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

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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 m^2 of surface and 500 nm thickness of $FAPbI_3$ or $FAPbBr_3$ 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 m^2 of surface and 500 nm thickness.
V_{m^2} is the volume of this thin-film. $V_{m^2} = 0.5\ cm^3$ and ρ_{FAPbX_3} is the crystal density obtained from cif files reported for the α-$FAPbI_3$[1] or $FAPbBr_3$[2].

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

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

Atomic weight percent of $FAPbI_3$ ($M_{wFAPbI3}$ = 632.98 mg/mmol)
C 1.90 %
H 0.80 %
N 4.43 %
Pb 32.73 %
I 60.15 %
Atomic weight percent of $FAPbBr_3$ ($M_{wFAPbBr3}$ = 491.98 mg/mmol)
C 2.44 %
H 1.02 %
N 5.69 %
Pb 42.12 %
Br 48.72 %

M_{wFA+} =45.06 mg/mmol; M_{wHCN} = 27.02 mg/mmol

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

$$W_{HCN/m^2} = W_{FAPbX_3/m^2} \cdot (\%\ CHN)_{FAPbX3} \cdot M_{w\,HCN}/M_{w\,FA}$$

The maximum observed hydrogen cyanide instantaneous partial pressure during low temperature heating tests was P_{HCN} = 1.36 10^{-7} torr at 85 ºC, see Figure S6. The equivalent HCN concentration in mg/m^3 is obtained as,

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

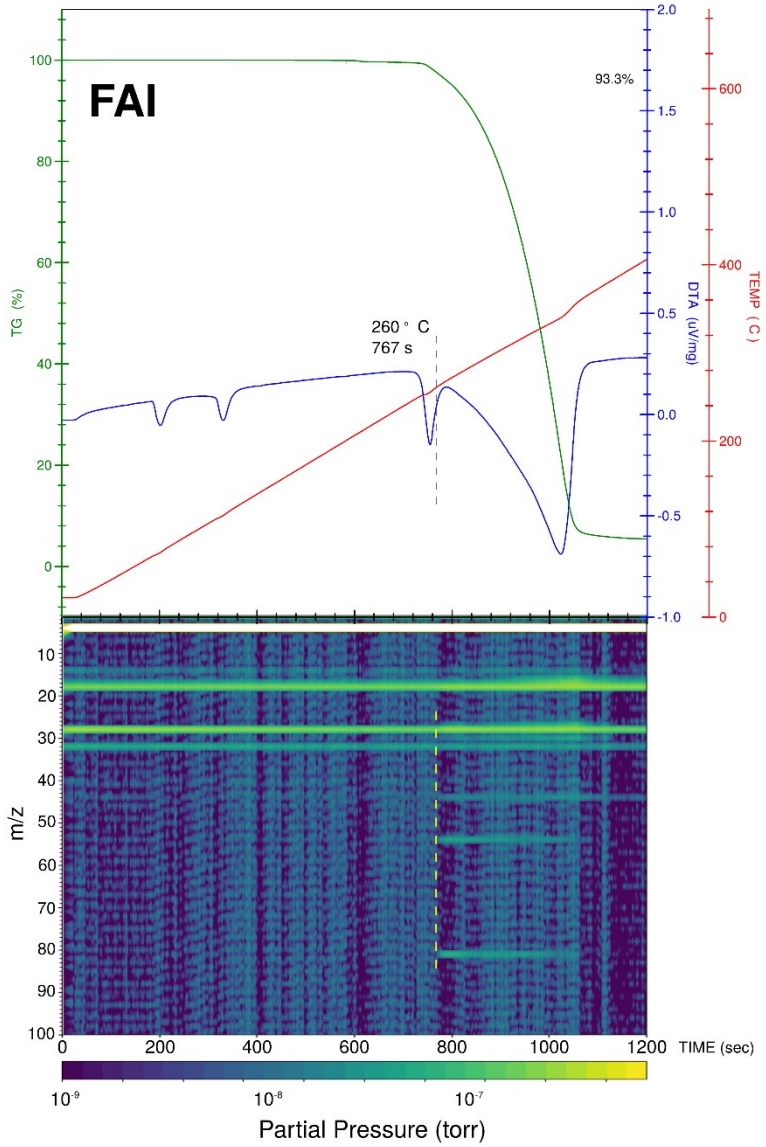


Figure S1. Tandem TG-DTA/MS coupled experiments for FAI. Top panel shows a one-step type mass loss TG pattern (green line). Bottom panel shows the MS traces simultaneously recorded (1-100 amu) during the experiments. Gray dash line indicates the initial temperature (time) of the first detection of the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

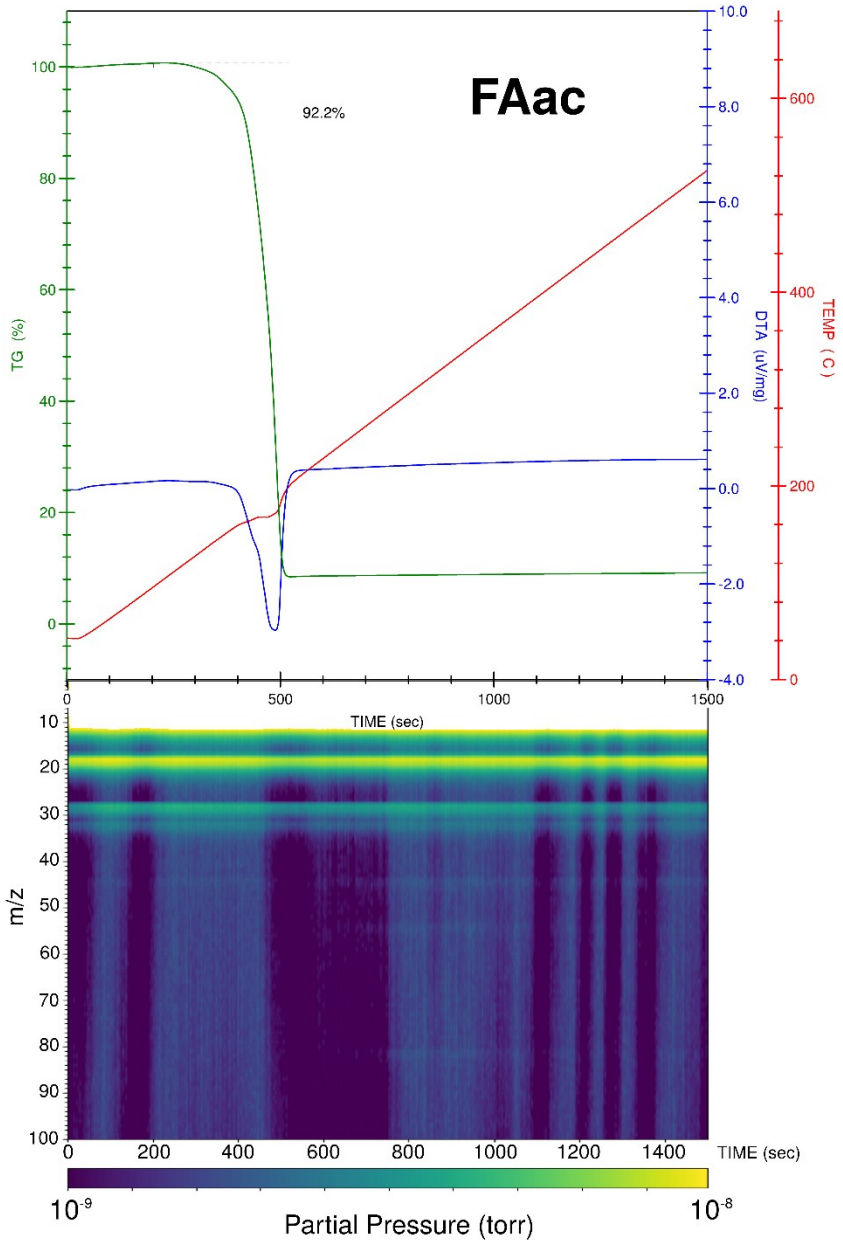


Figure S2. Tandem TG-DTA/MS coupled experiments for FAac (formamidinium acetate). Top panel shows a one-step type mass loss TG pattern (green line). Bottom panel shows the MS traces simultaneously recorded (1-100 amu) during the experiments. There is a concurrent process of sublimation of FAac obscuring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

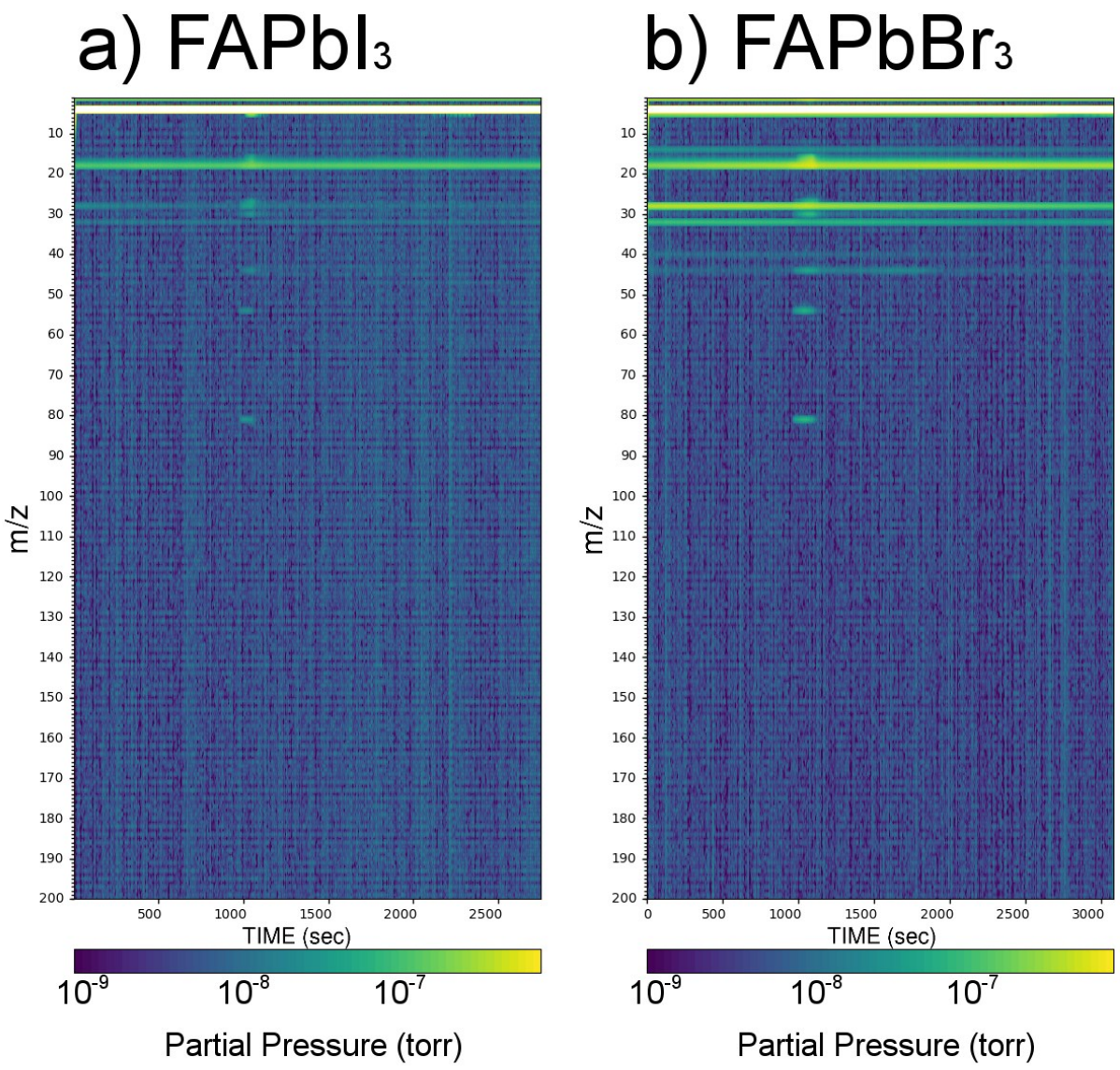


Figure S3. Full MS spectra (1-200 amu) for the tandem TG-DTA/MS coupled experiments shown in Figure 1 for a) $FAPbI_3$ and b) $FAPbBr_3$.

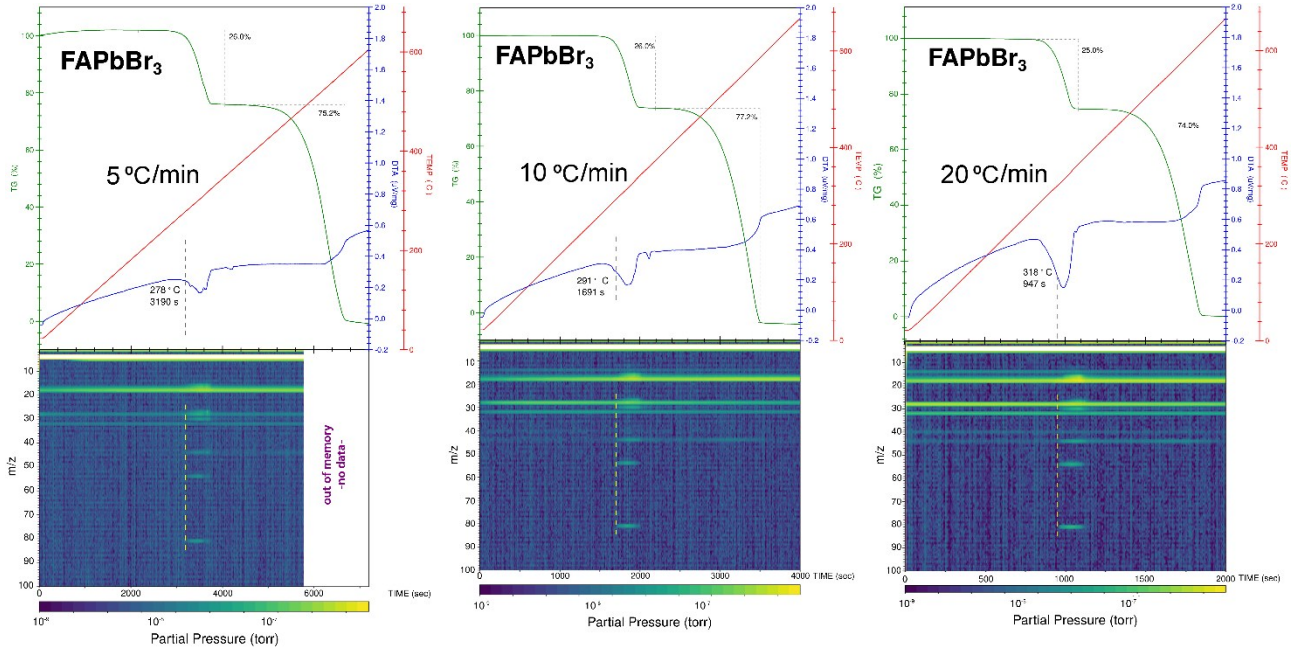
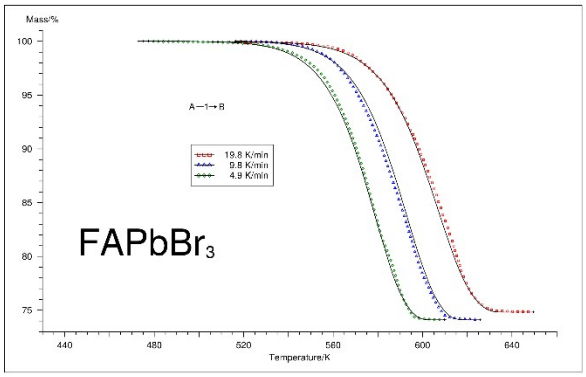
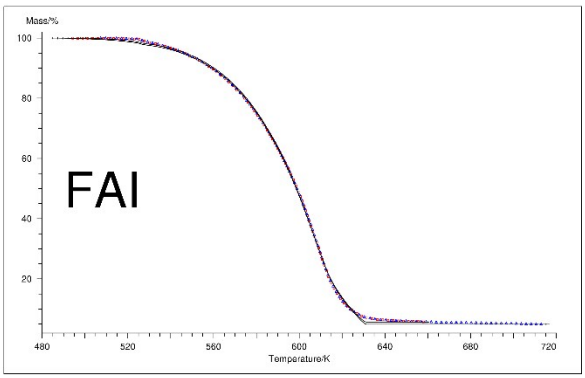
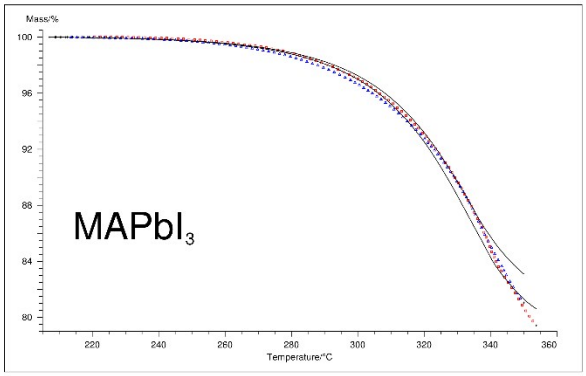
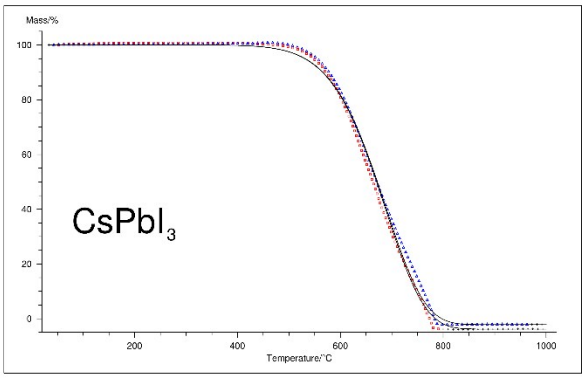


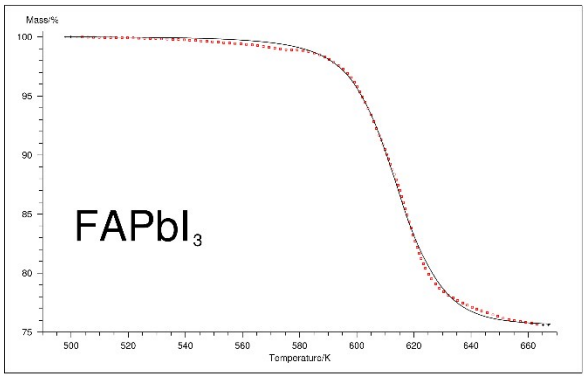
Figure S4. Tandem TG-DTA/MS coupled experiments for $FAPbBr_3$ at 3 different heating rates, 5 ºC/min (left), 10 ºC/min (center) and 20 ºC/min (right). Top panels show the archetypal two-step type mass loss TG patterns (green line) for $FAPbBr_3$. Bottom panels show MS traces simultaneously recorded (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.

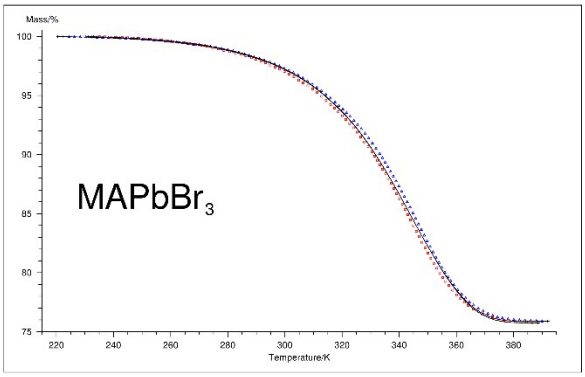


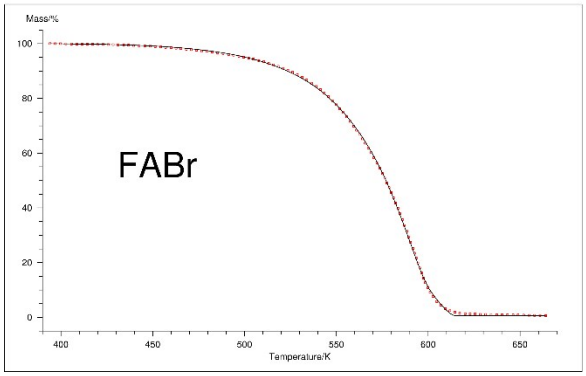












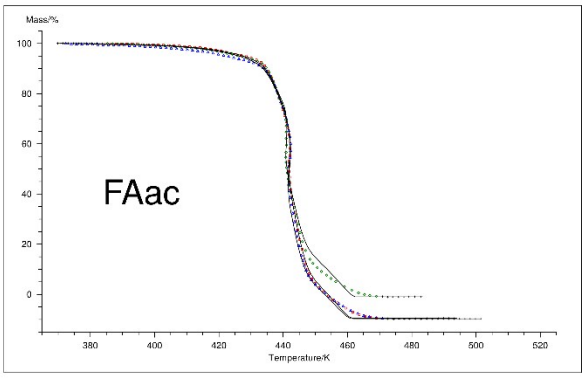


Figure S5. Graphical comparisons of the theoretical fittings (solid lines) and experimental data (symbols) for TG curves during the first mass loss step of $MAPbBr_3$, $FAPbBr_3$, $MAPbI_3$, $FAPbI_3$ and the unique mass loss step of precursors FAI, FABr and FAac, and all inorganic perovskite $CsPbI_3$.

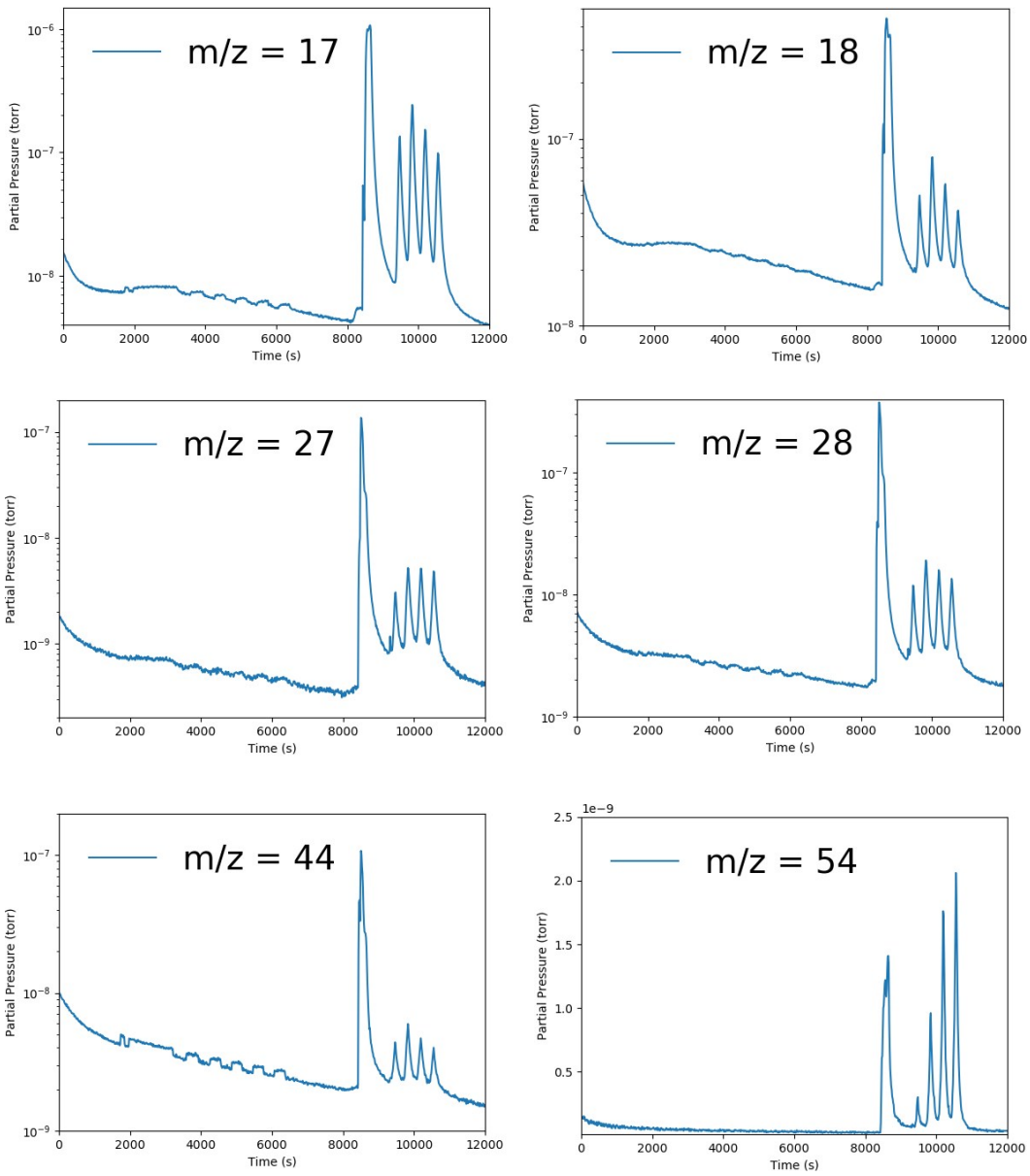


Figure S6. Raw m/z ratio traces (non-calibrated) recorded for NH_3 (17 amu), NH_4^+ (18 amu), HCN (27 amu), N_2^+ (28 amu), formamidine HCN_2H_3 (44 amu) and *sym*-triazine (54 amu) fragment.

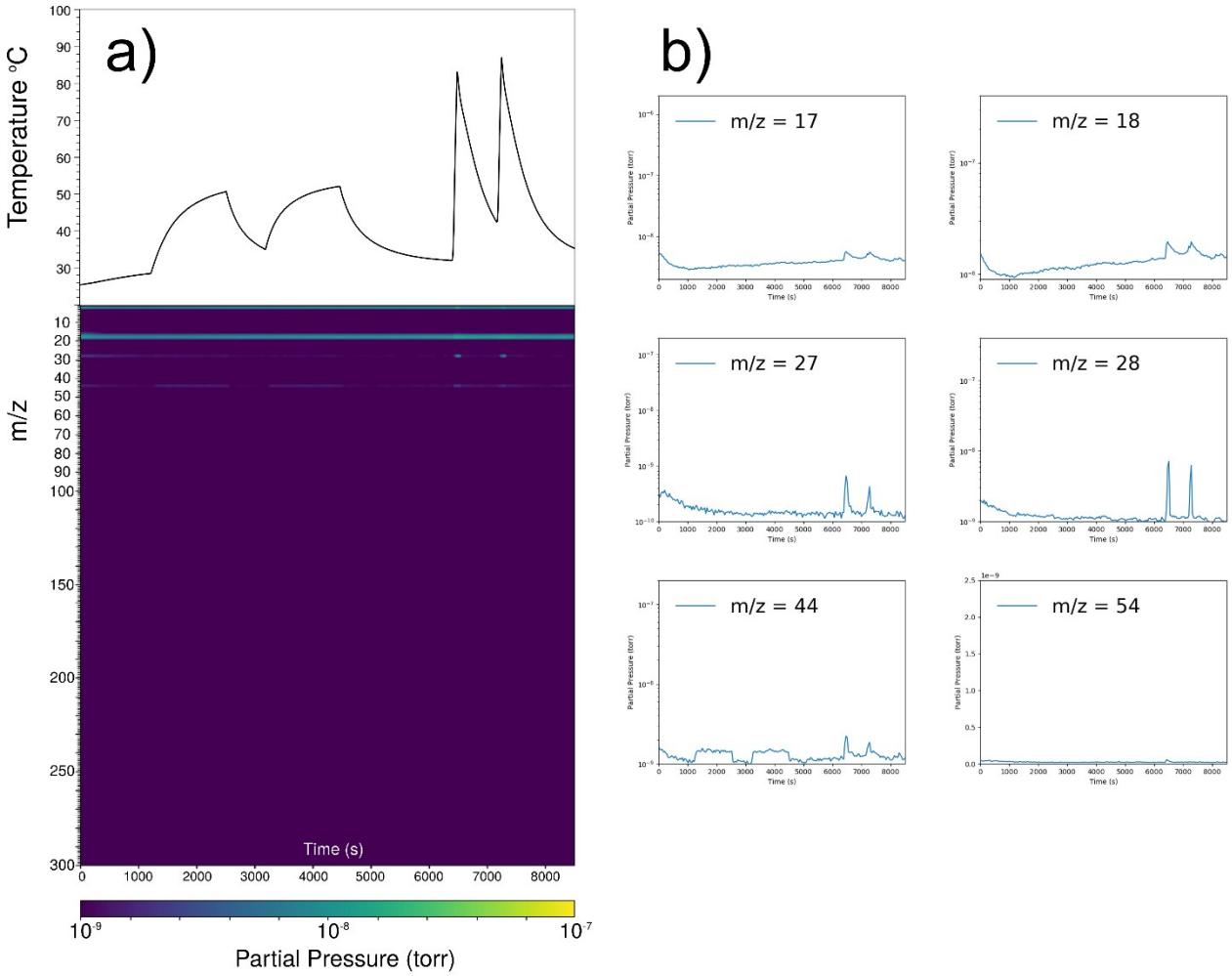


Figure S7. a) Mass spectrometry profiles of the empty 6-ways cross chamber recorded during illumination and heating-in-the-dark pulsed experiments. The sample holder temperature is recorded during light pulses and heating on/off intervals on the empty sample holder. b) Time dependent m/z traces of selected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

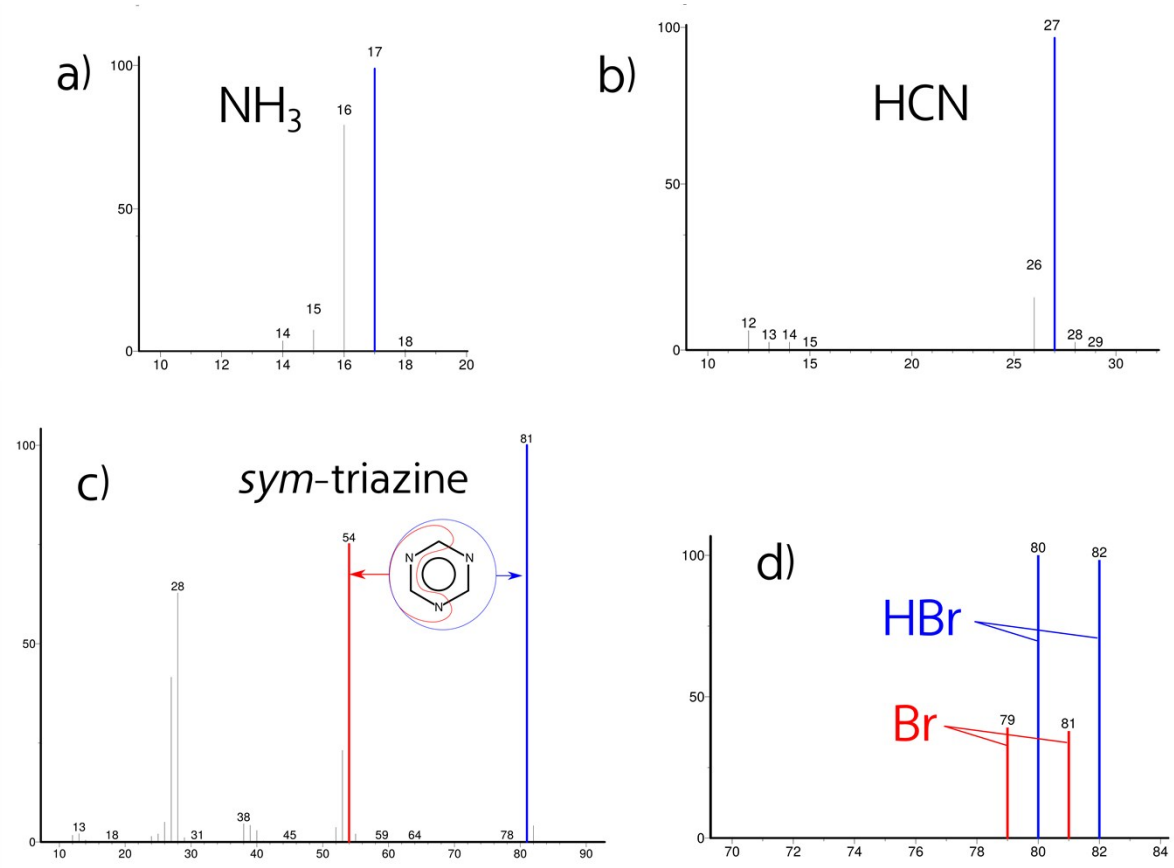


Figure S8. Fragmentation patterns m/z peaks retrieved from the NIST MS library data (http://webbook.nist.gov/chemistry/) for a) ammonia, b) hydrogen cyanide, c) *sym*-triazine and d) hydrogen bromide.

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.