

Thermal degradation of formamidinium based lead halide perovskites into *sym*-triazine and hydrogen cyanide observed by coupled thermogravimetry - mass spectrometry analysis

Emilio J. Juarez-Perez^{*a,b}, Luis K. Ono^a, Yabing Qi^{*,a}

***e-mail: ejjuarezperez@unizar.es; Yabing.Qi@OIST.jp**

^a*Energy Materials and Surface Sciences Unit (EMSSU), Okinawa Institute of Science and Technology Graduate University (OIST), 1919-1 Tancha, Onna-son, Okinawa 904-0495, Japan*

^b*ARAID Foundation, Institute of Nanoscience of Aragon (INA), University of Zaragoza. 50018 Zaragoza, Spain*

Detailed calculations for estimation of maximum release achievable per meter-square of FA based perovskite based solar cell and hydrogen cyanide instantaneous concentration observed during low temperature heating tests and.

Maximum release achievable per meter-square of FA based perovskite solar cell

The weight of one thin-film of 1 m² of surface and 500 nm thickness of FAPbI₃ or FAPbBr₃ is

$$W_{FAPbX_3/m^2} = V_{m^2} \cdot \rho_{FAPbX_3}$$

Where W_{FAPbX_3/m^2} is the weight of perovskite contained in the thin-film of 1 m² of surface and 500 nm thickness.

V_{m^2} is the volume of this thin-film. $V_{m^2} = 0.5 \text{ cm}^3$ and ρ_{FAPbX_3} is the crystal density obtained from cif files reported for the α -FAPbI₃¹ or FAPbBr₃².

$$W_{FAPbI_3/m^2} = 2505 \text{ mg}$$

$$W_{FAPbBr_3/m^2} = 1880 \text{ mg}$$

Atomic weight percent of FAPbI₃ ($M_{wFAPbI_3} = 632.98 \text{ mg/mmol}$)

C	1.90 %
H	0.80 %
N	4.43 %
Pb	32.73 %
I	60.15 %

Atomic weight percent of FAPbBr₃ ($M_{wFAPbBr_3} = 491.98 \text{ mg/mmol}$)

C	2.44 %
H	1.02 %
N	5.69 %
Pb	42.12 %
Br	48.72 %

$$M_{wFA^+} = 45.06 \text{ mg/mmol}; M_{wHCN} = 27.02 \text{ mg/mmol}$$

The maximum HCN release achievable per meter-square of FA based perovskite solar cell is,

$$W_{HCN/m^2} = W_{FAPbX_3/m^2} \cdot (\% CHN)_{FAPbX_3} \cdot M_{wHCN} / M_{wFA}$$

The maximum observed hydrogen cyanide instantaneous partial pressure during low temperature heating tests was $P_{HCN} = 1.36 \cdot 10^{-7} \text{ torr}$ at 85 °C, see Figure S6. The equivalent HCN concentration in mg/m³ is obtained as,

$$C_{\text{max} - HCN/m^2} = \frac{P_{HCN} M_{wHCN}}{S_{HCN} \cdot R \cdot T} \cdot \frac{W_{FAPbBr_3/m^2}}{W_{\text{sample}}}$$

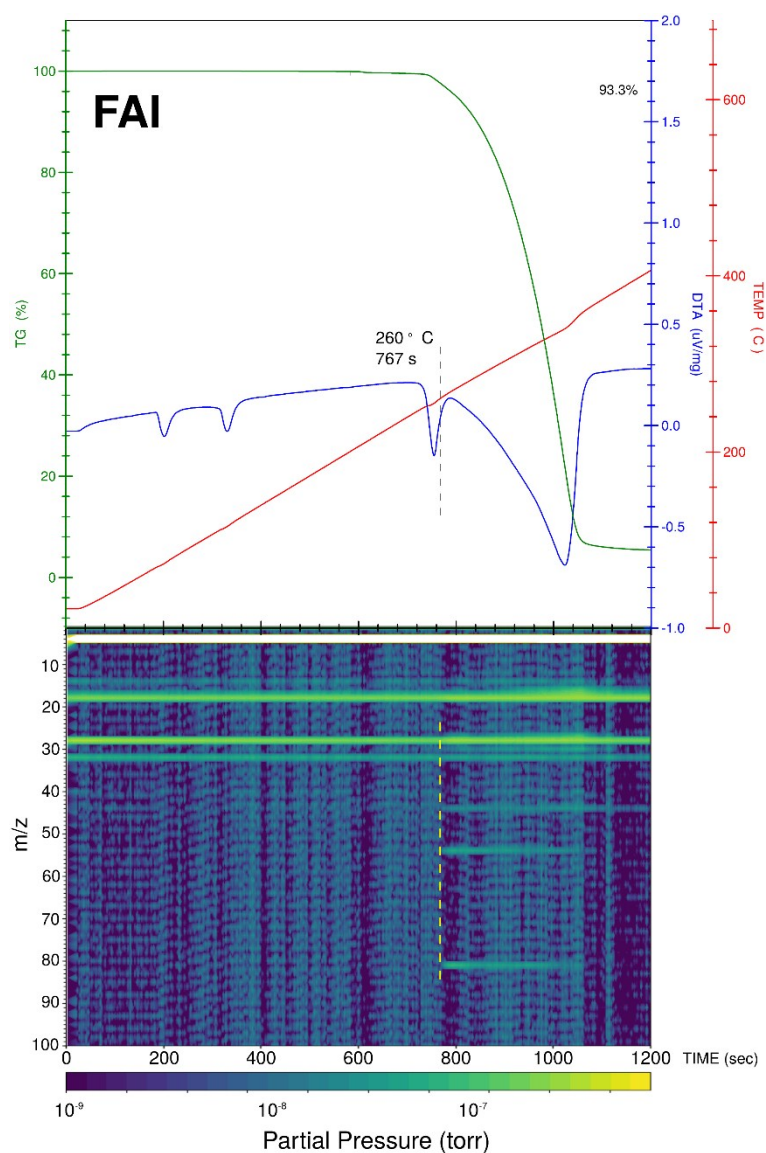


Figure S1. Tandem TG-DTA/MS coupled experiments for FAI. Top panel shows a one-step type mass loss TG pattern (green line). Bottom panel shows the MS traces simultaneously recorded (1-100 amu) during the experiments. Gray dash line indicates the initial temperature (time) of the first detection of the released gases during the high-temperature thermal degradation.

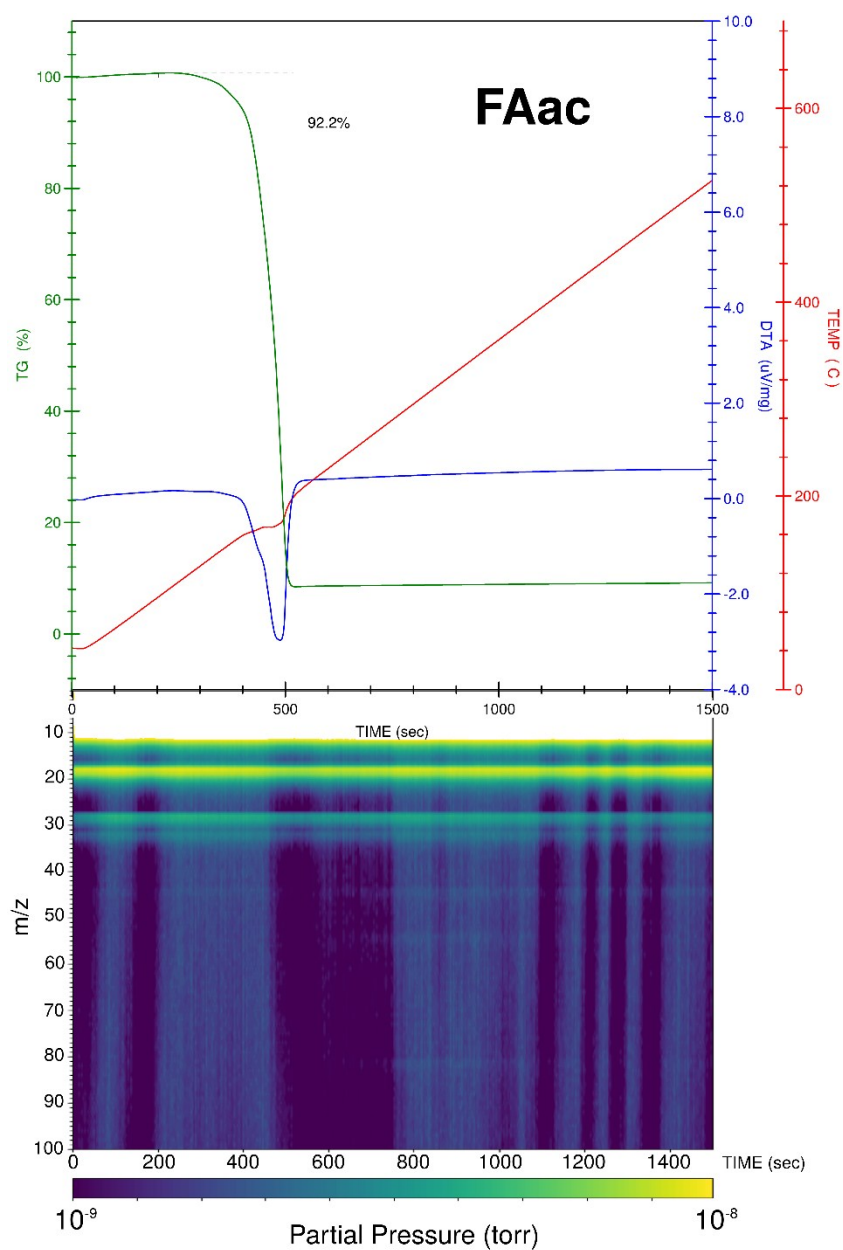


Figure S2. Tandem TG-DTA/MS coupled experiments for FAac (formamidine acetate). Top panel shows a one-step type mass loss TG pattern (green line). Bottom panel shows the MS traces simultaneously recorded (1-100 amu) during the experiments. There is a concurrent process of sublimation of FAac obscuring clear observation of released products during degradation.

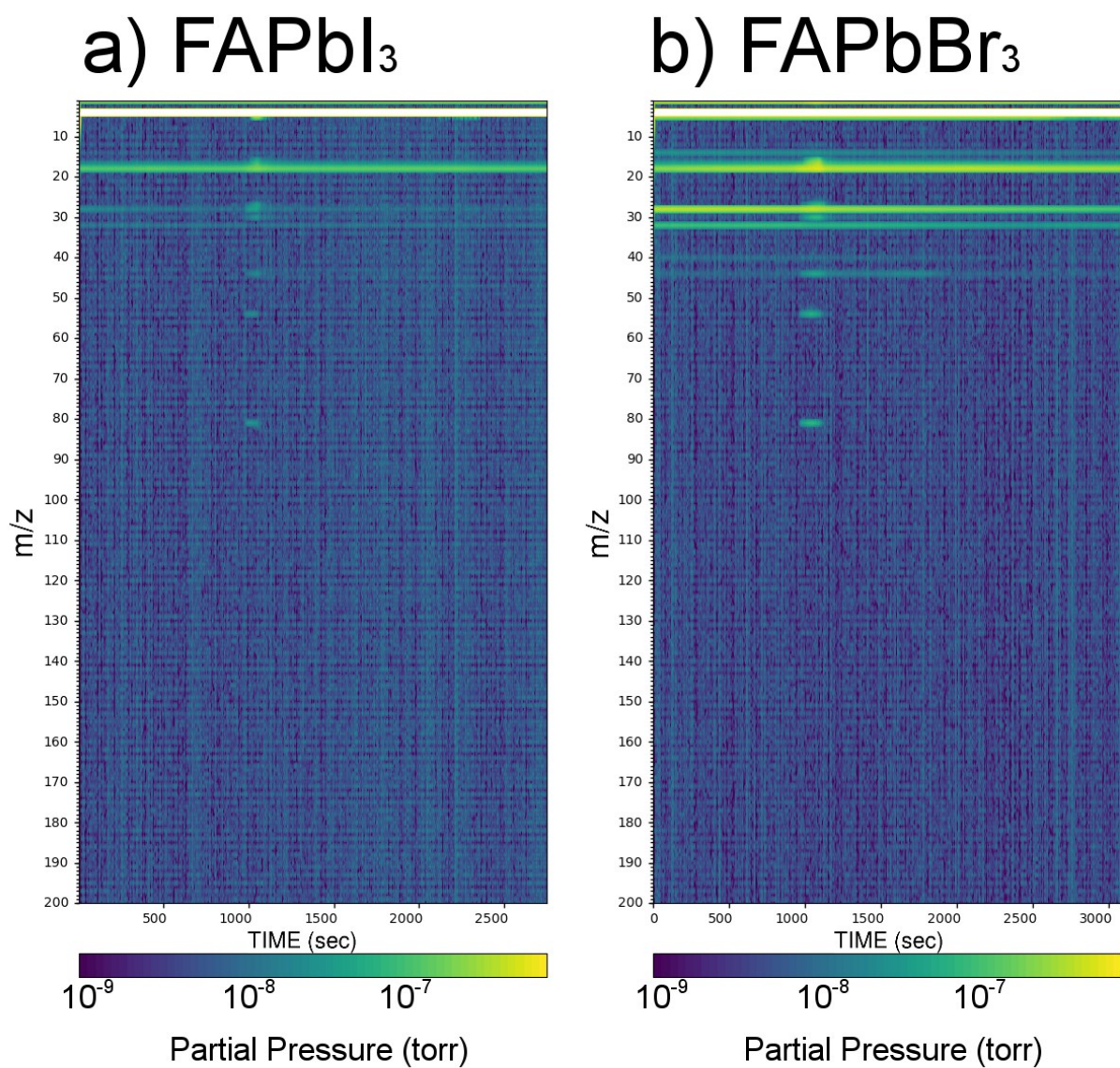


Figure S3. Full MS spectra (1-200 amu) for the tandem TG-DTA/MS coupled experiments shown in Figure 1 for a) FAPbI_3 and b) FAPbBr_3 .

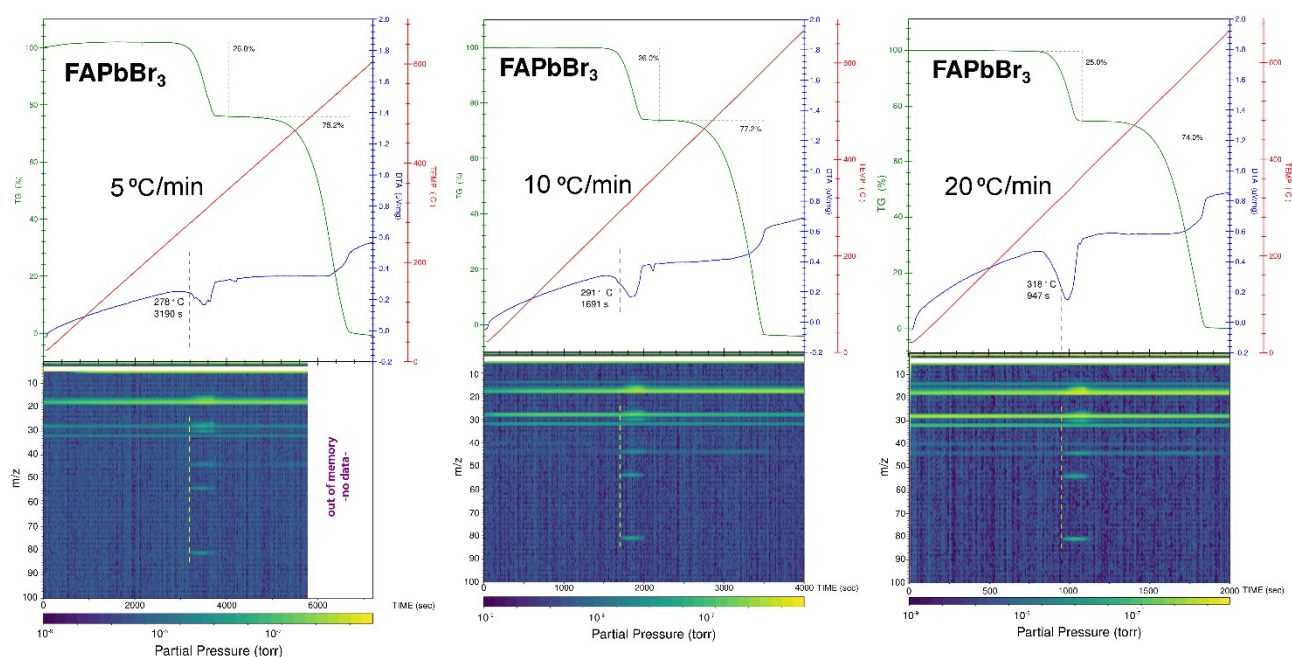


Figure S4. Tandem TG-DTA/MS coupled experiments for FAPbBr_3 at 3 different heating rates, 5 °C/min (left), 10 °C/min (center) and 20 °C/min (right). Top panels show the archetypal two-step type mass loss TG patterns (green line) for FAPbBr_3 . Bottom panels show MS traces simultaneously recorded (1-100 amu) during the experiments. Gray dash lines indicate the initial temperature (time) of the first detection of the released gases during the high-temperature thermal degradation.

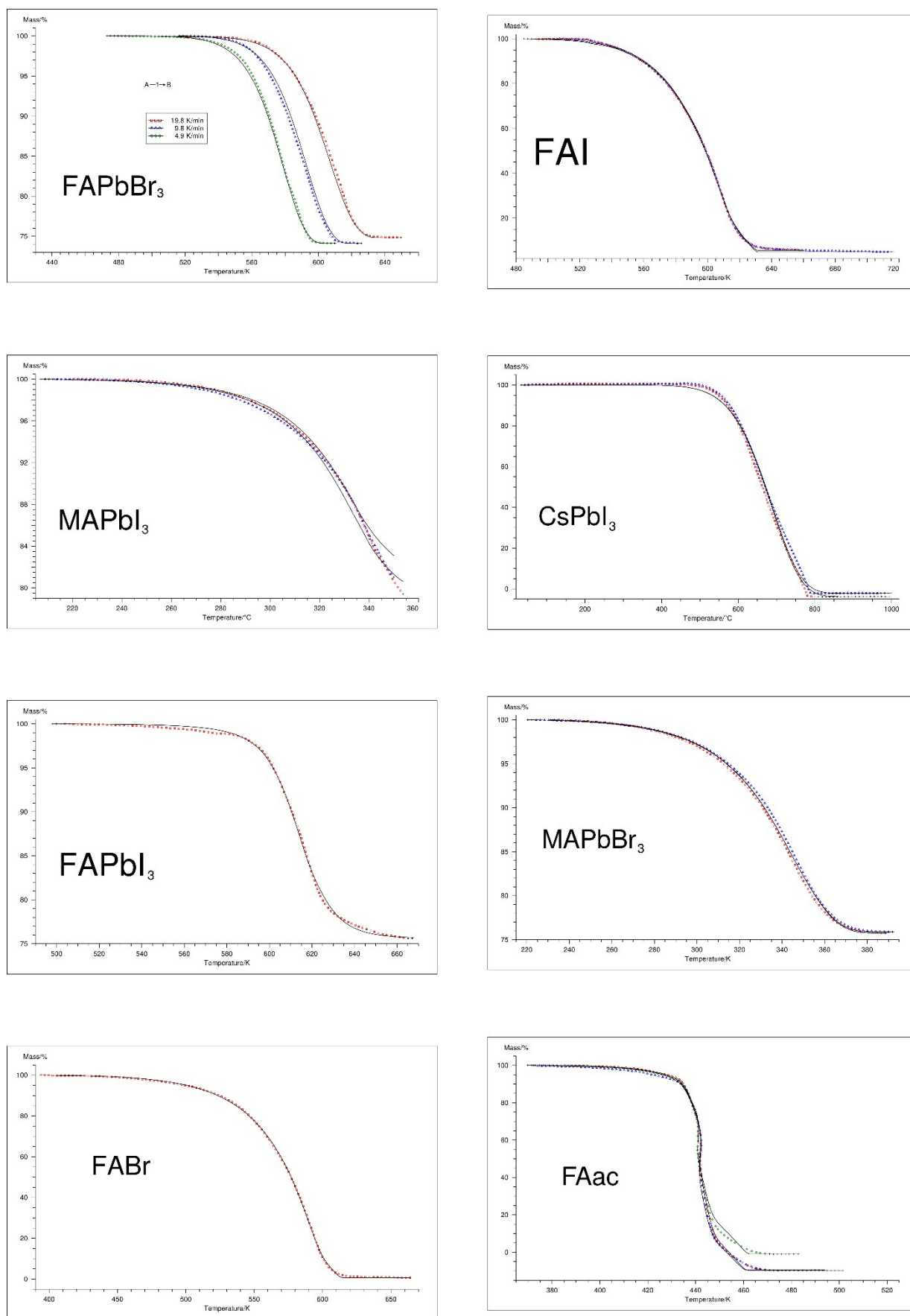


Figure S5. Graphical comparisons of the theoretical fittings (solid lines) and experimental data (symbols) for TG curves during the first mass loss step of MAPbBr₃, FAPbBr₃, MAPbI₃, FAPbI₃ and the unique mass loss step of precursors FAI, FABr and FAac, and all inorganic perovskite CsPbI₃.

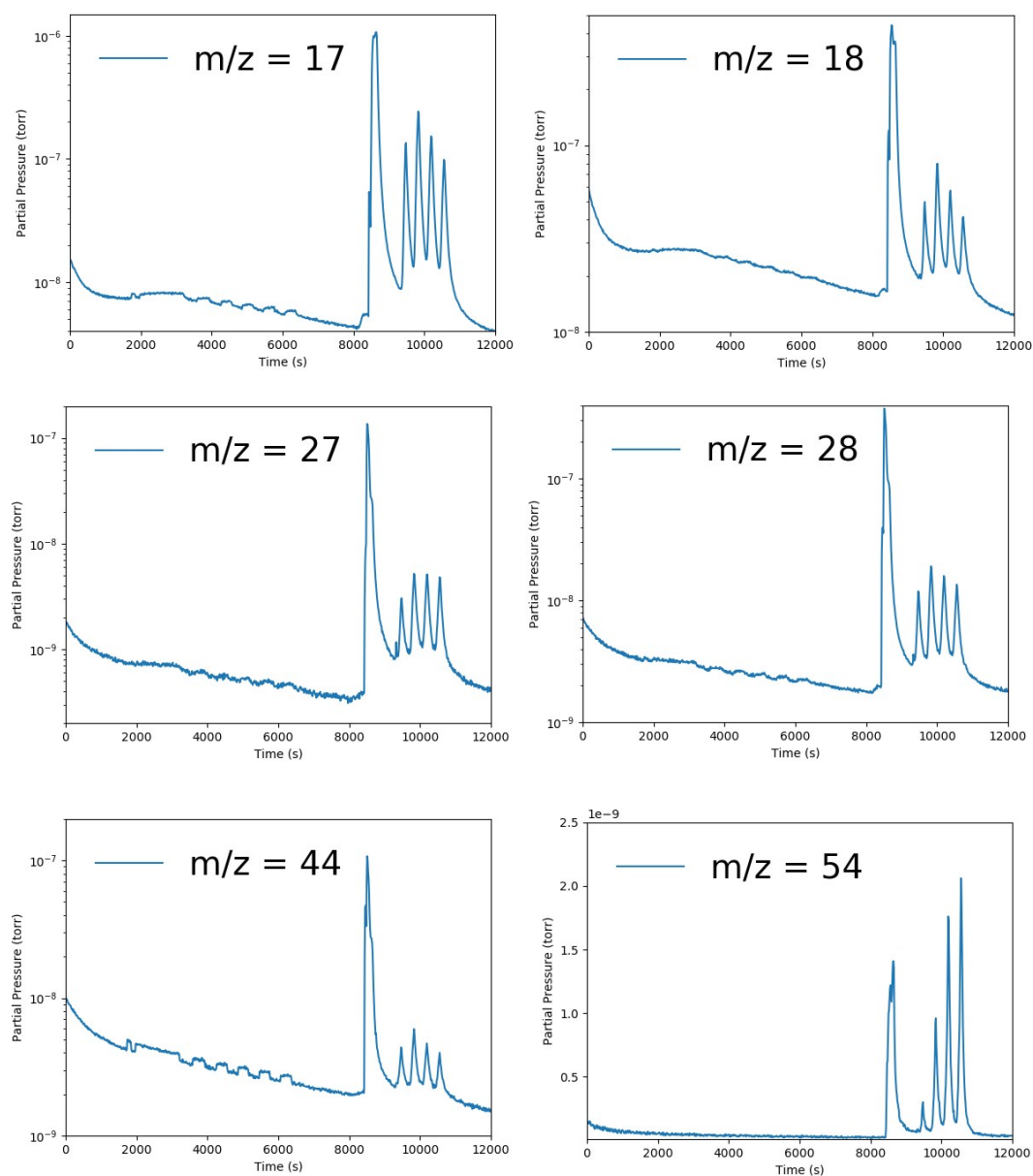


Figure S6. Raw m/z ratio traces (non-calibrated) recorded for NH₃ (17 amu), NH₄⁺ (18 amu), HCN (27 amu), N₂⁺ (28 amu), formamidine HCN₂H₃ (44 amu) and *sym*-triazine (54 amu) fragment.

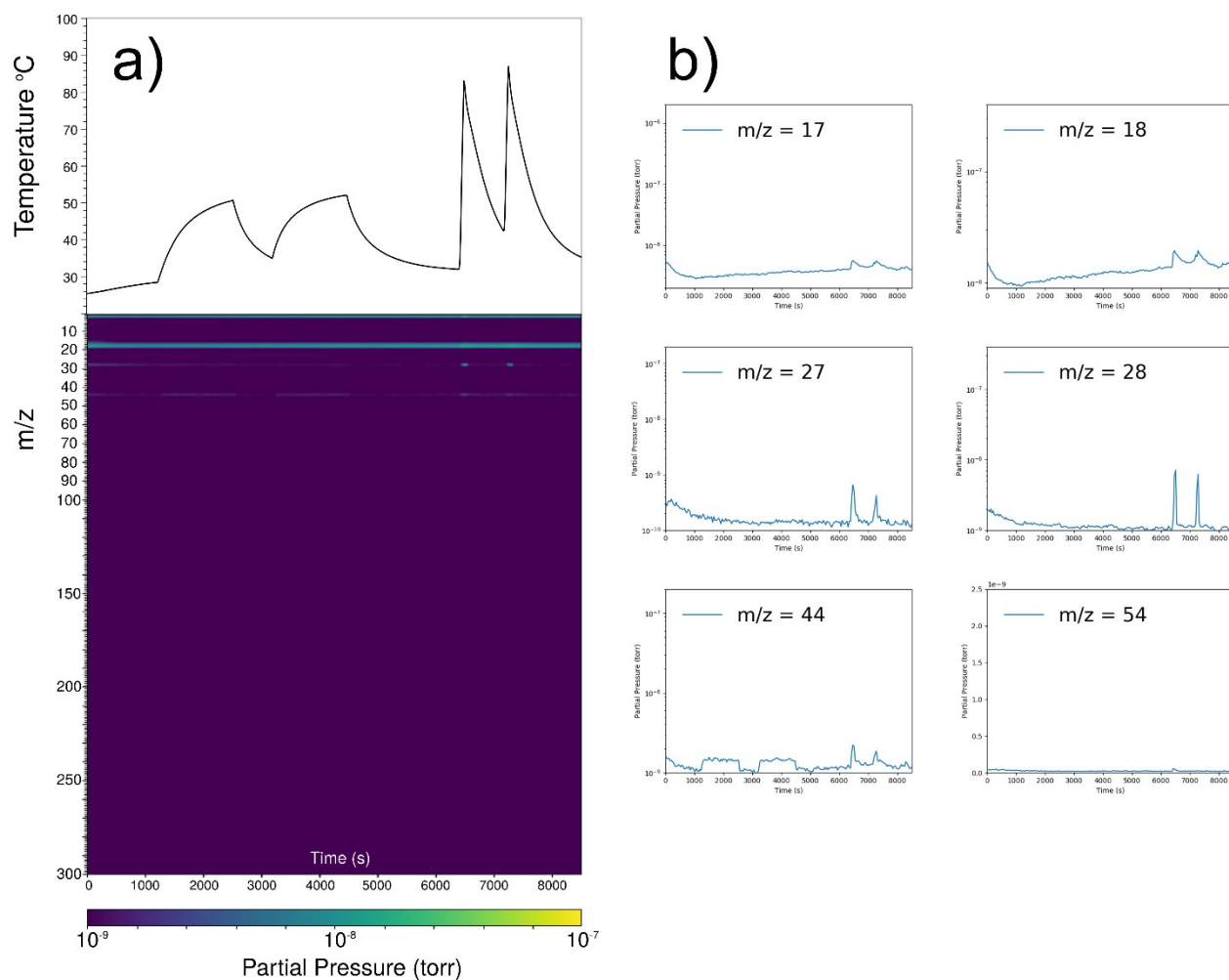


Figure S7. a) Mass spectrometry profiles of the empty 6-ways cross chamber recorded during illumination and heating-in-the-dark pulsed experiments. The sample holder temperature is recorded during light pulses and heating on/off intervals on the empty sample holder. b) Time dependent m/z traces of selected relevant amu registered during the thermal test of the chamber under light or dark conditions.

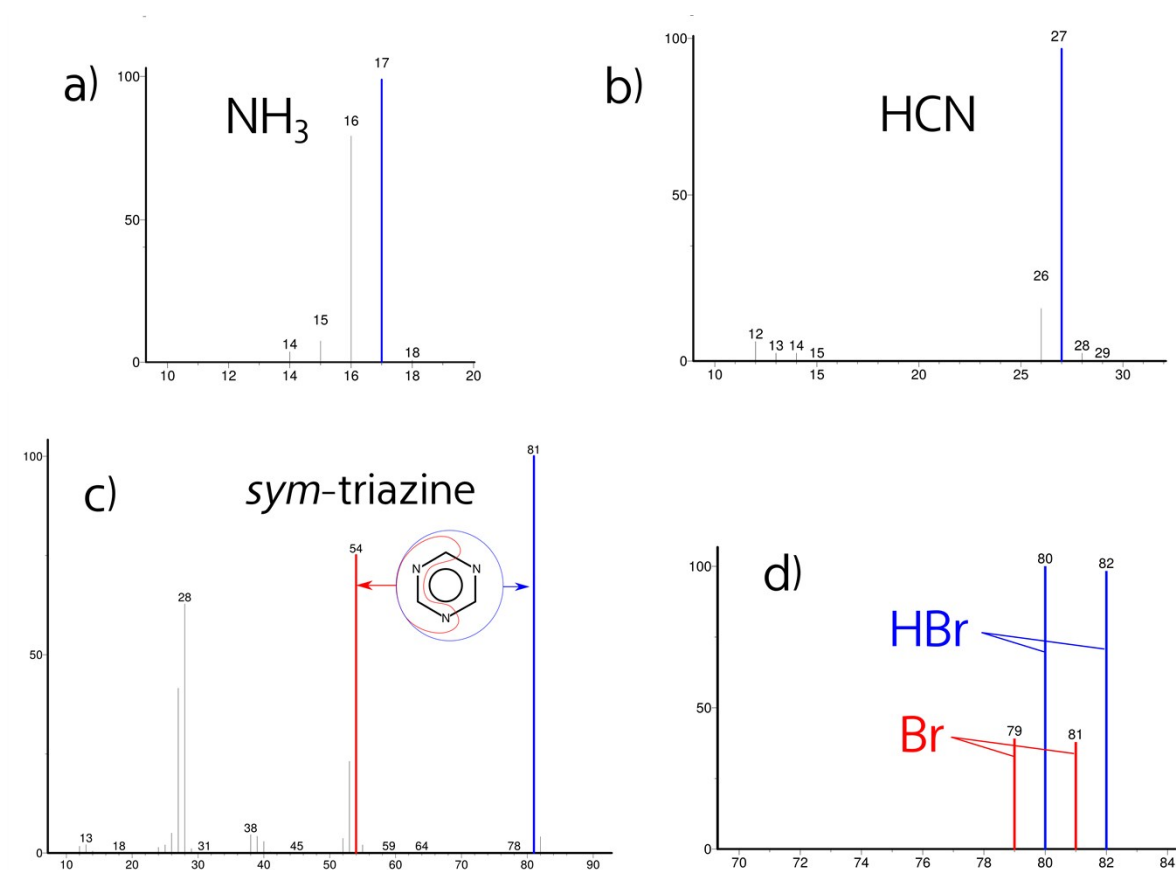


Figure S8. Fragmentation patterns m/z peaks retrieved from the NIST MS library data (<http://webbook.nist.gov/chemistry/>) for a) ammonia, b) hydrogen cyanide, c) *sym*-triazine and d) hydrogen bromide.

1. C. C. Stoumpos, C. D. Malliakas and M. G. Kanatzidis, *Inorg. Chem.*, 2013, **52**, 9019-9038.
2. S. Govinda, B. P. Kore, D. Swain, A. Hossain, C. De, T. N. Guru Row and D. Sarma, *The Journal of Physical Chemistry C*, 2018, **122**, 13758-13766.