

## SUPPLEMENTAY INFORMATION

### External standard calibration method for high-repetition-rate shock tube kinetic studies with synchrotron-based time-of-flight mass spectrometry

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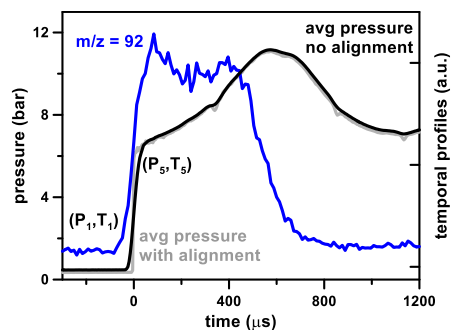


Fig S1. Pressure profile from 1 000 experiments from raw data (black) or with shifting for alignment (grey);  $m/z$  92 profile from 107 000 experiments, toluene pyrolysis, 0.1% in argon,  $T_5 = 1362 \pm 22$  K and  $P_5 = 6.6 \pm 0.2$  bar, photon energy 10.0 eV.

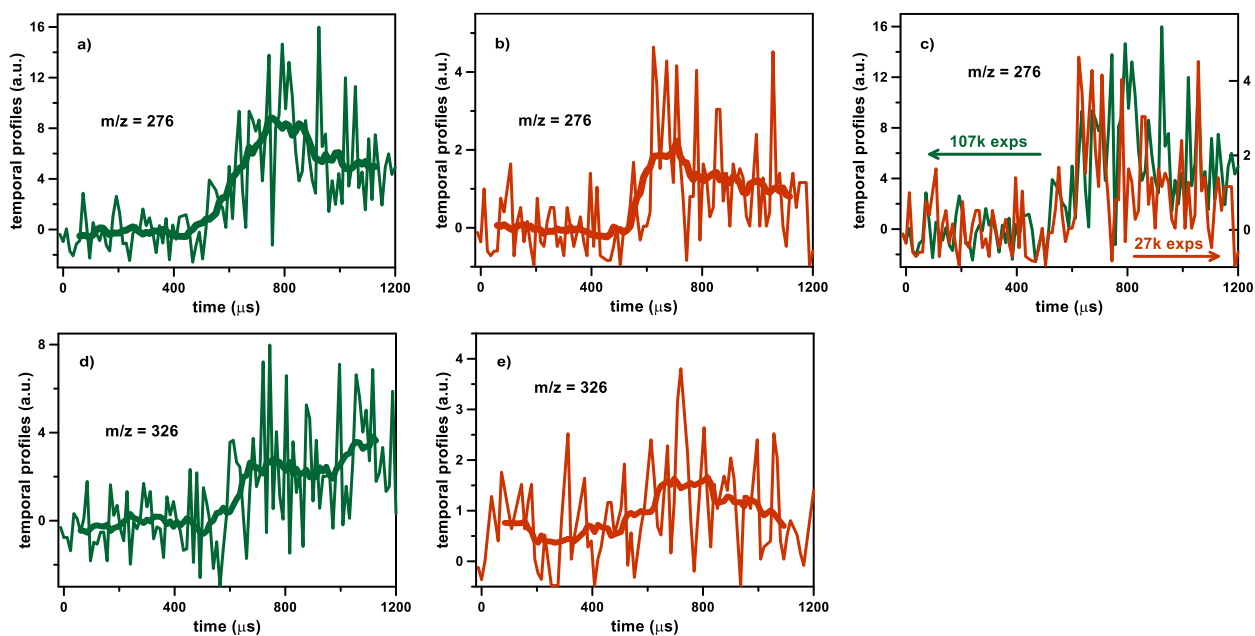


Fig. S2. Raw signals for a) to c)  $m/z$  276; d)-e)  $m/z$  326; toluene pyrolysis, at  $T = 1362 \pm 22$  K and  $P = 6.6 \pm 0.2$  bar, photon energy 10.0 eV. a)-d) 107 000 experiments; b)-e) 27 000 experiments. Bold lines obtained through running average fitting.

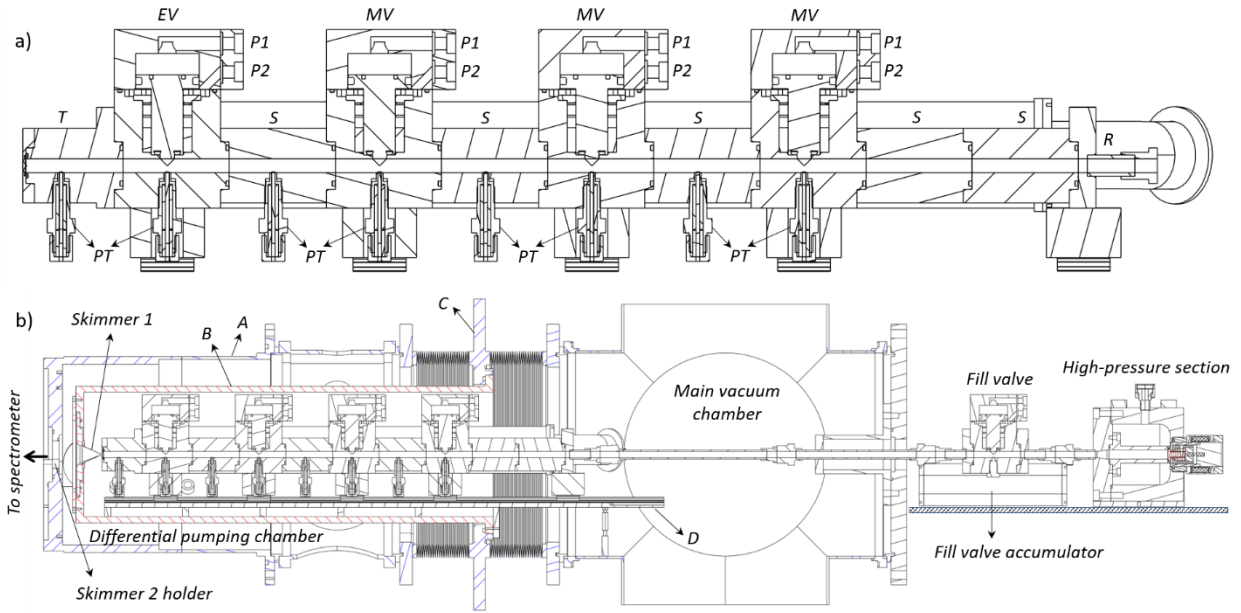


Fig. S3. a) Schematic of the low pressure section; b) HRRST/SAPHIRS coupling [from S. Nagaraju, R. S. Tranter, F. E. Cano Ardila, S. Abid, P. T. Lynch, G. A. Garcia, J. F. Gil, L. Nahon, N. Chaumeix, A. Comandini, Pyrolysis of ethanol studied in a new high-repetition-rate shock tube coupled to synchrotron-based double imaging photoelectron/photoion coincidence spectroscopy, *Comb. Flame*, 2021, 226, 53–68].