Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics
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Electronic Supplementary Information for

Internal energy deposition and ion fragmentation in atmospheric-pressure mid-infrared laser ablation electrospray ionization

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Initially, the ion transfer region of the mass spectrometer was characterized in survival yield (SY) experiments. The collected SY data were plotted as a function of the critical bond energies (see Table S1) to produce the sigmoidal curves in Figure S1a and to determine the internal energy distributions, P(E), of the generated ions (see Figure S1b). Increasing potential differences between the sampling and skimmer cones of the TOF instrument lead to decreasing the SY values, i.e., to shifting of the sigmoidal curves to higher critical energies (see Figure S1a). The calculated *P(E)* reveals that higher sampling cone potentials increased the average internal energies of the thermometer ions for both ESI and LAESI conditions (see Figure 1b). The means and the widths of the computed distributions, tabulated in Table S2, confirmed that LAESI and ESI generated ions with similar internal energies.

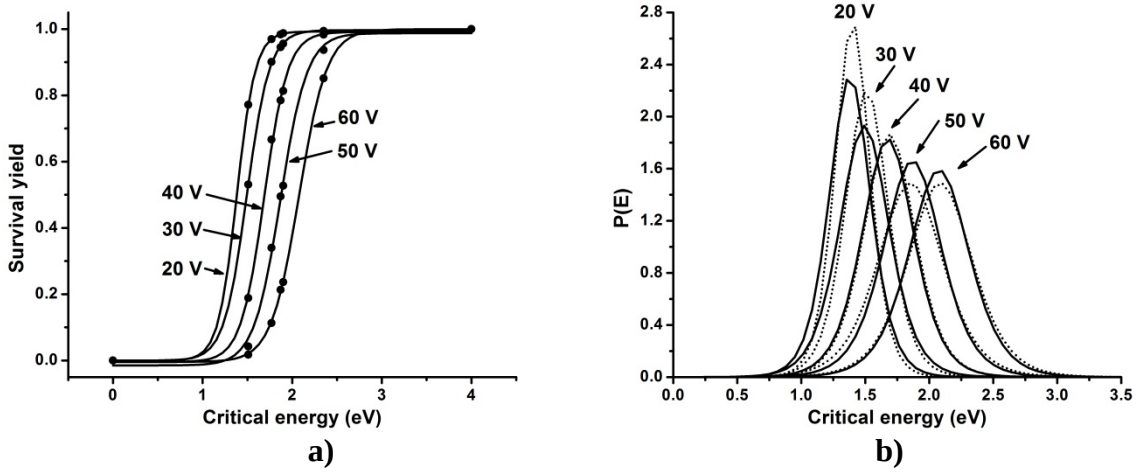

Figure S1. a) Sigmoidal SY curves for LAESI and **b)** internal energy distributions for ESI (dotted curves) and LAESI (solid curves) at different cone voltages. The extent of internal energy deposition by LAESI was indistinguishable from ESI, revealing a similarity in energy

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deposition in ion generation. Fitting parameters are summarized in Table S2. Error bars are within symbols.

Ion generation was also evaluated for large biomolecules with multiple potential fragmentation channels. Figure S2 shows the mass spectra obtained for the peptides substance P and angiotensin II. Both LAESI and ESI generated singly, doubly, and triply charged ions. No fragmentation was detected with either method. Ions in the low *m/z* region (*m/z* < 300) in Figures S2a and S2d correspond to the background from the electrospray solvent.

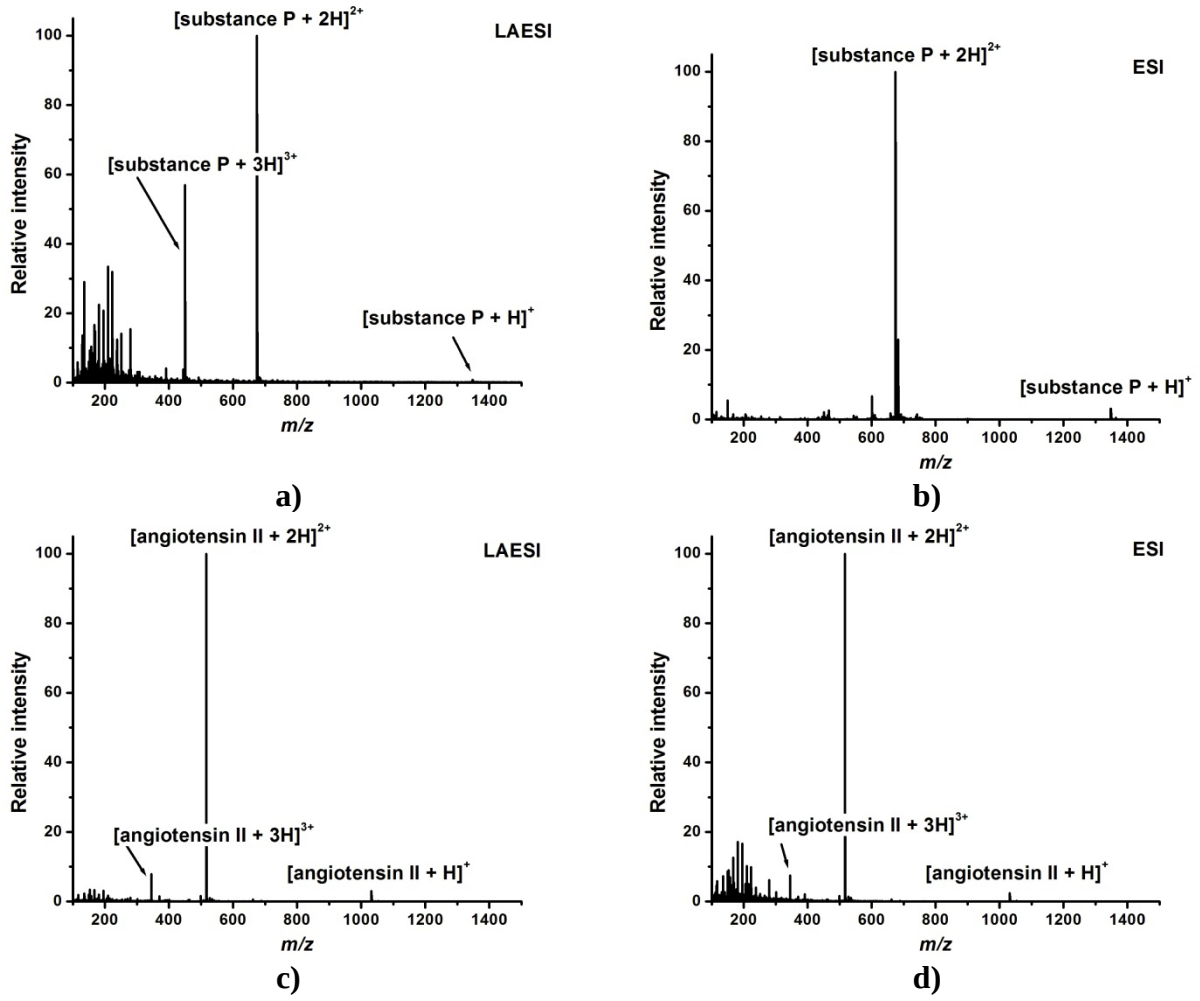

Figure S2. Comparison of peptide mass spectra in LAESI and ESI experiments. Both **a)** LAESI and **b)** ESI of substance P yielded singly (*m/z* 1347.7), doubly (*m/z* 674.4), and triply (*m/z* 449.9) charged species. Similarly, **c)** LAESI and **d)** ESI of angiotensin II solutions gave singly (*m/z* 1031.5), doubly (*m/z* 516.3), and triply charged (*m/z* 344.5) ions. No significant fragmentation was observed with either ionization method.

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Table S1. Benzyl-substituted benzylpyridinium ions and their critical bond energies, E_b, calculated using AM1 in References [1, 2].

Substituent of thermometer ion	Abbreviation	E_b (eV)	*m/z* (M^+)	*m/z* (F^+)
4-nitro-	$4NO_2$	2.35	215.1	136.0
3-methoxy-	3MO	1.95	200.1	121.1
4-chloro-	4Cl	1.90	204.1	125.0
3-methyl-	3M	1.90	184.1	105.1
4-fluoro-	4F	1.87	188.1	109.1
2-methyl-	2M	1.80	184.1	105.1
4-methyl-	4M	1.77	184.1	105.1
4-methoxy-	4MO	1.51	200.1	121.1

Table S2. Nonlinear regression results on measured survival yield data and calculated internal energy distribution parameters.

Instrument	Sampling cone potential* (V)	Sample phase	T_{sample} (°C)	Laser repetition rate (Hz)	Regression coefficient for sigmoidal fit		Mean and (width) of Gaussian (eV)	
					ESI	LAESI	ESI	LAESI
TOF MS	20	solution	25	10	0.997	0.999	1.40 (0.28)	1.38 (0.37)
	30	solution	25	10	0.997	0.999	1.51 (0.35)	1.49 (0.40)
	40	solution	25	10	0.997	0.998	1.68 (0.42)	1.69 (0.41)
	50	solution	25	10	0.983	0.997	1.85 (0.52)	1.87 (0.46)
	60	solution	25	10	0.998	0.999	2.09 (0.52)	2.08 (0.49)
	60	tissue	25	10	0.944	0.953	1.94 (0.64)	1.98 (0.65)
	8	tissue	0	10	-	0.994	-	1.53 (0.61)
Q-TOF MS	8	tissue	25	10	-	0.998	-	1.51 (0.41)
	8	tissue	25	20	-	0.998	-	1.51 (0.40)
	8	tissue	25	50	-	0.996	-	1.51 (0.42)
	8	solution	25	10	0.99129	-	1.57 (0.64)	-

*The sampling cone potential measures the sampling cone potential against the skimmer cone in the TOF MS instrument, whereas it denotes the potential applied against earth ground in the Q-TOF MS system.

References

[1] Gabelica, V.; De Pauw, E. Karas, M., *Int. J. Mass Spectrom.* **2004**, *231*, 189-195.
[2] Gabelica, V. De Pauw, E., *Mass Spectrometry Reviews* **2005**, *24*, 566-587.