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Internal Energy of Ions Produced by Laser Desorption/Ionization from Laser Induced Silicon Microcolumn Arrays JESSICA A. STOLEE, AKOS VERTES, George Washington University — Laser induced silicon microcolumn arrays (LISMA) were demonstrated as effective matrix-free laser desorption/ionization substrates for the mass spectrometry of biomolecules. Structure specific fragmentation of the produced ions primarily depends on their internal energy. To gain insight into the internal energy of ions laser desorbed from native LISMAs and LISMAs derivatized through silane chemistry, the cations of eight benzyl-substituted benzylpyridinium salts were used as thermometer ions (TI). Survival yields of their unimolecular decomposition were determined and correlated to their internal energy through RRKM calculations. On both native and perfluorophenyl-derivatized surfaces, TIs showed no change in their internal energy over a wide range of laser fluence. While the survival yields for these preformed ions are stable, results on peptides indicate fluence dependent fragmentation. These results point to a different fragmentation mechanism for peptides mediated by hydrogen radicals formed through the recombination of protons, produced from residual solvents, and electrons, emitted from the silicon surface upon laser irradiation.

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