surface induced dissociation (SID) is attractive because changing the internal excitation of ions is readily accomplished by small variations in the potential difference between the source and the surface. SPALDI has been successful in generating molecular ions using ranging in size from small organics such as $N(CH_3)_4^+$ to peptides without matrix assistance and with much lower laser flux than MALDI or laser desorption ionization (LDI), which leads to lower internal energy deposition in the source.

This optimized MALDI TOF SID instrument will have an observation time frame of hundreds of nanoseconds that may be extended to higher time frames with different ion extraction electrical fields and or different ion optical designs. In this model, the parent ion is assumed to undergo first-order unimolecular decay and the ion packets are assumed to possess Gaussian distribution until surface collision. The peak shape analysis model is implemented by the convolution of

the first-order unimolecular dissociation process with the arrival time distribution to the surface and the initial kinetic energy distribution from ionization.[3]

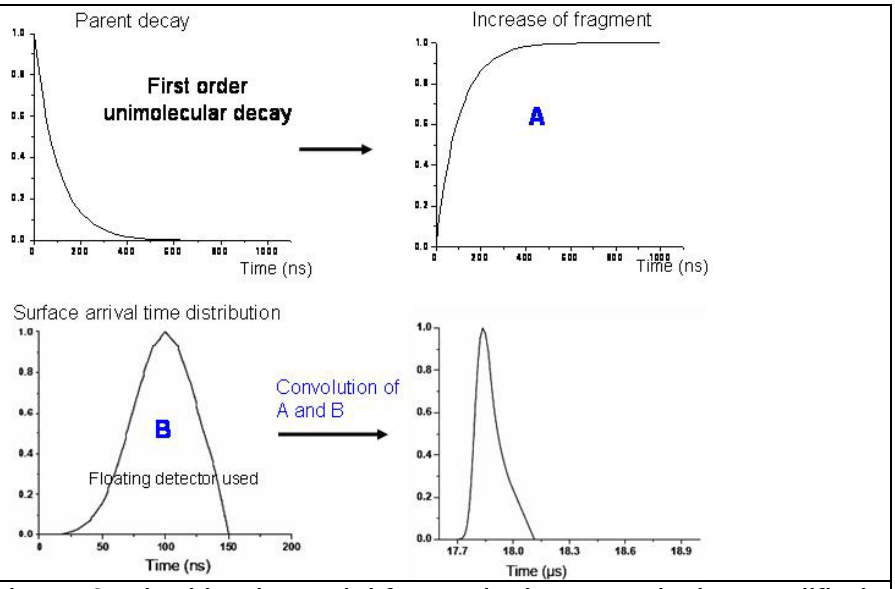


Figure 2. The kinetic model for peak shape analysis. Modified from ref. 3

The MALDI-TOF-SID-TOF instrument and SPALDI have been used to confirm the known $N(CH_3)_4^+$ and $N(CD_3)_4^+$ dissociation. This research suggests that MALDI-TOF-SID-TOF can be used for small ions dissociation kinetics and SPALDI makes colder ions than LDI. Fast fragmentation channels could be observed in the MALDI-TOF-SID-TOF instrument too. Various surfaces - Hydrogenated SAM surface and diamond surface – are being used or will be used to compare F-SAM results. This research can be broadened to characterization of different surfaces. In future, peptides such as RPPGFSPF, PPGFSPFR, KPPGFSPF, PPGFSPF, already known to have fast and slow fragmentation pathways, will be investigated based on our peak shape analysis model.

[1] X. Wen, S. Dagan, and V.H. Wysocki, *Anal. Chem.* 2007, 79, 434-444.
[2] C. Gamage, F. Fernández, K. Kuppannan, and V. Wysocki, Anal. Chem., 2004, 76, 5080-5091.
[3] C. Gamage, Ph. D. dissertation, U. of Arizona